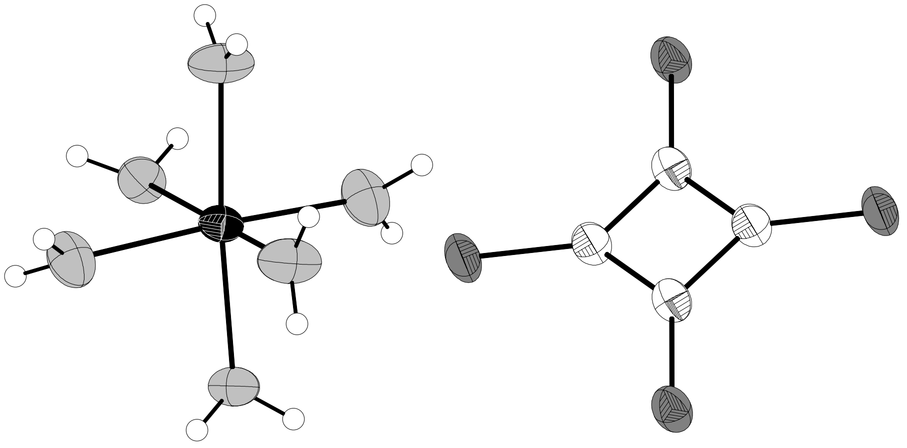
The Carbon Sulfide Anions $(C_4S_4)^{2-}$ and β-$(C_3S_5)^{2-}$ A Crystallographic Study on the Metal Salts and the Hydrolysis and Oxidation Properties



By

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The Carbon Sulfide Anions $(C_4S_4)^{2-}$ and β-$(C_3S_5)^{2-}$ A Crystallographic Study on the Metal Salts and the Hydrolysis and Oxidation Properties

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Younis Ben Amer

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ABSTRACT

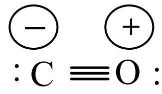
Tetrathiosquarate $(C_4S_4)^{2-}$ forms water soluble compounds of salt like character with the earth alkaline ions from Mg^{2+} to Ba^{2+}. While Ca^{2+} and Sr^{2+} yield almost isotypic tetrahydrates $M(C_4S_4)\cdot 4\ H_2O$, Mg^{2+} and Ba^{2+} show a different behaviour. For Mg^{2+} the formation of the discrete octahedral complex ions $[Mg(H_2O)_6]^{2+}$ is observed. Ba^{2+} forms a double salt $Ba_4K_2(C_4S_4)_5\cdot 16\ H_2O$ under inclusion of the potassium ions for the starting compound $K_2(C_4S_4)\cdot H_2O$. In all structures, the $(C_4S_4)^{2-}$ ions almost fulfil D_{4h} symmetry despite small derivations from the ideal symmetry are generally observed caused by the coordination to the cations. Tetrathiosquarate $(C_4S_4)^{2-}$ forms water soluble compounds of salt like character also with Mn^{2+} and Fe^{2+} ions. In both structures, water molecules are present as ligands and fill the coordination environment of the cations to octahedra. In the iron(II) salt $[Fe(H_2O)_2](C_4S_4)\cdot 4H_2O$, the Fe^{2+} ions are coordinated by two H_2O ligands and linked by bridging tetrathiosquarate ions to a one-dimensional strand. The Mn(II) salt $[Mn_4(OH)_4(H_2O)_4](C_4S_4)_2$ is made up of cube-shaped complexes $[Mn(OH)_4(H_2O)_4]^{4+}$, which are connected by tetrathiosquarate ions to a two-dimensional network, in which O–H···S and O–H···O bridging bonds connect the layers to a three-dimensional structure. β-$(C_3S_5)^{2-}$ turned out to be quite sensitive to oxidation, giving at room temperature in aqueous solution the $(C_6S_{10})^{2-}$ ion, which was isolated using Ca^{2+} and Sr^{2+} as $[Ca(H_2O)_7](C_6S_{10})$ and $[Sr(H_2O)_8](C_6S_{10})\cdot H_2O$. To further study the hydrolysis and oxidation processes, aqueous solutions of the potassium salt of β-$(C_3S_5)^{2-}$ were brought to crystallization using tetraphenylarsonium chloride, $[As(C_6H_5)_4]Cl$. By this method, several hydrolysis and oxidation products of β-$(C_3S_5)^{2-}$ could be trapped as the respective $[As(C_6H_5)_4]^+$ salts. Under air, crystals of $[As(C_6H_5)_4]_2(C_3S_5)\cdot 2H_2O$ could be isolated and crystals of $[As(C_6H_5)_4](HC_3S_5)$, containing the monoprotonated form of $(C_3S_5)^{2-}$, were found. $[As(C_6H_5)_4]_2(C_3S_6O_3)\cdot 3H_2O$ is the third isolated compound formed under air. The novel $(C_3S_6O_3)^{2-}$ ion is built of a planar C_3S_5 moiety with a pyramidal SO_3 group attached to the outer S atom of the C_3S_5 group. Under exclusion of air $[As(C_6H_5)_4](C_3S_4H)$ crystals were formed within few days. The anionic unit derives from $(C_3S_5)^{2-}$ by a C–S bond cleavage and the substitution of the sulfur atom by a hydrogen atom under formation of a new C–H bond.

Chapter One

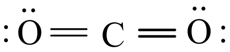
Introduction

1.1 Binary Compounds of Carbon with Oxygen and Sulfur

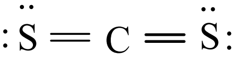
Carbon forms a large number of binary compounds and binary molecular anions with the elements oxygen and sulfur. The most important ones are of course carbon monoxide CO, carbon dioxide CO_2, and the carbonate ion CO_3^{2-}. Many analogies exist between the carbon-oxygen compounds and the carbon-sulfur compounds but there are also distinct differences. Carbon disulfide CS_2, and the trithiocarbonate ion CS_3^{2-} have their analogues with the respective carbon-oxygen composition. The sulfur analogue of carbon monoxide is carbon monosulfide CS. This is an unstable species, which can only be prepared at liquid nitrogen temperature. The number of known neutral molecules, only consisting of carbon and sulfur is, however, much higher than the respective number of molecular binary carbon oxides. Scheme 1 gives an overview on representative examples. A close chemical relation exists between carbon-oxygen anions (oxocarbons) and the respective sulfur analogues (thiocarbons). Some representative examples are collected in Scheme 2. Oxocarbons are compounds in which all or most of the carbon atoms are linked with each other in the form of carbonyl groups or in the form of hydrated carbonyl groups [1]. Among the oxocarbons the monocyclic dianions are the most interesting. They represent a series of polycarbonylated organic species with remarkable structural, chemical and electronic properties (Scheme 2). They can be characterized by the common formula $(C_nO_n)^{2-}$ in which n is a positive integer between 3 and 6. The monocyclic oxocarbon dianions are often described as aromatic, but most of them were predicted to have very small resonance energies. The planarity and cyclic conjugation of these dianions cannot be viewed as significant evidence of the existence of aromaticity, the deltate $(C_3O_3)^{2-}$ alone could be considered to be aromatic[2]. Deltic acid, $H_2C_3O_3$ (2,3-dihydroxycyclopropene-1-one) and its corresponding anion $(C_3O_3)^{2-}$ were synthesized in 1975 for the first time [3]. 3,4-Dihydroxycyclobut-3-ene-1,2-dione, which is commonly called squaric acid, $H_2C_4O_4$, was prepared for the first time in 1959 [4]. Today, squaric acid is produced on a small industrial scale by hydrolysis of perchlorocyclobutene in one step [5]. Although the special properties of oxocarbons have come to light only recently, their history begins at the very dawn of modern chemistry and involves many of the great chemists of the early nineteenth century [6]. The first scientist to have in hand an oxocarbon was probably Gmelin [7] who isolated dipotassium croconate, $K_2C_5O_5$, and croconic acid, $H_2C_5O_5$, 4,5-dihydroxy-4- cyclopentene-1,2,3-trione



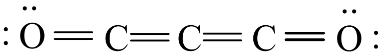
Carbon monoxide



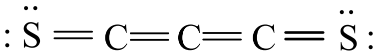
Carbon dioxide



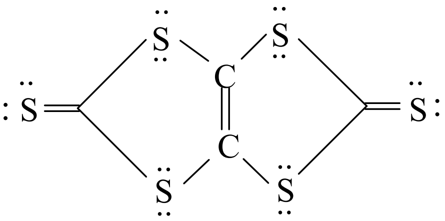
Carbon disulfide



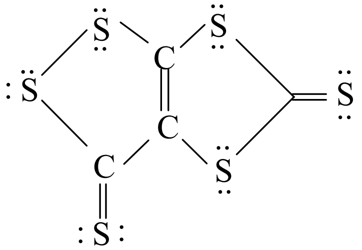
Carbon suboxide



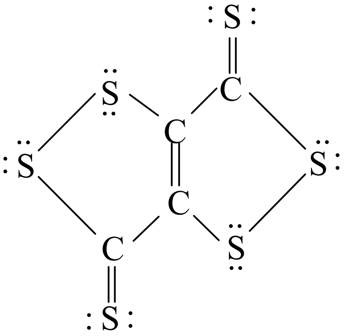
Carbon subsulfide



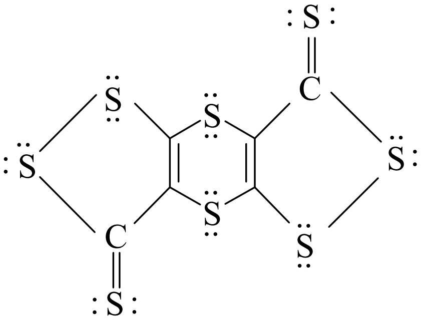
α, α–C_4S_6



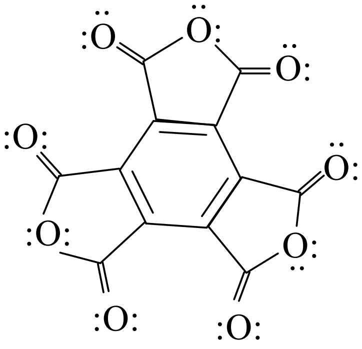
α, β–C_4S_6



β, β–C_4S_6

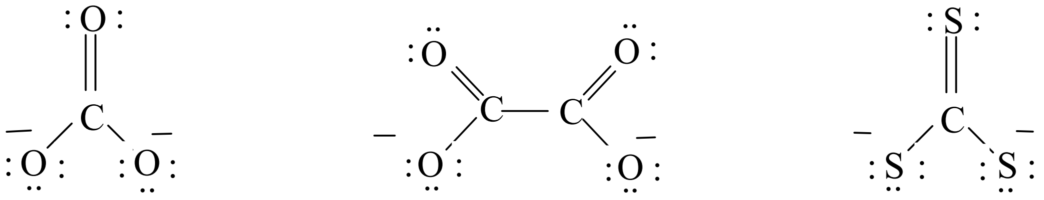


C_6S_8

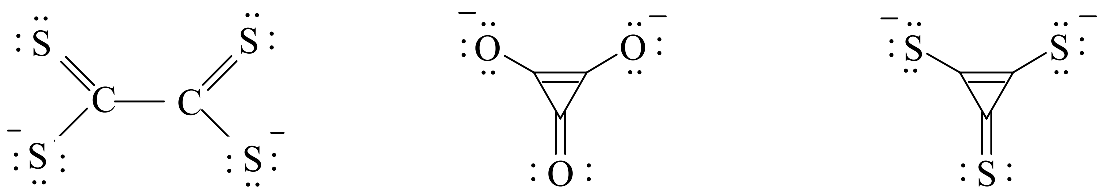


Mellitictrianhydride ($C_{12}O_9$)

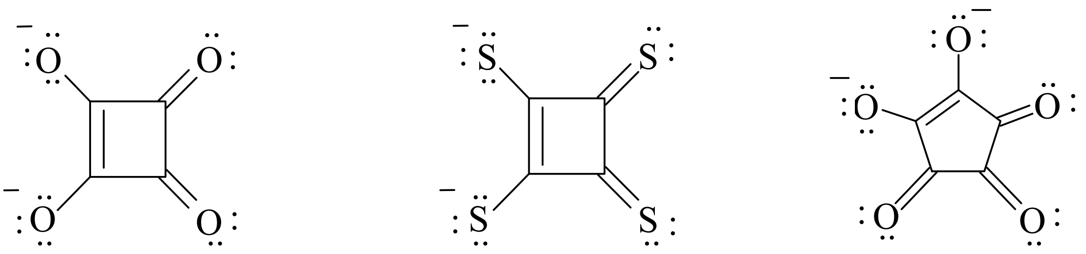
Scheme 1 Molecular structure and electron formula of selected neutral molecular carbon oxides and carbon sulfides.



Carbonate ion $(CO_3)^{2-}$ Oxalate ion $(C_2O_4)^{2-}$ Trithiocarbonate ion $(CS_3)^{2-}$



Tetrathiaoxalate ion $(C_2S_4)^{2-}$ Deltate ion $(C_3O_3)^{2-}$ Trithiodeltate ion$(C_3S_3)^{2-}$



Squarate ion $(C_4O_4)^{2-}$ Tetrathiosquarate ion $(C_4S_4)^{2-}$ Croconate ion $(C_5O_5)^{2-}$

Rhodizonate ion $(C_6O_6)^{2-}$ Benzene hexathiolate $(C_6S_6)^{6-}$

Scheme 2 Molecular structures and electronic formula of selected carbon- oxygen and carbon-sulfur anions.

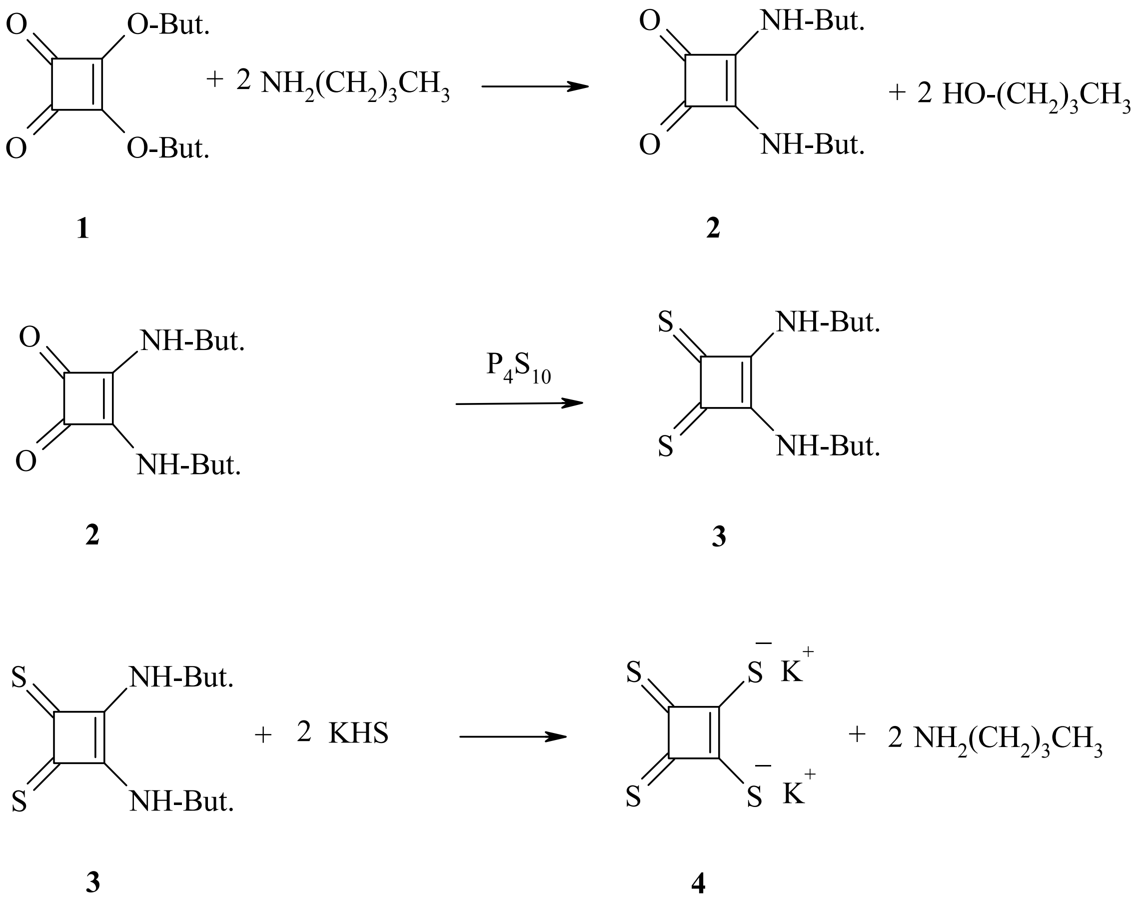
from a black residue formed in the reaction of potassium hydroxide with carbon. The chemistry of rhodizonic acid, $H_2C_6O_6$ (5, 6-dihydroxy-5-cyclohexene-1,2,3,4-tetraone), and its derivatives has been worked on even less than on croconates [6]. Rhodizonate $(C_6O_6)^{2-}$ was found together with croconate $(C_5O_5)^{2-}$ among the products of the reduction of potassium carbonate with charcoal in 1837 [8].

1.2 Thiocarbon Dianions $(C_nS_n)^{2-}$

Thiocarbon anions are the heavier analogues of the well-investigated nonbenzenoid aromatic oxocarbons [9]. The most interesting type of thiocarbon dianions can be characterized by the general formula $(C_nS_n)^{2-}$ in which n is a small positive integer [10]. The first synthesis of the aromatic dianion trithiodeltate $(C_3S_3)^{2-}$ was reported by Seitz et al. [11]. Using tetrachlorocyclopropene and $(CH_3)_3SiCH_2CH_2$-SH a symmetrical thioalkylsilyl substituted cyclopropenylium salt $((CH_3)_3SiCH_2CH_2\text{-}S)_3C_3^+$ was obtained, which gave the thione intermediate after reductive removal of one of the three alkylsilyl groups using zinc powder. Treatment with tetrabutylammoniumfluoride gave the deltate dianion, which was characterized as its sodium and methyltriphenylphosphonium salts. The spectroscopic data of this salt are in agreement with a planar symmetrical structure. The Raman and IR spectra show that the dianion has the proposed D_{3h} symmetry, which was also confirmed by the X-ray crystal structure determination. The sulfur analogue of the squarate dianion can be prepared using all highly activated squaric acid derivatives as easily available starting materials such as the dithioester, the dithioamide, the diamino dithiosquarate and tosyl substituted bis(amidine) of squaric acid. No literature was found pertaining $(C_5S_5)^{2-}$ and $(C_6S_6)^{2-}$, so these ions do not seem to be prepared yet. Fanghänel [12] prepared the sodium salt of $(C_6S_6)^{6-}$ and its X-ray structure was determined as $Na_2(H_4C_6S_6)\cdot 4NaOH\cdot 12H_2O$, which was obtained as single crystals from aqueous solution of $Na_6(C_6S_6)$ [13]. Not all thiocarbons are the monocyclic analogues of oxocarbons but there are noncyclic thiocarbon dianions which play an important role in coordination chemistry and have received some scientific interest. Those include the thiocarbonate ion $(CS_3)^{2-}$ which is the thiocarbon analogue of carbonate $(CO_3)^{2-}$, the perthiolate $(CS_4)^{2-}$ [14-17] which has no oxocarbon analogue, the tetrathiooxalate ion $(C_2S_4)^{2-}$, [18, 19] the thiocarbon analogue of oxalate $(C_2O_4)^{2-}$, and the cyclic $(C_3S_5)^{2-}$, which is known in two isomeric forms.

1.2.1 The Tetrathiosquarate Ion $(C_4S_4)^{2-}$

Seitz and coworkers [20] firstly prepared the tetrathiosquarate ion. They treated 2,4-bis(dimethylamino)cyclobutene-1,3-dithione or 3,4-dibutylamino-3-cyclobutene-1,2-dithione **3** with a freshly prepared solution of excess potassium hydrogen sulfide in dry ethanol. The product is the air stable orange yellow potassium salt of the 3-cyclobutene-1,2-dithione-3,4-dimercapto ion $K_2(C_4S_4)\cdot H_2O$ **4** in the form of the monohydrate which dissolves readily in water and can be recrystallized from aqueous ethanol. By heating in air above 120 ^oC, the water of crystallization is removed and a dark violet, strongly hygroscopic modification is formed, which readily reconverts to the hydrated salt when exposed to air. The characteristic orange color of the tetrathiosquarate dianion is due to an intense absorption at 430 nm. The very simple infrared spectrum is dominated by some intense sharp bands around 1240 cm^{-1}, which can be assigned to C–C–S vibrational frequencies. The ^{13}C-NMR spectrum in D_2O shows one signal at $\delta = 229.2$ ppm, indicating that all carbon atoms are equivalent. This is in line with the structure of the ion, determined by an X-ray crystal structure determination of $K_2(C_4S_4)\cdot H_2O$ [20].



Scheme 3 The reaction sequence for the synthesis of tetrathiosquarate according to Seitz [20].

In the crystal structure of $K_2(C_4S_4)\cdot H_2O$ the anions are essentially planar, the average bond distances for C–C and C–S bonds are 1.448(6) Å and 1.663(8) Å respectively. The ions deviate only slightly from ideal D_{4h} symmetry. The arrangement of the four sulfur atoms is a distorted square since the two independent S···S average distances are 3.77 Å for S(1) S(2), S(3)–S(4)and 3.83 Å for S(1)–S(4), S(2)–S(3). The coordination environment for both K^+ ions is rather irregular and can be considered as a distorted square antiprism in which each ion is connected to seven sulfur atoms of five anions with one anion acting as a

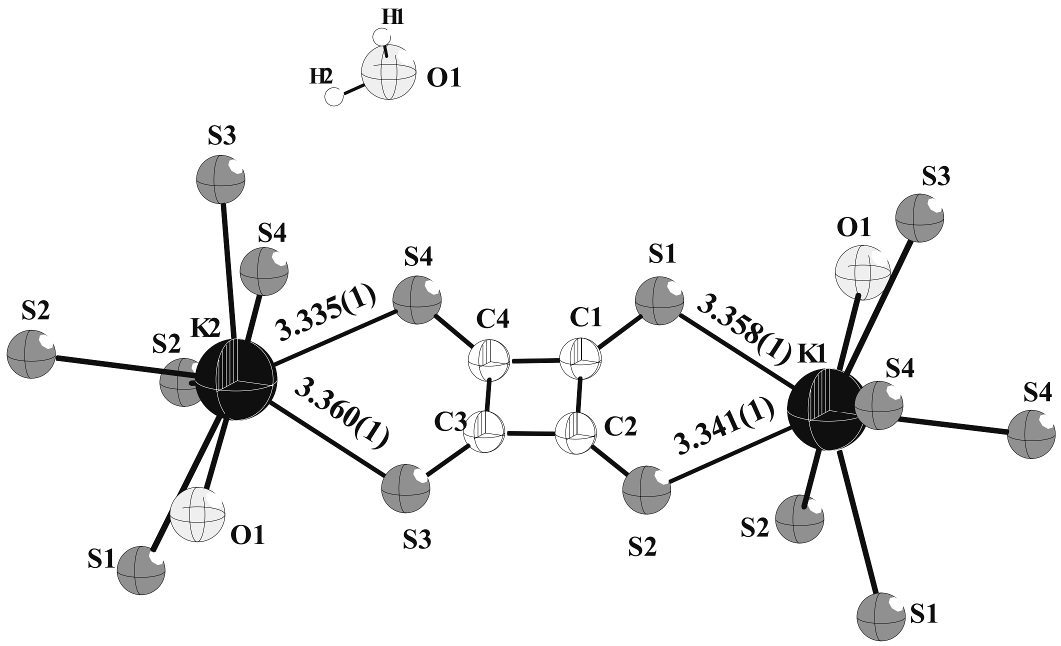


Figure 1 The ions K^+ and $(C_4S_4)^{2-}$ in the structure of $K_2(C_4S_4)\cdot H_2O$ and the coordination of the two independent K^+ ions.

bridging ligand between two cations and one oxygen atom of the water molecule (Figure 1), K(1)–O bond length is 2.911(1) Å and K(2)–O is 2.904(1) Å while the average bond lengths for K–S is 3.383 Å. In the unit cell both cations and anions are stacked along the c-axis (Figure 2) in which every anion is surrounded by six potassium ions. Free tetrathiosquaric acid, $H_2C_4S_4$, cannot be obtained from its dipotassium salt neither with sulfuric acid nor by an acidicly charged ion exchange resin. In both cases an insoluble yellow powder is formed, probably a polymer of the free acid. Beck and coworkers [21] prepared many compounds by reactions of the tetraphenylarsonium salt of tetrathiosquarate with $[(\pi\text{-}C_5H_5)\ (CO)_3M(BF_3)]$ with M = Mo,W or from the potassium salt of tetrathiosquarate with $[(CO)_5Re(H_2O)]^+\ [BF_4]^-$. In both cases the tetrathiosquarate ions react as a two or four dentate ligand, yielding stable compounds.

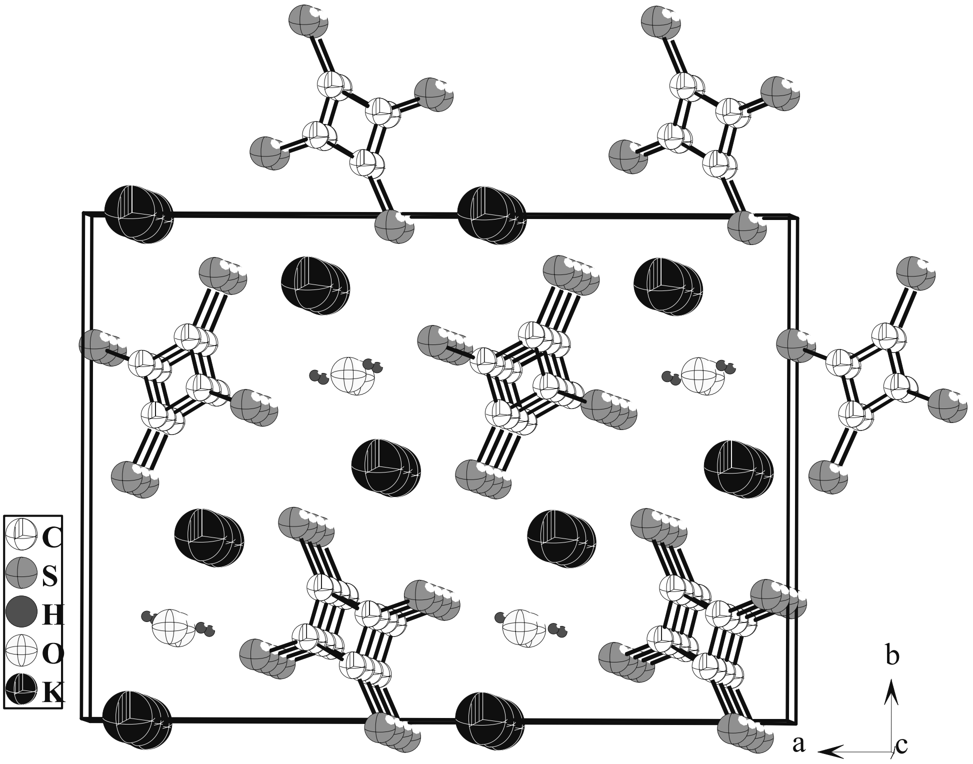
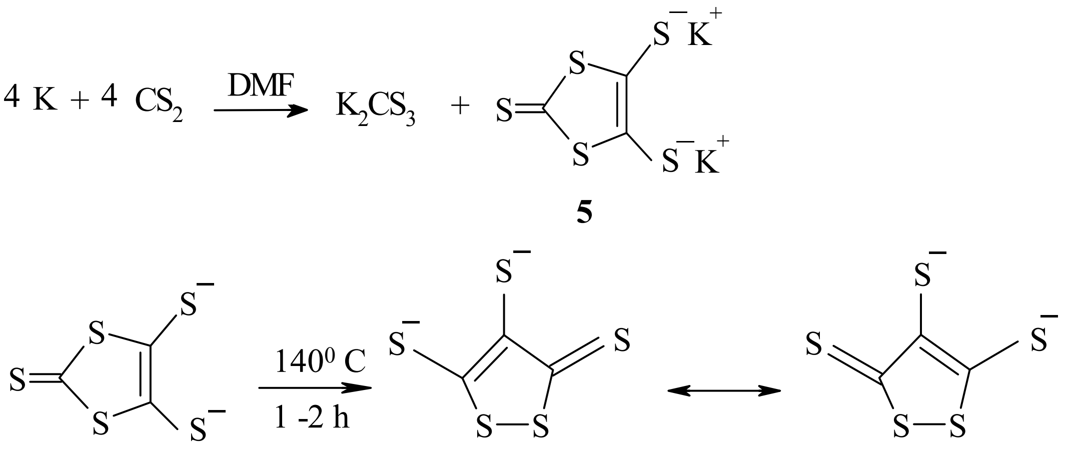


Figure 2 The unit cell of $K_2(C_4S_4)\cdot H_2O$.

Tetrathiosquarate appears in the complexes $[L_nM(C_4S_4)ML_n]^x$ (x =0, ML_n = $Mn(CO)_4$, $Rh(CO)_2$, Rh(COD) and Ir(COD); x =2-, ML_n=$Cr(CO)_4$, $Mo(CO)_4$, $W(CO)_4$ and $Re(CO)_3Br$) as a bischelate ligand. The reaction of $[AsPh_4]_2(C_4S_4)$ gives examples of tetrathiosquarate acting as a bridging bischelate ligand in the complexes $[(PPh_3)_2M(C_4S_4)$-$M(PPh_3)_2]$ (M =Cu,Ag,Rh), $[Ph_3PAu(C_4S_4)AuPPh_3]$, $[AsPh_4]_2[(Ph_3P)_2Pt(C_4S_4)Pt(PPh_3)_2]^{2-}$, $[(Et_3P)_2Pt\text{-}Pt(C_4S_4)Pt(PEt_3)_2]^{2+}(Cl^-)_2$,$[Cl_2Pd(C_4S_4)PdCl_2]$ and $Me_2Au(C_4S_4)AuMe_2$ and as a monochelate in $[AsPh_4]_2[(C_4S_4)Zn(C_4S_4)]$, $[(Ph_2PCH_2CH_2PPh_2)Ni(C_4S_4)]$ and $[AsPh_4]_2$ $[(C_4S_4)Ni(Py)_2(C_4S_4)]\cdot 2py$, of which the structure was determined crystallographically. Furthermore, many polymeric complexes, presumably with chain structures of approximate composition $[M^I_2(C_4S_4)]_n$ in which M^I is Cu, Ag, Au and $[M^{II}(C_4S_4)]_n$ with M^{II} = Cu, Zn, Cd, Hg, Fe, Co, Ni, Pd, Pt,Sn and Pb can be obtained from aqueous solutions of $K_2(C_4S_4)\cdot H_2O$ and the corresponding metal salts. Oligomeric complexes of the type $[AsPh_4]_2[(C_4S_4)M(C_4S_4)\ M(C_4S_4)]^{2-}$ with M = Mn, Fe, Co, Ni have been obtained from nonaqueous solutions [22]. Santos and Mutarelli [23] studied and compared the electronic absorption spectrum and Raman spectra of 10^{-3} M aqueous solutions of tetrathiosquarate with squarate ion. They found that the absence of enhanced totally-symmetric modes and the dispersion of the depolarization ratio are very strong indications that the Jahn – Teller effect is operative as already verified for the squarate ion. The vibrational force field on the basis of the observed infrared and Raman spectra and ab initio molecular orbital (MO) and density functional (DF) calculations of the tetrathiosquarate ion was analyzed [24].

1.2.2 1,2-Dithiole-3-Thione-4,5-Dithiolate Ion β-$(C_3S_5)^{2-}$

Steimecke et al. [25] reported that a mixture of dimethyl formamide (DMF), alkali metal and carbon disulfide CS_2 reacts to give the alkali metal salt of 1,3-dithiole-2-thione-4,5-dithiolate α-$(C_3S_5)^{2-}$ **5**. On heating the products to 120 – 140 °C for 1-2 h, the 1,3-dithiole-2-thione-4,5-dithiolate ion α-$(C_3S_5)^{2-}$ rearranges to 1,2-dithiole-3-thione-4,5-dithiolate β-$(C_3S_5)^{2-}$ **6** (Scheme 4).

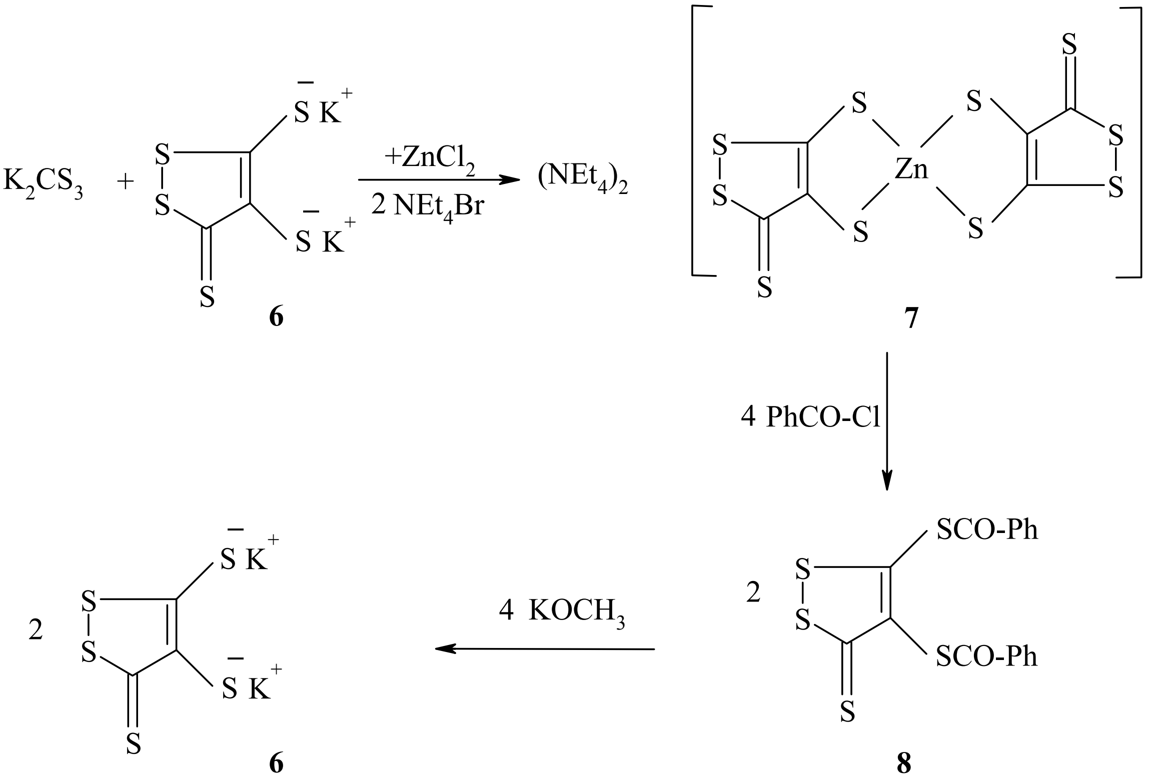


5

5 **6**

Scheme 4 The reaction sequence for the preparation of β-$(C_3S_5)^{2-}$ according to Steimecke [25].

6 is electronically more stable in comparison to **5** due to a higher extent of electron delocalization (as depicted in Scheme 4 with two mesomeric VB formulas). HMO-calculations on α-$(C_3S_5)^{2-}$ and ß-$(C_3S_5)^{2-}$ confirm the higher delocalization energy of the latter, i.e. the α-$(C_3S_5)^{2-}$ to ß-$(C_3S_5)^{2-}$ rearrangement (Steimecke rearrangement) is favored as can be seen from the lowering of the total π-electron energy. The rearrangement process depends on the solvent and on the temperature. On heating K_2 α-(C_3S_5) for 4 hours in acetonitrile or dimethylformamide at 80 °C there is no rearrangement, whereas heating for 3 hours in DMF at 100 °C is sufficient for nearly complete conversion. Using hexamethyl phosphoric triamide (HMPT) as solvent requires 120 °C but only 2 hours. Only ionic derivatives of α-$(C_3S_5)^{2-}$ can be thermally rearranged [26]. Sieler et al. [27] separated β-$(C_3S_5)^{2-}$ by complex formation with $ZnCl_2$ while $(CS_3)^{2-}$ stayed in solution. The zinc complex **7** is then treated with benzoyl chloride to give 4,5-bis(benzoyl-thio)-1,2-dithiole-3-thione **8**. Benzoyl groups are finally cleaved to give the free ion β-$(C_3S_5)^{2-}$ **6** with strong bases as methanolate (Scheme 5).



Scheme 5 The reaction sequence for the separation of K_2β-(C_3S_5) according to Sieler [27].

α- and β-$(C_3S_5)^{2-}$ can be used as ligands in metal complexes. Both act generally as bidentate ligands with two terminal S atoms. Several hundred complexes of α-$(C_3S_5)^{2-}$ have been reported up to now, but only a few complexes of β-$(C_3S_5)^{2-}$. A nickel chelate complex of β-$(C_3S_5)^{2-}$ with the composition $[N(C_4H_9)_4]_2[Ni(C_3S_5)_2]$ was prepared by Lindqvist et al. [28]. Olk et al. [29] synthesized the first trischelates of β-$(C_3S_5)^{2-}$ with the central ions

In(III), Tl(III) and V(IV), also the first x-ray structure of $[NBu_4]_2[V(\beta\text{-}C_3S_5)_3]$ was reported. The EPR parameters of this compound were measured in liquid and frozen acetonic solution and compared with those of the tris(maleonitrile-dithiolato)vanadate(IV) anion supporting a structure of the anion being between octahedral and trigonal prismatic. Starting from $\beta\text{-}(C_3S_5)^{2-}$ Rauchfuss et al. [30] prepared and identified crystalographically the neutral sulfur-carbon compounds C_4S_6, C_5S_7, C_8S_6. Reactions of the disodium salt of $\beta\text{-}(C_3S_5)^{2-}$ with sodium selenopentathionate-3-hydrate $Na_2[Se(S_2O_3)_2]\cdot 3H_2O$ and sodium telluropentathionatehydrate $Na_2[Te(S_2O_3)_2]\cdot 2H_2O$ in the presence of cations $[TeMe_3]^+$, $[AsPh_4]^+$, $[(C_5H_5)_2Co]^+$ and bis(triphenylphosphine)-iminium $(PPN)^+$, yielded the corresponding complexes of stoichiometry $[cation]_2[M(C_3S_5)_2]_2$, M=Se(II) or Te(II). These complexes are thermally unstable and undergo redox decomposition in solution. The reaction of these complexes with iodine or tetracyanoquinodimethane (TCNQ) gave a novel carbon sulfide C_6S_{10} [31]. Reynolds et al. [32] prepared an anionic tetrameric copper complex containing a planer eight-membered ring core $[NBu_4]_2$- $[Cu(\beta\text{-}C_3S_5)]_4$ using $[NBu_4]_2[Zn(\beta\text{-}C_3S_5)_2]$, $[NBu_4]_2$(tetrathiooxalate) and $CuCl_2$. The anion consists of four $\beta\text{-}(C_3S_5)^{2-}$ and four copper ion metal centers. Each $\beta\text{-}(C_3S_5)^{2-}$ ligand is coordinated to two Cu ions. In this complex the ligand shows a unique coordination behavior (Figure 1). A new sulfur-carbon anion $(C_6S_{10})^{2-}$ was prepared and crystalographically characterized by Rauchfuss et al. [33]. Red-orange crystals of the one-electron oxidized product $[Me_4N]_2$ (C_6S_{10}) were obtained by the treatment of $\alpha\text{-}(C_3S_5)_x$ with 1 equivalent of $[Me_4N]_2(C_3S_5)$. Figure 2 shows the structure of the anion. Additional insights into the redox properties of $[Me_4N]_2$ (C_3S_5) and $[Me_4N]_2(C_6S_{10})$ were obtained using cyclic voltammetry. Beck et al. [34] prepared $\beta\text{-}(C_6S_8)$ which is a second crystallographic form of C_6S_8 which was prepared earlier by Rauchfuss et al. [30]. C_6S_8 is now known in two forms, the planar $\alpha\text{-}(C_6S_8)$ and the bent, butterfly shaped $\beta\text{-}(C_6S_8)$.

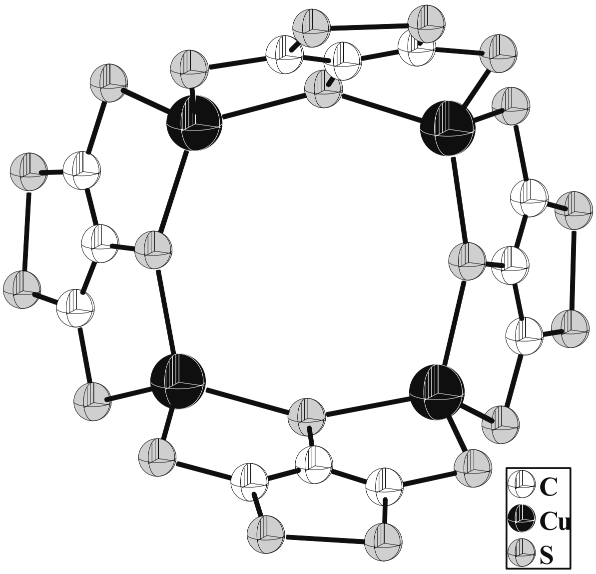


Figure 3 The complex $[Cu(\beta\text{-}C_3S_5)]_4^{2-}$ in the structure of the $[NBu_4]^+$ salt [32].

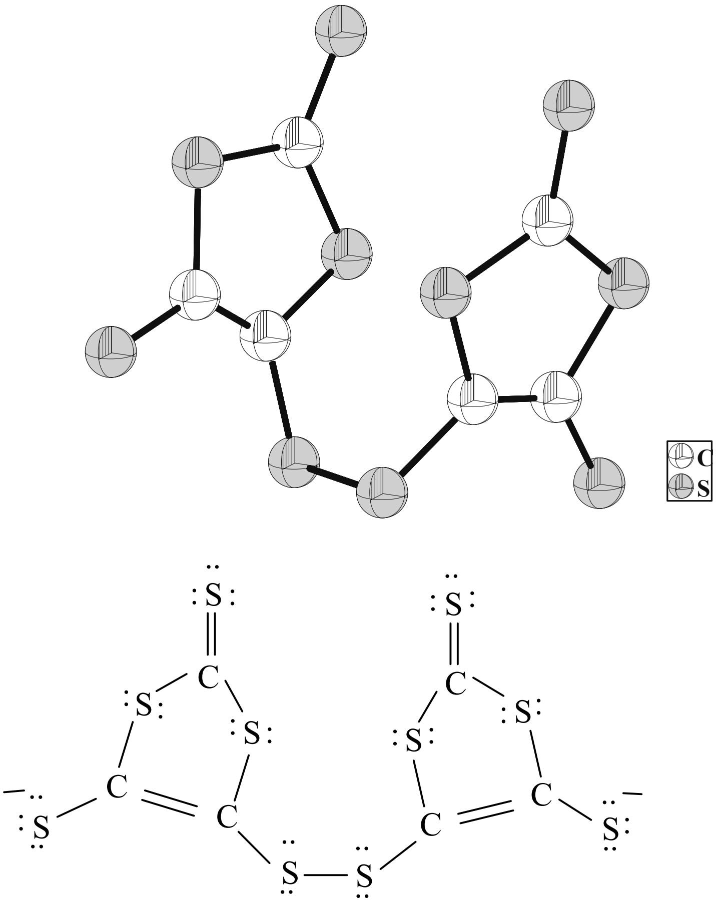


Figure 4 Molecular structure and electronic formula of the anion $(C_6S_{10})^{2-}$ as its $[NBu_4]^+$ salt [33].

The molecules in β-C_6S_8 are folded along the S-S axis of the central 1,4-dithine ring, the dihedral angle between the two planar C_3S_5 moieties is 133°. Beck et al. [35] prepared α,α–C_4S_6 and α,β–C_4S_6 by the reaction of the α and β forms of $(C_3S_5)^{2-}$ with thiophosgene respectively. α,α–C_4S_6 is unstable with respect to α,β–C_4S_6. The molecular rearrangement can be induced by a short thermal treatment at 150 °C. Only α,β-C_4S_6 formed a stable adduct with I_2 (α,β-$C_4S_6 \cdot I_2$) which was already known [36] but a second polymorph could be obtained.

In general, the chemistry of β-$(C_3S_5)^{2-}$ and $(C_4S_4)^{2-}$ ions is not well explored and the literature does not contain more than forty references on this subject. There are only some few reports on the structural chemistry of the simple salts of these two ions, only the crystal structures of $K_2C_4S_4 \cdot H_2O$ [20] and K_2β-(C_3S_5) [27] are reported. All the known complexes of these two ligands were so far prepared in nonaqueous solvents and there is no reference included the preparation of any metal complex of one of the two ligands in an aqueous solvent. For these reasons and the importance of these compounds a deeper knowledge of the simple salts of these two ligands is desirable. The work presented here deals with the so far unknown class of the earth alkaline and transition metal salts of $(C_4S_4)^{2-}$ and the aqueous chemistry of β-$(C_3S_5)^{2-}$.

Chapter Two

Experimental

2.1 Materials and Reagents

All purchased materials used in this work were of the highest available purity and used without further purification. They included 3,4-dihbutoxy-3-cyclobutene-1,2-dione (squaric acid dibutylester) **1**, N-butylamine $CH_3(CH_2)_3NH_2$, phosphorus pentasulfide P_4S_{10}, carbon disulfide CS_2, potassium metal, zinc chloride $ZnCl_2$, tetraethyl ammonium bromide $[NEt_4]Br$, benzoyl chloride C_6H_5COCl, potassium methoxide $KOCH_3$, metal(II) chloride hexahydrate, $MCl_2{\cdot}6H_2O$, M = Mg, Sr, Ba and Fe, metal (II)chloride tetrahydrate, $MCl_2{\cdot}4H_2O$, M = Ca and Mn, tetraphenylarsonium chloride $[As(C_6H_5)_4]Cl$. Potassium hydrogen sulfide KHS, was prepared from hydrogen sulfide H_2S and potassium ethoxide KOC_2H_5 as described [37]. The solvents used were tetrahydrofuran THF, ethanol CH_3CH_2OH, Acetone CH_3COCH_3, diethyl ether $C_2H_5OC_2H_5$, methylene chloride CH_2Cl_2, dimethylformamide DMF and distilled water.

2.2 Preparation of the Potassium Salt of Tetrathiosquarate

The synthesis of $K_2(C_4S_4){\cdot}H_2O$ involves three steps [20]. The reaction sequence is depicted in Scheme 3. 9.88 ml (0.10 mol) of n-butylamine were slowly added with a dropping funnel to 10.8 ml (0.05 mol) of squaric acid dibutylester **1** in 40 ml ethanol in a two neck round bottom flask cooled to 5 °C by an ice bath. The formed white precipitate of 3,4-dibutylamino-3-cyclobutene-1,2-dione (squaric acid dibutylamine) **2** was filtered and washed several times with ether.

4.48 g (0.02 mol) of **2** were dissolved in 400 ml of methylene chloride and 4.44 g (0.01 mol) of phosphorus pentasulfide were added in one portion and stirred for 3 hours. 100 ml of ethanol were added to the solution and stirred for 10 minutes, then the solvent was distilled off until one third of the original volume was reached and another 100 ml of ethanol were added. A yellow precipitate of **3** was formed which was filtered off, washed with ether and kept under vacuum over P_2O_5.

3.75 g (0.015 mol) of **3** and 2.25 g (0.03 mol) of freshly prepared of potassium hydrogen sulfide KHS were dissolved in 40 ml of ethanol and stirred for about 1 hour. Then 10-15 ml of ether was added to the solution and stirred for 15 minutes. The orange yellow precipitate of hydrated potassium salt of tetrathiosquarate $K_2(C_4S_4){\cdot}H_2O$ **4** was filtered and washed with ether. This product was purified by recrystallization. About 5 g of **4** were suspended in ethanol which was heated to the boiling point. Water was then added dropwise until all **4** dissolved in the boiling ethanol/water mixture. On slow cooling long, orange needle shaped crystals of **4** crystallized.

2.3 Preparation of the potassium salt of β-$(C_3S_5)^{2-}$

The reduction of CS_2 with potassium metal in dimethylformamide DMF gives a mixture of potassium trithiocarbonate K_2CS_3 and potassium-1,3-dithiole-2-thione-4,5-dithiolate, α-$(C_3S_5)^{2-}$ **5** (Scheme 4) which isomerizes quantitatively within 1-2 h at 120-140 °C to 1,2-dithiole-3-thione-4,5-dithiolate, β-$(C_3S_5)^{2-}$ **6**, which was separated by complex formation with $ZnCl_2$ and $[NEt_4]Br$ while $(CS_3)^{2-}$ stayed in solution. The zinc complex **7** is treated with benzoyl chloride to give 4,5-bis(benzoyl-thio)-1,2-dithiole-3-thione **8**. Benzoyl groups are cleaved with a strong base such as potassium methoxide CH_3OK in methanol [27]. $K_2\beta$-(C_3S_5) is obtained as a dark red powder, which is soluble in water.

2.4 Preparation of Tetrathiosquarate Salts

2.4.1 Preparation of Earth Alkaline Salts of Tetrathiosquarate

2.4.1.1 Preparation of $Mg(C_4S_4)\cdot 6H_2O$

The magnesium salt of tetrathiosquarate was prepared by mixing aqueous solutions of 0.203 g (0.001mol) of $MgCl_2\cdot 6H_2O$ in 10 ml H_2O and 0.272 g (0.001 mol) of $K_2(C_4S_4)\cdot H_2O$ in 10 ml H_2O. The resulting brownish-yellow solution slowly evaporated at room temperature to get a crystalline mixture of almost colorless crystals of KCl, and of light orange, block shaped crystals of $Mg(C_4S_4)\cdot 6H_2O$ which were separated by hand.

$$K_2(C_4S_4)\cdot H_2O + MgCl_2\cdot 6H_2O \longrightarrow Mg(C_4S_4)\cdot 6H_2O + 2\,KCl + H_2O$$

2.4.1.2 Preparation of $Ca(C_4S_4)\cdot 4H_2O$

The calcium salt of tetrathiosquarate was prepared by mixing aqueous solutions of 0.183 g (0.001mol) of $CaCl_2\cdot 4H_2O$ in 10 ml H_2O and 0.272 g (0.001 mol) of $K_2(C_4S_4)\cdot H_2O$ in 10 ml H_2O. The resulting brownish-yellow solution slowly evaporated at room temperature to get a crystalline mixture of almost colorless crystals of KCl, and of light red, block shaped crystals of $Ca(C_4S_4)\cdot 4H_2O$ which were separated by hand.

$$K_2(C_4S_4)\cdot H_2O + CaCl_2\cdot 4H_2O \longrightarrow Ca(C_4S_4)\cdot 4H_2O + 2\,KCl + H_2O$$

2.4.1.3 Preparation of $Sr(C_4S_4)\cdot 4H_2O$

The strontium salt of tetrathiosquarate was prepared by mixing aqueous solutions of 0.267 g (0.001mol) of $SrCl_2\cdot 6H_2O$ in 10 ml H_2O and 0.272 g (0.001 mol) of $K_2(C_4S_4)\cdot H_2O$ in 10 ml H_2O. The resulting brownish-yellow solution slowly evaporated at room temperature to get a crystalline mixture of almost colorless crystals of KCl, and of light red, block shaped crystals of $Sr(C_4S_4)\cdot 4H_2O$ which were separated by hand.

$$K_2(C_4S_4)\cdot H_2O + SrCl_2\cdot 6H_2O \longrightarrow Sr(C_4S_4)\cdot 4H_2O + 2\,KCl + 3H_2O$$

2.4.1.4 Preparation of $Ba_4K_2(C_4S_4)_5\cdot 16H_2O$

The mixed barium-potassium salt of tetrathiosquarate was prepared by mixing aqueous solutions of 0.316 g (0.001mol) of $BaCl_2\cdot 6H_2O$ in 10 ml H_2O and 0.341 g (0.00125 mol) of $K_2(C_4S_4)\cdot H_2O$ in 10 ml H_2O. On slow evaporation of the resulting brownish-yellow solution, dark red, block shaped crystals of $Ba_4K_2(C_4S_4)_5\cdot 16H_2O$ slowly precipitated. The crystals were filtered off.

$$5\,K_2(C_4S_4)\cdot H_2O + 4BaCl_2\cdot 6H_2O \longrightarrow Ba_4K_2(C_4S_4)_5\cdot 16H_2O + 8KCl + 13H_2O$$

2.4.2 Preparation of Transition Metal Salts of Tetrathiosquarate

2.4.2.1 Preparation of the Fe(II) Salt of Tetrathiosquarate

An aqueous concentrated solution of 0.235 g (0.001 mol) $FeCl_2\cdot 6H_2O$ in 10 ml water was added to an aqueous concentrated solution of 0.272 g (0.001 mol) $K_2(C_4S_4)\cdot H_2O$ in 10 ml water. A brown precipitate was formed immediately. The solution was filtered and the resulting brownish-yellow filtrate slowly evaporated at room temperature to get dark red, block shaped crystals of $[Fe(H_2O)_2](C_4S_4)\cdot 4H_2O$.

$$K_2(C_4S_4)\cdot H_2O + FeCl_2 \cdot 6H_2O \longrightarrow [Fe(H_2O)_2](C_4S_4)\cdot 4H_2O + 2\ KCl + H_2O$$

2.4.2.2 Preparation of the Mn(II) Salt of Tetrathiosquarate

An aqueous concentrated solution of 0.396 g (0.002 mol) $MnCl_2\cdot 4H_2O$ in 15 ml water was added to an aqueous concentrated solution of 0.272 g (0.001 mol) $K_2(C_4S_4)\cdot H_2O$ in 10 ml water. The brownish-yellow solution was slowly evaporated at room temperature to get bright red, cube shaped, small crystals with edge lengths of about 0.1 mm of $[Mn_4(OH)_4(H_2O)_4](C_4S_4)_2$ in small yield, less than 10 %.

$$2\ K_2(C_4S_4)\cdot H_2O + 4\ MnCl_2 \cdot 4H_2O \longrightarrow [Mn_4(OH)_4(H_2O)_4](C_4S_4)_2 + 4\ KCl + 10H_2O + 4HCl$$

2.5 Preparation of Metal Salts of 1,2-Dithiole-3-thione-4,5-dithiolate

2.5.1 Preparation of Ca^{2+} and Sr^{2+} Salts of β-$(C_3S_5)^{2-}$

Mixing of solutions of 0.183 g (0.001 mol) $CaCl_2\cdot 4H_2O$ in 10 ml water or 0.267 g (0.001 mol) $SrCl_2\cdot 6H_2O$ in 10 ml water and 0.549 g (0.002 mol) $K_2(C_3S_5)$ in 20 ml water in an open glass dish resulted in brownish-yellow solutions which were slowly evaporated at room temperature to get a crystalline mixture of almost colorless crystals of KCl and of orange and red octahedral shaped crystals of $[Ca(H_2O)_7](C_6S_{10})$ and $[Sr(H_2O)_8](C_6S_{10})\cdot H_2O$, respectively.

$$2\ K_2(C_3S_5) + \tfrac{1}{2}\ O_2 + CaCl_2\cdot 4H_2O + 4\ H_2O \longrightarrow [Ca(H_2O)_7](C_6S_{10}) + 2\ KCl + 2\ KOH$$

$$2\ K_2(C_3S_5) + \tfrac{1}{2}\ O_2 + SrCl_2\cdot 6H_2O + 4\ H_2O \longrightarrow [Sr(H_2O)_8](C_6S_{10})\cdot H_2O + 2KCl + 2KOH$$

2.5.2 Preparation of Tetraphenylarsonium Salts of β-$(C_3S_5)^{2-}$

2.5.2.1 Preparation in Air

Solutions of 0.79 g (0.0015mol) tetraphenylarsonium chloride $[As(C_6H_5)_4]Cl\cdot 6H_2O$ in 20 ml water and 10 ml ethanol and 0.275 g (0.001 mol) $K_2(C_3S_5)$ in 10 ml water were mixed in an open glass dish and 5 ml ethanol was added. The resulting yellowish orange solution was slowly evaporated at room temperature. Within one day light yellow crystals of $[As(C_6H_5)_4](HC_3S_5)$ and $[As(C_6H_5)_4]_2(C_3S_5)\cdot 2H_2O$ formed which were separated by hand. On keeping the glass dish covered with a glass plate to avoid rapid solvent evaporation light yellow orange crystals of $[As(C_6H_5)_4]_2(C_3S_6O_3)\cdot 3H_2O$ were formed.

$$3\,[As(C_6H_5)_4]Cl\cdot 6H_2O + 2\,K_2C_3S_5 \longrightarrow [As(C_6H_5)_4](HC_3S_5) + 3\,KCl + KOH + [As(C_6H_5)_4]_2(C_3S_5)\cdot 2H_2O + 3\,H_2O$$

$$2\,[As(C_6H_5)_4]_2(C_3S_5)\cdot 2H_2O + 3/2\,O_2 \longrightarrow [As(C_6H_5)_4]_2(C_3S_6O_3)\cdot 3H_2O + [As(C_6H_5)_4](C_3S_4H) + [As(C_6H_5)_4]OH$$

2.5.2.2 Under Exclusion of Air

Preparations were performed by mixing solutions of 0.526 g (0.001 mol) tetraphenylarsonium chloride $[As(C_6H_5)_4]Cl\cdot 6H_2O$ in 10 ml water and 5 ml ethanol and 0.136 g (0.0005 mol) $K_2(C_3S_5)$ in 10 ml water and 5 ml ethanol in a glass tube, equipped with a quick fit stopper. The tube was filled with argon gas, and tightly closed to prevent from air. After 5 to 6 days a few light brown crystals of $[As(C_6H_5)_4](C_3S_4H)$ appeared and a pale yellow powder was formed on the wall of the tube.

$$2\,[As(C_6H_5)_4]Cl\cdot 6H_2O + K_2(C_3S_5) \longrightarrow [As(C_6H_5)_4]C_3S_4H + [As(C_6H_5)_4]OH + 2\,KCl + 1/8\,S_8 + 5\,H_2O$$

2.6 Analyses and Physical Measurements

IR spectra in the region 400 – 4000 cm^{-1} were recorded with a Burker IFS 113v spectrometer at room temperature. Spectra of the solid samples were obtained in nujol mulls or in KBr pellets (1wt %). Raman spectra in the region 50–4000 cm^{-1} were recorded with FT Raman spectrometer RFS 100 Burker Neodym-YAG laser (λ= 1064 nm) at room temperature.

2.7 Crystallography

The diffraction quality of all crystals from compounds under study was checked out using a precession Buerger camera with image plate films. Data collection and unit cell determinations were carried out at room temperature using an automatic four-circle CAD-4 diffractometer for the crystal of $[Mg(H_2O)_6][C_4S_4]$ and a Nonius kappa-CCD diffractometer for crystals of all other compounds under study. The diffraction intensities were corrected for Lorenz, polarization and absorption effects. The structures of all crystals were solved with SHELXS97 [38] using direct methods. The refinements were performed with full matrix least squares on F^2 with the program SHELXL93 [39]. A geometrical analysis was performed using SHELXL93 [39]. The graphical representations were drawn with the program Diamond 2 [40].

Chapter Three

Results and Discussion

3.1 Earth Alkaline Tetrathiosquarate Salts

3.1.1 Structure Determination of $[Mg(H_2O)_6](C_4S_4)$

The crystals of this compound are sensitive towards the loss of water and were therefore sealed in glass capillaries. The diffraction quality of the crystals towards X-rays was checked by preliminary precession exposures. which showed the monoclinic symmetry. Data were collected at ambient temperature using a Nonius CAD–4 diffractometer equipped with Cu-Kα radiation (λ = 1.5418 Å). The space group is not unequivocal and could be derived from the data set as *C*2/*c* (№ 15) or *Cc* (№ 9) which can not be distinguished from the diffraction pattern. A structure model was obtained by direct method [38] and refined against F^2 with anisotropic displacement parameters for all non-hydrogen atoms in the centrosymmetric space group *C*2/*c* [39]. The H atoms were all identified in a difference Fourier synthesis. They were included as individual atoms with free positional and isotropic displacement parameters in the refinement. Crystallographic data and details of the structure analyses are given in Table 1. positional parameters. equivalent isotropic parameters for the non-H atoms and isotropic displacement parameters for H atoms in Table 2. anisotropic displacement parameters in Table 3 and some selected bond lengths and angles in Table 4.

Table 1 Crystallographic data and details of the structure determination $[Mg(H_2O)_6](C_4S_4)$.

Formula	$C_4H_{12}MgO_6S_4$
Lattice constants	a = 17.228(7) Å
	b = 5.919(2) Å, β = 104.73(3)°
	c = 13.148(4) Å
Volume of unit cell	1296.56 $Å^3$
Number of formula units	Z = 8
Density (calc.)	$\rho = 1.581$ g · cm^{-3}
Absorption coefficient	$\mu = 7.80$ cm^{-1}
Crystal system, space group	Monoclinic, *C*2/*c* (№ 15)
Diffractometer	CAD – 4
Radiation, wave length	Cu-Kα, λ = 1.5418 Å
Temperature of measurement	T = 293 K
Range of data collection	$2\theta < 44.15°$
Number of data collected	5678
Number of independent reflections, R_{merge}	801, 8.11%
Number of refined parameters	94
Ratio reflections/parameters	8.5
R(|F|) for all reflections	2.66%
R(|F|) for 768 reflections with $F_0 > 4\sigma(F_0)$	2.52 %
$wR(F^2)$	6.36 %
Largest electron density difference peak and hole	+0.18 / -0.23 e /Å3

Table 2 Positional parameters, equivalent isotropic parameters U_{eq} / Å^2 for the non-H atoms and isotropic displacement parameters for H atoms in the structure of [Mg(H_2O)$_6$](C_4S_4). Standard deviations are given in parentheses.

Atom	**x**	**y**	**z**	**U_{eq}**
Mg	1.0000	0.57999(13)	0.7500	0.0254(3)
S1	0.89638(3)	0.09352(8)	0.50126(5)	0.0332(3)
S2	0.73739(3)	-0.06860(10)	0.64052(5)	0.0441(3)
C1	0.80540(11)	0.1892(3)	0.49998(17)	0.0286(5)
C2	0.74496(12)	0.1284(3)	0.55411(18)	0.0297(5)
O1	1.08208(9)	0.8232(3)	0.72917(16)	0.0337(4)
H11	1.0894(15)	0.827(5)	0.669(3)	0.059(10)
H12	1.128(2)	0.840(6)	0.770(3)	0.094(12)
O2	0.92612(10)	0.3285(3)	0.77932(15)	0.0431(5)
H21	0.8882(16)	0.359(4)	0.802(2)	0.057(9)
H22	0.9328(17)	0.199(6)	0.770(3)	0.088(12)
O3	1.05260(11)	0.5999(3)	0.90762(15)	0.0413(5)
H31	1.0778(14)	0.707(5)	0.940(2)	0.057(9)
H32	1.0690(18)	0.492(5)	0.951(3)	0.081(11)

Table 3 Anisotropic displacement parameters U_{ij} [Å^2] for the non-H atoms in the structure of [Mg(H_2O)$_6$](C_4S_4). Standard deviations are given in parentheses.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{12}**	**U_{13}**	**U_{23}**
Mg	0.0289(5)	0.0195(5)	0.0306(7)	0	0.0131(5)	0
S1	0.0321(4)	0.0313(4)	0.0413(5)	0.0059(2)	0.0189(3)	0.0080(2)
S2	0.0347(4)	0.0482(1)	0.0552(1)	0.0076(2)	0.0224(1)	0.0288(1)
C1	0.032(1)	0.025(1)	0.030(1)	-0.0028(9)	0.011(1)	0.00005(0)
C2	0.030(1)	0.029(1)	0.032(1)	-0.0008(9)	0.011(1)	0.002(1)
O1	0.0351(9)	0.0340(9)	0.035(1)	-0.0072(7)	0.0153(9)	-0.0015(7)
O2	0.046(1)	0.027(1)	0.066(1)	-0.0056(7)	0.032(1)	-0.0022(8)
O3	0.055(1)	0.029(1)	0.035(1)	0.0009(8)	0.004(1)	-0.0003(8)

Table 4 Selected bond lengths / Å and angles /° for $[Mg(H_2O)_6](C_4S_4)$. Symmetry operations: I=1.5-x, 0.5-y, 1-z ; II= 2-x, y, 1.5-z.

Mg(1)–O(1)	2.084 (2)	Mg (1)–O(1)^{II}	2.084 (2)
Mg(1)–O(2)	2.058 (2)	Mg (1)–O(2)^{II}	2.058 (2)
Mg(1)–O(3)	2.043 (2)	Mg (1)–O(3)^{II}	2.043 (2)
C(1)–C(2)	1.448 (3)	S(1)–C(1)	1.663 (2)
C(1)–C(2)^{I}	1.453 (3)	S(2)–C(2)	1.656 (2)
C(2)–C(1)^{I}	1.453 (3)		
O(1)–Mg(1)–O(1)^{II}	92.6 (1)	O(2)–Mg (1)–O(3)	89.29 (7)
O(1)–Mg(1)O(2)^{II}	90.14 (8)	O(3)–Mg(1)–O(3)^{II}	173.4 (1)
O(1)–Mg(1)–O(2)	175.53(7)	O(1)^{II}–Mg(1)–O(3)^{II}	87.29 (8)
C(1)–C(2)–C(1)^{I}	89.39 (2)	S(1)–C(1)–C(2)	134.77(2)
C(2)–C(1)–C(2)^{I}	90.61 (1)	S(2)–C(2)–C(1)	134.75(2)

3.1.2 Discussion of the Structure of $[Mg(H_2O)_6](C_4S_4)$

The crystal structure of $[Mg(H_2O)_6](C_4S_4)$ is built of octahedral $[Mg(H_2O)_6]^{2+}$ complexes and of planar $(C_4S_4)^{2-}$ ions (Figure 5). Mg atoms are located on the special positions 4*e* on twofold axes giving the $[Mg(H_2O)_6]^{2+}$ complexes crystallographic C_2 symmetry. The twofold axes bisect the O(1)–O(1)^{II} and O(2)–O(2)^{II} edges of the MgO_6 octahedra passing through Mg. The Mg–O bonds of 2.043 to 2.084 Å are rather uniform. but the O–Mg–O angles of 87.29 to 95.49° show substantial deviations from octahedral symmetry (Table 3). The H atoms of the six H_2O ligands are pointing to different directions according to the C_2 point symmetry of the complexes.

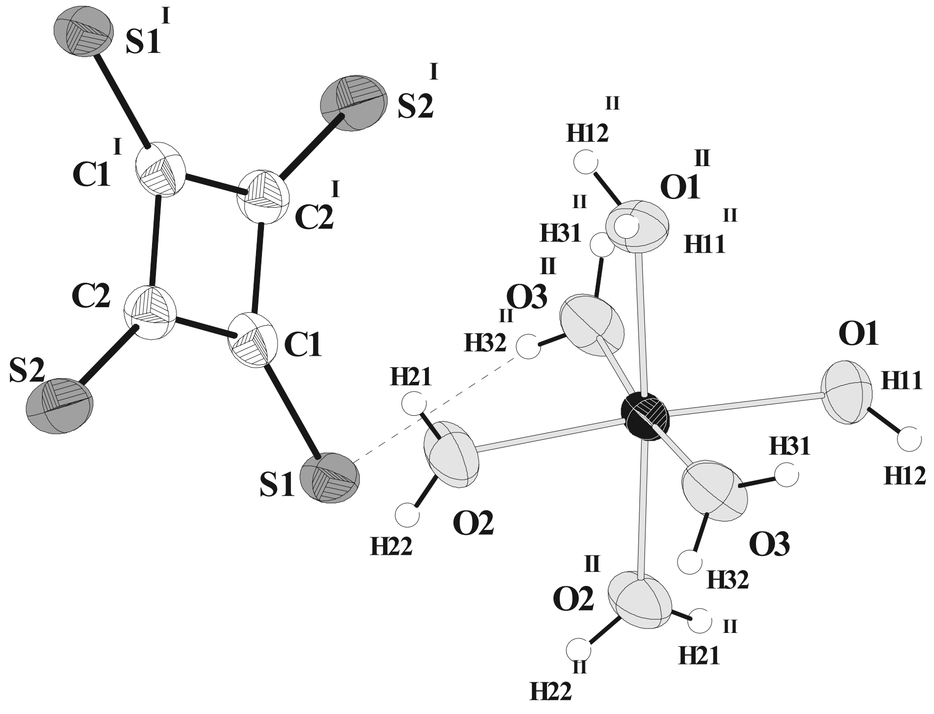


Figure 5 The ions $[Mg(H_2O)_6]^{2+}$ and $(C_4S_4)^{2-}$ in the structure of $[Mg(H_2O)_6]$ (C_4S_4). Thermal ellipsoids are drawn to include a probability density of 50%. Symmetry operations: I =1.5-x, 0.5-y, 1-z ; II = 2-x, y, 1.5-z.

The tetrathiosquarate ions are located at inversion centers. giving the ions crystallographic C_i symmetry (Figure 5). The anions are essentially planar. The largest deviation from the least squares plane through all four carbon atoms observed for C(1) and C(1)^I with only 0.005 Å, with C–C bonds of 1.443 and 1.448 Å. C–S bonds of 1.656 and 1.663 Å the ions deviate only slightly from ideal D_{4h} symmetry. Even the two independent S···S distances are almost identical (3.79 and 3.81Å). The observed structural parameters are close to those observed for $K_2(C_4S_4)\cdot H_2O$, where, however, a larger deviation from ideal structural parameters was found [20].

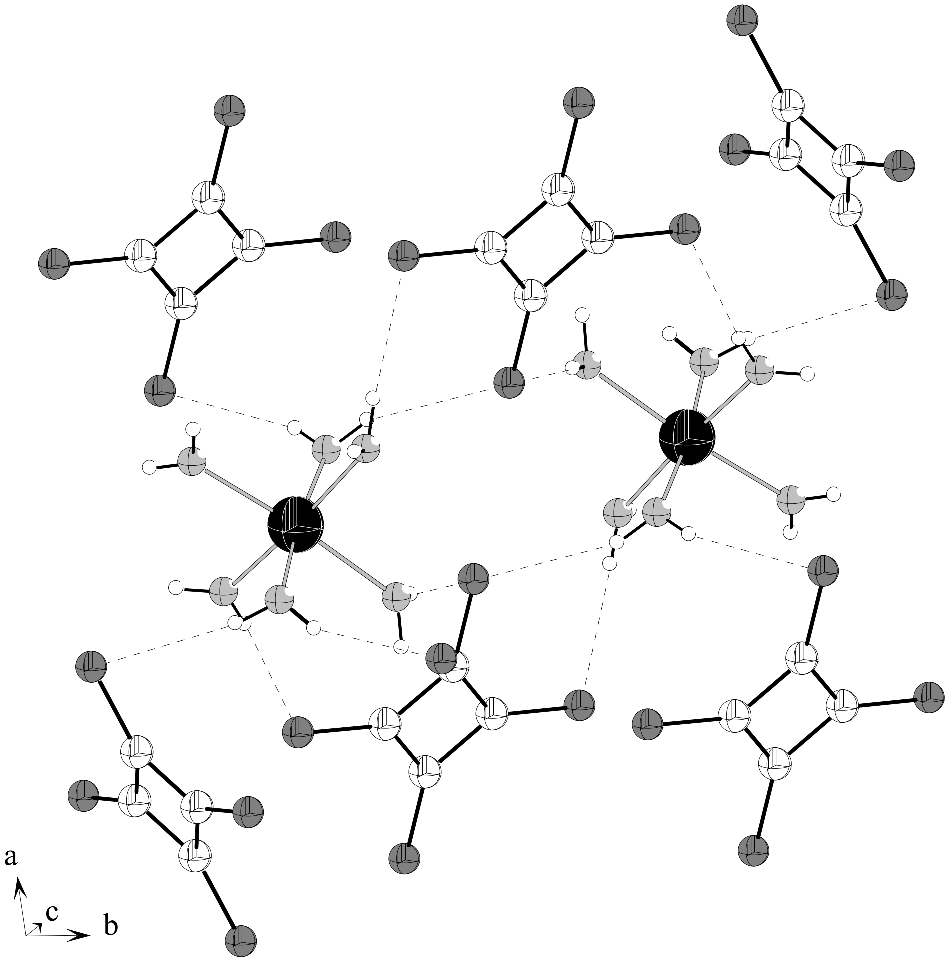


Figure 6 The interconnection of the $[Mg(H_2O)_6]^{2+}$ and $(C_4S_4)^{2-}$ ions by O–H···O and O–H···S bridges in the structure of $[Mg(H_2O)_6](C_4S_4)$.

The $[Mg(H_2O)_6]^{2+}$ complexes and the $(C_4S_4)^{2-}$anions are connected via a three-dimensional net of O–H···O and O–H···S bridges (Figure 6). O–H···O bridges connect the $[Mg(H_2O)_6]^{2+}$ complexes to a one-dimensional strand along the *b*-axis with O(1)·····O(2) distances of 2.994 Å and H(22)·····$O(1)^{II}$ distances of 2.241 Å. Several O·····S distances shorter than the sum of van der Waals radii (3.32 Å [41]) are observed {O(1)·····$S(1)^{II}$ 3.183. O(1)·····$S(2)^{II}$ 3.211. O(2)·····$S(2)^{I}$ 3.306. O(3)·····$S(1)^{II}$ 3.195 and O(3)·····$S(1)^{II}$ 3.264 Å} with O–H···O and O–H···S angles between 154.5 to 174.3°. Each $[Mg(H_2O)_6]^{2+}$ is connected with two neighbored Mg complexes and six $(C_4S_4)^{2-}$ ions. Hydrogen bridges with H·····A < r(A) + 2.0 Å of 2.41 Å for H(22)·····O(1)^{II} to 2.501 Å for H(21)·····S(2)^{I} are observed [42]. In the unit cell, cations and anions are arranged regularly. Each cation is surrounded by six anions and each anion by six cations in distorted octahedral fashions (Figure 7). Simplifying the crystal structure to the positions of the Mg^{2+} and the inversion centers in the $(C_4S_4)^{2-}$ ions allows for the investigation of the packing. These centers of gravity of the ions form the motif of the simple rock salt structure type (Figure 8).

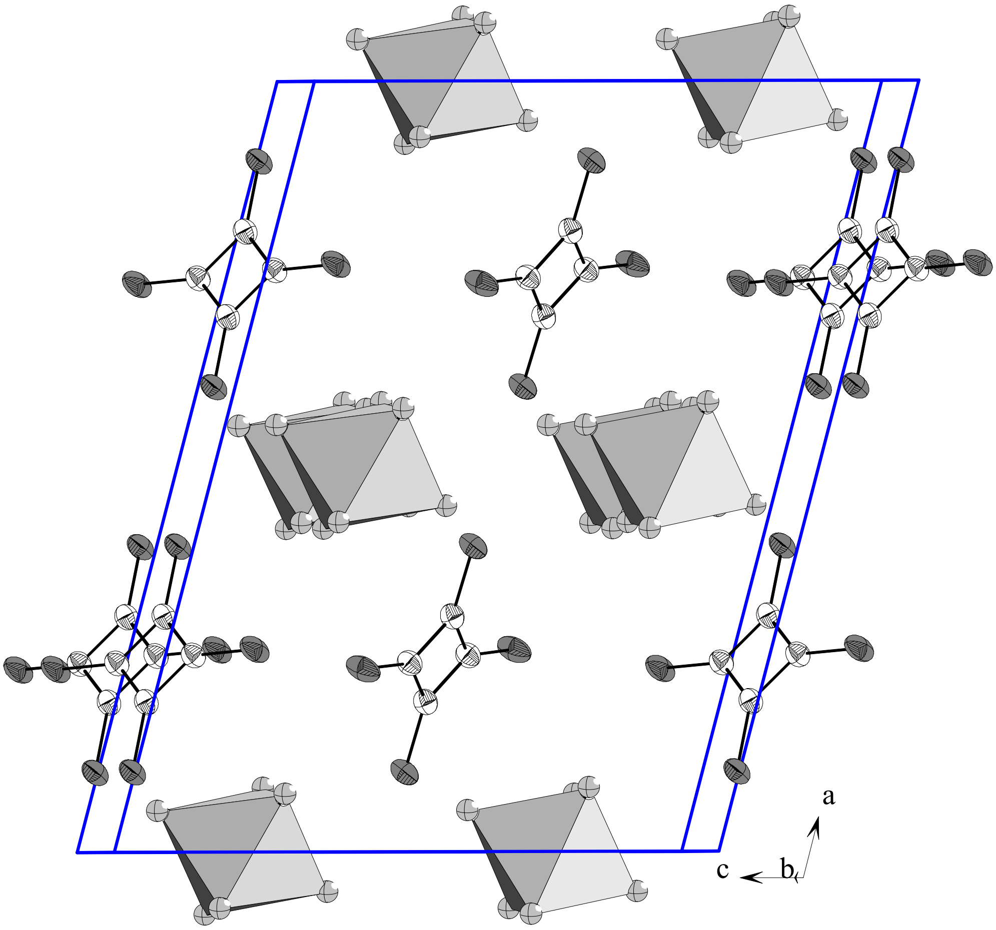


Figure 7 The unit cell of $[Mg(H_2O)_6](C_4S_4)$ in a view slightly inclined to the *b*-axis. $[Mg(H_2O)_6]^{2+}$ complexes are depicted as massive octahedra.

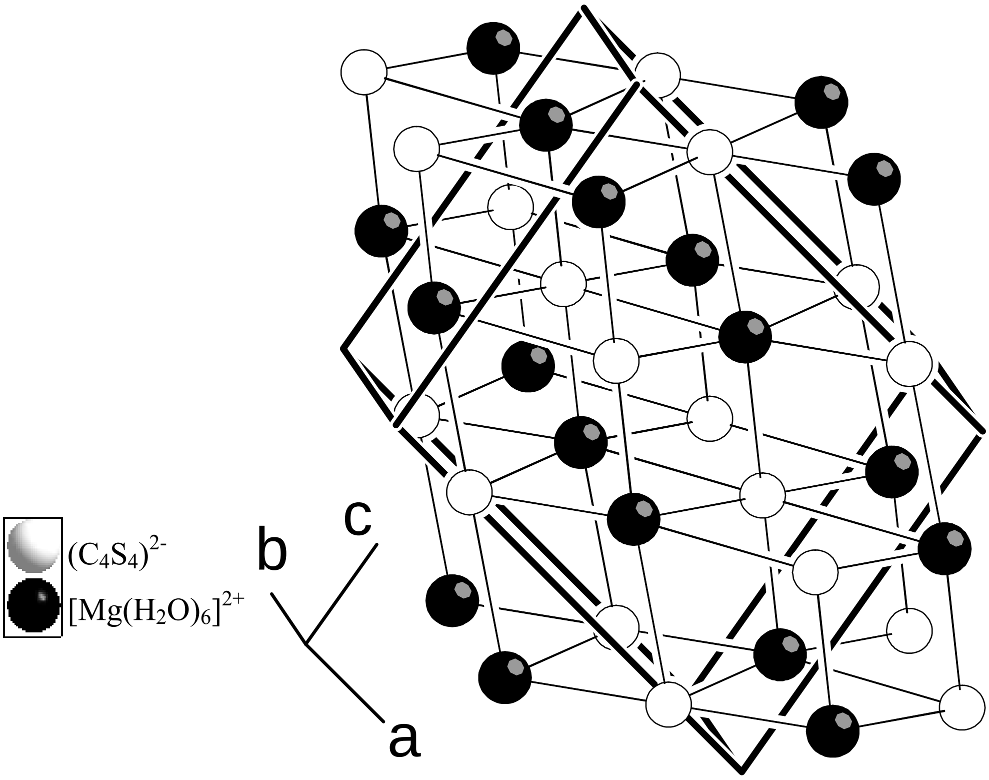


Figure 8 The simplified structure of $[Mg(H_2O)_6](C_4S_4)$. The complex cations and the anions are represented as black and white spheres. The crystallographic unit cell of $[Mg(H_2O)_6](C_4S_4)$ is shown with bold lines. The thin lines between the spheres representing the cations and anions show the three-dimensional net of the NaCl structure type.

3.1.3 Structure Determination of $[Ca(H_2O)_4](C_4S_4)$

The crystals of this compound are sensitive towards the loss of water and were therefore sealed in glass capillaries. The diffraction quality of the crystals towards X-rays was checked by preliminary precession exposures, which showed the monoclinic symmetry. Data were collected at ambient temperature using a Nonius kappa-CCD diffractometer equipped with Mo-Kα radiation (λ=0.7107 Å). The space group could be derived from the data set either as $P2_1$ (№ 4) or $P2_1/m$ (№ 11). A structure model was obtained by direct method [38] and refined against F^2 with anisotropic displacement parameters for all non-hydrogen atoms in the centrosymmetric space group $P2_1/m$ [39]. The H atoms were identified as small maxima in a difference Fourier synthesis. The quality of the data set did not allow for a refinement as atoms with free parameters. So the hydrogen atoms bound to oxygen atoms O(1), O(2), O(3) and O(4) were included in the refinement applying restraints (constant O–H distance of 0.85 Å, fixing the O–H–O angle by a constant H–H distance of 1.3 Å, isotropic displacement factors fixed to 1.3 of the attached O atoms). The localization of the H atoms bound to O atoms O(5) and O(6) was not possible. These atoms were omitted from the refinement. Crystallographic data and details of the structure analyses are given in Table 5, positional parameters, equivalent isotropic parameters for the non-H atoms and isotropic displacement parameters for H atoms in Table 6, anisotropic displacement parameters in Table 7 and some selected bond lengths and angles in Table 8.

Table 5 Crystallographic data and details of the structure determination of $[Ca(H_2O)_4](C_4S_4)$.

Formula	$C_4H_8CaO_4S_4$
Lattice constants	a = 7.8515(3) Å
	b = 12.7705(5) Å, β = 93.2280(2)°
	c = 10.6010(4) Å
Volume of unit cell	1061.25 $Å^3$
Number of formula units	Z = 8
Density (calc.)	$\rho = 1.805$ g · cm^{-3}
Absorption coefficient	$\mu = 13.6$ cm^{-1}
Crystal system, space group	Monoclinic, *P*2$_1$/*m* (№ 11)
Diffractometer	Nonius kappa-CCD
Radiation, wave length	Mo-Kα, λ = 0.7107 Å
Temperature of measurement	T = 293 K
Range of data collection	$2\theta < 50.04°$
Number of data collected	3759
Number of independent reflections, R_{merge}	1832, 3.12%
Number of refined parameters	143
Ratio reflections/parameters	12.8
R(|F|) for all reflections	7.66%
R(|F|) for 1019 reflections with $F_0 > 4\sigma(F_0)$	3.47%
$wR(F^2)$	10.31 %
Largest electron density difference peak and hole	+0.39 / -0.34 e /$Å^3$

Table 6 Positional parameters, equivalent isotropic parameters U_{eq} / Å^2 for the non-H atoms and isotropic displacement parameters for H atoms in the structure of [Ca(H_2O)$_4$](C_4S_4). Standard deviations are given in parentheses.

Atom	**x**	**y**	**z**	**U_{eq}**
Ca1	0.6294(1)	0.2500	0.8183(1)	0.0278(3)
Ca2	1.1200(1)	0.2500	0.6823(1)	0.0289(3)
S1	0.6489(2)	0.1048(1)	1.0577(1)	0.0416(4)
S2	0.6019(2)	0.0100(1)	1.4144(2)	0.0415(4)
S3	1.1100(2)	0.1045(1)	0.4437(1)	0.0414(4)
S4	1.1447(2)	0.0997(2)	0.0868(2)	0.0457(4)
O1	0.9385(6)	0.2500	0.8797(4)	0.034(1)
O2	0.3308(6)	0.2500	0.8812(4)	0.041(1)
O3	0.8163(7)	0.2500	0.6216(5)	0.049(1)
O4	0.4201(6)	0.2500	0.6194(4)	0.034(1)
O5	1.1250(9)	0.0735(3)	0.7470(6)	0.073(1)
O6	0.6275(9)	0.0758(3)	0.7526(6)	0.076(1)
C1	0.6339(6)	0.1942(5)	1.1687(5)	0.027(1)
C2	0.6158(6)	0.1937(5)	1.3053(5)	0.029(1)
C3	1.1223(6)	0.1929(5)	0.3323(5)	0.026(1)
C4	1.1347(6)	0.1933(5)	0.1948(5)	0.030(1)
H1	0.961(6)	0.197(1)	0.924(3)	0.06(2)
H2	0.314(6)	0.199(1)	0.934(3)	0.06(2)
H3	0.763(9)	0.199(2)	0.583(7)	0.21(5)
H4	0.468(8)	0.199(1)	0.584(6)	0.14(4)

Table 7 Anisotropic displacement parameters U_{ij} /Å^2 for the non-H atoms in the structure of $[Ca(H_2O)_4](C_4S_4)$. Standard deviations are given in parentheses.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{12}**	**U_{13}**	**U_{23}**
Ca1	0.0287(6)	0.0278(7)	0.0271(6)	0	0.0029(5)	0
Ca2	0.0311(6)	0.0283(7)	0.0273(6)	0	0.0029(5)	0
S1	0.0667(9)	0.0309(8)	0.0280(8)	0.0033(6)	0.0083(6)	-0.0045(6)
S2	0.0646(9)	0.0331(8)	0.0268(7)	-0.0024(6)	0.0036(5)	0.0034(6)
S3	0.0668(9)	0.0305(8)	0.0274(8)	-0.0049(6)	0.0067(6)	0.0035(6)
S4	0.0736(9)	0.0369(8)	0.0267(7)	0.0120(7)	0.0035(6)	-0.0067(6)
O1	0.033(2)	0.043(3)	0.025(2)	0	-0.002(2)	0
O2	0.038(2)	0.060(3)	0.027(2)	0	0.007(2)	0
O3	0.044(3)	0.067(4)	0.035(3)	0	-0.001(2)	0
O4	0.034(2)	0.040(3)	0.028(2)	0	0.003(2)	0
O5	0.150(4)	0.029(1)	0.039(2)	0.008(3)	0.000(2)	-0.002(3)
O6	0.146(4)	0.032(2)	0.045(2)	0.009(4)	-0.022(2)	-0.009(3)
C1	0.030(2)	0.027(2)	0.025(2)	-0.004(2)	0.004(2)	-0.002(2)
C2	0.031(2)	0.033(3)	0.021(2)	-0.004(2)	0.001(2)	-0.005(2)
C3	0.030(2)	0.028(3)	0.021(2)	-0.003(2)	-0.001(2)	-0.004(2)
C4	0.032(2)	0.032(3)	0.026(2)	-0.002(2)	0.002(2)	-0.005(2)

Table 8 Selected bond lengths / Å and angles /° for $[Ca(H_2O)_4](C_4S_4)$. Symmetry operations: I= x, 0.5-y, z; II= 1+x, y, z. Standard deviations are given in parentheses.

Ca(1)–O(1)	2.477 (5)	Ca(2)–O(1)	2.598 (5)
Ca(1)–O(2)	2.473 (5)	Ca(2)–O(2)^{II}	2.606 (5)
Ca(1)–O(3)	2.616 (6)	Ca(2)–O(3)	2.435 (6)
Ca(1)–O(4)	2.599 (5)	Ca(2)–O(4)^{II}	2.485 (5)
Ca(1)–O(6)	2.331 (4)	Ca(2)–O(5)^{I}	2.356 (4)
Ca(1)–O(6)^{I}	2.331 (4)	Ca(2)–O(5)	2.356 (4)
Ca(1)–S(1)	3.140 (2)	Ca(2)–S(4)	3.136 (2)
Ca(1)–S(1)^{I}	3.140 (2)	Ca(2)–S(4)^{I}	3.136 (2)
S(1)–C(1)	1.648 (6)	S(3) – C(3)	2.640 (6)
S(2)–C(2)	1.671 (7)	S(4) – C(4)	2.660 (6)
C(1)–C(2)	1.463 (6)	C(3) – C(4)	1.466 (6)
C(1)–C(1)^{I}	1.43 (1)	C(3) – C(3)^{I}	1.46 (1)
C(2)–C(2)^{I}	1.44 (1)	C(4) – C(4)^{I}	1.45 (1)
O(1)–Ca(1)–O(6)	93.91 (2)	O(3)–Ca(2)–O(2)^{II}	141.41(2)
O(1)–Ca(1)–O(2)	149.18(2)	O(5)–Ca(2)–O(4)^{II}	76.42 (1)
S(3)^{I}–Ca(1)–S(3)	72.37 (1)	S(4)^{I}–Ca(1)–S(4)	72.67 (1)
C(1)–C(1)^{I}–C(2)^{I}	90.3 (4)	C(3)–C(3)^{I}–C(4)^{I}	89.8 (4)
C(1)^{I}–C(2)^{I}–C(2)	89.7 (4)	C(3)^{I}–C(3)^{I}–C(4)	90.2 (4)

3.1.4 Discussion of the Structure of $[Ca(H_2O)_4](C_4S_4)$

In the crystal structure of $[Ca(H_2O)_4](C_4S_4)$ the two crystallographically independent Ca^{2+} ions are coordinated each by the oxygen atoms of six water molecules and by two sulfur atoms of one $(C_4S_4)^{2-}$ ion, which therefore acts as bidentate ligand (Figure 9). The coordination environment for both Ca^{2+} ions is rather irregular and can be considered as a distorted square antiprism or a bicapped trigonal prism. A mirror plane bisects the two CaO_6S_2 polyhedra with the atoms Ca(1), Ca(2), O(1), O(2), O(3) and O(4) located in the mirror plane.

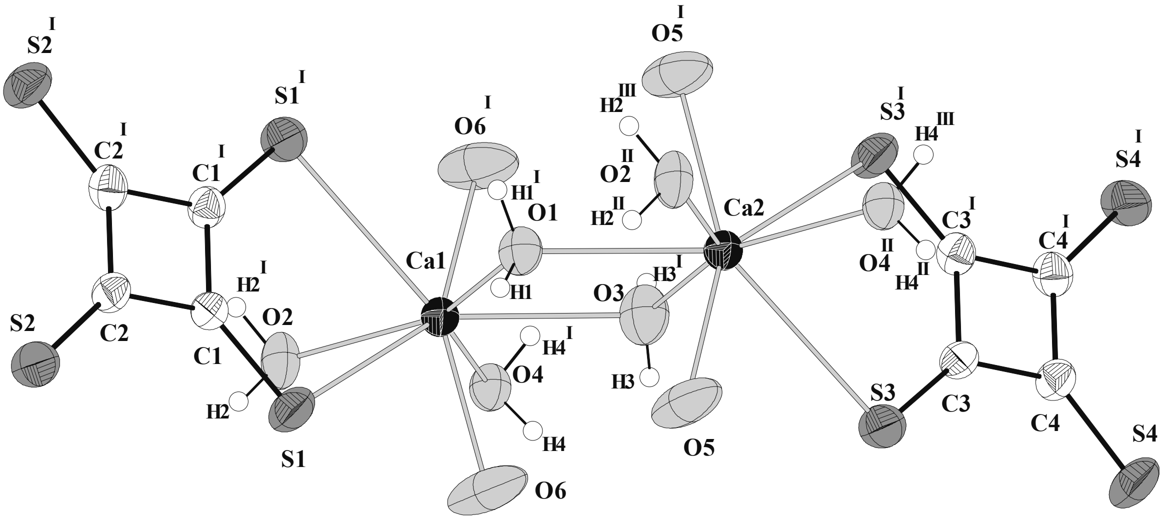


Figure 9 A section of the crystal structure of $[Ca(H_2O)_4](C_4S_4)$. Thermal ellipsoids are drawn to include a probability density of 50%. H atoms are drawn with arbitrary radii. Symmetry operations: I =x, 0.5-y, z ; II = 1+x, y, z ; III =1+x, 0.5-y, z.

The Ca^{2+} ions exhibit two short bonds to O(5) and O(6) of the terminal H_2O ligands of 2.356 and 2.331 Å respectively. The bonds to the bridging atoms of averaged 2.533 Å are markedly longer. The Ca(1)–S(1) (3.140 Å) and Ca(2)–S(3) (3.136 Å) bonds are as expected much longer than the Ca–O bonds. The mirror plane perpendicular to the molecular plane bisects both independent $(C_4S_4)^{2-}$ ions giving them C_S symmetry. The deviations from planarity (maximally 0.002 Å for C(2) and $C(2)^{I}$, 0.008 Å for C(3) and

C(3)^{I}) are very small. The C – C bond lengths (averaged 1.45 ± 0.02 Å) and the C – S bonds (averaged 1.655 ± 0.015 Å) are uniformly distributed; the C–C–C angles deviate with maximally 0.27° from rectangularity. For both $(C_4S_4)^{2-}$ ions there is, however, a significant deviation from the ideal D_{4h} symmetry observed. The S····S distances in the outer perimeter of the rings are averaged 3.83 Å for the non coordinating S atoms but are only 3.71 Å for the S(1) ····S(1)^{I} and the S(3) ····S(3)^{I} edges. The electrostatic interaction between cations and anions thus cause a substantial deformation of the $(C_4S_4)^{2-}$ ions. In the crystal the coordination polyhedra of the Ca^{2+} ions are connected by common edges O(1)–O(3) and O(2)–O(4) to infinite stands running along the crystallographic *a*-axis (Figure 10). The $(C_4S_4)^{2-}$ ions are stacked in a nearly coplanar fashion along the *a*-axis. The distance of the molecular planes through neighbored $(C_4S_4)^{2-}$ ions amounts half the length of the *a*-axis (3.93 Å).

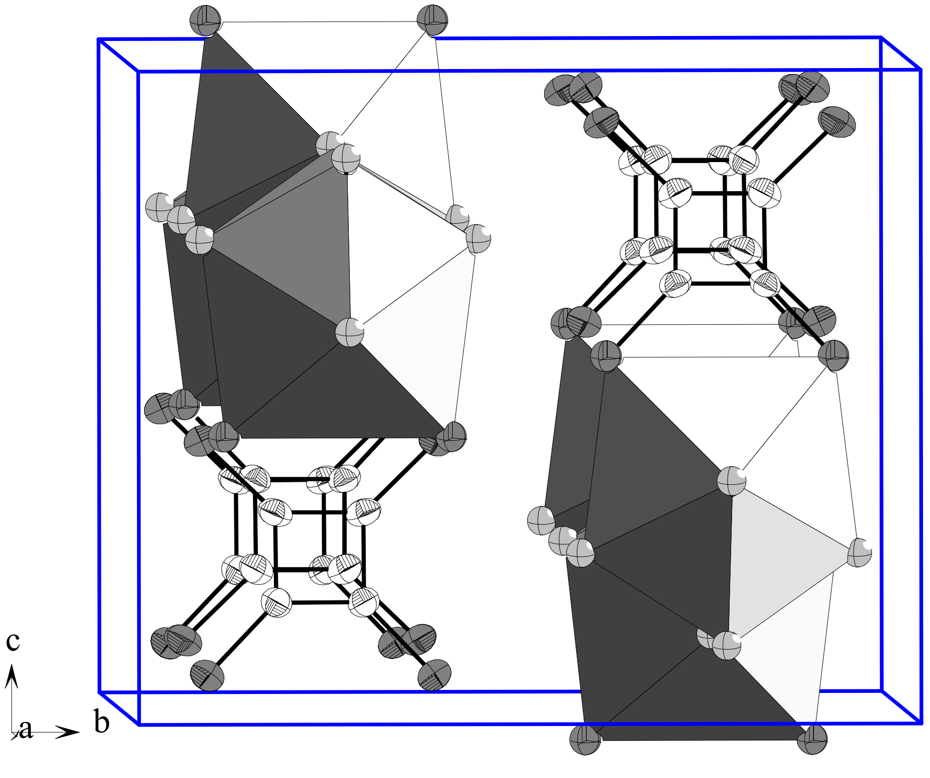


Figure 10 The unit cell of $[Ca(H_2O)_4](C_4S_4)$ in a view slightly inclined along the *a*-axis. The coordination polyhedra of the Ca^{2+} ions are shown as massive polyhedra.

3.1.5 Structure Determination of [Sr(H_2O)$_4$](C_4S_4)

The crystals of this compound are sensitive towards the loss of water and were therefore sealed in glass capillaries. The diffraction quality of the crystals towards X-rays was checked by preliminary precession exposures, which showed the orthorhombic symmetry. The diffraction quality of the crystals, despite they were of beautiful dark red color. transparent and of well defined shape, was generally very low. A large series of crystals had to be checked and tested until a suitable specimen was found. Data were collected at ambient temperature using a Nonius kappa-CCD diffractometer equipped with Mo-Kα radiation (λ=0.7107 Å). The space group could be derived from the data set as *Pnma* (№ 62). A structure model was obtained by direct method [38] and refined against F^2 with anisotropic displacement parameters for all non-hydrogen atoms [39]. The H atoms were identified as small maxima in a difference Fourier synthesis. The quality of the data set did not allow for a refinement as atoms with free parameters. So the hydrogen atoms were not included in the refinement. Crystallographic data and details of the structure analyses are given in Table 9, positional parameters, equivalent isotropic parameters for the non-H atoms in the structure in Table 10, anisotropic displacement parameters in Table 11 and some selected bond lengths and angles in Table 12.

Table 9 Crystallographic data and details of the structure determination of $[Sr(H_2O)_4](C_4S_4)$.

Formula	$C_4H_8O_4S_4Sr$
Lattice constants	a = 8.1494(1) Å
	b = 12.907(2) Å
	c = 10.790(2) Å
Volume of unit cell	1134.96 $Å^3$
Number of formula units	Z = 4
Density (calc.)	$\rho = 1.96\ g \cdot cm^{-3}$
Absorption coefficient	$\mu = 54.7\ cm^{-1}$
Crystal system, space group	Orthorhombic, *Pnma* (№ 62).
Diffractometer	Nonius kappa-CCD
Radiation, wave length	Mo-Kα, λ = 0.7107Å
Temperature of measurement	T = 293 K
Range of data collection	$2\theta < 50.32°$
Number of data collected	2034
Number of independent reflections, R_{merge}	755, 9.58%
Number of refined parameters	64
Ratio reflections/parameters	11.8
R(|F|) for all reflections	10.61%
R(|F|) for 408 reflections with $F_0 > 4\sigma(F_0)$	3.84 %
$wR(F^2)$	7.90 %
Largest electron density difference peak and hole	+0.41 / -0.33 e /$Å^3$

Table 10 Positional parameters, equivalent isotropic parameters U_{eq} / Å^2 for the non-H atoms in the structure of $[Sr(H_2O)_4](C_4S_4)$. Standard deviations are given in parentheses.

Atom	**x**	**y**	**z**	**U_{eq}**
Sr	0.6296(1)	0.2500(0)	0.81491(8)	0.0419(3)
S1	0.6374(5)	0.1046(2)	1.0563(2)	0.0621(6)
S2	0.6278(6)	0.1010(2)	1.4078(2)	0.0778(7)
O1	0.9482(9)	0.2500(0)	0.8894(7)	0.066(3)
O2	0.331(1)	0.2500(0)	0.887(1)	0.157(7)
O3	0.576(3)	0.0666(5)	0.7524(6)	0.126(7)
C1	0.642(1)	0.1971(6)	1.1666(6)	0.046(2)
C2	0.636(2)	0.1960(6)	1.3021(7)	0.061(2)

Table 11 Anisotropic displacement parameters U_{ij} [Å^2] for the non-H atoms in the structure of $[Sr(H_2O)_4](C_4S_4)$. Standard deviations are given in parentheses.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{12}**	**U_{13}**	**U_{23}**
Sr	0.0488(6)	0.0384(5)	0.0397(6)	0.0019(6)	0	0
S1	0.0940(2)	0.0439(1)	0.0477(1)	0.0010(1)	0.0039(1)	0.00019(9)
S2	0.1093(2)	0.0480(1)	0.0761(2)	-0.0095(1)	-0.0193(2)	0.0195(1)
C1	0.0749(5)	0.0414(4)	0.0482(4)	0.0150(5)	0.0161(5)	-0.0010(3)
C2	0.0570(4)	0.0573(5)	0.0702(5)	0.0402(5)	0.0052(5)	0.0147(4)
O1	0.1023(9)	0.0895(9)	0.2867(3)	-0.0020(8)	0	0
O2	0.0680(5)	0.0274(4)	0.0970(7)	-0.0010(4)	0	0
O3	0.2063(9)	0.0701(4)	0.0469(3)	0.0194(5)	-0.0512(6)	-0.0092(3)

Table 12 Selected bond lengths / Å and angles / º for $[Sr(H_2O)_4](C_4S_4)$. Symmetry operations: I=-0.5+x, 0.5-y, 0.5-z , II= 0.5+x, 0.5-y, 0.5-z , III=x, y, 0.5-z. Standard deviations are given in parentheses.

Sr(1)–O(1)	2.54 (1)	Sr(1)$^{\mathbf{I}}$–O(2)	2.684 (8)
Sr(1)–O(1)^{II}	2.74 (2)	S(1)–C(1)	1.697 (9)
Sr(1)–O(2)	2.669 (9)	S(2)–C(2)	1.674 (9)
Sr(1)–O(2)^{II}	2.684 (8)	S(1)^{III}–C(1)^{III}	1.697 (9)
Sr(1)–O(3)	2.497 (8)	S(2)^{III}–C(2)^{III}	1.674 (9)
Sr(1)–O(3)$^{\mathbf{I}}$	2.497 (8)	C(1)–C(2)	1.466(11)
Sr(1)–S(1)	2.213 (2)	C(1)^{III}–C(2)^{III}	1.466(11)
Sr(1)–S(1)^{I}	2.213 (2)	C(1)–C(1)^{III}	1.372(17)
Sr(1)$^{\mathbf{I}}$–O(1)	2.744 (2)	C(2)–C(2)^{III}	1.397(19)
O(2)–Sr(1)–O(3)	81.6 (2)	Sr(1)$^{\mathbf{I}}$–Sr(1)$^{\mathbf{I}}$–O(3)	93.0 (3)
O(1)–Sr(1)–O(2)^{II}	144.7 (4)	Sr(1)$^{\mathbf{I}}$–Sr(1)$^{\mathbf{I}}$–O(1)	179.0 (4)
S(1)^{III}–Sr(1)–S(1)	71.70 (8)	S(1)^{III}–Sr(1)$^{\mathbf{I}}$–S(1)	71.70 (8)
C(1)–C(2)–C(2)^{III}	89.53 (1)	C(1)–C(1)^{III}–C(2)^{III}	90.47 (1)
C(2)–C(1)–C(1)^{III}	90.47 (1)	C(2)–C(2)^{III}–C(1)^{III}	89.53 (1)

3.1.6 Discussion of the Structure of $[Sr(H_2O)_4](C_4S_4)$

The Sr^{2+} ion is coordinated by the O atoms of six H_2O molecules and by two S atoms of one $C_4S_4^{2-}$ ion, which therefore acts as a chelating ligand (Figure 11). The coordination environment for the Sr^{2+} ion can be considered as a distorted square antiprism or a bicapped trigonal prism. A mirror plane bisects the SrO_6S_2 polyhedra with the atoms Sr, O(1), and O(2) located in the mirror plane. The Sr^{2+} ion exhibits three short and three longer Sr−O bonds. The short bonds of average length of 2.5 Å are observed between Sr and the atoms $H_2O(3)$, $H_2O(3)^{III}$, and $H_2O(2)^{II}$ of the terminal H_2O molecules, the longer bonds of average length of 2.7 Å between Sr and bridging $H_2O(1)$ and $H_2O(2)$ molecules and the terminal $H_2O(1)^{II}$ molecule. The two Sr−S bonds of 3.2 Å are of equal lengths. A mirror plane bisects the $C_4S_4^{2-}$ ion giving it crystallographic C_S symmetry. The deviations from planarity (maximally 0.034 Å for C(1) and $C(1)^{I}$) are very small, the C−C bond lengths (averaged 1.41 ± 0.03 Å) and the C−S bonds (averaged 1.68 ± 0.01 Å) are uniformly distributed. the C−C−C angles deviate less than 1° from rectangularity. The connection of the coordination polyhedra follows the pattern observed for the Ca analogue. The SrO_6S_2 polyhedra are connected by common edges O(1)−O(2) to infinite strands running along the crystallographic *a*-axis (Figure 12). The $C_4S_4^{2-}$ ions are stacked almost perpendicular to this axis. The angle between the plane through all atoms of the $C_4S_4^{2-}$ ion and the propagation direction of the strand is 1.2°.

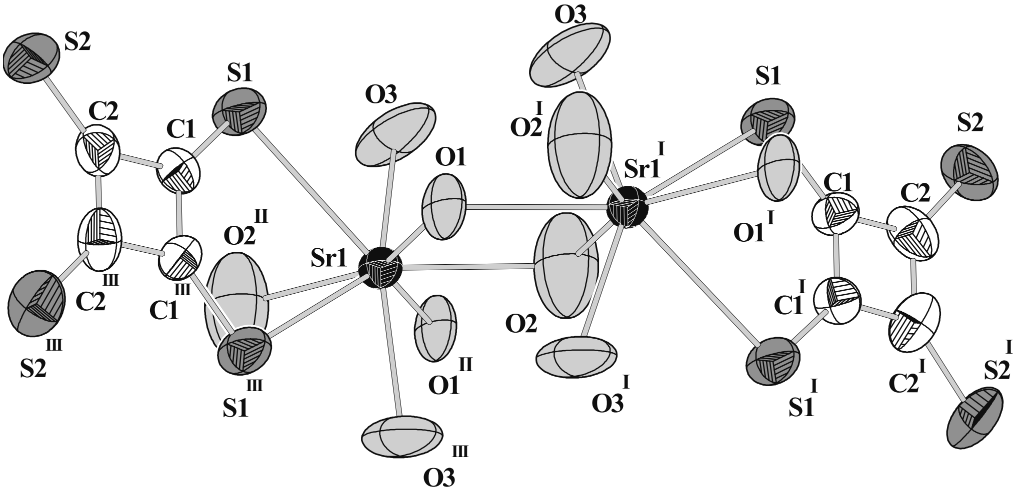


Figure 11 A section of the structure of $[Sr(H_2O)_4](C_4S_4)$. Thermal ellipsoids are drawn to include a probability density of 50%. Symmetry operations: I=-0.5+x, y, 1.5-z; II= 0.5+x, y, 1.5-z ; III=x, 0.5-y, z.

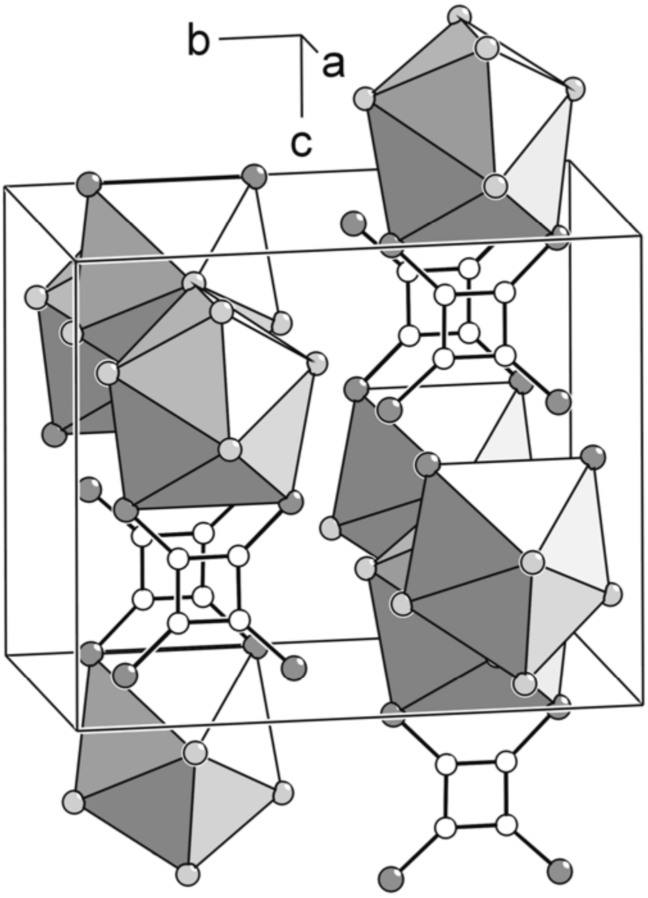
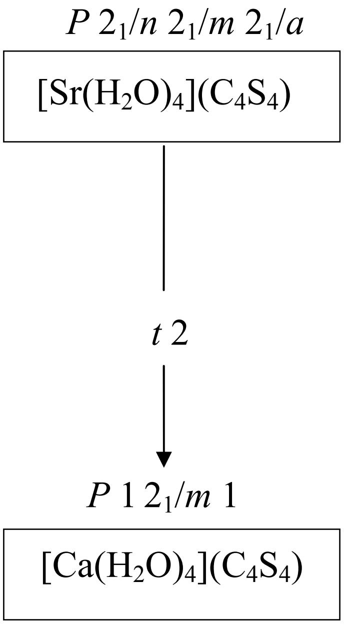


Figure 12 The unit cell of $[Sr(H_2O)_4](C_4S_4)$ in a view along the *a*-axis. The coordination of the Sr^{2+} ions is shown as massive polyhedra.

3.1.7 Comparison of the Structures of $[M(H_2O)_4](C_4S_4)$ with M= Ca , Sr

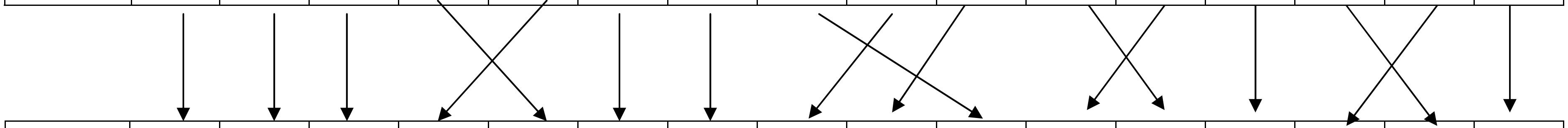
The crystal structure of $[Sr(H_2O)_4](C_4S_4)$ is closely related to the structure of the Ca^{2+} containing analogue $[Ca(H_2O)_4](C_4S_4)$, $[Sr(H_2O)_4](C_4S_4)$ however, belongs to the orthorhombic crystal system while the Ca containing analogue crystallizes with monoclinic symmetry. The lattice constants of both compounds are similar and the monoclinic angle of $[Ca(H_2O)_4](C_4S_4)$, β=93.228(2)°, deviates not strongly from rectangularity. The unit cell volumes of 1061.25 $Å^3$ for $[Ca(H_2O)_4](C_4S_4)$ and 1134.96 $Å^3$ for $[Sr(H_2O)_4](C_4S_4)$ show the expected relation due to the larger ion radius of Sr^{2+} relative to Ca^{2+}. The space groups of the two structures show a straightforward supergroup-subgroup relation of the *translationsgleich* type of index 2: $Pnma \text{ — } t2 \rightarrow P12_1/m1$ [41]. Scheme 6 shows this relation in form of a "Bärnighausen tree". The consequence is that the special positions 4*c* in *Pmna* are split into two independent positions 2*e* in $P2_1/m$, and the general positions 8*d* in *Pnma* are split into two independent general positions 4*f* in $P2_1/m$. Table 13 contains all atom positions of $[Sr(H_2O)_4](C_4S_4)$ and one respective symmetry related position x+0.5, y, -z+0.5. A clear relation to the atom positions of $[Ca(H_2O)_4](C_4S_4)$ is present. Each two symmetry related positions of the Sr containing structure have their almost identical but symmetry independent positions in the structure of the Ca analogue. In Figure 13 the two structures are compared by views of the unit cells in all three crystallographic directions. A substantial difference is visible in the view along the *b*-axis. In the structure of $[Ca(H_2O)_4](C_4S_4)$, the angle between the planes of the $C_4S_4^{2-}$ ions and the direction of the *a*-axis amounts 8.7° while the respective angle in the Sr containing structure amounts only 1.2°.



Scheme 6 The supergroup-subgroup relation between the space groups *Pmna* and $P2_1/m$ depicted as a Bärnighausen tree.

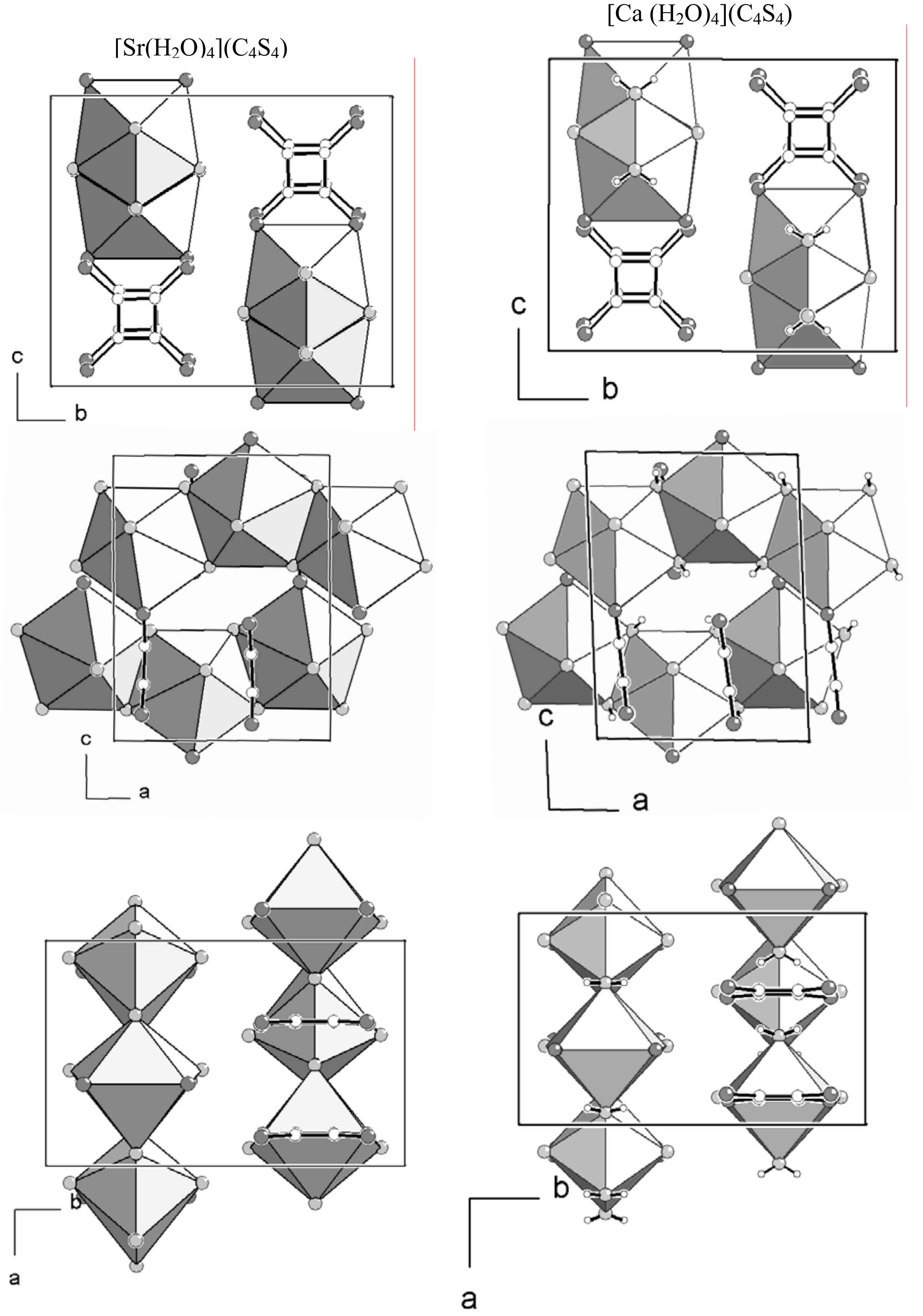
Table 13 Comparison of the positions for [Sr(H_2O)$_4$](C_4S_4) and [Ca(H_2O)$_4$](C_4S_4). The symmetry operation I= x+0.5, y, z+0.5 has been applied for all atoms coordinates of [Sr(H_2O)$_4$](C_4S_4). The arrows indicate the respective atom position in the structure of [Ca(H_2O)$_4$](C_4S_4).

	Sr	Sr^I	S1	S1^I	S2	S2^I	O1	O1^I	O2	O2^I	O3	O3^I	C1	C1^I	C2	C2^I
Wyckoff Position	4c (.m.)	4c (.m.)	8d	8d	8d	8d	4c (.m.)	4c (.m.)	4c (.m.)	4c (.m.)	8d	8d	8d	8d	8d	8d
x	0.6296	1.1296	0.6374	1.1374	0.6278	1.1278	0.9428	1.4428	0.3312	0.8312	0.5761	0.5761	0.6419	1.1419	0.6362	1.1362
y	0.2500	0.2500	0.1046	0.1046	0.1010	0.1010	0.2500	0.2500	0.2500	0.2500	0.0666	0.0666	0.1971	0.1971	0.1960	0.1960
z	0.8149	0.6851	1.0563	0.4437	1.4078	0.0922	0.8894	0.610	0.8865	0.6135	0.7524	0.7524	1.1666	0.3334	1.3021	0.1979



	Ca1	Ca2	S1	S2	S3	S4	O1	O2	O3	O4	O5	O6	C1	C2	C3	C4
Wyckoff Position	2e (.m.)	2e (.m.)	4f	4f	4f	4f	2e (.m.)	2e (.m.)	2e (.m.)	2e (.m.)	4f	4f	4f	4f	4f	4f
x	0.6294	1.1200	0.6489	0.6019	1.1000	1.1447	0.9385	0.3308	0.8163	0.4201	1.1250	0.6275	0.6339	0.6158	1.1223	1.1347
y	0.2500	0.2500	0.1048	0.1010	0.1045	0.0997	0.2500	0.2500	0.2500	0.2500	0.0735	0.0758	0.1942	0.1937	0.1929	0.1933
z	0.8183	0.6823	1.0577	1.4144	0.4437	0.0868	0.8797	0.8812	0.6216	0.6194	0.7470	0.7526	1.1687	1.3035	0.3323	0.1948

Figure 13 A view of the unit cells of $[Sr(H_2O)_4](C_4S_4)$ and $[Ca(H_2O)_4](C_4S_4)$ along the *a,b* and *c*-axes.



3.1.8 Structure Determination of $[Ba_4K_2(H_2O)_{16}](C_4S_4)_5$

The crystals of this compound are slightly sensitive towards the loss of water and were therefore sealed in glass capillaries. The diffraction quality of the crystal towards X-rays was checked by preliminary precession exposures, which showed the orthorhombic symmetry. Data were collected at ambient temperature using a Nonius kappa-CCD diffractometer equipped with Mo-Kα radiation (λ=0.7107 Å). The space group could be derived from the data set as *Pbca* (№ 61). A structure model was obtained by direct method [38] and refined against F^2 with anisotropic displacement parameters for all non-hydrogen atoms [39]. The H atoms were all identified in a difference Fourier synthesis. They were included as individual atoms with free positional and isotropic displacement parameters in the refinement. Crystallographic data and details of the structure analyses are given in Table 14, positional parameters, equivalent isotropic parameters for the non-H atoms and isotropic displacement parameters for H atoms in Table 15, anisotropic displacement parameters in Table 16 and selected bond lengths and angles in Table 17.

Table 14 Crystallographic data and details of the structure determination of $[Ba_4K_2(H_2O)_{16}](C_4S_4)_5$.

Formula	$C_{10}H_{32}Ba_2KO_{16}S_{10}$
Lattice constants	a = 15.875(3) Å
	b = 21.325(5) Å
	c = 16.119(1) Å
Volume of unit cell	5456.70 $Å^3$
Number of formula units	Z = 8
Density (calc.)	$\rho = 2.19\ g \cdot cm^{-3}$
Absorption coefficient	$\mu = 38.2\ cm^{-1}$
Crystal system, space group	Orthorhombic, *Pbca* (№ 61)
Diffractometer	Nonius kappa-CCD
Radiation, wave length	Mo-Kα, $\lambda = 0.7107$ Å
Temperature of measurement	T = 293 K
Range of data collection	$2\theta < 60°$
Number of data collected	202926
Number of independent reflections, R_{merge}	7864, 10.81%
Number of refined parameters	344
Ratio reflections/parameters	22.8
R(|F|) for all reflections	6.21%
R(|F|) for 5637 reflections with $F_0 > 4\sigma(F_0)$	3.32 %
$wR(F^2)$	7.77 %
Largest electron density difference peak and hole	+1.24 / -1.17 e /$Å^3$

Table 15 Positional parameters, equivalent isotropic parameters U_{eq} / Å^2 for the non-H atoms and isotropic displacement parameters for H atoms in the structure of $[Ba_4K_2 (H_2O)_{16}](C_4S_4)_5$. Standard deviations are given in parentheses.

Atom	**x**	**y**	**z**	**U_{eq}**
Ba1	0.31798(1)	0.31905(1)	-0.23589(1)	0.02625(6)
Ba2	0.15727(1)	0.49792(1)	-0.27106(1)	0.03000(6)
K	0.15463(5)	0.14885(4)	-0.26757(5)	0.0420(2)
C1	-0.0102(2)	0.5087(1)	-0.0614(2)	0.0230(6)
C2	-0.0636(2)	0.5016(1)	0.0115(2)	0.0227(6)
C3	0.4289(2)	0.3806(1)	-0.0212(2)	0.0230(6)
C4	0.4885(2)	0.4041(1)	-0.0808(2)	0.0224(6)
C5	0.5465(2)	0.4212(1)	-0.0153(1)	0.0239(6)
C6	0.014(1)	0.6023(1)	-0.4542(1)	0.0254(6)
C7	0.4830(2)	0.3110(1)	-0.4472(1)	0.0260(7)
C8	0.4120(2)	0.1880(1)	-0.0040(1)	0.0252(6)
C9	0.4686(1)	0.2028(1)	-0.0721(1)	0.0231(6)
C10	0.5399(2)	0.2007(1)	-0.0158(1)	0.0260(6)
O1	0.2135(2)	0.2352(1)	-0.1513(2)	0.0404(6)
O2	0.3186(2)	0.2121(1)	-0.3339(2)	0.0379(6)
O3	0.1658(3)	0.3073(3)	-0.3212(3)	0.0584(9)
O4	0.3003(2)	0.4290(1)	-0.3334(2)	0.0321(5)
O5	0.1777(2)	0.3884(1)	-0.1732(2)	0.0331(5)
O6	0.3142(2)	0.5097(1)	-0.1838(2)	0.0536(9)
O7	0.1826(2)	0.6083(1)	-0.1872(2)	0.0417(6)
O8	0.2507(2)	0.5737(1)	-0.3722(2)	0.0337(6)
S1	-0.0261(5)	0.5224(5)	-0.162(5)	0.0329(2)
S2	-0.1659(5)	0.5031(4)	0.0300(5)	0.0321(2)
S3	0.3343(5)	0.3485(1)	-0.0296(5)	0.0313(2)
S4	0.4885(5)	0.4103(4)	-0.1838(5)	0.0304(2)
S5	0.6402(5)	0.4545(5)	-0.0149(5)	0.0385(2)
S6	0.0177(5)	0.6074(5)	-0.3515(5)	0.0350(2)

Table 15 continued

S7	0.4959(6)	0.3190(6)	-0.3462(5)	0.0455(3)
S8	0.3100(5)	0.1736(4)	0.0079(5)	0.0334(2)
S9	0.4630(5)	0.2159(4)	-0.1740(5)	0.0311(2)
S10	0.6428(5)	0.2069(6)	-0.0243(6)	0.0459(3)
H11	0.176(3)	0.251(3)	-0.129(3)	0.07(2)
H12	0.246(4)	0.223(3)	-0.110(4)	0.11(2)
H21	0.309(3)	0.222(2)	-0.379(3)	0.04(1)
H22	0.361(3)	0.191(2)	-0.339(3)	0.06(2)
H31	0.153(4)	0.270(3)	-0.362(5)	0.12(2)
H32	0.149(5)	0.319(5)	-0.325(6)	0.11(4)
H41	0.341(3)	0.447(2)	-0.340(3)	0.06(2)
H42	0.299(3)	0.414(2)	-0.380(3)	0.06(1)
H51	0.140(3)	0.370(2)	-0.160(3)	0.05(2)
H52	0.189(3)	0.399(3)	-0.128(4)	0.10(2)
H61	0.352(3)	0.498(2)	-0.193(3)	0.05(1)
H62	0.311(3)	0.525(3)	-0.128(4)	0.09(2)
H71	0.153(3)	0.639(3)	-0.192(3)	0.07(2)
H72	0.188(3)	0.600(3)	-0.136(4)	0.09(2)
H81	0.283(3)	0.557(2)	-0.404(2)	0.04(1)
H82	0.222(3)	0.592(2)	-0.397(3)	0.05(1)

Table 16 Anisotropic displacement parameters U_{ij} / Å^2 for the non-H atoms in the structure of $[Ba_4K_2(H_2O)_{16}](C_4S_4)_5$. Standard deviations are given in parentheses.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{12}**	**U_{13}**	**U_{23}**
Ba1	0.0199(8)	0.0302(8)	0.0282(8)	0.0009(6)	-0.0001(6)	-0.0011(7)
Ba2	0.0209(8)	0.0390(1)	0.0298(9)	-0.0006(6)	-0.0017(6)	-0.0031(7)
K	0.0319(3)	0.0413(4)	0.0522(4)	0.0012(3)	0.0007(3)	0.0100(3)
C1	0.020(1)	0.017(1)	0.032(1)	-0.001(1)	-0.001(1)	0.0004(1)
C2	0.019(1)	0.019(1)	0.032(1)	-0.0007(1)	-0.001(1)	0.001(1)
C3	0.022(1)	0.019(1)	0.029(1)	-0.001(1)	-0.002(1)	0.000(1)
C4	0.020(1)	0.021(1)	0.026(1)	-0.0007(1)	-0.002(1)	0.002(1)
C5	0.021(1)	0.020(1)	0.031(1)	-0.002(1)	-0.002(1)	0.002(1)
C6	0.021(1)	0.022(1)	0.032(1)	0.0009(1)	-0.0003(1)	-0.0005(1)
C7	0.023(1)	0.019(1)	0.037(1)	-0.001(1)	-0.004(1)	0.007(1)
C8	0.022(1)	0.023(1)	0.030(1)	-0.0009(1)	0.003(1)	-0.003(1)
C9	0.023(1)	0.020(1)	0.028(1)	0.001(1)	0.0009(1)	-0.002(1)
C10	0.021(1)	0.018(1)	0.040(1)	0.0003(1)	0.001(1)	-0.004(1)
O1	0.047(1)	0.031(1)	0.042(1)	-0.007(1)	0.003(1)	-0.000(1)
O2	0.043(1)	0.026(1)	0.044(1)	0.005(1)	0.003(1)	0.004(1)
O3	0.032(1)	0.044(1)	0.096(1)	0.011(1)	0.011(1)	0.025(1)
O4	0.034(1)	0.026(1)	0.038(1)	-0.001(1)	-0.0009(1)	0.000(1)
O5	0.032(1)	0.027(1)	0.039(1)	-0.003(1)	-0.002(1)	0.003(1)
O6	0.028(1)	0.032(1)	0.102(2)	0.002(1)	0.011(1)	0.016(1)
O7	0.053(1)	0.030(1)	0.043(1)	-0.002(1)	0.005()	0.005(1)
O8	0.037(1)	0.030(1)	0.035(1)	-0.005(1)	0.004(1)	-0.002(1)
S1	0.0251(3)	0.0165(3)	0.0569(4)	0.0011(2)	0.00004(3)	-0.0037(3)
S2	0.0169(3)	0.0274(3)	0.0521(4)	-0.0029(2)	-0.0006(3)	-0.0007(3)
S3	0.0243(3)	0.0227(3)	0.0470(4)	-0.0008(2)	-0.0129(3)	0.0015(3)
S4	0.0296(3)	0.0173(3)	0.0443(4)	-0.0013(2)	-0.0118(3)	0.0012(3)
S5	0.0250(3)	0.0283(3)	0.0629(3)	-0.0006(3)	-0.0180(3)	0.0049(3)
S6	0.0298(4)	0.0174(3)	0.0575(5)	-0.0005(2)	-0.0008(3)	0.0015(3)
S7	0.0276(4)	0.0181(3)	0.0905(7)	-0.0020(3)	-0.0124(4)	0.0124(4)
S8	0.0211(3)	0.0320(4)	0.0475(4)	-0.0022(3)	-0.0033(3)	-0.0081(3)
S9	0.0285(3)	0.0172(3)	0.0480(4)	0.0019(2)	0.0060(3)	-0.0047(3)
S10	0.0201(3)	0.0272(4)	0.0909(7)	0.0003(3)	-0.0034(4)	-0.0085(4)

Table 17 Selected bond lengths / Å and angles / ° for $[Ba_4K_2(H_2O)_{16}](C_4S_4)_5$. Symmetry operations: I= 0.5-x, -0.5-y, z; II=-x, 1-y, -z; III=-x, -0.5+y, -0.5-z; IV = -0.5+x, y, -0.5-z; V= 0.5-x, 1-y, -0.5+z; VI=-0.5+x, 0.5-y,-z; VII= x, 0.5-y, -0.5+z. Standard deviations are given in parentheses.

Ba(1)–O(1)	2.796 (3)	Ba(2)–O(4)	2.886 (2)
Ba(1)–O(2)	2.774 (3)	Ba(2)–O(5)	2.834 (3)
Ba(1)–O(3)	2.791 (3)	Ba(2)–O(6)	2.872 (3)
Ba(1)–O(4)	2.837 (3)	Ba(2)–O(7)	2.745 (3)
Ba(1)–O(5)	2.859 (3)	Ba(2)–O(8)	2.732 (2)
Ba(1)–S(3)	3.3946(8)	Ba(2)–S(1)	3.4412(9)
Ba(1)–S(4)	3.4378(9)	Ba(2)–S(6)^{V}	3.471 (1)
Ba(1)–S(7)^{VII}	3.337 (1)	K(1)–O(1)	2.790 (3)
K(1)–S(6)^{VI}	3.456 (1)	K(1)–O(8)^{I}	2.767 (3)
C(1)–C(2)	1.456 (4)	S(1)–C(1)	1.664 (3)
C(1)–C(2)^{I}	1.438 (4)	S(3)–C(3)	1.653 (3)
C(3)–C(4)	1.440 (4)	S(5)–C(5)	1.650 (3)
C(3)–C(6)	1.466 (4)	S(7)–C(7)	1.648 (3)
C(9)–C(10)	1.451 (4)	S(9)–C(9)	1.664 (3)
O(1)–Ba(1)–O(2)	75.84 (8)	Ba(1)–O(5)–Ba(2)	108.64(1)
O(1)–Ba(1)–O(4)	137.80(8)	O(5)–Ba(2)–O(6)	72.66 (1)
S(3)–Ba(1)–S(7)	117.18 (1)	S(6)–Ba(2)–S(1)	63.18 (0)
C(2)–C(1)–C(2)^{II}	90.29 (1)	C(4)–C(3)–C(6)	89.98 (1)
C(1)–C(2)^{II}–C(2)^{II}	89.71 (1)	C(7)–C(8)–C(9)	89.56 (1)

3.1.9 Discussion of the structure of $[Ba_4K_2 (H_2O)_{16}](C_4S_4)_5$

The crystal structure of $[Ba_4K_2(H_2O)_{16}](C_4S_4)_5$ is surprisingly complex with a large orthorhombic unit cell with a volume of almost 5500 Å^3. In the asymmetric unit, there are two symmetry independent Ba^{2+} ions, one K^+ ion, and three independent $C_4S_4^{2-}$ ions, one of which is located at an inversion centre. Within a sphere of 3.6 Å radius the two Ba^{2+} ions have the coordination number 9, both are bound to five H_2O molecules and three $(C_4S_4)^{2-}$ ions, one of which acts as chelating ligand. The K^+ ion exhibits coordination number 10 and is bound to six H_2O molecules and to three $(C_4S_4)^{2-}$ ions (Figure 14). As expected the Ba–O and Ba–S bond lengths are elongated each by about 0.3 Å and 0.2 Å in comparison to the respective bonds in $[Ca(H_2O)_4](C_4S_4)$ and $[Sr(H_2O)_4](C_4S_4)$ respectively. The high coordination number of the K^+ ion causes an elongation of the K–O bonds. In $K_2C_4S_4 \cdot H_2O$, K^+ exhibits coordination number 8 by seven sulphur atoms and one oxygen atom with mean bond lengths K–S = 3.58 Å and K–O = 2.91Å [20]. In the structure of $[Ba_4K_2(H_2O)_{16}](C_4S_4)_5$, the K–S bonds have an average length of 3.52 Å, the K–O bonds of 3.08 Å. The $Ba(1)S_4O_5$. $Ba(2)S_4O_5$, and the KS_4O_6 polyhedra are connected via common edges and corners to a two-dimensional sheet spread out parallel to the *a*-*b*-plane (Figure 15). Bridging $(C_4S_4)^{2-}$ ions link these sheets to a three-dimensional network. The molecules are connected through intermolecular hydrogen bonds between the hydrogen atoms of water molecules and the sulphur atoms of the anion. The H····S bond lengths with H····A < r(A) + 2.0 Å vary from 2.371 to 2.949 Å (Figure 17).

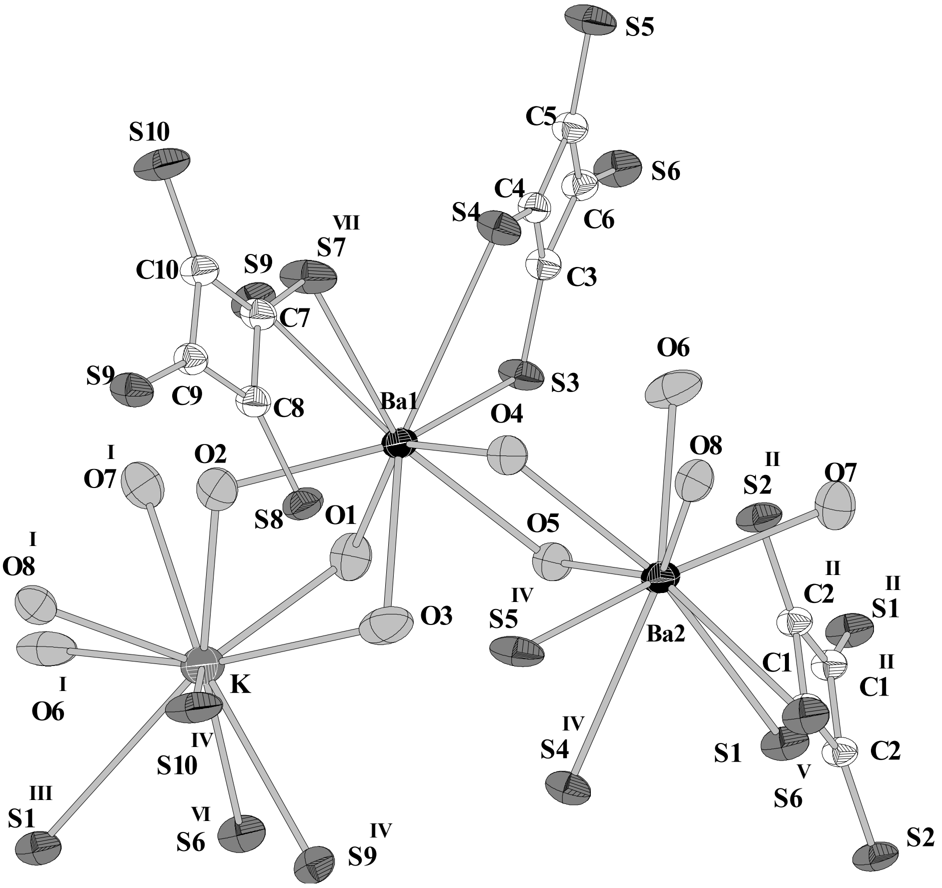


Figure 14 Section of the structure of $[Ba_4K_2(H_2O)_{16}](C_4S_4)_5$. Thermal ellipsoids are drawn to include a probability density of 50%.

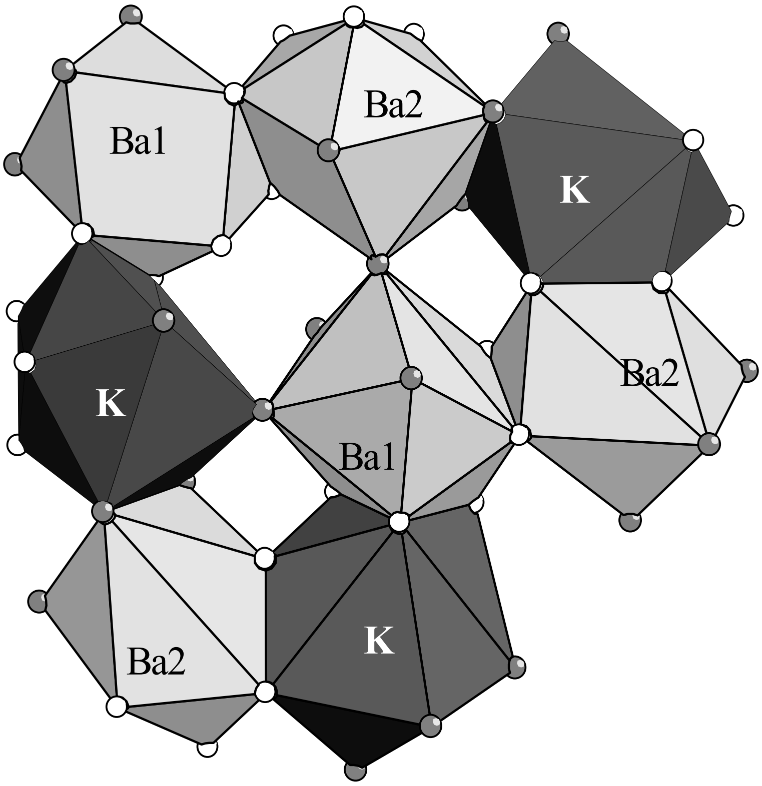


Figure 15 A section of a layer of coordination polyhedra of the Ba^{2+} and the K^{+} ions showing their interconnection via common corners and edges.

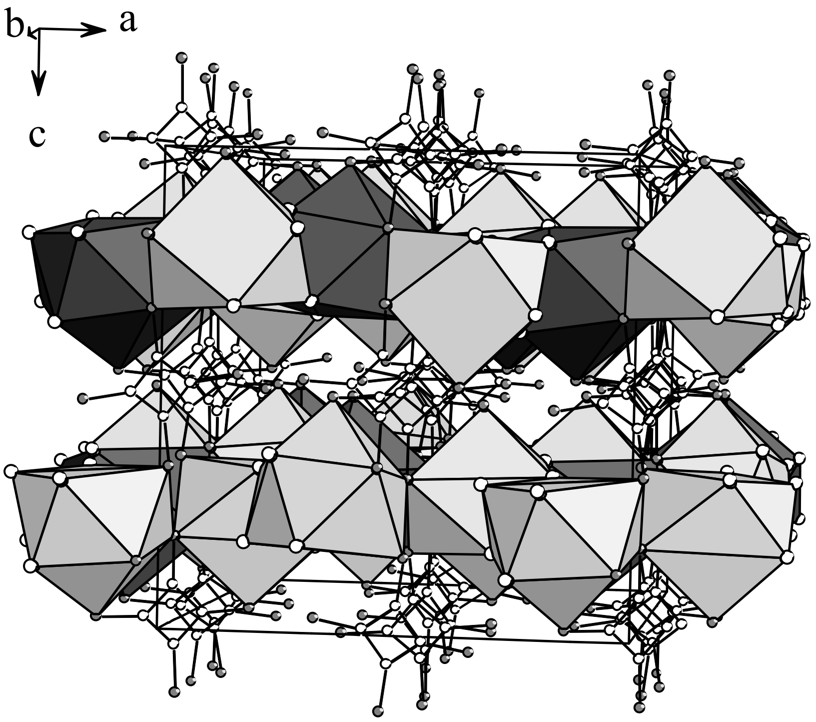


Figure 16 The unit cell of $[Ba_4K_2(H_2O)_{16}](C_4S_4)_5$ in a perspective view along the *b*-axis showing the coordination of the Ba^{2+} and the K^+ ions as massive polyhedra.

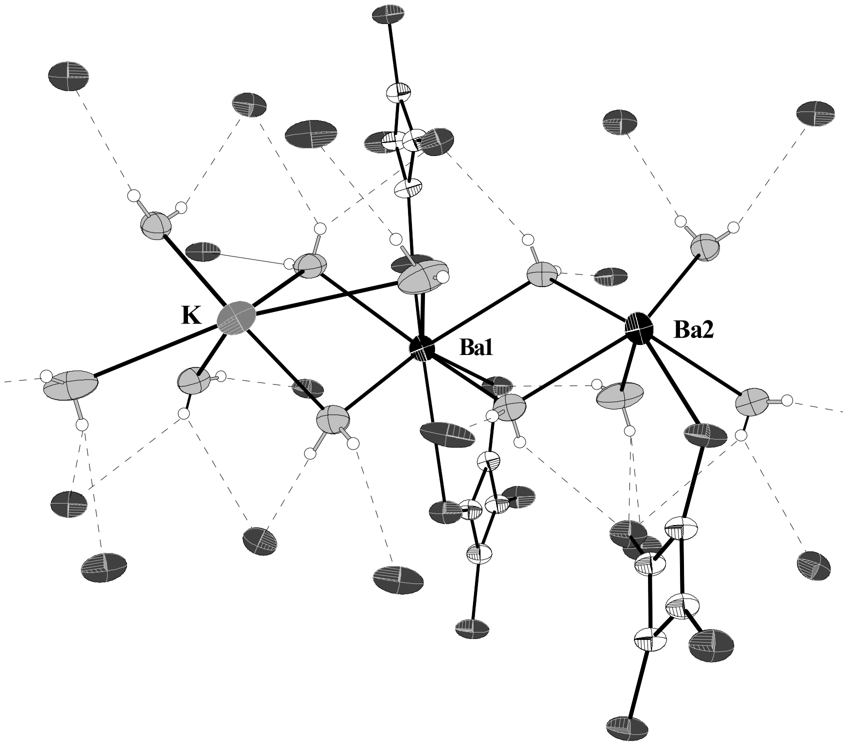


Figure 17 O–H···S hydrogen bridges in the structure of $[Ba_4K_2(H_2O)_{16}](C_4S_4)_5$. Shown is a section of the structure with the two independent Ba^{2+} ions and the K^+ ion and all H_2O molecules attached to the cations. All sulfur atoms around the hydrogen atoms of the water molecules are included. Thermal ellipsoids are drawn to include a probability density of 50%.

3.1.10 IR and Raman Spectroscopy of Earth Alkaline Tetrathiosquarates

The IR and Raman spectra of the four earth alkaline tetrathiosquarate compounds are closely related. The observed IR spectra of $[Mg(H_2O)_6](C_4S_4)$ and $[Ca(H_2O)_4](C_4S_4)$ are shown in Figure 18 and of $[Sr(H_2O)_4](C_4S_4)$ and $[Ba_4K_2(H_2O)_{16}](C_4S_4)_5$ in Figure 19**.** IR spectra of all compounds show broad bands at 3394, 3387, 3352 and 3314 cm^{-1} which are assigned to O–H stretching vibrations of the water molecules present in the compounds. The IR spectra are each dominated by two absorptions at 1231, 756 cm^{-1} for $[Mg(H_2O)_6](C_4S_4)$, 1250, 763 cm^{-1} for $[Ca(H_2O)_4](C_4S_4)$, 1243, 762 cm^{-1} for $[Sr(H_2O)_4](C_4S_4)$ and $[Ba_4K_2(H_2O)_{16}](C_4S_4)_5$. The absorption bands 1231-1250 cm^{-1} are split into two bands which are separated by about 10 cm^{-1}. The observed Raman spectra of $[Mg(H_2O)_6](C_4S_4)$ and $[Ca(H_2O)_4](C_4S_4)$ are shown in Figure 20 and of $[Sr(H_2O)_4](C_4S_4)$ and $[Ba_4K_2(H_2O)_{16}](C_4S_4)_5$ shown in Figure 21**.** Each Raman spectrum show three strong lines at 1083, 445, 419 cm^{-1} for $[Mg(H_2O)_6](C_4S_4)$, 1083, 450, 421 cm^{-1} for $[Ca(H_2O)_4](C_4S_4)$, 1083, 445, 419 cm^{-1} for $[Sr(H_2O)_4](C_4S_4)$ and 1083, 445, 419 for $[Ba_4K_2(H_2O)_{16}](C_4S_4)_5$ and additionally weak lines at 1171. 1179. 1193 and 1184 cm^{-1}. The IR and Raman frequencies of the investigated compounds are collected in Table 18. A vibrational analysis of the tetrathiosquarate ion has been performed [24]. All the observed IR and Raman bands are in line with literature data and can be attributed to the normal modes of a D_{4h} symmetric $(C_4S_4)^{2-}$ ion. The splitting of the 1231-1250 cm^{-1} IR-active e_u bands may be due to the loss of the degenerate character by the low point symmetry of the ions in the crystal and the resulting distortion. Weak absorption bands in the IR spectra at 1615-1638 cm^{-1} cannot be explained by normal modes of the $(C_4S_4)^{2-}$ ion and are attributed to C=O vibrations probably caused by the presence of trithiosquarate $(C_4OS_3)^{2-}$ or dithiosquarate $(C_4O_2S_2)^{2-}$.1,2-Dithiosquarate shows two strong IR absorptions at 1708 and 1627 cm^{-1} of which the 1708 cm^{-1} absorption is attributed to ν_s(C=O) [42]. The IR spectrum of 1,3-dithiosquarate has a strong absorption at 1545 cm^{-1} attributed to ν(OCCO) [43]. Since the starting material used, $K_2(C_4S_4)$ ·H2O, showed weak IR absorptions in the 1608 cm^{-1} region indicating the presence of oxygen containing impurities. Partial hydrolysis of tetrathiosquarate by the long exposure to water during the preparation process plays apparently only a minor role.

Table 18 Infrared and Raman data (cm^{-1}) for earth alkaline tetrathiosquarates and $K_2(C_4S_4)\cdot H_2O$.

	Infrared spectra				Raman spectra				
	OH stretch	CS stretch	CC and CS stretch	C S stretch	CS stretch	CC and CS stretch	Ring def.	CS out of plane def.	CS in plane def.
$K_2(C_4S_4)\cdot H_2O$[20]	3464 b	1608 s	1243m	753 s	1181w	1089s	447s	418s	180w
$[Mg (H_2O)_6](C_4S_4)$	3394 b	1636 s	1231m	756 s	1171w	1083s	445s	419s	156w
$[Ca_2(H_2O)_6](C_4S_4)_2$	3387 b	1638 s	1250 m	763 s	1197w	1083s	450s	421s	183w
$[Sr(H_2O)_4](C_4S_4)$	3352 b	1632 s	1243 m	762 s	1193 w	1079 s	446 s	419 s	175 w
$Ba_2K(H_2O)_8(C_4S_4)_{25}$	3314 b	1615 s	1243 m	768 s	1184 w	1086 s	452 s	424 s	156 w

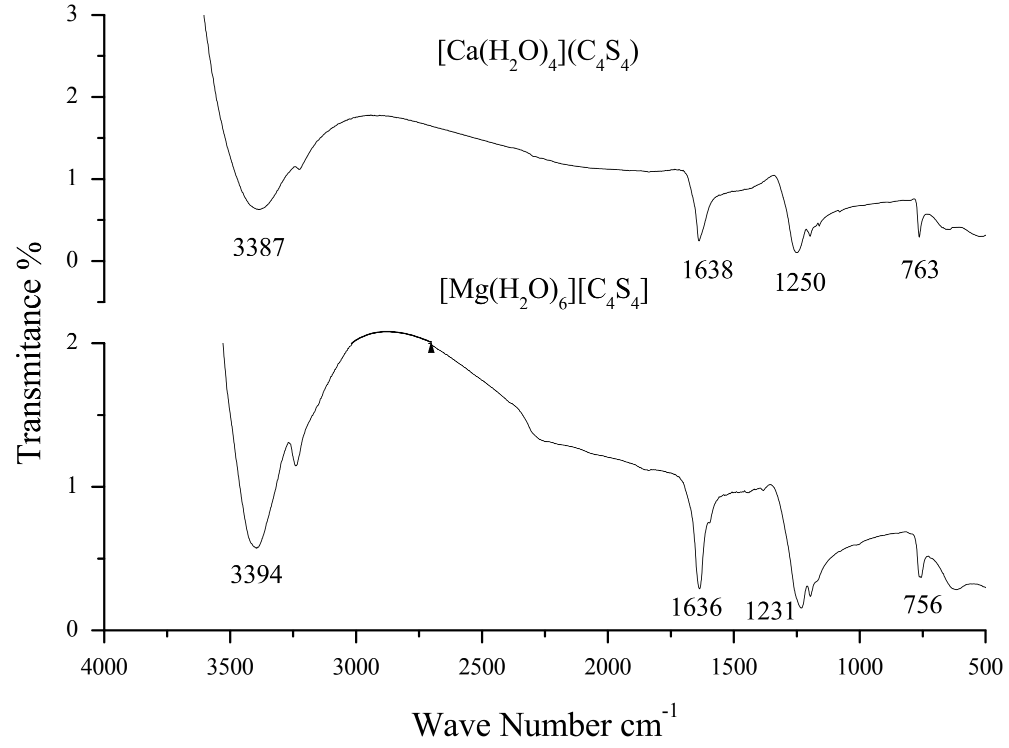


Figure 18 IR spectra for $[Mg(H_2O)_6](C_4S_4)$ and $[Ca(H_2O)_4](C_4S_4)$.

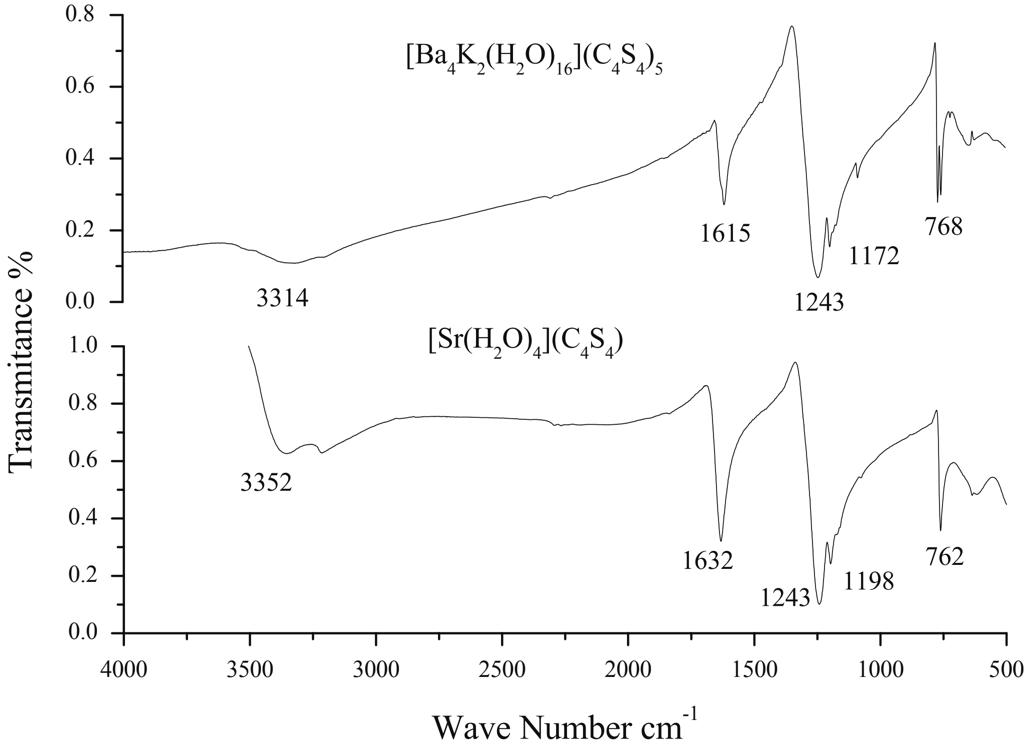


Figure 19 IR spectra for $[Sr(H_2O)_4](C_4S_4)$ and $[Ba_4K_2(H_2O)_{16}](C_4S_4)_5$.

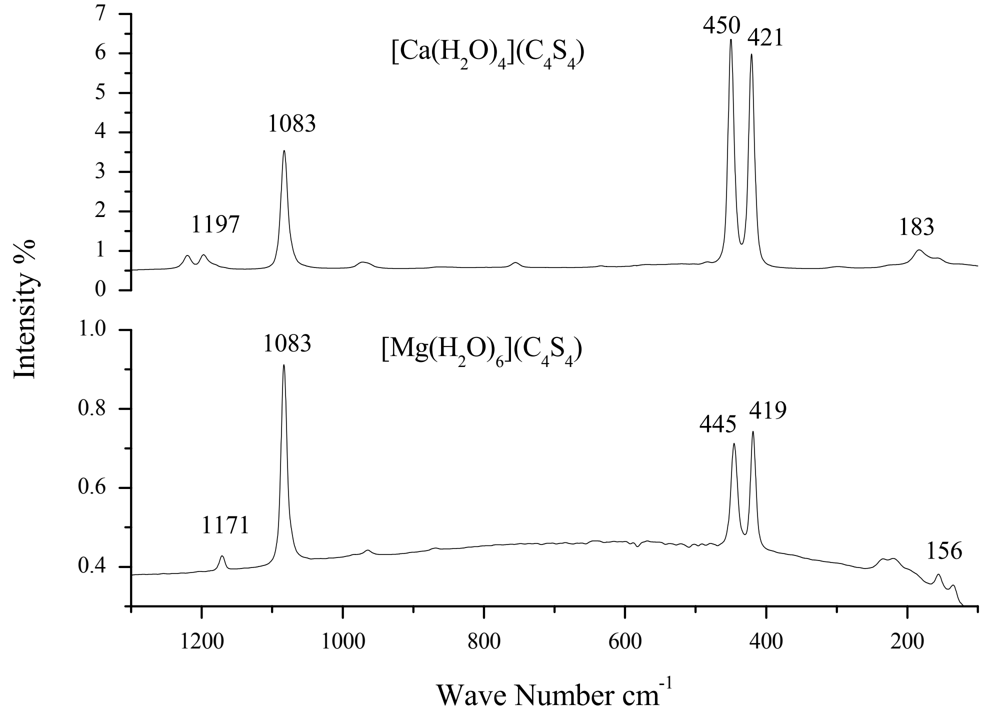


Figure 20 Raman spectra for [Mg(H2O)6](C4S4) and [Ca(H2O)4](C4S$_4$).

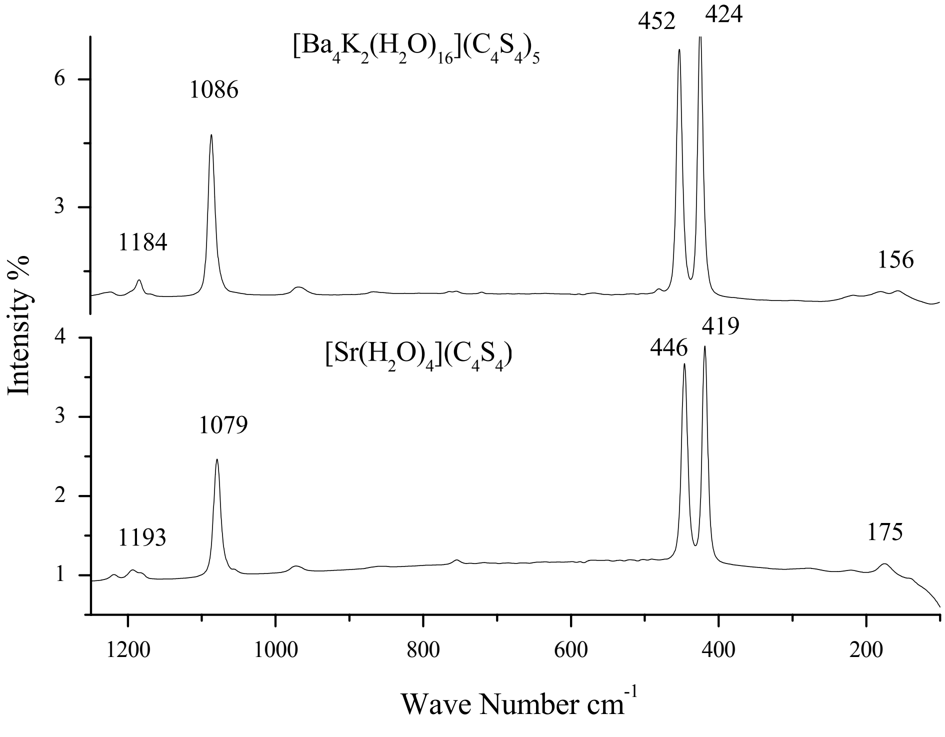


Figure 21 Raman spectra for [Sr(H$_2$O)$_4$](C$_4$S$_4$) and [Ba$_4$K$_2$(H$_2$O)$_{16}$](C$_4$S$_4$)

3.1.11 Discussion and Comparison of Earth Alkaline Tetrathiosquarate Salts

Tetrathiosquarate $(C_4S_4)^{2-}$ forms water soluble compounds of salt-like character with the earth alkaline ions from Mg^{2+} to Ba^{2+}. While Ca^{2+} and Sr^{2+} yield almost isotypic tetrahydrates $[M(H_2O)_4](C_4S_4)$, Mg^{2+} and Ba^{2+} show a different behaviour. For Mg^{2+} the formation of the discrete octahedral complex ion $[Mg(H_2O)_6]^{2+}$ is observed, Ba^{2+} forms a double salt with the used starting compound $K_2C_4S_4{\cdot}H_2O$. $[Ba_2K(H_2O)_{16}](C_4S_4)_5$ is the least soluble of the series. The Ca^{2+}, Sr^{2+}, and Ba^{2+} containing salts show high coordination numbers for the earth alkaline ions, which are linked by bridging H_2O molecules and bridging tetrathiosquarate ions to one-dimensional strands for Ca^{2+} and Sr^{2+} or to a three-dimensional network for $[Ba_2K(H_2O)_{16}](C_4S_4)_5$. In all structures, the $(C_4S_4)^{2-}$ ions almost fulfill D_{4h} symmetry despite small deviations from the ideal symmetry are generally observed caused by the coordination to the cations. The smaller, less polarizable ion Mg^{2+} prefers a coordination environment by the harder ligand H_2O, while the larger and softer cations Ca^{2+}, Sr^{2+}, and Ba^{2+} are bound to both, H_2O and the sulfur atoms of the $(C_4S_4)^{2-}$ anion.

3.2 Manganese (II) and Iron (II) Tetrathiosquarates

3.2.1 Structure Determination of $[Mn_4(OH)_4(H_2O)_4](C_4S_4)_2$

The crystals of this compound are slightly sensitive towards the loss of water and were therefore sealed in glass capillaries. The diffraction quality of the crystals towards X-rays was checked by preliminary precession exposures, which showed the tetragonal symmetry. Data were collected at ambient temperature using a Nonius kappa-CCD diffractometer equipped with Mo-Kα radiation (λ=0.7107 Å). The space group could be derived from the data set as $P\,4_2/nmc$ (№ 137). A structure model was obtained by direct method [38] and refined against F^2 with anisotropic displacement parameters for all non-hydrogen atoms [39]. The H atoms were all identified in a difference Fourier synthesis. They were included as individual atoms with free positional and isotropic displacement parameters in the refinement. Crystallographic data and details of the structure analysis are given in Table 19, positional parameters, equivalent isotropic parameters for the non-H atoms and isotropic displacement parameters for H atoms in Table 20, anisotropic displacement parameters for the non-H atoms in Table 21 and selected bond lengths and angles in Table 22.

Table 19 Crystallographic data and details of the structure determination of $[Mn_4(OH)_4(H_2O)_4](C_4S_4)_2$.

Formula	$C_8H_{12}O_8Mn_4S_8$
Lattice constants	a = b = 11.3418(2) Å
	c = 8.3029(2) Å
Volume of unit cell	1068.06 $Å^3$
Number of formula units	Z = 4
Density (calc.)	$\rho = 2.21\ g \cdot cm^{-3}$
Absorption coefficient	$\mu = 31.3\ cm^{-1}$
Crystal system, space group	Tetragonal, $P4_2/nmc$ (№ 137)
Diffractometer	Nonius kappa-CCD
Radiation, wave length	Mo-Kα, λ = 0.7107 Å
Temperature of measurement	T = 293 K
Range of data collection	2θ < 49.99°
Number of data collected	1861
Number of independent reflections, R_{merge}	486, 6.83%
Number of refined parameters	46
Ratio reflections/parameters	10.6
R (|F|) for all reflections	7.75%
R (|F|) for 356 reflections with $F_0 > 4\sigma(F_0)$	3.56 %
$wR(F^2)$	8.93 %
Largest electron density difference peak and hole	+0.75 / -0.30 e /$Å^3$

Table 20 Positional parameters, equivalent isotropic parameters U_{eq} / Å^2 for the non-H atoms and isotropic displacement parameters for H atoms in the structure of $[Mn_4(OH)_4(H_2O)_4](C_4S_4)_2$.

Atom	**x**	**y**	**z**	**U_{eq}**
Mn	0.75	0.39955(8)	0.11516(12)	0.0366(4)
S	0.58881(10)	0.57752(10)	0.12032(18)	0.0406(4)
C	0.6858(4)	0.6851(3)	0.1193(6)	0.0273(10)
O1	0.3745(4)	0.75	-0.1237(6)	0.0369(11)
O2	0.7500	0.4055(6)	-0.1499(7)	0.0626(16)
H1	0.75	0.399(13)	-0.252(3)	0.19(7)
H2	0.75	0.478(4)	-0.124(19)	0.4(2)
H3	0.442(6)	0.75	-0.081(14)	0.19(5)

Table 21 Anisotropic displacement parameters U_{ij} /Å^2 for the non-H atoms in the structure of $[Mn_4(OH)_4(H_2O)_4](C_4S_4)_2$. Standard deviations are given in parentheses.

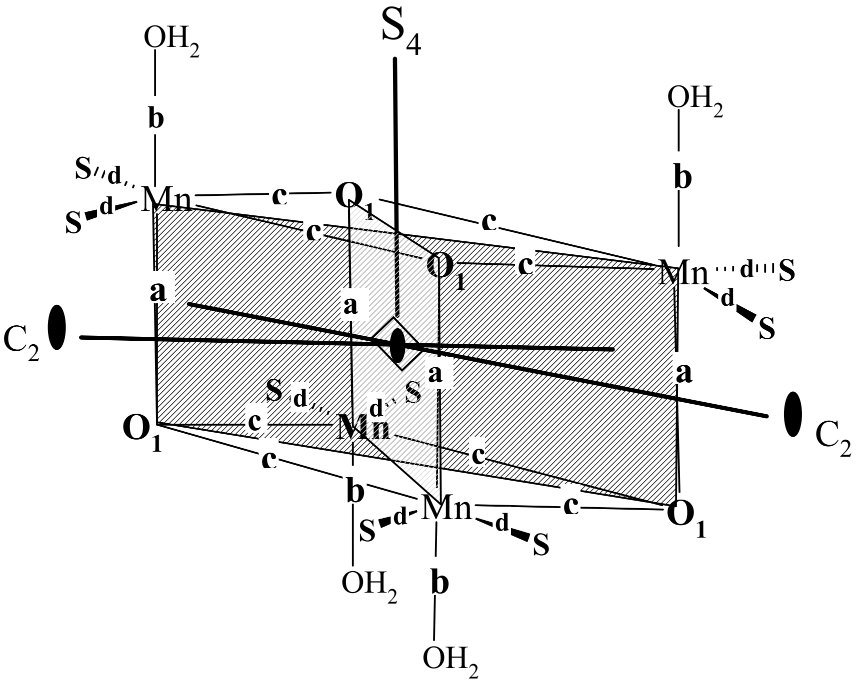
Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{12}**	**U_{13}**	**U_{23}**
Mn	0.0398(8)	0.0273(7)	0.0429(7)	0	0	0.0029(7)
S	0.0278(8)	0.0269(8)	0.0669(9)	-0.0057(5)	-0.0004(8)	-0.0005(8)
C	0.026(2)	0.019(2)	0.036(3)	0.00002(3)	-0.0005(3)	0.0006(2)
O1	0.039(3)	0.028(3)	0.044(3)	0	0.016(3)	0
O2	0.077(5)	0.061(5)	0.050(4)	0	0	-0.0027(3)

Table 22 Selected bond lengths /Å and angles /° for $[Mn_4(OH)_4(H_2O)_4](C_4S_4)_2$. Symmetry operations: I= 1-x, 1-y, -z ; II =-0.5+x, 0.5+y, -z ; III=y, 1.5-x, -0.5+z ; IV= 1.5-x, y, z.

Mn–O(1)^{I}	2.208(3)	Mn^{I}–O(1)	2.208(3)
Mn–O(1)^{VI}	2.208(3)	Mn^{II}–O(1)	2.208(3)
Mn–O(1)^{VII}	2.187(5)	Mn^{III} –O(1)	2.187(5)
Mn–O(2)	2.202(6)	C–C^{IV}	1.457(8)
Mn–S	2.724(1)	C–C^{V}	1.471(8)
Mn^{IV}–S^{IV}	2.724(1)	S–C	1.643(4)
O(1)^{I}–Mn–O(1)^{VII}	82.4 (2)	O(1)^{I}–Mn–S^{IV}	98.1 (1)
O(2)–Mn–O(1)^{VII}	174.3(2)	O(2)–Mn–S^{IV}	89.6 (1)
O(1)^{VI}–Mn–O(1)^{I}	79.5 (2)	O(1)^{I}–Mn–S	176.4(1)
C–C^{V}–C^{IV}	90.00(0)	S–Mn–S	84.3 (0)
C^{IV}–C–S	132.0(1)	S^{III}–Mn^{III}–S^{III}	84.3 (0)

3.2.2 Discussion of the Structure of $[Mn_4(OH)_4(H_2O)_4](C_4S_4)_2$

The structure consists of a cube–shaped cation $[Mn(\mu_3\text{-}OH)(H_2O)]_4^{4+}$, and tetrathiosquarate anions $(C_4S_4)^{2-}$ (Figures 22 and 23). Each manganese(II) is sixfold coordinated and bound to three oxygen atoms of hydroxide groups, two sulfur atoms of a tetrathiosquarate unit and one oxygen atom of a water molecule. The coordination environment around each metal center is a distorted octahedron in which angles are 82.4(2)° to 98.0(1)°, 174.3(2)° and 176.4(1)°. The $[Mn_4(H_2O)_4(OH)_4]^{4+}$ clusters are centered around the special positions 2*b* $\frac{3}{4}\frac{1}{4}\frac{1}{4}$ and $\frac{1}{4}\frac{3}{4}\frac{3}{4}$ in the unit cell.



Scheme 7 Schematic structure of the cube-shaped $[Mn(\mu_3\text{-}OH)(H_2O)_4]_4^{4+}$ in the structure of $[Mn_4(OH)_4(H_2O)_4](C_4S_4)_2$. The symmetry operations are given in the symbols according to the *International Tables for Crystallography*. Additionally the respective Schönfließ notations are given. The unique distances are a=2.187(5). b=2.202(6). c=2.208(3) and d=2.724(1)Å.

These positions have the site symmetry $\bar{4}m2$, in Schönfließ notation this is equivalent to D_{2d}. In the center of each cluster a $\bar{4}$ center is present; two perpendicular mirror planes bisect the clusters with all atoms of the Mn_4O_4 core located in the mirror planes. Between the mirror planes two perpendicular twofold axes are present running through the faces of the Mn_4O_4 cube. Scheme 7 shows a schematic representation of the cluster and the symmetry operations. There are only a few independent bond lengths in cluster present as depicted in Scheme 7. A subtle distortion in the manganese coordination geometry is found. The Mn–O distances average is 2.199 Å, which is a typical value of Mn^{2+}–O distances [44]. A significant flattening occurs along the $H_2O(2)$–Mn–O(1) bond vector involving the terminal water ligand, which produces distinct classes of Mn–O and Mn–S bond lengths. The bonds perpendicular to the molecular S_4 axis, designated c and d in Scheme 7, are longer than those parallel to the molecular S_4 axis. The Mn···Mn distances also reflect the alternating Mn–O and Mn–S bond lengths. The two face diagonals perpendicular to the S_4 axis are 0.11 Å longer than the four other diagonals. The O···O distances within the core of 2.813(2) Å and 2.879(2) Å are beyond the van der Waals radii of O atoms. The $(C_4S_4)^{2-}$ anions have *mm*2 symmetry. They are made up by only one independent sulfur atom and one independent carbon atom. The two mirror planes bisect the (C_4S_4) moiety perpendicular to the C–C bonds. The symmetry corresponds to the Schönfließ point group C_{2v}. Since the mirror planes do not pass through the C–S bonds, (C_4S_4) must be planar to fulfill this symmetry despite there is no mirror plane parallel to the plane of the ring. This special symmetry conditions cause all four C–S bonds to be of equal lengths but allow for two different C–C bonds. The anion is slightly distorted with $C–C^{IV}=1.457(8)$ Å and $C–C^{V}=1.471(8)$ Å. All C-C-C angles are 90.0° and the C–S distance is 1.643(4) Å. The anion is planar in which all SC–CS torsion angles are 0°. The S····S distances in the outer perimeter of the rings are 3.91 Å for the non coordinating S atoms but are only 3.66 Å for the coordinating edges. Anions and cations are stacked along the *c*-axis. Each $[Mn_4(OH)_4(H_2O)_4]^{4+}$ cluster is attached to four $(C_4S_4)^{2-}$ ions with each anion acting as a chelating ligand to two Mn^{2+} ions at opposite sides. A two-dimensional network of $[Mn_4(OH)_4(H_2O)_4]^{4+}$ clusters and square planar $(C_4S_4)^{2-}$ ions results (Figure 24). This network is made up of large rings consisting of four clusters and four $(C_4S_4)^{2-}$ anions. The center of each of these rings is filled by a $[Mn_4(OH)_4(H_2O)_4]^{4+}$ cluster of the next layer (Figure 25). The $[Mn_4(H_2O)_4(OH)_4]^{4+}$ complexes and the $(C_4S_4)^{2-}$anions are connected via a three-dimensional net of O–H···O and O–H···S bridges (Figure 26). O–H···O bridges connect the $[Mn(OH)(H_2O)]_4^{+}$ complexes to one-dimensional strands along the *c*-axis with an O(2)·····O(2) distance of 2.997 Å, and H(1)·····O(2) distance of 2.570 Å, and an O(2)·····S(1) distance of 3.491 Å, and H(2)·····S(1) distance of 2.958 Å, O–H···O and O–H···S angles are 111.99° and 122.75°, respectively.

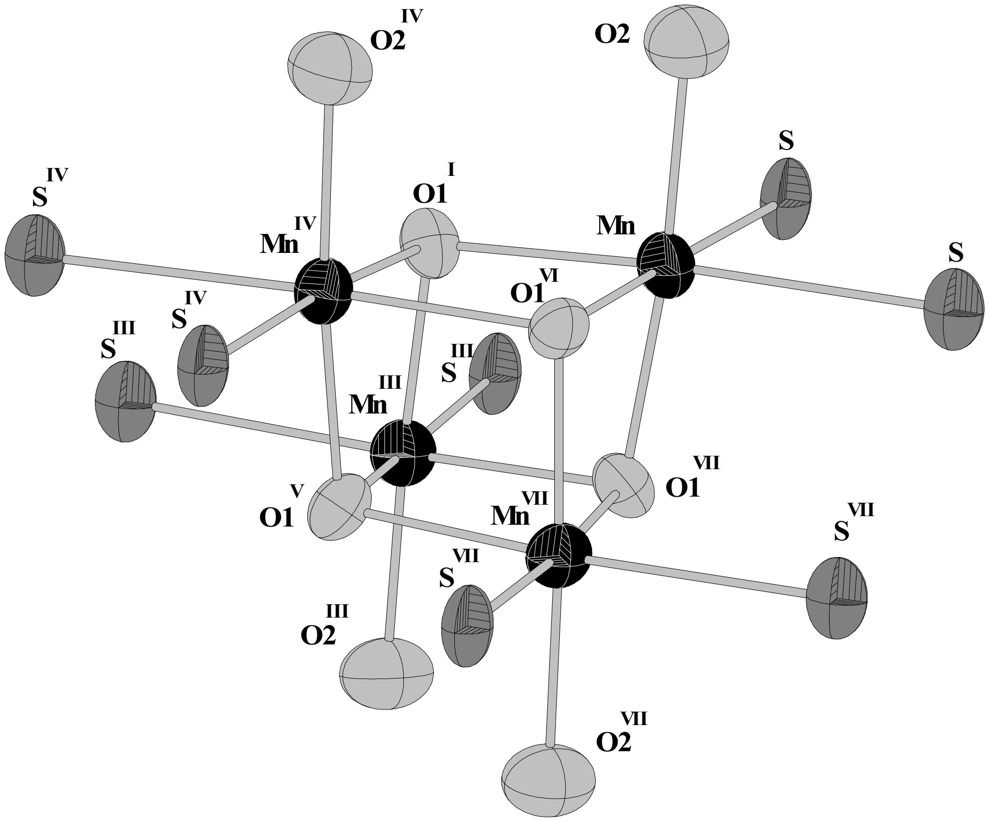


Figure 22 Cuban like core of the $[Mn_4(OH)_4(H_2O)_4](C_4S_4)_2$ structure. Thermal ellipsoids are drawn to include a probability density of 50%. Symmetry operations: I= 1-x, 1-y, -z ; II =-0.5+x, 0.5+y, -z ; III=y, 1.5-x, -0.5+z ; IV= 1.5-x, y, z; V=x, 1.5-y, z; VI=0.5+x, 1-y, -z; VII=1.5-y, x, 0.5+z.

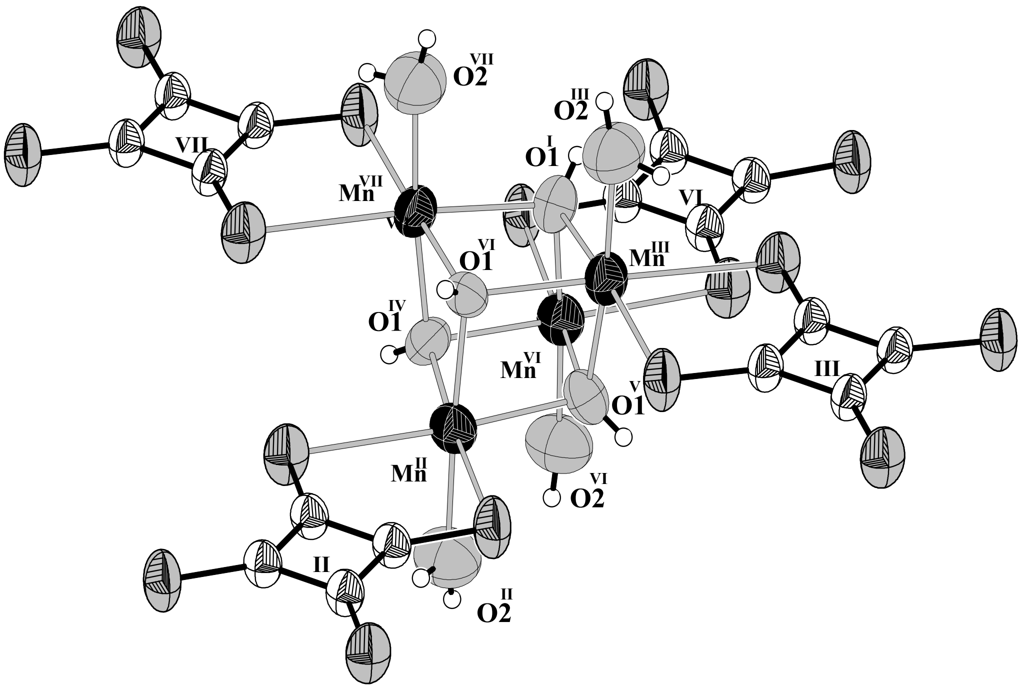


Figure 23 Section of the structure of $[Mn_4(OH)_4(H_2O)_4](C_4S_4)_2$. Thermal ellipsoids are drawn to include a probability density of 50%. For the $(C_4S_4)^{2-}$ ions the symmetry code is given in the centre of the rings.

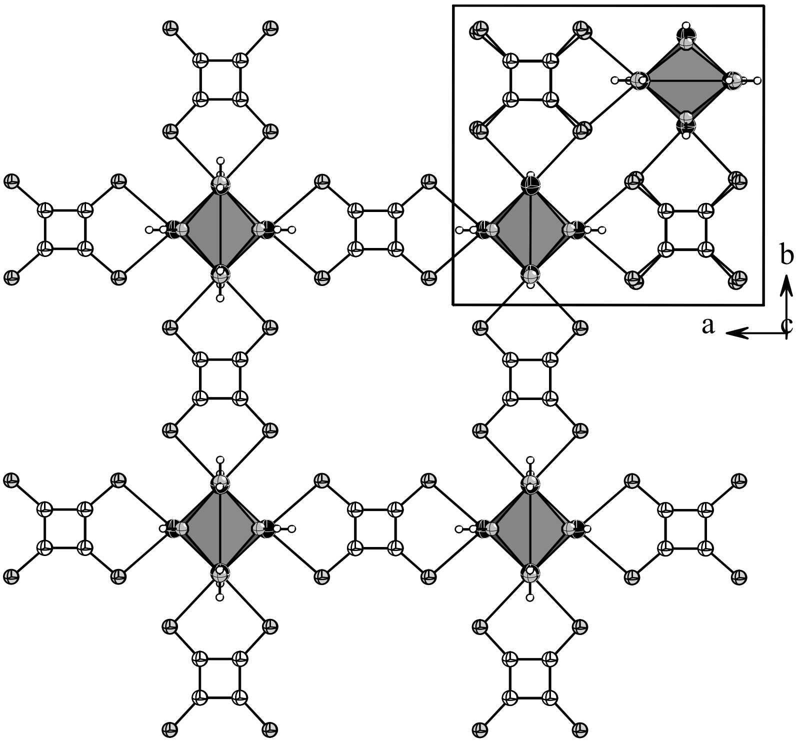


Figure 24 The structure of $[Mn_4(OH)_4(H_2O)_4](C_4S_4)_2$ in a view along the *c*-axis. The unit cell is shown and a larger section of one layer of $[Mn_4(OH)_4(H_2O)_4]^{4+}$ clusters, which are connected by $(C_4S_4)^{2-}$ anions.

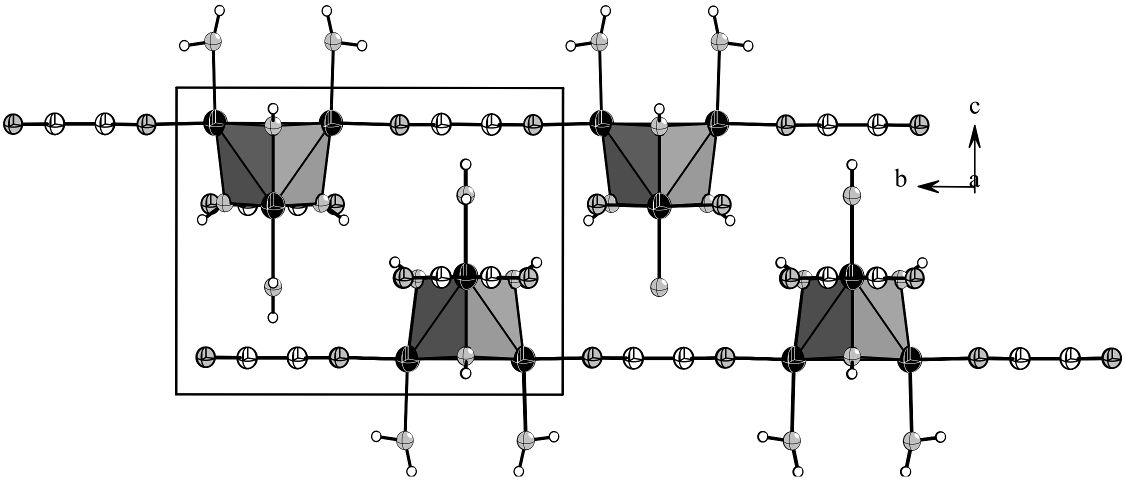


Figure 25 The unit cell of $[Mn_4(OH)_4(H_2O)_4](C_4S_4)_2$ in a view along the *a*-axis. Sections of layers in the structure of $[Mn_4(OH)_4(H_2O)_4](C_4S_4)_2$ are shown and their stacking along the crystallographic *c*-axis.

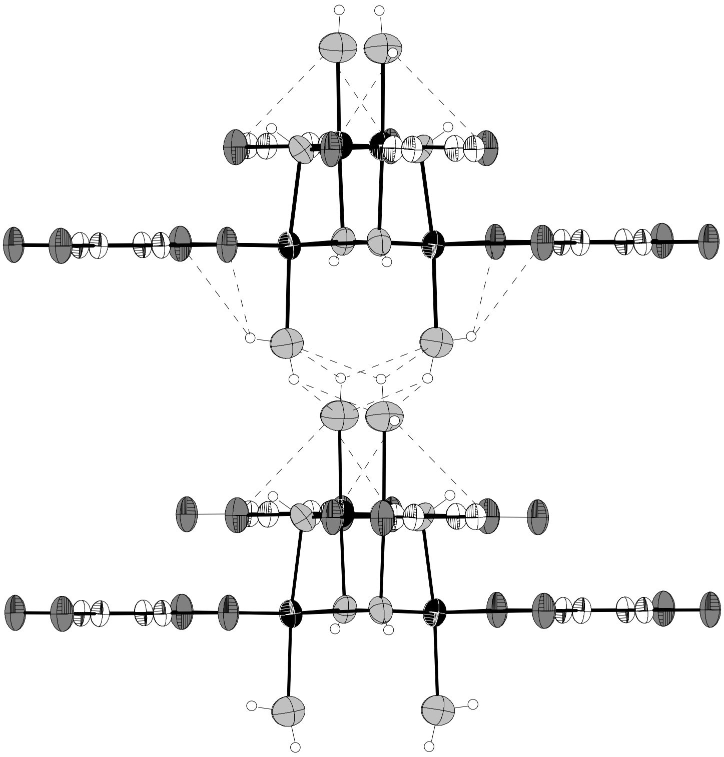


Figure 26 The interconnection of $[Mn_4(OH)_4(H_2O)_4]^{4+}$ clusters by O–H···S and O–H···O bridges. All S···H contacts shorter than 3.20 Å and O···H contacts shorter than 2.55 Å are depicted as dotted lines.

3.2.3 Structure Determination of $[Fe(H_2O)_2](C_4S_4)\cdot 4H_2O$

The crystals of this compound are slightly sensitive towards the loss of water and were therefore sealed in glass capillaries. The diffraction quality of the crystals towards X-rays was checked by preliminary precession exposures, which showed the monoclinic symmetry. Data were collected at ambient temperature using a Nonius kappa-CCD diffractometer equipped with Mo-Kα radiation (λ=0.7107 Å). The space group could be derived from the data set as the triclinic group $P\bar{1}$ (№ 2). A structure model was obtained by direct method [38] and refined against F^2 with anisotropic displacement parameters for all non-hydrogen atoms [39]. The refinement confirmed the centrosymmetry of the structure. The H atoms were all identified in a difference Fourier synthesis. They were included as individual atoms with free positional and isotropic displacement parameters in the refinement. Crystallographic data and details of the structure analysis are given in Table 23, positional parameters, equivalent isotropic parameters for the non-H atoms and isotropic displacement parameters for H atoms in Table 24, anisotropic displacement parameters for the non-H atoms in Table 25 and selected bond lengths and angles in Table 26.

Table 23 Crystallographic data and details of the structure determination of $[Fe(H_2O)_2](C_4S_4)\cdot 4H_2O$. Standard deviations are given in parentheses.

Formula	$C_4H_{12}FeO_6S_4$
Lattice constants	a =6.3381(3) Å, α =72.318(3)° b =7.3026(4) Å, β =73.316(3)° c =7.6097(3) Å, γ =81.411(3)°
Volume of unit cell	320.70 $Å^3$
Number of formula units	Z = 1
Density (calc.)	$\rho = 1.76\ g \cdot cm^{-3}$
Absorption coefficient	$\mu = 18.3\ cm^{-1}$
Crystal system, space group	Triclinic, $P\bar{1}$ (№ 2)
Diffractometer	Nonius kappa-CCD
Radiation, wave length	Mo-Kα, λ = 0.7107 Å
Temperature of measurement	T = 293 K
Range of data collection	$2\theta < 55.10°$
Number of data collected	2899
Number of independent reflections, R_{merge}	1463, 2.01%
Number of refined parameters	94
Ratio reflections/parameters	15.7
R (|F|) for all reflections	3.74%
R (|F|) for 1206 reflections with $F_0 > 4\sigma(F_0)$	2.65%
$wR(F^2)$	5.91%
Largest electron density difference peak and hole	+0.60 / -0.31 e /$Å^3$

Table 24 Positional parameters, equivalent isotropic parameters U_{eq} / Å^2 for the non-H atoms and isotropic displacement parameters for H atoms in the structure of $[Fe(H_2O)_2](C_4S_4)\cdot4H_2O$. Standard deviations are given in parentheses.

Atom	**x**	**y**	**z**	**U_{eq}**
Fe	0.0000	0.5000	0.5000	0.02499(13)
S1	0.27989(7)	0.39327(7)	0.70380(6)	0.03027(14)
S2	0.27377(7)	0.38266(7)	0.22926(6)	0.02951(14)
C1	0.1123(3)	0.4559(3)	0.8896(2)	0.0253(4)
C2	0.1092(3)	0.4513(3)	0.0839(2)	0.0243(4)
O1	0.1089(2)	0.7864(2)	0.3857(2)	0.0342(3)
O2	0.7190(3)	0.0552(3)	0.3939(4)	0.0467(5)
O3	0.3370(4)	0.8811(3)	0.0043(3)	0.0518(5)
H1	0.164(4)	0.817(4)	0.286(4)	0.050(9)
H2	0.172(6)	0.813(6)	0.457(6)	0.113(14)
H3	0.717(6)	0.085(5)	0.321(4)	0.049(13)
H4	0.849(8)	-0.043(7)	0.377(7)	0.159(17)
H5	0.421(6)	0.784(5)	-0.004(5)	0.085(12)
H6	0.256(8)	0.935(7)	-0.029(7)	0.15(2)

Table 25 Anisotropic displacement parameters U_{ij} / Å^2 for the non-H atoms in the structure of $[Fe(H_2O)_2](C_4S_4)\cdot4H_2O$. Standard deviations are given in parentheses.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{12}**	**U_{13}**	**U_{23}**
Fe	0.0274(2)	0.0339(2)	0.0160(2)	-0.0027(2)	-0.0064(2)	-0.0092(2)
S2	0.0269(3)	0.0459(3)	0.0190(2)	0.0032(2)	-0.0096(2)	-0.0130(2)
S1	0.0266(3)	0.0477(3)	0.0201(2)	0.0030(2)	-0.0069(2)	-0.0163(2)
C1	0.0268(9)	0.0333(9)	0.0189(9)	-0.0025(8)	-0.0065(8)	-0.0107(8)
C2	0.0255(9)	0.0321(9)	0.0170(9)	-0.0026(8)	-0.0061(8)	-0.0083(8)
O1	0.0361(9)	0.0405(9)	0.0264(9)	-0.0079(7)	-0.0033(7)	-0.0115(7)
O2	0.051(1)	0.042(1)	0.052(1)	-0.0007(9)	-0.022(1)	-0.0116(9)
O3	0.056(1)	0.050(1)	0.0386(9)	0.004(1)	-0.0031(9)	-0.0074(8)

Table 26 Selected bond lengths / Å and angles / °for $[Fe(H_2O)_2](C_4S_4)\cdot 4H_2O$. Symmetry operations: I= -x, 1-y, 1-z ; II= x, y, -1+z.

Fe(1)–O(1)	2.142(3)	C(1)–S(1)^{I}	1.650(3)
Fe(1)–O(1)^{I}	2.142(3)	C(2)^{I}–S(2)^{I}	1.653(2)
Fe(1)–S(1)	2.567(4)	C(1)^{I}–C(2)^{I}	1.463(0)
Fe(1)–S(2)	2.562(5)	C(1)–C(2)^{I}	1.452(2)
Fe(1)–S(1)^{I}	2.567(4)	C(1)^{I}–C(2)	1.452(2)
Fe(1)–S(2)^{I}	2.562(5)	C(1)–C(2)	1.463(0)
O(1)–Fe–O(1)^{I}	180.0(0)	C(1)–C(2)^{I}–C(1)^{I}	90.37(14)
O(1)–Fe –S(2)	92.35(4)	C(2)–C(1)^{I}–C(2)^{I}	89.63(14)
O(1)– Fe –S(1)^{I}	87.65(4)	C(1)^{II}–C(2)^{I}–C(1)^{I}	90.37(14)
S(1)– Fe –S(2)	90.61(1)	C(2)–C(1)–C(2)^{I}	89.63(14)
S(1)^{I}– Fe –S(2)	89.39(1)	C(1)–C(2)–C(1)^{I}	90.37(14)

3.2.4 Discussion of the Structure of $[Fe(H_2O)_2](C_4S_4)\cdot 4H_2O$

The structure of $[Fe(H_2O)_2](C_4S_4)\cdot 4H_2O$ is built of one-dimensional polymeric strands. Tetrathiosquarate ions act as bridging ligands between Fe^{2+} ions making up the linear chain –Fe–C_4S_4–Fe–C_4S_4–. The six-coordinate iron atom is located on a crystallographic center of symmetry and is coordinated by two bidentate tetrathiosquarate anions occupying the equatorial positions and by two water molecules occupying the axial positions (Figure 27). The FeS_4 unit is required by symmetry to be planar. The O–Fe–O linear unit is positioned normal to the FeS_4 plane. The Fe–O bond length is 2.142(3) Å, while the respective Fe–S bonds to S(1) and S(2) are longer and amount to 2.567(4) and 2.562(5)Å, respectively (Table 16). The angles in the octahedral arrangement are 180° and near to 90°, only differing by ±2.45°. The anions are located at a center of symmetry. They are planar with C–C bonds of 1.452 and 1.463 Å and C–S bonds of 1.650 and 1.653 Å. The ions deviate only slightly from ideal D_{4h} symmetry. The S···S distances in the outer perimeter of the $(C_4S_4)^{2-}$ ion show, however, significant deviations from square symmetry. The short $S(2)\cdots S(1)^{I}$ and $S(1)^{II}\cdots S(2)^{I}$ (3.81 Å) distances are observed between the coordinating S atoms, which are attached to the same Fe atom. The S···S distances in the direction of the chain $S(1)^{I}\cdots S(2)^{I}$ and $S(1)^{II}\cdots S(2)$ are longer (3.97 Å). In the unit cell, the $[Fe(H_2O)_2(C_4S_4)]_n$ chains are running along the *c*-axis (Figure 28). All chains are identical by translational symmetry and within the chains the (C_4S_4) groups are identical too, so all (C_4S_4) groups in the structure are arranged parallel to each other (Figure 29). The structure contains four additional water molecules per formula unit. The chains are connected by the water molecules $H_2O(2)$ and $H_2O(3)$ via a three-dimensional net of O–H···O and O–H···S bridges (Figure 30) with O·····O distances from 2.768 to 3.039 Å and H·····O distances of 1.917 to 2.611 Å. The O(3)·····S(2) distance is 3.331 Å, which amounts the sum of van der Waals radii (3.32 Å [45]) with O–H···O and O–H···S angles between 146.4 to 174.6°. Hydrogen bridges with H·····A < r(A) + 2.0 Å of 1.92 Å for H(4)·····O(1) to 2.611 Å for H(5)·····S(2) are observed [46].

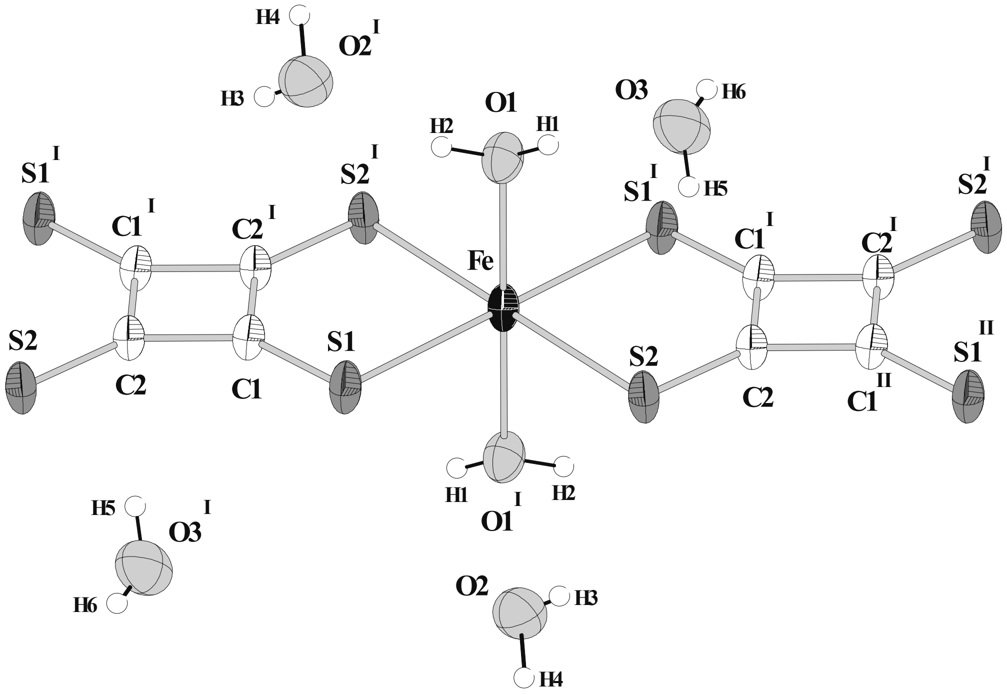


Figure 27 Section of the structure of $[Fe(H_2O)_2](C_4S_4)\cdot 4H_2O$. Thermal ellipsoids are drawn to include a probability density of 50%. Symmetry operations: I= -x, 1-y, 1-z; II=x, y, -1+z.

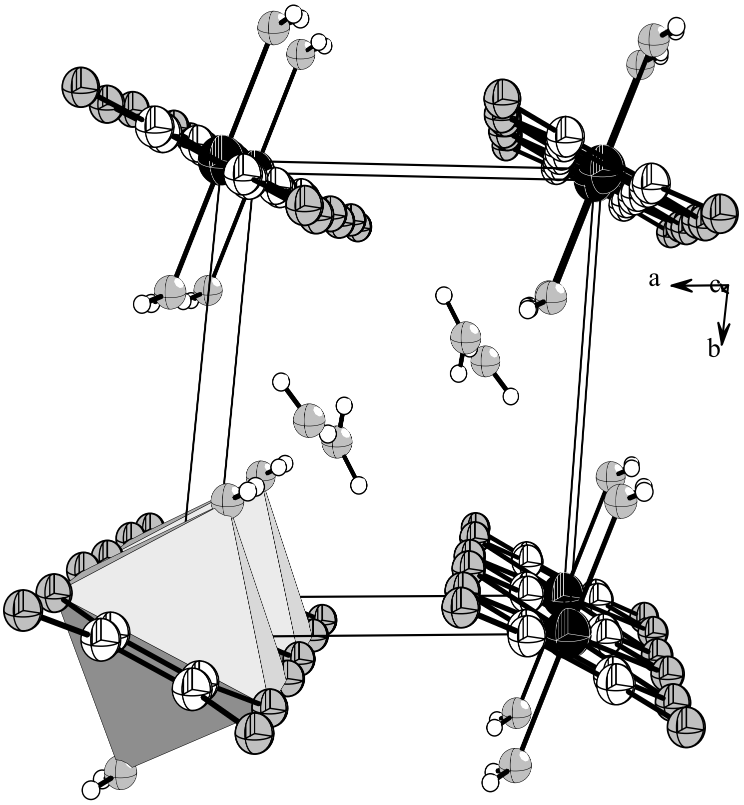


Figure 28 The chains in the structure of $[Fe(H_2O)_2](C_4S_4)\cdot 4H_2O$ in a view along the *c*-axis. For one of the translational equivalent chains, the coordination of the Fe^{2+} ions is shown as massive octahedra.

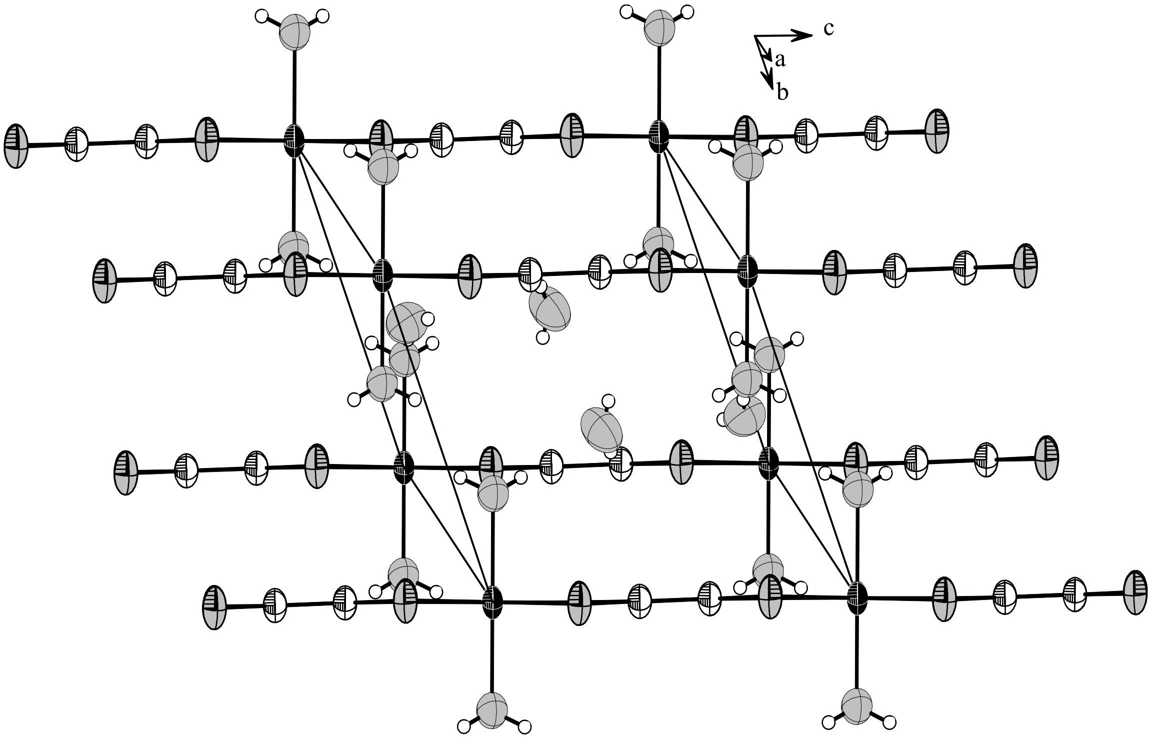


Figure 29 The structure of $[Fe(H_2O)_2](C_4S_4)\cdot 4H_2O$ in a view perpendicular to the chains and in the plane of the (C_4S_4) groups.

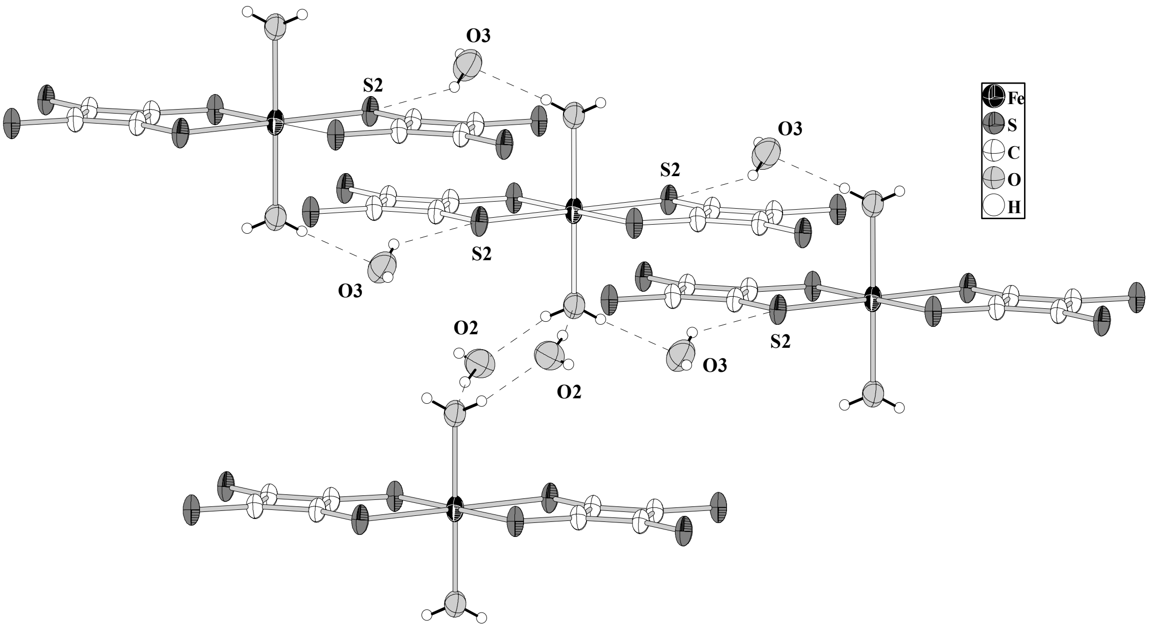


Figure 30 The interconnection of the $[Fe(H_2O)_2](C_4S_4)\cdot 4H_2O$ chains by O–H···S and O–H···O bridges.

3.2.5 Discussion and Comparison of Transition Metal Tetrathiosquarate Salts

Tetrathiosquarate $(C_4S_4)^{2-}$ is known to form water insoluble precipitations with most transition metals [21,22]. This shows that $(C_4S_4)^{2-}$ acts as a ligand using all four S atoms to form irregular, amorphous networks with transition metal ions. This stands in contrast to the behavior of $(C_4S_4)^{2-}$ towards alkaline and earth alkaline ions. Here, high solubility of the respective metal salts is observed and no precipitations occur. This is caused by the concurrence of $(C_4S_4)^{2-}$ and H_2O as ligands towards the mono- and divalent main group element ions. In all salts with these hard cations there are always water molecules present acting as ligands towards the metal ions and $(C_4S_4)^{2-}$ does not replace them completely. This situation changes on going to the transition metal ions, when $(C_4S_4)^{2-}$ becomes a stronger ligand in comparison to H_2O. The soft ligand $(C_4S_4)^{2-}$ replaces all or mostly all harder H_2O ligands from the hexaqua complexes $[M(H_2O)_6]^{2+}$ in the solution. Since $(C_4S_4)^{2-}$ is a polydentate ligand, the formation of irregular networks is probable and occurs with all transition metal ions. Surprisingly it was now observed that for the transition metal ions Fe^{2+} and Mn^{2+} crystalline compounds can be obtained from aqueous solutions. In both structures, water molecules are present as ligands and fill the coordination polyhedra of the cations to octahedra. However, the observations of W. Beck et al. [21,22] are still valid since the yield of the crystalline polymeric Mn^{2+} and Fe^{2+} compounds are low and the major part of the product is obtained as a brown powder insoluble in water. In the iron (II) salt, the Fe^{2+} ions are linked by bridging tetrathiosquarate ions and two H_2O molecules to a one-dimensional strand. The four uncoordinated H_2O molecules of each formula unit bridge the strands together through O–H···S and O–H···O hydrogen bonds. The Mn^{2+} salt is made up of interesting cube-shaped complexes $[Mn(OH)_4(H_2O)_4]^{4+}$ which are connected by tetrathiosquarate ions to a two-dimensional network, in which O–H···S and O–H···O bridging bonds connect the layers to a three-dimensional structure. The $Mn_4(OH)_4$ cuboidal cluster core has already been reported. In 1991 M. Zaworotko et al. prepared $[Mn(CO)_3(\mu_3\text{-}OH)]_4$ from $Mn_2(CO)_{10}$ and $(CH_3)_3NO{\cdot}2H_2O$ in tetrahydrofurane (THF) as solvent in quantitative yield [47]. This carbonyl molecule has T_d molecular symmetry while in the crystal (space group $P\bar{3}$) only a threefold axis through a Mn atom and an opposite OH group is present [48]. Figure31 gives a view of this molecule. The

Mn–O bond lengths are 2.032 Å and are thus closely related to the Mn–OH bonds found in $[Mn_4(H_2O)_4(OH)_4]^{4+}$ (average 2.19 Å). In a series of publications of the Zaworotko group, it could be shown that the OH groups are strong hydrogen bond donors able to act as nodal points in three dimensional network structures [49-53].

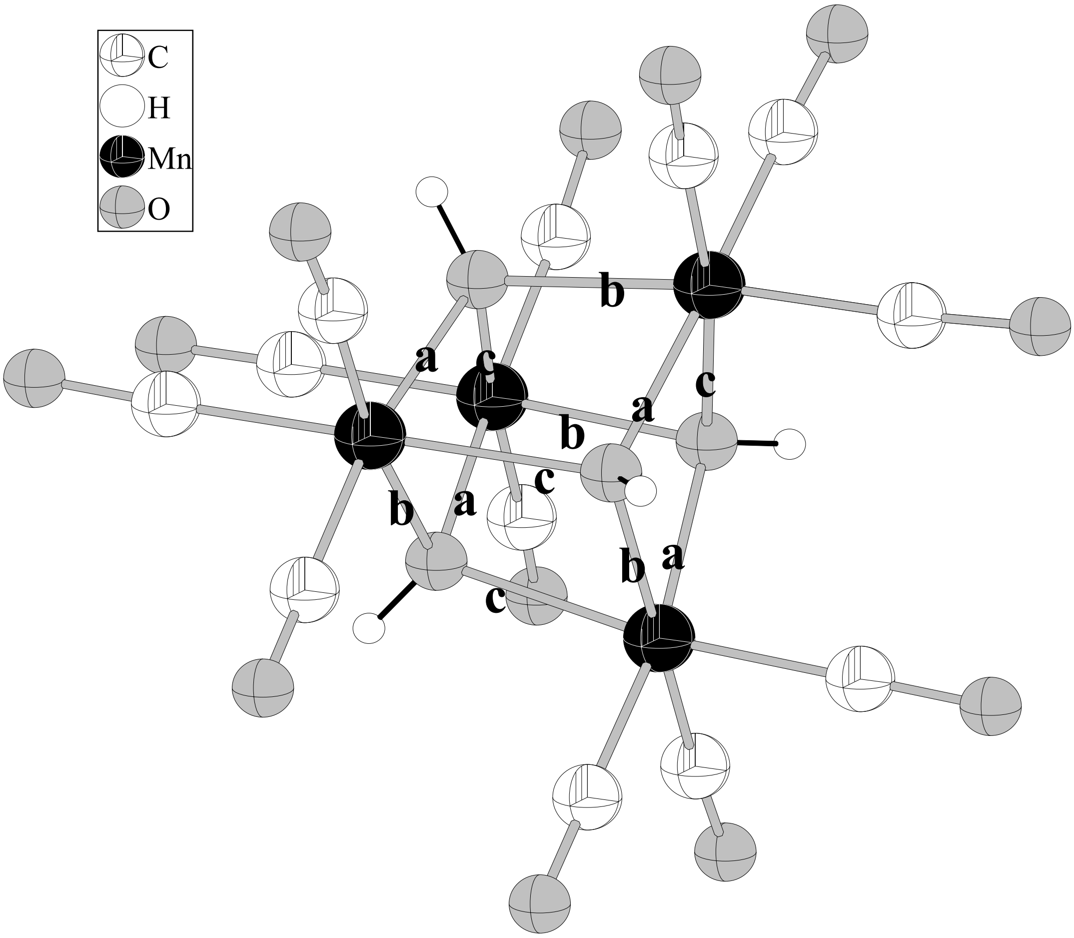


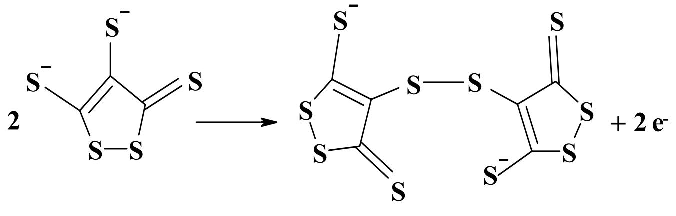
Figure 31 Cuban like core of $[Mn(CO)_3(\mu_3\text{-}OH)]_4$ [47]. The unique Mn–O distances are a=2.023(4), b=2.031(4) and c=2.044(4)Å.

3.3 Reactions of β-$(C_3S_5)^{2-}$ in Aqueous Solution

Tetrathiosquarate ions are hydrolytically of surprising stability. The experiments performed during this work showed that aqueous solutions of $(C_4S_4)^{2-}$ do not completely decompose even on prolonged time and exposure to air and light. Simple salts of the dimercapto-dithiole-thione ions, α and β-$(C_3S_5)^{2-}$, are sparingly known. α-$(C_3S_5)^{2-}$ is described to be a hydrolytically and thermal unstable molecule [26]. It was recommended to perform all reactions with a freshly prepared sample. This is in line with our observations. Dark red Na_2(α-C_3S_5) decomposes at room temperature, even in the absence of air within some days under change of color to brown-green. The behavior of the isomeric form β-$(C_3S_5)^{2-}$ is not mentioned in the literature. The samples of Na_2(β-C_3S_5), however, seem to be stable, since no change of color is observed even over months. So a study was undertaken analogously to the reactions of $(C_4S_4)^{2-}$ with earth alkaline ions. In contrast to $(C_4S_4)^{2-}$, β-$(C_3S_5)^{2-}$ turned out to be quite sensitive to oxidation, giving the $(C_6S_{10})^{2-}$ ion. To study the hydrolysis and oxidation processes, aqueous solutions of β-$(C_3S_5)^{2-}$ were brought to crystallization using tetraphenylarsonium chloride, $[As(C_6H_5)_4]Cl$. By this method, several hydrolysis and oxidation products of β-$(C_3S_5)^{2-}$ could be trapped as the respective $[As(C_6H_5)_4]^+$ salts. In the following paragraphs tentative reaction equations were set up to explain the formation of $(C_6S_{10})^{2-}$, $(C_3S_6O_3)^{2-}$, $(HC_3S_5)^-$ and $(C_3S_4H)^{2-}$. The reaction paths presented were assumed to be most probable one.

3.3.1 Oxidation of β-$(C_3S_5)^{2-}$ by Air and the Formation of $(C_6S_{10})^{2-}$

In aqueous solution the 4,5-dimercapto-1,2-dithiole-3-thione ion β-$(C_3S_5)^{2-}$ is oxidized to give the $(C_6S_{10})^{2-}$ ion under formation of a new S–S bond. This oxidation is caused by the oxygen of air (equations 1 and 2).



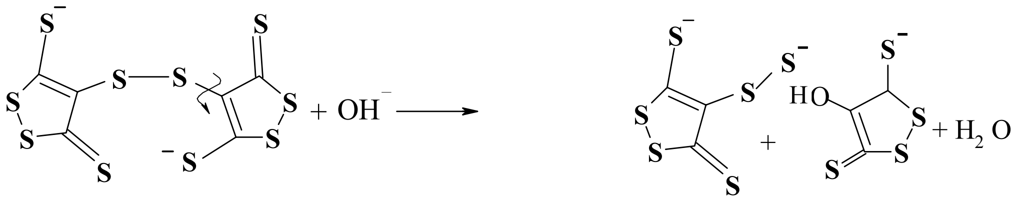
Oxidation (1)

$$1/2\ O_2 + OH_2 + 2e^- \longrightarrow 2\ OH^-$$

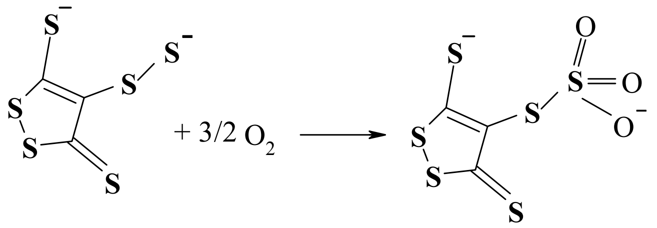
Reduction (2)

3.3.2 Oxidation by Air and the Formation of the $(C_3S_6O_3)^{2-}$ Ion

The formation of $(C_3S_6O_3)^{2-}$ can be understood by a three step reaction. According to equations (1) and (2), β-$(C_3S_5)^{2-}$ is oxidized by air to $(C_6S_{10})^{2-}$. In a second step, a C–S bond of the dimeric molecule is cleaved probably by nucleophilic attack of hydroxide ions leaving $(C_3S_6)^{2-}$ and $(HOC_3S_4)^{-}$, the respective persulfidic species (equation 3). $(C_3S_6)^{2-}$ is then oxidized by oxygen to $(C_3S_6O_3)^{2-}$ according to equation (4)



(3)



(4)

3.3.3 The Formation of the $(HC_3S_5)^{-}$ Ion

The formation of the monoprotonated ion $(HC_3S_5)^{-}$ can be straightforward understood by protolysis involving the solvent water. The Cl^{-} ion of $[As(C_6H_5)_4]Cl$ has basic properties and shifts the equilibrium slightly to the right side according to equation (5). $(C_3S_5)^{2-}$, however is a strong base. It is protonated by HCl and by H_2O to $(HC_3S_5)^{-}$ (equations 6 and 7).

$$[As\,(C_6H_5)_4]^{+} + Cl^{-} + H_2O \rightleftharpoons [As\,(C_6H_5)_4]^{+} + HCl + OH^{-} \qquad (5)$$

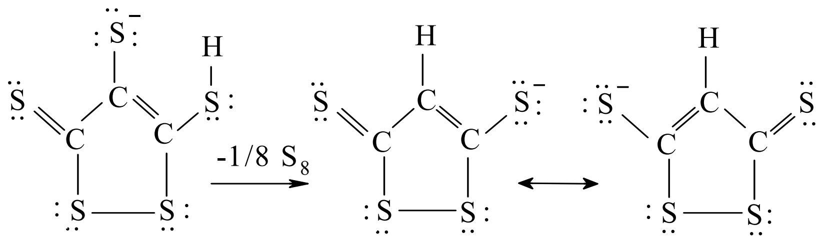
$$(C_3S_5)^{2-} + HCl \rightleftharpoons (HC_3S_5)^{-} + Cl^{-} \qquad (6)$$

$$(C_3S_5)^{2-} + H_2O \rightleftharpoons (HC_3S_5)^{-} + OH^{-} \qquad (7)$$

3.3.4 The Formation of the $(C_3S_4H)^-$ Ion Under Exclusion of Air

It can be assumed that in the aqueous solution $(HC_3S_5)^-$ ions are present. This ion can undergo an intramolecular hydrogen migration accompanied by the cleavage of elemental sulfur under exclusion of air. Equation 9 gives the mesomeric forms of this ion.

$$HC_3S_5^- \longrightarrow C_3S_4H^- + 1/8\ S_8\downarrow \qquad (8)$$



(9)

3.4 Calcium and Strontium Salts of $(C_6S_{10})^{2-}$

3.4.1 Structure Determination of $[Ca(H_2O)_7](C_6S_{10})$

The crystals of this compound are slightly sensitive towards air and were therefore sealed in glass capillaries. The diffraction quality of the crystals towards X-rays was checked by preliminary precession exposures, which showed the triclinic symmetry. Data were collected at ambient temperature using a Nonius kappa-CCD diffractometer equipped with Mo-Kα radiation (λ=0.7107 Å). The space group could be derived from the data set as $P\bar{1}$ (№ 2). A structure model was obtained by direct method [38] and refined against F^2 with anisotropic displacement parameters for all non-hydrogen atoms [39]. The refinement showed the structure to be centrosymmetric and $P\bar{1}$ to be the correct space group. The H atoms were all identified in a difference Fourier synthesis. They were included as individual atoms with free positional and isotropic displacement parameters in the refinement. Crystallographic data and details of the structure analyses are given in Table 27, positional parameters, isotropic equivalent parameters for the non-H atoms and displacement isotropic parameters for H atoms in Table 28, anisotropic displacement parameters for the non-H atoms in Table 29 and selected bond lengths and angles in Table 30.

Table 27 Crystallographic data and details of the structure determination of $[Ca(H_2O)_7](C_6S_{10})$.

Formula	$C_6H_{14}CaO_7S_{10}$
Lattice constants	a = 10.710(2)Å, α =112.99(6)°
	b = 10.718(3)Å, β =97.93(2)°
	c = 10.887(3)Å, γ =108.69(3)°
Volume of unit cell	1039.02 Å^3
Number of formula units	Z = 2
Density (calc.)	ρ = 1.787g · cm^{-3}
Absorption coefficient	μ =13.3 cm^{-1}
Crystal system, space group	Triclinic, $P\bar{1}$ (№ 2)
Diffractometer	Nonius kappa-CCD
Radiation, wave length	Mo-Kα, λ = 0.7107 Å
Temperature of measurement	T = 293 K
Range of data collection	$2\theta < 55°$
Number of data collected	31500
Number of independent reflections, R_{merge}	4730, 6.26%
Number of refined parameters	217
Ratio reflections/parameters	21.79
R(|F|) for all reflections	4.94%
R(|F|) for 3757 reflections with $F_0 > 4\sigma(F_0)$	3.10%
wR(F^2)	5.06%
Largest electron density difference peak and hole	+0.34 / -0.33 e /Å^3

Table 28 Positional parameters, equivalent isotropic parameters U_{eq} / Å^2 for the non-H atoms and displacement isotropic parameters for H atoms in the structure of $[Ca(H_2O)_7](C_6S_{10})$. Standard deviations are given in parentheses.

Atom	x	y	z	U_{eq}
Ca1	0.33637(4)	0.53572(5)	0.27423(4)	0.0303(1)
S1	-0.00189(6)	1.02487(7)	0.18918(6)	0.0423(1)
S2	0.12166(5)	0.78746(5)	0.56195(5)	0.0297(1)
S3	0.28455(5)	0.99605(6)	0.41955(5)	0.0323(1)
S4	0.41845(5)	1.16974(6)	0.94737(6)	0.0337(1)
S5	0.31782(5)	0.83260(6)	0.67389(5)	0.0294(1)
S6	-0.16771(6)	0.44539(7)	0.24821(8)	0.0497(2)
S7	-0.10229(5)	0.78494(6)	0.26023(5)	0.0302(1)
S8	-0.21004(5)	0.77315(6)	0.40264(6)	0.0310(1)
S9	0.30718(6)	1.01165(7)	1.09970(6)	0.0385(1)
S10	0.20815(6)	0.78424(7)	1.02596(7)	0.0421(2)
C1	-0.0809(2)	0.9637(2)	0.2900(2)	0.0252(4)
C2	0.1340(2)	0.9681(2)	0.6047(2)	0.0227(4)
C3	0.2030(2)	1.0476(2)	0.5399(2)	0.0235(4)
C4	0.3407(2)	1.0039(2)	0.9468(2)	0.0261(4)
C5	0.2966(2)	0.8598(2)	0.8383(2)	0.0246(4)
C6	0.2310(2)	0.7388(2)	0.8624(2)	0.0302(4)
O1	0.5014(2)	0.6663(2)	0.5025(2)	0.0397(4)
O2	0.4941	0.4135(2)	0.2589(2)	0.0412(4)
O3	0.4545(2)	0.7788(2)	0.2971(2)	0.0384(4)
O4	0.1554(2)	0.6103(3)	0.2369(2)	0.0447(4)
O5	0.3602(2)	0.5052(3)	0.0412(2)	0.0538(5)
O6	0.1688(3)	0.2909(3)	0.1166(4)	0.0714(7)
O7	0.2101(3)	0.4445(4)	0.4144(3)	0.0660(7)

Table 28 continued

H1	0.554(3)	0.747(4)	0.527(3)	0.055(9)
H2	0.495(3)	0.648(3)	0.562(3)	0.061(10)
H3	0.479(3)	0.343(4)	0.180(4)	0.085(12)
H4	0.565(4)	0.456(4)	0.280(4)	0.086(14)
H5	0.501(3)	0.846(4)	0.367(4)	0.079(12)
H6	0.487(4)	0.802(5)	0.235(5)	0.116(15)
H7	0.174(4)	0.690(5)	0.281(5)	0.115(18)
H8	0.072(4)	0.559(4)	0.229(4)	0.091(12)
H9	0.343(6)	0.436(7)	-0.001(6)	0.150(27)
H10	0.324(6)	0.524(7)	0.001(6)	0.154(28)
H11	-0.141(6)	0.752(7)	0.945(7)	0.153(30)
H12	-0.130(7)	0.756(8)	0.856(7)	0.188(33)
H13	0.161(5)	0.377(5)	0.385(5)	0.105(19)
H14	0.213(5)	0.501(6)	0.492(6)	0.139(22)

Table 29 Anisotropic displacement parameters U_{ij} [Å^2] for the non-H atoms in the structure of [Ca(H_2O)$_7$](C_6S_{10}). Standard deviations are given in parentheses.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{12}**	**U_{13}**	**U_{23}**
Ca1	0.0323(2)	0.0268(2)	0.0309(2)	0.0109(2)	0.0104(2)	0.0134(2)
S1	0.0492(3)	0.0521(4)	0.0430(3)	0.0244(3)	0.0279(3)	0.0310(3)
S2	0.0351(3)	0.0214(3)	0.0267(3)	0.0086(2)	0.0050(2)	0.0095(2)
S3	0.0308(3)	0.0322(3)	0.0286(3)	0.0097(2)	0.0127(2)	0.0103(2)
S4	0.0412(3)	0.0265(3)	0.0336(3)	0.0124(2)	0.0149(2)	0.0139(2)
S5	0.0344(3)	0.0325(3)	0.0299(3)	0.0199(2)	0.0158(2)	0.0157(2)
S6	0.0514(4)	0.0274(3)	0.0721(5)	0.0138(3)	0.0295(3)	0.0230(3)
S7	0.0318(3)	0.0284(3)	0.0305(3)	0.0148(2)	0.0106(2)	0.0116(2)
S8	0.0316(3)	0.0243(3)	0.0384(3)	0.0100(2)	0.0138(2)	0.0159(2)
S9	0.0440(3)	0.0438(3)	0.0284(3)	0.0153(3)	0.0168(2)	0.0178(3)
S10	0.0435(3)	0.0497(4)	0.0462(3)	0.0166(3)	0.0223(3)	0.0337(3)
C1	0.0214(9)	0.0279(10)	0.024(1)	0.0088(8)	0.0029(7)	0.0121(8)
C2	0.0219(9)	0.0201(10)	0.0222(9)	0.0066(7)	0.0028(7)	0.0092(8)
C3	0.0191(9)	0.0221(10)	0.0224(9)	0.0056(7)	0.0014(7)	0.0077(8)
C4	0.0232(9)	0.0349(11)	0.027(1)	0.0154(8)	0.0091(8)	0.0173(9)
C5	0.0227(9)	0.0288(11)	0.027(1)	0.0132(8)	0.0084(8)	0.0152(9)
C6	0.026(1)	0.0320(11)	0.041(1)	0.0143(8)	0.0120(9)	0.023(1)
O1	0.045(1)	0.0384(11)	0.0313(9)	0.0114(8)	0.0140(7)	0.0160(8)
O2	0.038(1)	0.0363(10)	0.040(1)	0.0150(8)	0.0098(8)	0.0102(8)
O3	0.0395(9)	0.0317(9)	0.0345(9)	0.0064(7)	0.0079(8)	0.0139(8)
O4	0.037(1)	0.0424(11)	0.059(1)	0.0183(8)	0.0200(8)	0.025(1)
O5	0.071(1)	0.0456(13)	0.037(1)	0.020(1)	0.0153(9)	0.015(1)
O6	0.073(1)	0.0329(11)	0.070(2)	-0.001(1)	0.010(1)	0.009(1)
O7	0.064(1)	0.0672(16)	0.062(1)	0.005(1)	0.024(1)	0.041(1)

Table 30 Selected bond lengths / Å and angles / ° for $[Ca(H_2O)_7](C_6S_{10})$.

Ca(1)–O(1)	2.485 (2)	C(5)–C(6)	1.404 (4)
Ca(1)–O(2)	2.373 (2)	S(2)–S(5)	2.078 (1)
Ca(1)–O(3)	2.396 (5)	S(9)–S(10)	2.072 (2)
Ca(1)–O(4)	2.432 (5)	S(1)–C(1)	1.687 (3)
Ca(1)–O(5)	2.396 (2)	S(4)–C(4)	1.702 (2)
Ca(1)–O(6)	2.365 (3)	S(5)–C(5)	1.758 (2)
Ca(1)–O(7)	2.446 (2)	S(6)–C(6)	1.695 (8)
C(1)–C(2)	1.406 (3)		
O(1)–Ca(1)–O(2)	76.54 (2)	O(6)–Ca(1)–O(3)	118.45(3)
O(2)–Ca(1)–O(3)	138.90(3)	O(2)–Ca(1)–O(4)	83.36(2)
O(4)–Ca(1)–O(5)	109.31(2)	O(6)–Ca(1)–O(1)	89.21(2)
C(1)–C(2)–C(6)	119.66(3)	S(10)–C(6)–S(1)	115.73(3)
C(4) –C(3)–C(5)	118.51(4)	S(6) –C(5)–S(7)	115.49(2)
C(1)–S(2)–S(1)	94.82(2)	C(2)–S(4)–S(5)	101.17(3)

3.4.2 Discussion of the Structure of $[Ca(H_2O)_7](C_6S_{10})$

The structure consists of discrete anions and cations without any significant close atom-atom contacts among them. Some intermolecular S···S nonbonded contacts within the sum of Van der Waals radii (3.7Å, represented by dashed lines) are observed along the *b*-axis (Figure 32). The calcium ion is bound to seven oxygen atoms of water molecules. The geometry about the metal center is a distorted pentagonal bipyramid, in which O–Ca–O angles in the equatorial positions are 76.44(2)° for O(1)–Ca–O(5) to 76.90(2)° for O(3)–Ca–O(5) and 166.80(3)° for the apical positions O(4)–Ca–O(6). The Ca–O bond lengths are rather uniform and range from 2.361(3) Å for O(6) to 2.483(2) Å for O(1). The anion consists of two essentially planar C_3S_5 subunits interconnected by a disulfide group. The two molecular planes consisting of S(2), S(5), and C_3S_5 make up an interplanar angle of 101° (Figure 33). The C(1)-C(2)-S(2)-S(5) and C(6)-C(5)-S(5)-S(2) torsion angles are 77.88(4)° and 78.42(4)°, respectively. In contrast to this, in diphenyldisulfide the phenyl rings are only torsioned by 19.82° and 1.06° [54]. These differences are not surprising, accounting the steric influence of the thione substituents. A plot of S–S bond lengths vs CS–SC torsion angles, in which all structures containing the C–S–S–C unit were included except those where the S–S bond is part of a ring, as gathered from the Cambridge Structural Database (based on version 5.18, 1999) [55] shows that the largest density of data points is concentrated in the bond length region between 2.00 and 2.07 Å with torsion angles between 75° and 90°. MO calculations suggest that C–S–S–C dihedral angles near 90° are stabilized by a weak bonding interaction between the C–S σ* orbital located on one sulfur atom and the $3p_z$ lone pair on the other sulfur atom [56]. The C(2)-S(2)-S(5)-C(5) torsion angle for the anion structure is -86.26(3)° and the S(2)–S(5) bond length is 2.078(1) Å. This values fall within the trend made by other disulfides [57]. In the packing, the disulfide bond is located parallel to the *bc* plane (Figure 32). The $[Ca(H_2O)_7]^{2+}$ complexes and the $(C_6S_{10})^{2-}$ anions are connected via a three-dimensional net of O–H···O and O–H···S bridges along the *c*-axis (Figure 34) with 2.285(3) Å for H(6)·····O(4), and H·····S average distance of 2.475 Å, O(3)·····O(4) distance of 3.04 Å, and O·····S average distance of 3.280 Å. The O(3)–H(6)···O(4) angle is 170.64°, and O–H···S average angles are 167.814°. Every $[Ca(H_2O)_7]^{2+}$ is connected to three neighbored $(C_6S_{10})^{2-}$ ions.

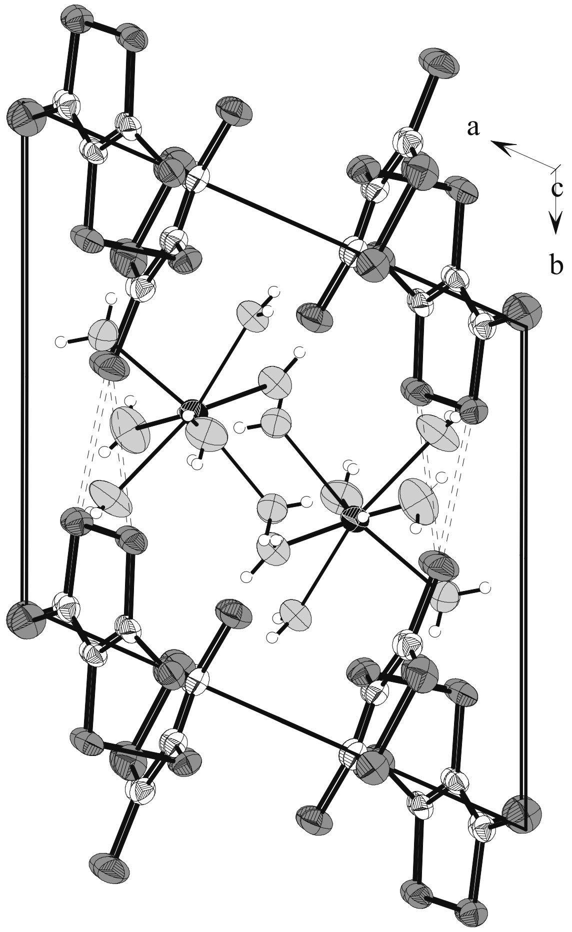


Figure 32 The unit cell of $[Ca(H_2O)_7](C_6S_{10})$ in a view along the *c*-axis.

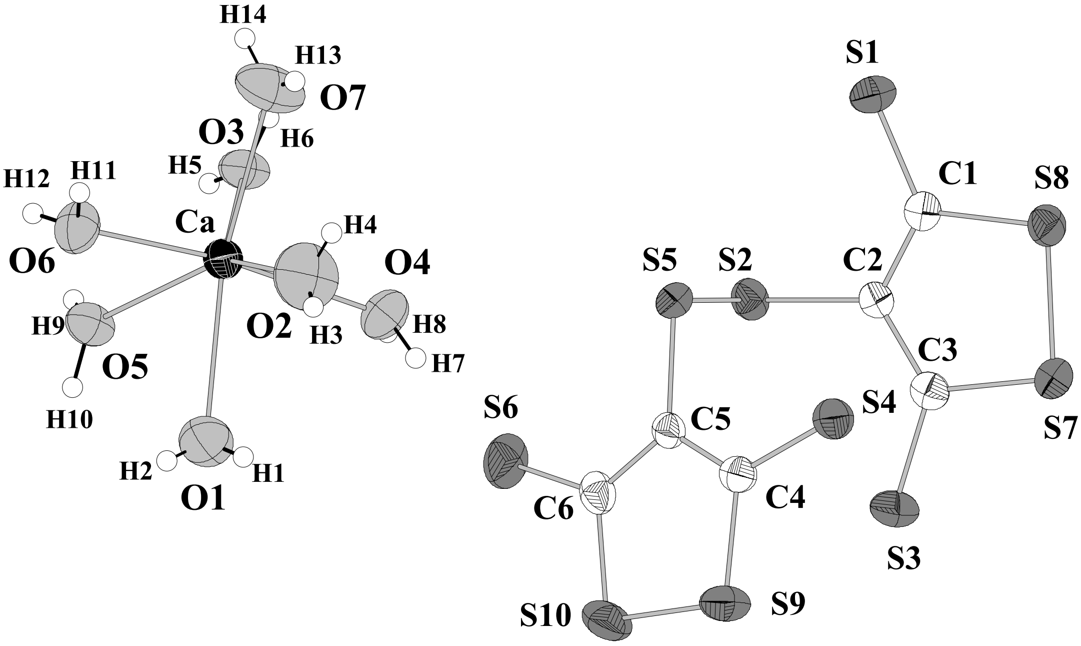


Figure 33 The ions in the structure of $[Ca(H_2O)_7](C_6S_{10})$. Thermal ellipsoids are drawn to include a probability density of 50%.

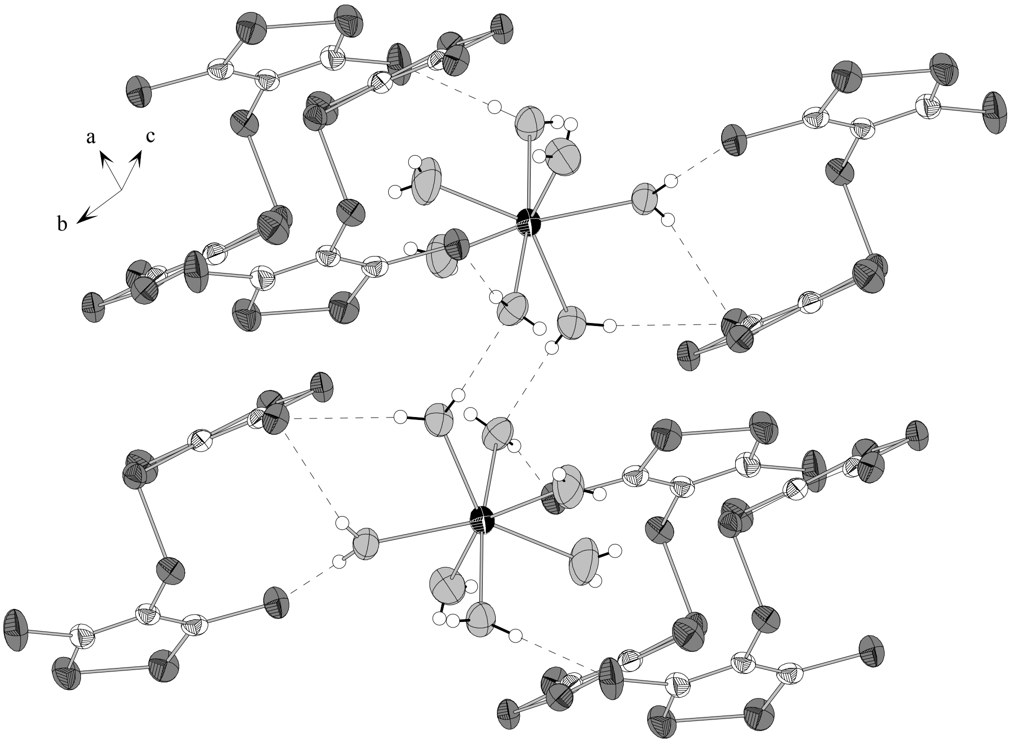


Figure 34 The interconnection of cations and anions in the structure of $[Ca(H_2O)_7](C_6S_{10})$ by O–H···S and O–H···O bridges.

3.4.3 Structure Determination of $[Sr(H_2O)_8](C_6S_{10})\cdot H_2O$

The crystals of this compound are sensitive towards the loss of water and were therefore sealed in glass capillaries. The diffraction quality of the crystals towards X-rays was checked by preliminary precession exposures which showed the triclinic symmetry. Data were collected at ambient temperature using a Nonius kappa-CCD diffractometer equipped with Mo-Kα radiation (λ=0.7107 Å). The space group could be derived from the data set as triclinic $P\bar{1}$ (№ 2). A structure model was obtained by direct method [38] and refined against F^2 with anisotropic displacement parameters for all non-hydrogen atoms [39]. The localization of the H atoms bound to the O atoms was not possible. These atoms were omitted from the refinement. Crystallographic data and details of the structure analyses are given in Table 31, positional parameters, isotropic equivalent parameters for the non-H atoms in Table 32, anisotropic displacement parameters for the non-H atoms in Table 33 and selected bond lengths and angles in Table 34.

Table 31 Crystallographic data and details of the structure determination $[Sr(H_2O)_8](C_6S_{10})\cdot H_2O$. Standard deviations are given in parentheses.

Formula	$C_6H_{18}O_9S_{10}Sr$
Lattice constants	a = 10.7100(9) Å, α =87.117(4)°
	b = 12.7497(9) Å, β =75.003(4)°
	c = 19.5076(9) Å, γ =69.430(3)°
Volume of unit cell	2406.54 $Å^3$
Number of formula units	Z = 4
Density (calc.)	$\rho = 1.723\ g \cdot cm^{-3}$
Absorption coefficient	$\mu = 31.51 cm^{-1}$
Crystal system, space group	Triclinic, $P\bar{1}$ (№ 2)
Diffractometer	Nonius kappa-CCD
Radiation, wave length	Mo-Kα, λ = 0.7107 pm
Temperature of measurement	T = 293 K
Range of data collection	$2\theta < 50.29°$
Number of data collected	15919
Number of independent reflections, R_{merge}	8349, 7.98%
Number of refined parameters	469
Ratio reflections/parameters	17.80
R(|F|) for all reflections	15.29%
R(|F|) for 4094 reflections with $F_0 > 4\sigma(F_0)$	6.17%
$wR(F^2)$	10.0 %
Largest electron density difference peak and hole	+1.3 / -0.46 e /$Å^3$

Table 32 Positional parameters, equivalent isotropic parameters U_{eq} / Å^2 for the non-H atoms in the structure of $[Sr(H_2O)_8](C_6S_{10})\cdot H_2O$. Standard deviations are given in parentheses.

Atom	**x**	**y**	**z**	**U_{eq}**
Sr1	0.15521(8)	0.72374(6)	0.46431(3)	0.0630(2)
Sr2	0.30058(8)	0.88520(6)	0.08984(3)	0.0644(2)
S1	-0.9172(2)	1.0063(2)	0.70228(9)	0.0675(5)
S2	-0.7651(2)	1.1035(1)	0.80150(8)	0.0530(5)
S3	-0.4601(2)	1.1177(2)	0.7051(1)	0.0800(6)
S4	-0.8044(3)	1.3509(2)	0.9256(1)	0.0843(7)
S5	-0.9113(2)	1.2613(2)	0.7991(1)	0.0594(5)
S6	-0.8023(3)	1.3566(2)	0.6391(1)	0.0963(8)
S7	-0.3725(2)	0.7118(2)	0.5512(1)	0.0696(6)
S8	-0.2420(2)	0.7940(2)	0.67166(9)	0.0558(5)
S9	-0.4588(2)	0.8387(2)	0.83418(9)	0.0737(6)
S10	0.0523(2)	0.7458(2)	0.7613(1)	0.0742(6)
S11	-0.1040(2)	0.6324(2)	0.67147(8)	0.0586(5)
S12	-0.2844(3)	0.4896(2)	0.7810(1)	0.0787(5)
S13	-0.6800(2)	0.9876(2)	0.58498(9)	0.0784(6)
S14	-0.5100(2)	1.0264(2)	0.58737(9)	0.0773(6)
S15	0.3388(3)	0.4565(2)	0.8124(1)	0.0962(7)
S16	-0.6634(3)	1.4594(2)	0.7068(1)	0.0989(8)
S17	-0.6043(2)	0.7180(2)	0.6699(1)	0.0671(5)
S18	-0.6372(2)	0.7678(2)	0.77431(9)	0.0631(5)
S19	-0.0550(2)	0.6373(2)	0.8839(1)	0.0732(6)
S20	-0.1726(2)	0.5388(2)	0.8896(1)	0.0730(6)
C1	-0.7640(7)	1.0254(5)	0.6734(3)	0.052(2)
C2	-0.6942(7)	1.0637(5)	0.7110(3)	0.049(2)
C3	-0.5662(7)	1.0714(5)	0.6756(3)	0.053(2)
C4	-0.7669(7)	1.3802(5)	0.8389(4)	0.058(2)

Table 32 continued

C5	-0.8124(7)	1.3468(5)	0.7844(3)	0.056(2)
C6	-0.7692(8)	1.3808(6)	0.7164(3)	0.061(2)
C7	-0.4479(7)	0.7378(5)	0.6385(3)	0.052(2)
C8	-0.4021(7)	0.7747(5)	0.6923(3)	0.050(2)
C9	-0.4860(7)	0.7934(5)	0.7623(3)	0.049(2)
C10	-0.0405(7)	0.6630(6)	0.7937(4)	0.055(2)
C11	-0.1076(7)	0.6141(6)	0.7618(3)	0.055(2)
C12	-0.1847(7)	0.5524(5)	0.8026(3)	0.055(2)
O1	0.2929(10)	0.5499(6)	0.3820(4)	0.159(4)
O2	0.4020(6)	0.7294(6)	0.4511(3)	0.107(2)
O3	-0.1073(8)	0.8504(7)	0.5020(4)	0.238(7)
O4	0.2579(11)	0.5703(7)	0.5468(4)	0.161(4)
O5	-0.0249(10)	0.6172(9)	0.4927(4)	0.162(3)
O6	0.0753(8)	0.7406(6)	0.3472(3)	0.132(3)
O7	0.1528(7)	0.9182(6)	0.4139(4)	0.133(3)
O9	0.3228(8)	1.0723(5)	0.0359(3)	0.110(2)
O8	0.0963(8)	0.8073(6)	0.5902(3)	0.122(2)
O10	0.2596(7)	0.8985(6)	-0.0359(3)	0.113(2)
O11	0.5211(7)	0.7370(6)	0.0121(3)	0.117(2)
O12	0.2230(5)	1.0283(5)	0.1956(3)	0.087(2)
O13	0.5248(6)	0.8914(6)	0.1137(3)	0.100(2)
O14	0.2261(11)	0.7184(8)	0.0817(4)	0.170(4)
O15	0.2905(14)	0.7743(7)	0.2043(5)	0.194(5)
O16	0.0381(6)	0.9822(7)	0.1128(3)	0.116(2)
O17	0.4708(9)	0.5737(8)	-0.0594(4)	0.155(3)
O18	-0.0616(9)	0.8571(8)	0.0263(4)	0.149(3)

Table 33 Anisotropic displacement parameters U_{ij} /Å^2 for the non-H atoms in the structure of $[Sr(H_2O)_8](C_6S_{10})\cdot H_2O$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{12}**	**U_{13}**	**U_{23}**
Sr1	0.0736(5)	0.0660(5)	0.0553(4)	-0.0322(4)	-0.0149(3)	-0.0011(3)
Sr2	0.0670(5)	0.0721(5)	0.0582(4)	-0.0353(4)	-0.0064(3)	-0.0031(3)
S1	0.072(1)	0.071(1)	0.064(1)	-0.034(1)	-0.0124(9)	-0.0005(9)
S2	0.058(1)	0.052(1)	0.0453(9)	-0.0191(8)	-0.0072(7)	0.0046(7)
S3	0.067(1)	0.111(2)	0.068(1)	-0.043(1)	-0.011(1)	0.008(1)
S4	0.097(2)	0.085(1)	0.062(1)	-0.010(1)	-0.032(1)	-0.008(1)
S5	0.051(1)	0.062(1)	0.057(1)	-0.0133(9)	-0.0068(8)	-0.0056(8)
S6	0.153(2)	0.082(1)	0.058(1)	-0.0444(8)	-0.031(1)	0.012(1)
S7	0.067(1)	0.080(1)	0.0577(9)	-0.0164(6)	-0.018(1)	-0.0124(9)
S8	0.056(1)	0.056(1)	0.0590(8)	-0.0259(5)	-0.0127(9)	0.0053(8)
S9	0.080(2)	0.097(1)	0.0532(9)	-0.0459(6)	-0.010(1)	-0.0085(9)
S10	0.055(1)	0.074(1)	0.103(1)	-0.0320(6)	-0.025(1)	0.005(1)
S11	0.054(1)	0.059(1)	0.0538(8)	-0.0133(5)	-0.008(1)	-0.006(1)
S12	0.100(1)	0.073(1)	0.083(1)	-0.0529(6)	-0.025(1)	0.003(1)
S13	0.092(2)	0.092(1)	0.0502(9)	-0.0400(6)	-0.003(1)	-0.011(1)
S14	0.077(1)	0.091(1)	0.0519(9)	-0.0317(6)	0.007(1)	-0.0011(9)
S15	0.110(2)	0.081(2)	0.114(1)	-0.0482(7)	-0.036(1)	-0.007(1)
S16	0.131(1)	0.069(2)	0.096(1)	-0.0512(8)	-0.007(1)	0.007(1)
S17	0.065(1)	0.075(1)	0.0733(9)	-0.0341(5)	-0.024(1)	-0.0027(9)
S18	0.056(1)	0.071(1)	0.0651(9)	-0.0297(5)	-0.011(1)	0.0082(8)
S19	0.079(1)	0.079(1)	0.0723(9)	-0.0306(6)	-0.032(1)	-0.0006(1)
S20	0.087(1)	0.070(1)	0.0637(9)	-0.0287(6)	-0.022(1)	0.012(1)
C1	0.063(4)	0.048(3)	0.045(3)	-0.022(2)	-0.008(3)	0.005(3)
C2	0.049(4)	0.035(3)	0.050(3)	-0.006(2)	-0.001(3)	0.002(3)
C3	0.055(4)	0.049(4)	0.053(3)	-0.025(2)	-0.001(3)	0.004(3)
C4	0.061(4)	0.037(4)	0.071(3)	-0.004(2)	-0.025(2)	-0.013(4)
C5	0.065(4)	0.036(4)	0.056(4)	-0.011(3)	-0.011(3)	0.001(3)
C7	0.060(4)	0.047(4)	0.053(4)	-0.021(3)	-0.017(3)	0.006(3)

Table 33 continued

C8	0.046(5)	0.046(4)	0.055(4)	-0.013(3)	-0.009(3)	-0.003(3)
C9	0.060(5)	0.038(4)	0.055(4)	-0.017(3)	-0.023(3)	0.004(3)
C10	0.036(4)	0.048(4)	0.073(4)	-0.005(3)	-0.013(3)	-0.004(3)
C11	0.046(4)	0.053(4)	0.064(4)	-0.016(3)	-0.012(3)	-0.002(3)
C12	0.055(4)	0.043(4)	0.059(4)	-0.012(3)	-0.006(3)	-0.006(3)
O1	0.220(9)	0.104(5)	0.125(5)	0.023(5)	-0.100(6)	0.042(4)
O2	0.092(5)	0.146(6)	0.108(4)	-0.067(4)	-0.032(3)	0.013(4)
O3	0.083(5)	0.48(2)	0.088(5)	-0.032(8)	-0.030(4)	0.073(7)
O4	0.248(9)	0.141(6)	0.164(6)	-0.122(7)	-0.115(7)	0.102(5)
O5	0.168(8)	0.206(9)	0.138(6)	-0.100(7)	-0.034(5)	0.006(6)
O6	0.161(7)	0.129(6)	0.100(4)	-0.020(5)	-0.068(4)	-0.001(4)
O7	0.113(6)	0.090(5)	0.182(7)	-0.032(4)	-0.027(5)	0.043(4)
O8	0.162(6)	0.162(6)	0.078(4)	-0.100(5)	-0.025(4)	-0.019(4)
O9	0.140(6)	0.096(5)	0.114(4)	-0.064(4)	-0.039(4)	0.029(4)
O10	0.110(5)	0.158(6)	0.076(4)	-0.057(4)	-0.018(3)	-0.007(4)
O11	0.109(5)	0.116(5)	0.120(5)	-0.022(4)	-0.037(4)	-0.042(4)
O12	0.065(4)	0.091(4)	0.101(4)	-0.022(3)	-0.014(3)	-0.032(3)
O13	0.069(4)	0.134(5)	0.096(4)	-0.023(4)	-0.031(3)	-0.037(3)
O14	0.242(9)	0.180(8)	0.136(6)	-0.158(8)	-0.009(6)	-0.011(5)
O15	0.355(9)	0.111(6)	0.139(6)	-0.130(8)	-0.044(7)	0.052(5)
O16	0.073(4)	0.208(7)	0.080(4)	-0.068(5)	-0.014(3)	-0.003(4)
O17	0.132(6)	0.199(8)	0.141(4)	-0.084(6)	0.002(5)	-0.065(6)
O18	0.156(7)	0.189(8)	0.134(6)	-0.072(6)	-0.076(5)	0.023(5)

Table 34 Selected bond lengths / Å and angles / ° for $[Sr(H_2O)_8](C_6S_{10})\cdot H_2O$. Standard deviations are given in parentheses.

Sr(1)–O(1)	2.528 (7)	Sr(2)–O(9)	2.621 (4)
Sr(1)–O(2)	2.622 (1)	Sr(2)–O(10)	2.593 (2)
Sr(1)–O(3)	2.640 (6)	Sr(2)–O(11)	2.587 (8)
Sr(1)–O(4)	2.583 (6)	Sr(2)–O(12)	2.596 (7)
Sr(1)–O(5)	2.651 (3)	Sr(2)–O(13)	2.606 (2)
Sr(1)–O(6)	2.613 (3)	Sr(2)–O(14)	2.557 (2)
Sr(1)–O(7)	2.631 (4)	Sr(2)–O(15)	2.568 (5)
Sr(1)–O(8)	2.589 (5)	Sr(2)–O(16)	2.569 (4)
C(1) –C(2)	1.397 (3)	C(10) –C(11)	1.407 (2)
S(2) –S(5)	2.075 (2)	S(8) –S(11)	2.076 (2)
O(1)–Sr(1)–O(2)	081.68 (1)	O(9)–Sr(2)–O(14)	147.31 (0)
O(2)–Sr(1)–O(5)	152.44 (0)	O(12)–Sr(2)–O(16)	073.21 (0)
O(6)–Sr(1)–O(8)	144.74 (1)	O(10)–Sr(2)–O(15)	143.79 (1)
C(1)–C(2)–C(3)	119.30 (1)	C(2)–S(2)–S(5)	102.41 (4)
C(7)–C(8)–C(9)	117.66 (1)	C(8)–S(8)–S(11)	102.97 (4)

3.4.4 Discussion of the Structure of $[Sr(H_2O)_8](C_6S_{10})\cdot H_2O$

The unit cell of $[Sr(H_2O)_8](C_6S_{10})\cdot H_2O$ contains four Sr^{2+} cations, four $(C_6S_{10})^{2-}$ anions and four non-coordinated water molecules. In the asymmetric unit there are two independent ions of each kind.

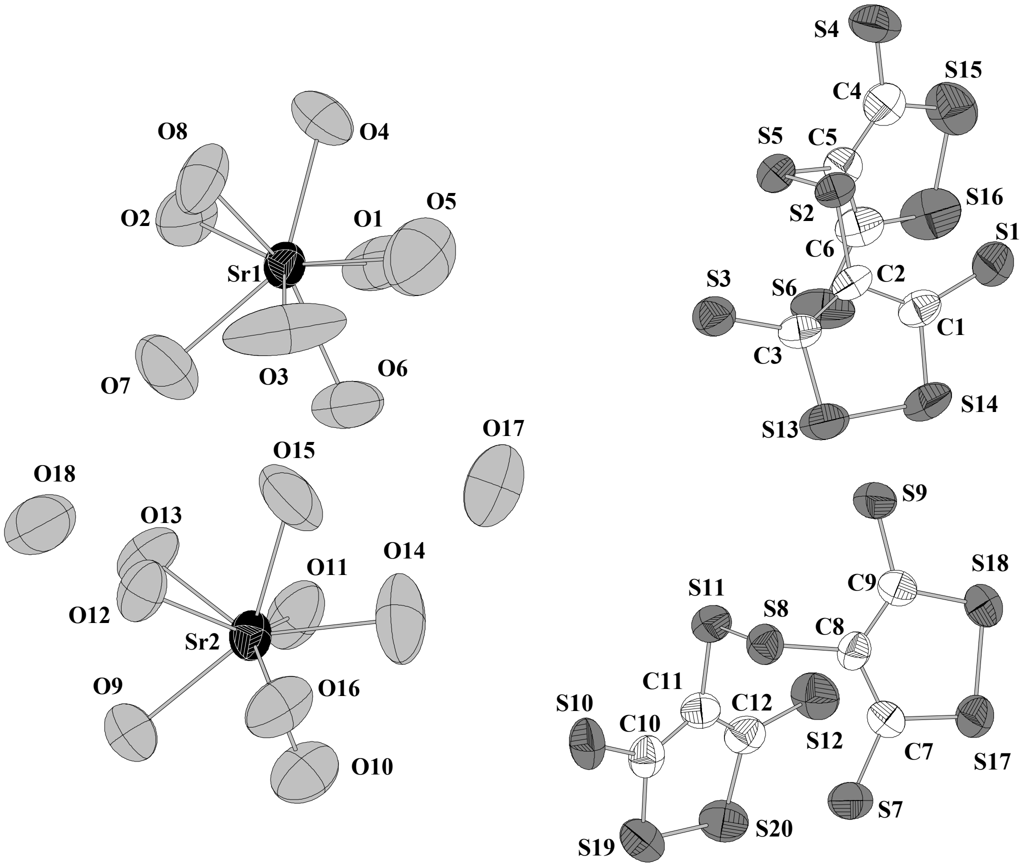


Figure 35 The ions in the structure of $[Sr(H_2O)_8](C_6S_{10})\cdot H_2O$. Thermal ellipsoids are drawn to include a probability density of 50%.

The two crystallographically independent Sr^{2+} ions are coordinated each by the oxygen atoms of eight water molecules (Figure 35). The coordination environment for both Sr^{2+} ions is rather irregular and can be considered as a distorted square antiprism or a bicapped trigonal prism. The Sr–O bond lengths are rather long, in average 2.607 Å for Sr(1) and 2.587 Å for Sr(2). There are no short contacts between strontium and sulfur atoms of the $C_6S_{10}^{2-}$ ions. The torsion angles at the disulfide groups C(2)-S(2)-S(5)-C(5) and C(8)-S(8)-

S(11)-C(11) torsion angles are -82.26(1)° and 83.39(1)° respectively. The S(2)–S(5) and S(8)–S(11) bond lengths are 2.075(4) Å and 2.076(4) Å, which falls within the trend made by other disulfides [54,57]. The average bond lengths C–S 1.703 Å and C–C 1.402 Å in $(C_6S_{10})^{2-}$ are intermediate between double and single bond values [58]. The S–S distances corresponds to a single bond which is also consistent with the C–S–S angle inside the C_3S_5 ring. The structure contains two additional water molecules with O(17) and O(18) per formula unit.

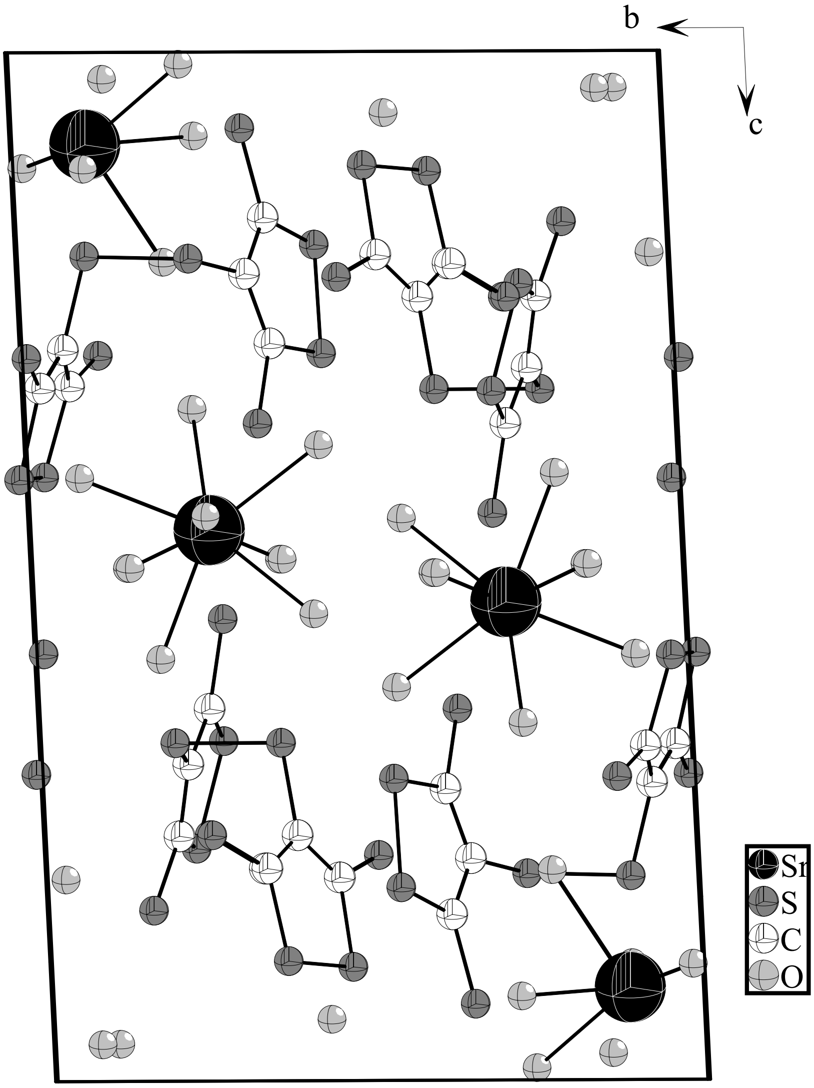


Figure 36 The unit cell of $[Sr(H_2O)_8](C_6S_{10})\cdot H_2O$ in a view slightly inclined to the [110] direction.

3.4.5 Discussion and Comparison of $(C_6S_{10})^{2-}$ Anions

The hydrolysis and oxidation behavior of the β isomeric form of $(C_3S_5)^{2-}$ is not mentioned in the literature. Solid samples of $Na_2(\beta\text{-}C_3S_5)$, however, seem to be stable, since no change of color is observed even over months. It was now found that in aqueous solution the 4,5-dimercapto-1,2-dithiole-3-thione ion $\beta\text{-}(C_3S_5)^{2-}$ is easily oxidized under dimerizatin to give the $(C_6S_{10})^{2-}$ ion under formation of a new S–S bond. $[Ca(H_2O)_7](C_6S_{10})$ and $[Sr(H_2O)_8][C_6S_{10}]\cdot H_2O$ were both prepared from aqueous solutions in the presence of air and crystallographically studied on single crystals. In $[Ca(H_2O)_7](C_6S_{10})$ there is only one $(C_6S_{10})^{2-}$ ion in the asymmetric unit (Figure 37). The anion consists of two essentially planar C_3S_5 subunits interconnected by a disulfide group. The two molecular planes of the C_3S_5 subunits make up an interplanar angle of 101°. The C(1)-C(2)-S(2)-S(5) and C(6)-C(5)-S(5)-S(2) torsion angles are -77.88(4)° and -78.42(4)°, respectively. The C(2)-S(2)-S(5)-C(5) torsion angle for the anion structure is -86.26(3)° and the S(2)–S(5) bond length is 2.078(1) Å.

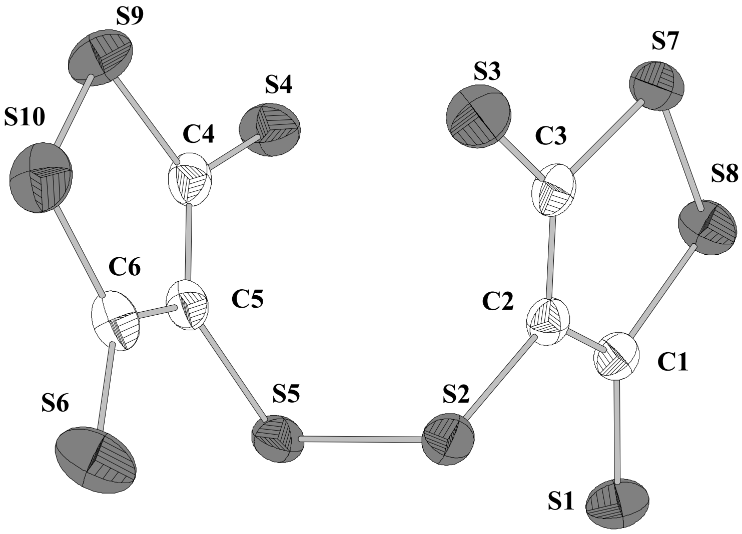
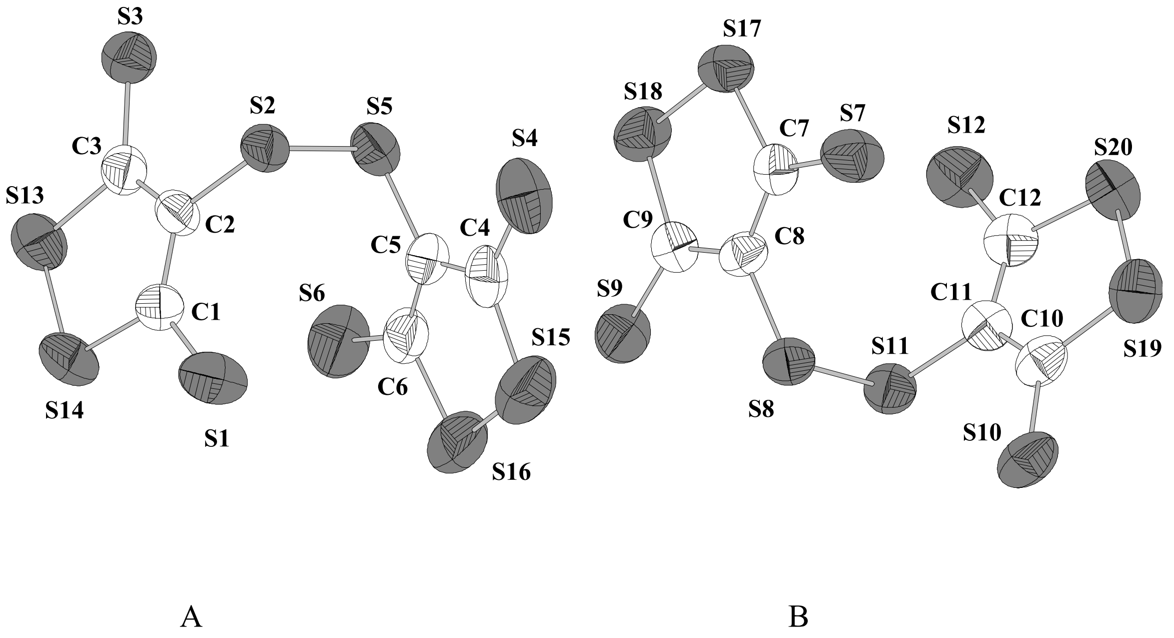


Figure 37 The anion $(C_6S_{10})^{2-}$ in the structure of $[Ca(H_2O)_7](C_6S_{10})$.

In $[Sr(H_2O)_8][C_6S_{10}]\cdot H_2O$ there are two $(C_6S_{10})^{2-}$ ions in the asymmetric unit (Figure 38). The two molecular planes consisting the two C_3S_5 subunits make up an interplanar angle of 102.4° for ion A and 102.6° for ion B. The C(3)-C(2)-S(2)-S(5) and C(4)-C(5)-S(5)-S(2) torsion angles for the anion A are -78.97(1)° and -77.22(1)°, respectively, and the C(9)-C(8)-S(8)-S(11) and C(10)-C(11)-S(11)-S(8) torsion angles for the anion B are 80.31(1)° and 77.29(1)°, respectively. The torsion angles at the disulfide groups C(2)-S(2)-S(5)-C(5) and C(8)-S(8)-S(11)-C(11) are -82.26(1)° and 83.39(1)° respectively. The S(2)–S(5) and S(8)–S(11) bond lengths are 2.075(4) Å and 2.076(4) Å. In the anions of $[Ca(H_2O)_7](C_6S_{10})$ and $[Sr(H_2O)_8][C_6S_{10}]\cdot H_2O$ the average bond lengths C–S are 1.72 and 1.71 Å respectively and C–C bond length average is 1.40 Å for both structures, these bonds are intermediate between double and single bond values [58]. The S–S distances corresponds to a single bond which is also consistent with the C–S–S angle inside the C_3S_5 rings.



A

B

Figure 38 The anions $(C_6S_{10})^{2-}$ in the structure of $[Sr(H_2O)_8](C_6S_{10})\cdot H_2O$.

The structural parameters of the three $(C_6S_{10})^{2-}$ ions are summarized in Table 35. The structural parameters of the three crystallographically independent $(C_6S_{10})^{2-}$ ions included in the two compounds, with torsion angles almost identical with only 3° difference and almost the same disulfide bond lengths allow for the interpretation that the most stable conformation for the $(C_6S_{10})^{2-}$ ion is present in the two compounds even though the cation is not identical.

Table 35 Comparison of characteristic structural parameters of the $(C_6S_{10})^{2-}$ ions in the structures of $[Ca(H_2O)_7](C_6S_{10})$ and $[Sr(H_2O)_8](C_6S_{10})\cdot H_2O$.

Ion	**Interplanar angle of the two C_3S_5 subunits /°**	**Torsion angle C–S–S–C of the disulfide bond /°**	**Torsion angle C–C–S–S /°**	**Length of the disulfide S–S bond /Å**
$(C_6S_{10})^{2-}$ in the structure of $[Ca(H_2O)_7](C_6S_{10})$	101.36	86.26	77.88 78.42	2.077
$(C_6S_{10})^{2-}$ A in the structure of $[Sr_2(H_2O)_{16}](C_6S_{10})_2\cdot 2H_2O$	102.4	82.26	77.22 78.97	2.075
$(C_6S_{10})^{2-}$ B in the structure of $[Sr_2(H_2O)_{16}](C_6S_{10})_2\cdot 2H_2O$	102.6	83.39	77.29 80.31	2.076

3.5 Tetraphenylarsonium Salts of β-$(C_3S_5)^{2-}$

3.5.1 Tetraphenylarsonium Salts Prepared in Air

3.5.1.1 Structure Determination of $[As(C_6H_5)_4]_2(C_3S_5)\cdot 2H_2O$

The crystals of this compound are sensitive towards the loss of water and were therefore sealed in glass capillaries. The diffraction quality of the crystals towards X-rays was checked by preliminary precession exposures, which showed the triclinic symmetry. Data were collected at ambient temperature using a Nonius kappa-CCD diffractometer equipped with Mo-Kα radiation (λ=0.7107 Å). The space group could be derived from the data set as triclinic, $P\,\bar{1}$ (№ 2). A structure model was obtained by direct method [38] and refined against F^2 with anisotropic displacement parameters for all non-hydrogen atoms [39]. Hydrogen atoms attached to the carbon atoms of the phenyl rings were located in idealized, calculated positions and refined in a riding model with B_{iso} fixed to 1.2 B_{iso} of the resprective carbon atoms. The localization of the H atoms bound to O atoms of the two water molecules was not possible. These atoms were omitted from the refinement. Crystallographic data and details of the structure analyses are given in Table 36, positional parameters, isotropic equivalent parameters for the non-H atoms in Table 37, anisotropic displacement parameters for the non-H atoms in Table 38 and selected bond lengths and angles in Table 39.

Table 36 Crystallographic data and details of the structure determination $[As(C_6H_5)_4]_2(C_3S_5)\cdot 2H_2O$.

Formula	$As_2C_{51}H_{44}O_2S_5$
Lattice constants	a =12.812(1)Å, α=72.70(4)°
	b =13.886(1)Å, β=71.62(4)°
	c =16.912(1)Å, γ=64.53(4)°
Volume of unit cell	2531.50 $Å^3$
Number of formula units	Z = 2
Density (calc.)	$\rho = 1.305\ g \cdot cm^{-3}$
Absorption coefficient	$\mu = 15.6\ cm^{-1}$
Crystal system, space group	Triclinic, $P\bar{1}$ (№ 2)
Diffractometer	Nonius kappa-CCD
Radiation, wave length	Mo-Kα, λ = 0.7107 Å
Temperature of measurement	T = 293 K
Range of data collection	$2\theta < 49.99°$
Number of data collected	17029
Number of independent reflections, R_{merge}	8242, 9.73%
Number of refined parameters	663
Ratio reflections/parameters	12.4
R (|F|) for all reflections	18.77%
R (|F|) for 3399 reflections with $F_0 > 4\sigma(F_0)$	7.39%
$wR(F^2)$	24.35%
Largest electron density difference peak and hole	+0.61 / -0.24 e /$Å^3$

Table 37 Positional parameters, equivalent isotropic parameters U_{eq} /Å^2 for the non-H atoms in the structure of $[As(C_6H_5)_4]_2(C_3S_5)\cdot 2H_2O$.

Atom	x	y	z	U_{eq}
As1	0.72634(9)	0.03589(8)	0.44290(6)	0.077(1)
As2	0.89027(9)	0.46337(8)	0.18565(6)	0.076(1)
S1	0.8324(6)	0.0588(4)	-0.0705(3)	0.168(2)
S2	0.7023(6)	0.2781(5)	-0.2327(6)	0.205(3)
S3	0.9019(5)	0.3844(4)	-0.3488(3)	0.155(2)
S4	1.0646(4)	0.2271(3)	-0.2483(3)	0.132(2)
S5	1.0364(4)	0.1097(3)	-0.1437(3)	0.138(2)
O1	1.3445(18)	0.0149(17)	0.173(2)	0.30(1)
O2	0.5863(13)	0.5427(15)	-0.3225(10)	0.210(7)
C1	0.8900(19)	0.1426(14)	-0.1500(13)	0.155(6)
C2	0.8443(16)	0.2296(13)	-0.2089(10)	0.124(5)
C3	0.9197(15)	0.2830(11)	-0.2674(8)	0.119(5)
C4	0.7490(8)	-0.1049(7)	0.5118(6)	0.074(3)
C5	0.6103(10)	0.1418(8)	0.5086(6)	0.083(3)
C6	0.6715(10)	0.0462(9)	0.3466(6)	0.086(3)
C7	0.8777(10)	0.0547(8)	0.4008(7)	0.081(3)
C8	0.8149(11)	0.6115(7)	0.1398(6)	0.079(3)
C9	1.0549(9)	0.4243(8)	0.1665(6)	0.078(3)
C10	0.8219(10)	0.4410(8)	0.3048(6)	0.082(3)
C11	0.8646(11)	0.3745(9)	0.1328(6)	0.089(3)
C12	0.8549(13)	-0.3003(10)	0.5293(10)	0.106(4)
C13	0.6780(11)	-0.1154(9)	0.5948(7)	0.089(3)
C14	0.6454(11)	-0.0347(10)	0.3370(7)	0.089(3)
C15	0.8357(11)	-0.1957(8)	0.4816(8)	0.088(3)
C16	0.8958(13)	0.1285(11)	0.4287(9)	0.101(4)
C17	0.6648(13)	0.1361(12)	0.2816(7)	0.107(4)
C18	0.5068(9)	0.2098(8)	0.4814(7)	0.079(3)
C19	0.6303(12)	0.1514(10)	0.5814(7)	0.091(3)
C20	0.5964(12)	0.0625(13)	0.2057(9)	0.104(4)

Table 37 continued

C21	0.6983(12)	-0.2199(10)	0.6398(8)	0.099(4)
C22	0.5523(14)	0.2243(12)	0.6275(10)	0.109(4)
C23	1.0648(13)	0.0159(13)	0.3052(11)	0.117(4)
C24	0.7793(16)	-0.308(1)	0.6148(10)	0.116(5)
C25	0.6069(16)	-0.021(1)	0.2658(10)	0.128(5)
C26	1.0069(15)	0.1408(11)	0.3948(10)	0.109(4)
C27	0.8196(14)	0.4129(13)	0.0631(8)	0.111(4)
C28	0.8835(13)	0.6703(9)	0.0853(8)	0.097(4)
C29	0.8696(14)	0.4446(10)	0.3617(7)	0.100(4)
C30	1.1020(11)	0.4877(11)	0.1885(7)	0.091(3)
C31	0.7136(13)	0.4243(9)	0.3309(8)	0.100(4)
C32	0.6961(15)	0.6597(11)	0.1603(8)	0.111(4)
C33	1.2974(14)	0.3711(14)	0.1358(9)	0.115(4)
C34	1.2194(16)	0.4619(14)	0.1723(9)	0.121(5)
C35	0.8473(14)	0.2321(17)	0.0608(10)	0.117(5)
C36	0.6386(18)	0.7724(15)	0.1242(9)	0.136(6)
C37	1.1350(13)	0.3383(11)	0.1271(8)	0.105(4)
C38	0.6641(17)	0.4071(11)	0.4165(9)	0.118(5)
C39	1.2535(16)	0.3148(16)	0.1169(10)	0.130(5)
C40	0.4415(16)	0.2938(11)	0.6024(9)	0.117(5)
C41	1.0873(14)	0.0846(11)	0.3362(10)	0.103(4)
C42	0.6186(16)	0.1466(17)	0.2169(9)	0.139(6)
C43	0.9597(14)	0.0035(10)	0.3394(8)	0.104(4)
C44	0.4182(13)	0.2860(10)	0.5323(9)	0.101(4)
C45	0.713(2)	0.4179(11)	0.4713(9)	0.133(7)
C46	0.9024(12)	0.2626(9)	0.1684(8)	0.095(3)
C47	0.8085(16)	0.3430(17)	0.0267(9)	0.125(5)
C48	0.8147(17)	0.4336(12)	0.4476(9)	0.116(4)
C49	0.7055(19)	0.8260(12)	0.0766(10)	0.115(5)
C50	0.828(2)	0.7835(12)	0.0519(11)	0.128(6)
C51	0.8889(15)	0.1957(13)	0.1277(12)	0.121(5)

Table 38 Anisotropic displacement parameters U_{ij} /Å^2 for the non-H atoms in the structure of $[As(C_6H_5)_4]_2(C_3S_5)\cdot 2H_2O$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{12}**	**U_{13}**	**U_{23}**
As1	0.089(2)	0.067(1)	0.082(1)	-0.0303(7)	-0.0296(6)	-0.0107(5)
As2	0.091(2)	0.072(1)	0.069(1)	-0.0301(7)	-0.0166(6)	-0.0173(5)
S1	0.226(6)	0.146(4)	0.148(4)	-0.097(4)	-0.022(3)	-0.025(3)
S2	0.187(5)	0.158(5)	0.306(8)	-0.068(4)	-0.125(5)	-0.010(5)
S3	0.197(5)	0.132(3)	0.122(3)	-0.032(3)	-0.052(3)	-0.028(2)
S4	0.140(3)	0.125(3)	0.140(3)	-0.045(2)	-0.030(2)	-0.046(2)
S5	0.161(4)	0.118(3)	0.153(3)	-0.039(2)	-0.063(3)	-0.037(2)
O1	0.17(1)	0.22(2)	0.48(4)	-0.09(1)	0.02(2)	-0.09(2)
O2	0.17(1)	0.27(2)	0.22(1)	-0.11(1)	-0.11(1)	0.03(1)
C1	0.19(2)	0.11(1)	0.19(2)	-0.03(1)	-0.07(1)	-0.07(1)
C2	0.16(1)	0.10(1)	0.13(1)	-0.049(9)	-0.05(1)	-0.017(8)
C3	0.15(1)	0.106(9)	0.091(8)	-0.041(9)	-0.015(8)	-0.036(7)
C4	0.078(6)	0.056(5)	0.090(6)	-0.020(4)	-0.036(5)	-0.002(4)
C5	0.108(8)	0.075(6)	0.077(6)	-0.038(6)	-0.022(5)	-0.019(4)
C6	0.100(7)	0.086(6)	0.080(6)	-0.045(6)	-0.014(5)	-0.018(5)
C7	0.089(7)	0.073(6)	0.089(6)	-0.030(5)	-0.038(5)	-0.008(5)
C8	0.106(9)	0.058(5)	0.076(6)	-0.028(6)	-0.028(5)	-0.014(4)
C9	0.085(7)	0.079(6)	0.065(5)	-0.022(5)	-0.019(5)	-0.013(4)
C10	0.097(8)	0.075(6)	0.069(6)	-0.040(5)	0.006(5)	-0.019(4)
C11	0.118(8)	0.096(7)	0.070(6)	-0.048(6)	-0.024(6)	-0.023(5)
C12	0.115(1)	0.076(7)	0.13(1)	-0.020(6)	-0.055(8)	-0.015(7)
C13	0.104(8)	0.084(7)	0.073(6)	-0.043(6)	-0.024(6)	0.009(5)
C14	0.113(8)	0.096(7)	0.079(6)	-0.051(6)	-0.024(6)	-0.025(5)
C15	0.098(8)	0.076(7)	0.088(6)	-0.026(6)	-0.030(6)	-0.010(5)
C16	0.106(9)	0.103(9)	0.113(9)	-0.048(7)	-0.050(7)	-0.004(6)
C17	0.13(1)	0.13(1)	0.078(7)	-0.073(6)	-0.032(6)	0.010(7)
C18	0.088(7)	0.071(6)	0.086(6)	-0.026(5)	-0.034(5)	-0.013(5)
C19	0.088(8)	0.087(7)	0.096(7)	-0.021(6)	-0.028(6)	-0.021(6)
C20	0.105(9)	0.12(1)	0.090(8)	-0.044(8)	-0.030(7)	-0.016(8)
C21	0.103(9)	0.073(8)	0.092(7)	-0.019(7)	-0.029(6)	0.006(6)
C22	0.13(1)	0.101(9)	0.116(9)	-0.052(9)	-0.045(9)	-0.016(8)
C23	0.082(9)	0.13(1)	0.16(1)	-0.047(8)	-0.039(8)	-0.031(9)
C24	0.16(1)	0.077(8)	0.12(1)	-0.051(9)	-0.07(1)	0.026(7)
C25	0.17(1)	0.16(1)	0.097(9)	-0.09(1)	-0.024(6)	-0.05(1)
C26	0.13(1)	0.085(8)	0.14(1)	-0.052(8)	-0.07(1)	-0.001(8)
C27	0.13(1)	0.119(9)	0.092(8)	-0.063(9)	-0.024(7)	-0.013(7)
C28	0.100(8)	0.067(6)	0.119(9)	-0.022(6)	-0.035(7)	-0.014(6)
C29	0.13(1)	0.100(8)	0.078(7)	-0.043(7)	-0.029(7)	-0.019(5)
C30	0.079(8)	0.109(8)	0.087(7)	-0.039(6)	-0.012(5)	-0.022(6)
C31	0.13(1)	0.068(6)	0.098(8)	-0.041(6)	-0.008(7)	-0.025(5)
C32	0.12(1)	0.087(8)	0.093(8)	-0.014(7)	-0.019(7)	-0.005(6)
C33	0.085(9)	0.13(1)	0.115(9)	-0.021(9)	-0.026(8)	-0.025(8)

Table 38 continued

C34	0.13(1)	0.15(1)	0.108(9)	-0.06(1)	-0.031(8)	-0.035(9)
C35	0.13(1)	0.16(1)	0.093(9)	-0.09(1)	-0.003(8)	-0.044(9)
C36	0.13(1)	0.13(1)	0.090(8)	-0.02(1)	0.014(9)	-0.031(8)
C37	0.10(1)	0.106(9)	0.110(9)	-0.029(7)	-0.020(7)	-0.041(7)
C38	0.17(1)	0.103(9)	0.078(8)	-0.075(9)	0.013(8)	-0.027(6)
C39	0.10(1)	0.14(1)	0.12(1)	-0.02(1)	0.0005(8)	-0.056(9)
C40	0.15(1)	0.083(8)	0.105(9)	-0.044(9)	0.0003(9)	-0.035(7)
C41	0.098(9)	0.086(8)	0.13(1)	-0.028(7)	-0.054(8)	-0.005(7)
C42	0.16(1)	0.17(1)	0.094(9)	-0.09(1)	-0.053(9)	0.039(9)
C43	0.14(1)	0.085(7)	0.116(9)	-0.052(7)	-0.041(8)	-0.029(6)
C44	0.100(9)	0.079(7)	0.12(1)	-0.028(6)	-0.023(7)	-0.030(7)
C45	0.18(2)	0.093(8)	0.075(8)	-0.038(9)	0.03(1)	-0.025(6)
C46	0.117(9)	0.081(7)	0.091(7)	-0.046(6)	-0.022(6)	-0.014(6)
C47	0.16(1)	0.16(1)	0.090(8)	-0.09(1)	-0.039(8)	-0.028(9)
C48	0.14(1)	0.13(1)	0.080(8)	-0.047(9)	-0.011(8)	-0.034(7)
C49	0.14(1)	0.078(8)	0.104(9)	-0.024(9)	-0.022(9)	-0.019(7)
C50	0.21(2)	0.088(9)	0.11(1)	-0.07(1)	-0.07(1)	-0.005(7)
C51	0.14(1)	0.108(9)	0.12(1)	-0.054(9)	-0.001(9)	-0.054(9)

Table 39 Selected bond lengths / Å and angles / ° for $[As(C_6H_5)_4]_2(C_3S_5)\cdot 2H_2O$.

As(1)–C(4)	1.920 (5)	As(2)–C(8)	1.890 (5)
As(1)–C(5)	1.911 (6)	As(2)–C(9)	1.887 (3)
As(1)–C(6)	1.894 (2)	As(2)–C(10)	1.906 (4)
As(1)–C(7)	1.948 (3)	As(2)–C(11)	1.883 (2)
C(1)–C(2)	1.379 (4)	S(1)–C(1)	1.662 (4)
C(2)–C(3)	1.417 (4)	S(2)–C(2)	1.780 (3)
C(1)–S(5)	1.757(2)	S(3)–C(3)	1.643 (5)
C(3)–S(4)	1.812(3)	S(4)–S(5)	2.078(2)
C(4)–As(1)–C(5)	108.33 (1)	C(8)–As(2)–C(9)	111.72 (1)
C(5)–As(1)–C(6)	109.74 (0)	C(9)–As(2)–C(10)	111.06 (1)
C(6)–As(1)–C(7)	107.01 (1)	C(10)–As(2)–C(11)	109.53 (0)
C(1)–S(5)–S(4)	95.38(1)	C(3)–S(4)–S(5)	95.91(0)
C(1)–C(2)–C(3)	120.53(1)	C(1)–C(2)–S(2)	126.98(1)

3.5.1.2 Discussion the structure of $[As(C_6H_5)_4]_2(C_3S_5)\cdot 2H_2O$

The crystal structure consists of one independent $(C_3S_5)^{2-}$ ion, two tetraphenylarsonium ions, and two non-coordinated water molecules (Figure 39). In the $(C_3S_5)^{2-}$ ligands, the S(4)–S(5) bond is 2.074(6) Å as expected. The C(1)–S(5) and C(3)–S(4) bond distances are 1.757(2) Å and 1.812(3) Å respectively, similar to other $(C_3S_5)^{2-}$ compounds. The terminal C–S average bond is 1.698 Å, which is shorter than expected [32]. The C–C bond lengths of averaged 1.398 Å are observed to be slightly longer than usual [26,29].

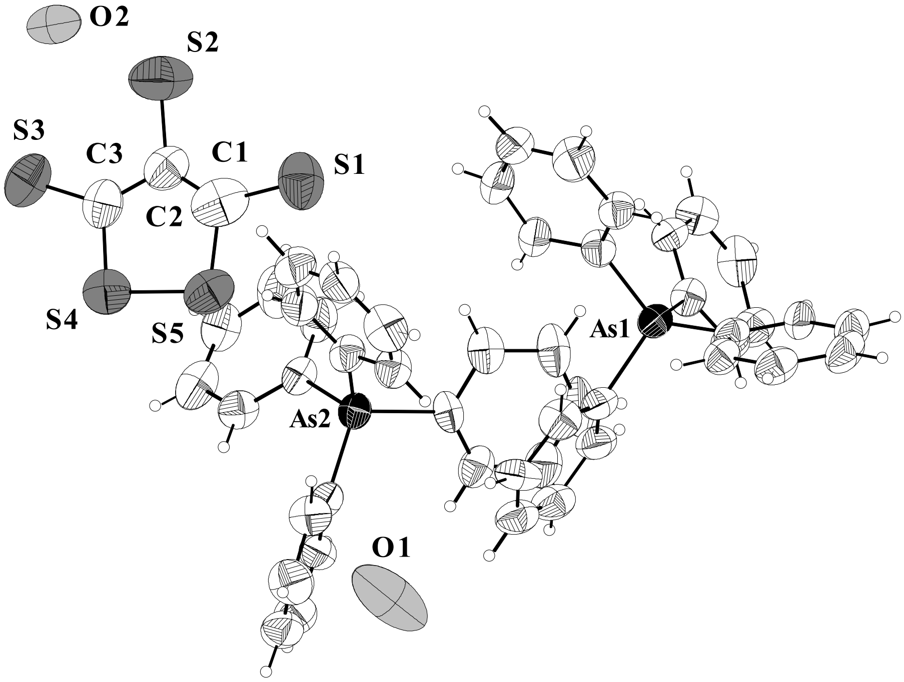


Figure 39 The ions in the structure of $[As(C_6H_5)_4]_2(C_3S_5)\cdot 2H_2O$. Thermal ellipsoids are drawn to include a probability density of 50%.

As expected, the structure of the $(C_3S_5)^{2-}$ ion is fairly close to planarity. However, C(2) and S(2) atoms deviate significantly from the plane of all other atoms as evident from torsional angles, which deviate from ideal 180°. The structure of this compound bears mentioning because the $(C_3S_5)^{2-}$ ion with its high charge is not coordinated or derivatized. The most basic atoms on the anion are expected to be the thiolate sulfur atoms, yet the nearest S····H contact is 2.89 Å, which is observed to a hydrogen atom of the $[As(C_6H_5)_4]^+$ cation; therefore, the $(C_3S_5)^{2-}$ anion may be regarded as well isolated. The formation of the free anion as the arsonium salt may be explained by the finding that $(C_3S_5)^{2-}$ is a weaker Bronsted base as expected, especially in comparison with other dithiolenes[33]. Also the size of the cation plays an important role here, since a bigger size of the counter-cations keeps the anions apart from each other.

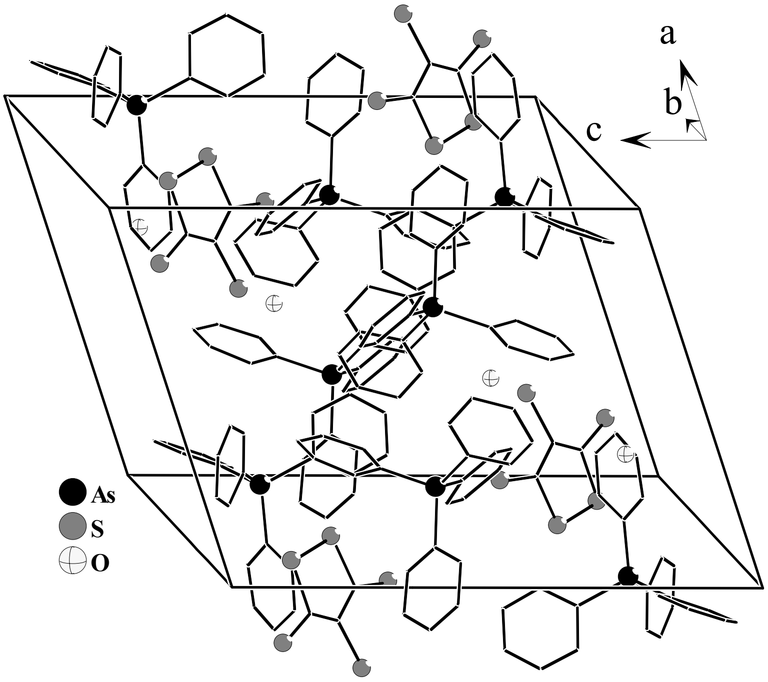


Figure 40 The unit cell of $[As(C_6H_5)_4]_2(C_3S_5)\cdot 2H_2O$. Tetraphenylarsonium cations are drawn in a simplified way and all hydrogen atoms are omitted.

As seen in representation of the unit cell in (Figure 40), there are no S····S interactions between neighbouring anions within distances equal or less the sum of the van der Waals radii (3.70 Å[59]). There are two $[As(C_6H_6)_4]^+$ cations in the asymmetric unit. The two cations each exhibit a tetrahedrally coordinated As atom. As–C bond lengths for As(1) and As(2) are in average 1.918 and 1.891Å, respectively. The deviations from a regular tetrahedral arrangement around As atoms are small with C–As–C bond angles ranging from 107.01(1) to 113.20(1). The crystal structure is dominated by the stacks of the bulky cations along the *a*-axis (Figure 41). As a result. there is no strong interaction between the $(C_3S_5)^{2-}$ units; the shortest S····S distance is S(1)····S(5) 4.10 Å.

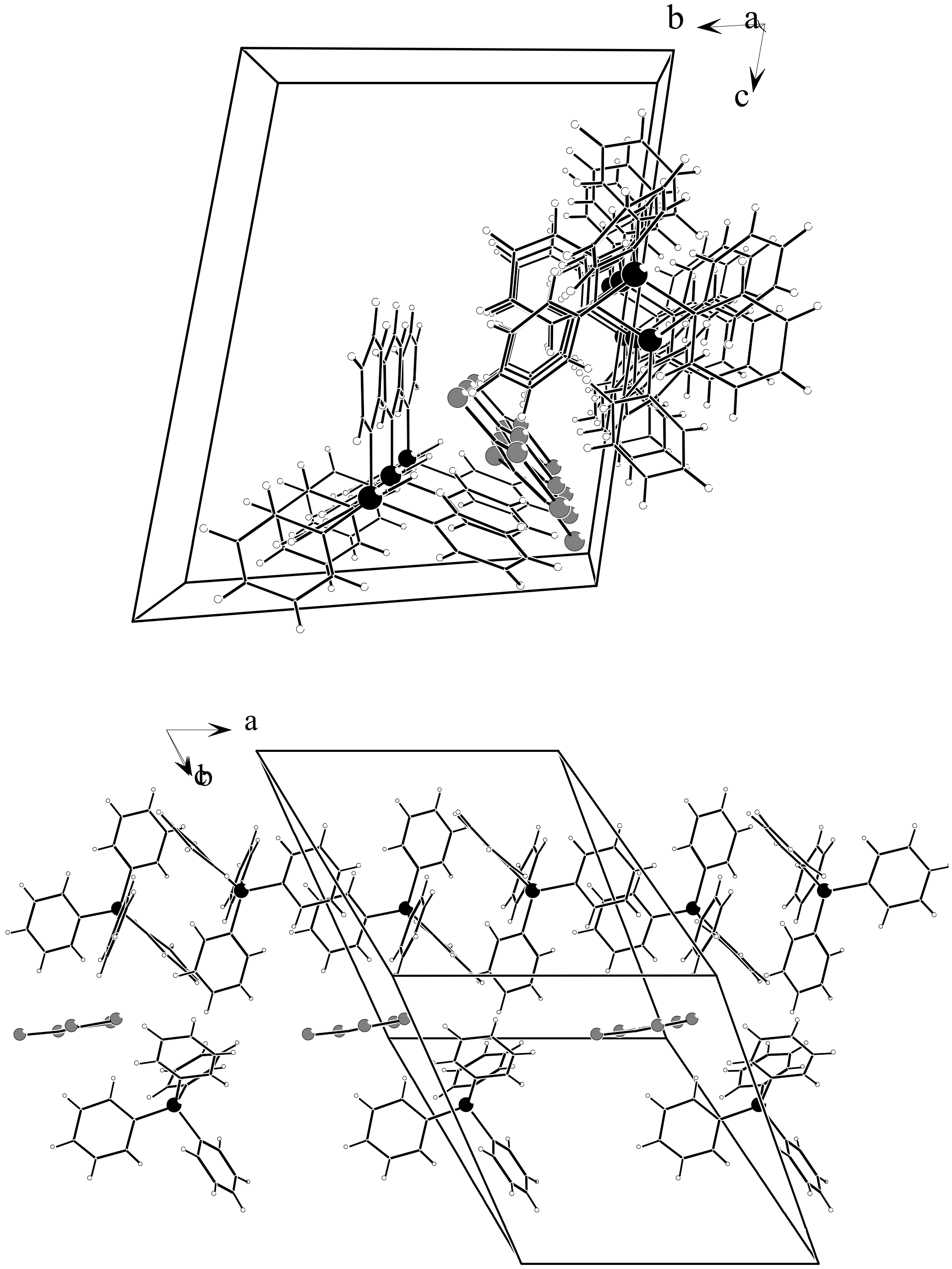


Figure 41 The stack of $[As(C_6H_5)_4]^+$ ions in a view along *a* and *b*-axis in the structure of $[As(C_6H_5)_4]_2(C_3S_5)\cdot 2H_2O$.

3.5.1.3 Structure Determination of $[As(C_6H_5)_4](HC_3S_5)$

The crystals of this compound are slightly sensitive towards the air and were therefore sealed in glass capillaries. The diffraction quality of the crystals towards X-rays was checked by preliminary precession exposures, which showed the triclinic symmetry. Data were collected at ambient temperature using a Nonius kappa-CCD diffractometer equipped with Mo-Kα radiation (λ=0.7107 Å). The space group could be derived from the data set as monoclinic, *C* 2/*c* (№ 15). A structure model was obtained by direct method [38] and refined against F^2 with anisotropic displacement parameters for all non-hydrogen atoms [39]. Hydrogen atoms attached to the carbon atoms of the phenyl rings were located in idealized, calculated positions and refined in a riding model with B_{iso} fixed to 1.2 B_{iso} of the resprective carbon atom. Hydrogen atom attached to the sulfur atom was refined with fixed thermal parameters. Crystallographic data and details of the structure analyses are given in Table 40, positional parameters, isotropic equivalent parameters for the non-H atoms in Table 41, anisotropic displacement parameters for the non-H atoms in Table 42, and selected bond lengths and angles in Table 43.

Table 40 Crystallographic data and details of the structure determination $[As(C_6H_5)_4](HC_3S_5)$.

Formula	$AsC_{27}H_{21}S_5$
Lattice constants	a =18.6435(7) Å
	b =13.6112(5) Å, β= 98.739(2)°
	c =21.5525(6) Å
Volume of unit cell	5405.68 $Å^3$
Number of formula units	Z = 8
Density (calc.)	$\rho = 1.427\ g \cdot cm^{-3}$
Absorption coefficient	$\mu = 16.6\ cm^{-1}$
Crystal system, space group	Monoclinic, *C* 2/*c* (№ 15)
Diffractometer	Nonius kappa-CCD
Radiation, wave length	Mo-Kα, λ = 0.7107 Å
Temperature of measurement	T = 293 K
Range of data collection	$2\theta < 50.21°$
Number of data collected	37253
Number of independent reflections, R_{merge}	4565, 8.38%
Number of refined parameters	301
Ratio reflections/parameters	15.5
R (|F|) for all reflections	12.83%
R (|F|) for 2483 reflections with $F_0 > 4\sigma(F_0)$	6.01 %
$wR(F^2)$	18.81 %
Largest electron density difference peak and hole	+0.82 / -0.34 e /$Å^3$

Table 41 Positional parameters, equivalent isotropic parameters U_{eq} /Å^2 for the non-H atoms in the structure of [As(C_6H_5)$_4$](HC_3S_5).

Atom	**x**	**y**	**z**	**Ueq**
As1	0.36210(5)	0.15489(6)	0.33860(3)	0.0607(3)
S1	0.1320(2)	0.0631(2)	0.1447(1)	0.108(1)
S2	0.2817(3)	-0.0793(2)	0.1640(2)	0.178(2)
S3	0.3799(2)	-0.0467(3)	0.0460(2)	0.136(1)
S4	0.1894(2)	0.1383(3)	0.0322(1)	0.117(1)
S5	0.2767(2)	0.0979(3)	-0.0040(2)	0.125(1)
C1	0.2018(7)	0.0580(9)	0.0964(6)	0.108(4)
C2	0.2601(8)	0.0031(8)	0.0996(5)	0.101(4)
C3	0.3067(9)	0.0102(8)	0.0530(5)	0.129(5)
C4	0.3862(5)	0.0192(6)	0.3341(3)	0.066(2)
C5	0.2636(4)	0.1615(6)	0.3527(3)	0.063(2)
C6	0.4217(5)	0.2135(6)	0.4081(3)	0.064(2)
C7	0.3745(5)	0.2171(6)	0.2621(3)	0.065(2)
C8	0.2491(5)	0.1631(7)	0.4131(4)	0.082(2)
C9	0.4759(5)	0.1602(8)	0.4444(4)	0.088(3)
C10	0.1210(6)	0.1573(9)	0.3734(5)	0.103(3)
C11	0.1374(5)	0.1567(8)	0.3144(5)	0.093(3)
C12	0.2073(5)	0.1599(7)	0.3018(4)	0.082(2)
C13	0.3342(6)	-0.0517(6)	0.3421(4)	0.080(3)
C14	0.4728(7)	-0.1077(9)	0.3223(5)	0.099(3)
C15	0.4558(6)	-0.0076(7)	0.3246(4)	0.083(3)
C16	0.3953(12)	0.3618(9)	0.2027(6)	0.171(8)
C17	0.4237(9)	-0.1748(8)	0.3306(4)	0.098(3)
C18	0.4087(6)	0.3135(7)	0.4206(4)	0.084(3)
C19	0.3681(6)	0.1661(7)	0.2072(4)	0.092(3)
C20	0.4514(7)	0.3607(9)	0.4714(5)	0.100(3)
C21	0.3776(7)	0.2129(9)	0.1522(4)	0.097(3)
C22	0.5046(7)	0.3061(12)	0.5075(5)	0.105(4)
C23	0.5178(6)	0.2104(12)	0.4944(5)	0.108(4)
C24	0.3548(8)	-0.1495(7)	0.3400(4)	0.097(3)
C25	0.3907(7)	0.3079(10)	0.1494(5)	0.102(3)
C26	0.3911(10)	0.3155(10)	0.2608(5)	0.155(6)
C27	0.1775(6)	0.1599(9)	0.4238(5)	0.102(3)
H1	0.232(4)	-0.053(5)	0.209(3)	0.0500

Table 42 Anisotropic displacement parameters U_{ij} /Å^2 for the non-H atoms in the structure of $[As(C_6H_5)_4](HC_3S_5)$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{12}**	**U_{13}**	**U_{23}**
As1	0.0725(5)	0.0572(5)	0.0514(4)	-0.0039(4)	0.0066(3)	-0.0015(4)
S1	0.172(3)	0.078(2)	0.081(2)	0.020(2)	0.039(2)	0.003(1)
S2	0.291(6)	0.074(2)	0.132(3)	-0.050(3)	-0.093(3)	0.037(2)
S3	0.106(3)	0.130(3)	0.172(3)	0.001(2)	0.017(2)	-0.036(2)
S4	0.128(2)	0.134(3)	0.089(2)	0.020(2)	0.014(2)	0.041(2)
S5	0.136(3)	0.136(3)	0.103(3)	0.013(2)	0.020(2)	0.005(2)
C1	0.102(9)	0.089(8)	0.123(9)	-0.001(7)	-0.017(7)	-0.008(6)
C2	0.137(11)	0.075(7)	0.084(7)	-0.027(7)	-0.003(7)	-0.002(5)
C3	0.156(12)	0.065(6)	0.139(10)	-0.007(7)	-0.065(10)	-0.015(7)
C4	0.087(3)	0.058(5)	0.051(4)	0.002(4)	0.005(4)	-0.004(4)
C5	0.072(5)	0.060(5)	0.057(4)	-0.005(4)	0.013(4)	0.001(4)
C6	0.072(5)	0.065(5)	0.055(4)	-0.009(4)	0.009(4)	-0.003(4)
C7	0.083(6)	0.057(5)	0.055(4)	-0.004(4)	0.015(4)	0.002(4)
C8	0.081(6)	0.103(7)	0.064(5)	0.011(6)	0.014(4)	0.0002(48)
C9	0.077(6)	0.126(8)	0.060(5)	-0.023(6)	0.005(4)	0.003(5)
C10	0.097(7)	0.114(9)	0.097(7)	0.014(7)	0.013(6)	0.012(6)
C11	0.074(6)	0.120(8)	0.083(6)	-0.001(6)	0.009(5)	0.013(6)
C12	0.078(6)	0.086(6)	0.078(5)	-0.013(5)	-0.003(4)	-0.008(5)
C13	0.111(8)	0.057(5)	0.071(5)	-0.020(5)	0.011(5)	-0.001(4)
C14	0.108(9)	0.087(8)	0.097(7)	0.027(7)	0.0002(62)	-0.011(6)
C15	0.092(7)	0.075(6)	0.084(6)	0.010(5)	0.016(5)	-0.007(5)
C16	0.355(3)	0.084(8)	0.089(8)	-0.067(11)	0.074(11)	-0.007(6)
C17	0.149(11)	0.076(7)	0.069(6)	0.007(8)	0.018(6)	-0.003(5)
C18	0.104(7)	0.079(6)	0.067(5)	-0.017(5)	0.007(5)	-0.019(4)
C19	0.126(8)	0.097(7)	0.057(5)	-0.029(6)	0.025(5)	-0.020(5)
C20	0.104(8)	0.117(9)	0.081(6)	-0.033(7)	0.020(6)	-0.036(6)
C21	0.138(9)	0.099(8)	0.056(5)	-0.033(7)	0.021(5)	-0.004(5)
C22	0.097(8)	0.156(12)	0.065(6)	-0.020(8)	0.017(6)	-0.031(7)
C23	0.081(7)	0.173(13)	0.068(6)	-0.016(7)	0.007(5)	-0.017(7)
C24	0.148(10)	0.060(5)	0.083(6)	-0.013(7)	0.013(6)	0.006(5)
C25	0.119(9)	0.120(9)	0.072(6)	-0.004(7)	0.029(6)	0.015(6)
C26	0.297(20)	0.097(8)	0.078(7)	-0.060(11)	0.055(9)	-0.011(6)
C27	0.084(7)	0.142(9)	0.086(6)	0.006(7)	0.032(5)	-0.003(6)

Table 43 Selected bond lengths / Å and angles / ° for $[As(C_6H_5)_4](HC_3S_5)$.

As(1)–C(4)	1.907 (8)	C(3)–S(5)	1.729 (2)
As(1)–C(5)	1.909 (8)	C(1)–S(4)	1.739 (2)
As(1)–C(6)	1.898 (7)	S(1)–C(1)	1.794 (1)
As(1)–C(7)	1.897 (7)	S(2)–C(2)	1.789 (1)
S(4)–S(5)	1.991 (5)	S(3)–C(3)	1.586 (2)
C(1)–C(2)	1.318 (2)	S(2)–H(1)	1.326 (1)
C(2)–C(3)	1.431 (2)		
C(4)–As(1)–C(5)	107.14 (4)	C(3)–S(5)–S(4)	96.16(0)
C(5)–As(1)–C(6)	108.42 (3)	C(1)–C(2)–S(2)	119.38(1)
C(6)–As(1)–C(7)	111.33 (3)	C(1)–C(2)–C(3)	120.86(1)
C(1)–S(4)–S(5)	96.78 (1)	S(1)–C(1)–S(4)	114.53 (1)

3.5.1.4 Discussion the structure of $[As(C_6H_5)_4](HC_3S_5)$

The unit cell contains eight cations $[As(C_6H_5)_4]^+$ and eight anions $(HC_3S_5)^-$. There is no significant contact present between the arsonium ion and the sulfur atoms of the anion within a distance equal or less than the sum of the van der Waals radii (3.65 Å). The closest S····H contact to a hydrogen atom of the $[As(C_6H_5)_4]^+$ ion is 2.93 Å; therefore, the $(HC_3S_5)^-$ anion may be regarded as isolated. $(HC_3S_5)^-$ is a weak Bronsted base when compared with other dithiolenes, and has a pK_a in water of 5.31 [60], which explains the possibility of isolating it as the arsonium salt [33]. For comparison, ethane-1.2-dithiolate ion in the monoprotonated form has a pK_a of 12.13, and even monoprotonated 1,2-dicyanoethane-1,2-dithiolate ion, with the electron-withdrawing substituents lowering the basicity, has a pK_a value of 7.55 [61].

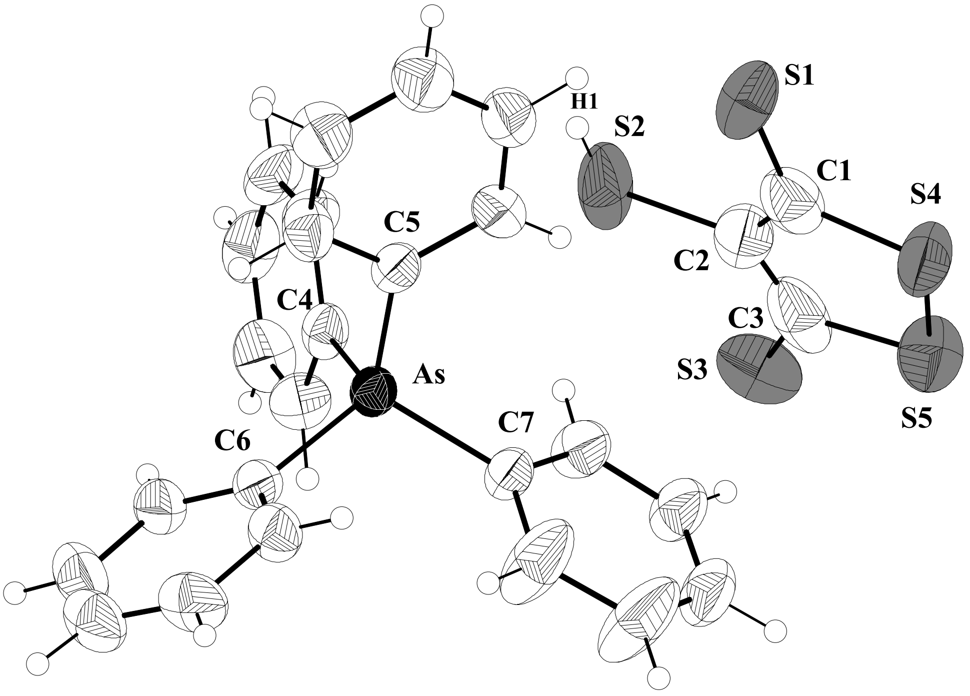
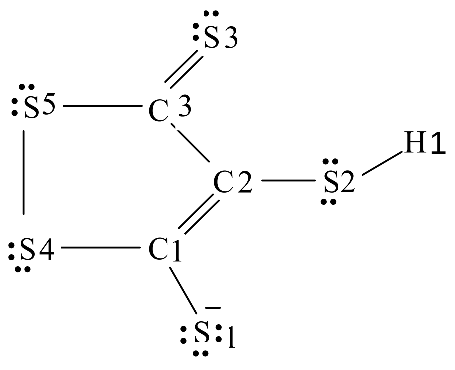


Figure 42 The ions in the structure of $[As(C_6H_5)_4](HC_3S_5)$. Thermal ellipsoids are drawn to include a probability density of 50%.

No S····S interactions found between neighboring anions in distances equal or less than the sum of the van der Waals radii (3.70 Å[59]). In the $(HC_3S_5)^-$ ions, the S(4)–S(5) bond is 1.991(2) Å which is shorter than that found in $[As(C_6H_5)_4]_2(C_3S_5)\cdot 2H_2O$. The C(1)–S(4) and C(3)–S(5) bond distances are 1.739(2) Å and 1.729(3) Å respectively, similar to other $(C_3S_5)^{2-}$ ions. The terminal C–S bonds are of different lengths. C(3)–S(3) is the shortest bond and amount to1.586(2), C(1)–S(1) and C(2)–S(2) amount 1.794(1) Å and 1.789(1) respectively, which are equal to the value for a single C−S bond [62]. The C(1)–C(2) and C(2)–C(3) bond lengths are 1.318(2) Å (similar to that found for $(Bu_4N)_2\,[V(C_3S_5)_3]$ [29]) and 1.431(2) Å(similar to that found for the planar $(Bu_4N)_2\,[Ni(C_3S_5)_2]$ with 1.42 Å [28]). These bond lengths proved that the protonation of S2 atom in C_3S_5 ring suppressed the resonance through C–C and terminal C–S bonds giving the $(HC_3S_5)^-$ ion the localized electron structure shown in Scheme 8.



Scheme 8 Molecular structures and electronic formula of $(HC_3S_5)^-$ ion.

As expected, the $(HC_3S_5)^-$ ion is fairly close to planarity. The hydrogen atom H(1) has been refined with fixed thermal parameters. However, the hydrogen atom H(1) deviates from the plane of the C_3S_5 ring as evident from torsion angle C–C–S–H which amounts 172.68°. In the unit cell the anions and cations are stacking a long *b*-axis Figure 43. The packing of this compound is dominated by that of the bulky cations As a result there is no strong interaction between the anions. The As–C bond average is 1.902 Å and C–C bond length in the phenyl rings ranging from 1.325 to 1.419 Å. C–As–C angles ranging from 107.14 to 111.33 °, indicating $[As(C_6H_5)_4]^+$ ions of regular structure.

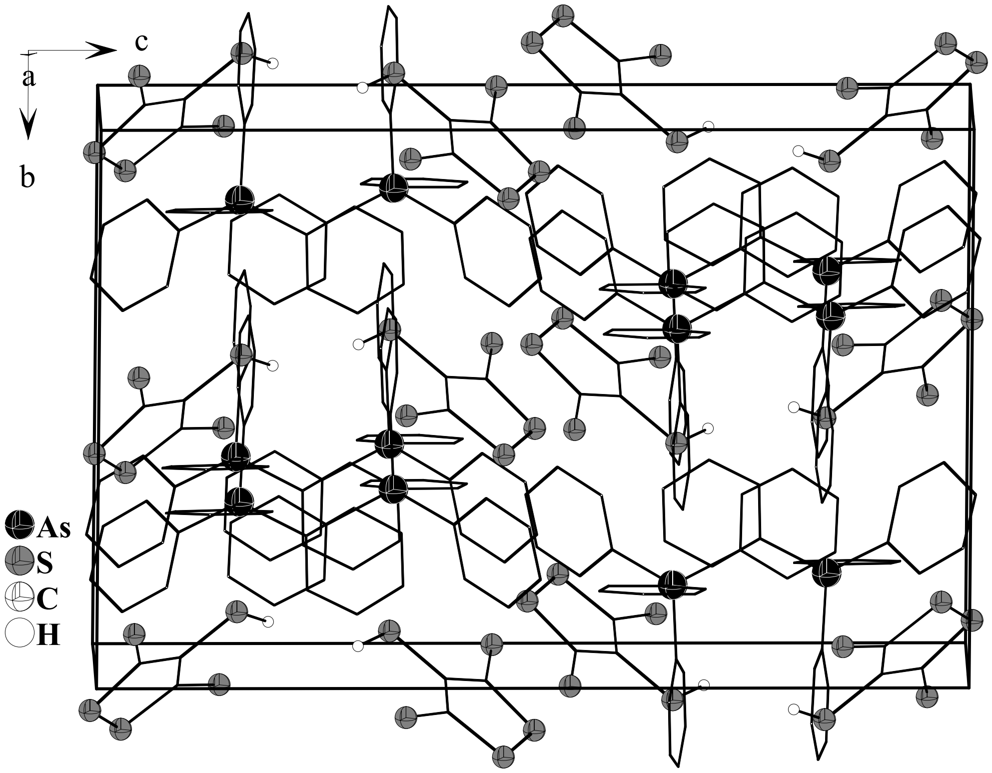


Figure 43 The unit cell of $[As(C_6H_5)_4](HC_3S_5)$ in a view slightly inclined along *a*-axis.

3.5.1.5 Structure Determination of $[As(C_6H_5)_4]_2(C_3S_6O_3)\cdot 3H_2O$

The crystals of this compound are sensitive towards the loss of water and were therefore sealed in glass capillaries. The diffraction quality of the crystals towards X-rays was checked by preliminary precession exposures, which showed the triclinic symmetry. Data were collected at ambient temperature using a Nonius kappa-CCD diffractometer equipped with Mo-Kα radiation (λ=0.7107 Å). The space group could be derived from the data set as triclinic, $P\bar{1}$ (№ 2). A structure model was obtained by direct method [38] and refined against F^2 with anisotropic displacement parameters for all non-hydrogen atoms [39]. Hydrogen atoms attached to the carbon atoms of the phenyl rings were located in idealized, calculated positions and refined in a riding model with B_{iso} fixed to 1.2 B_{iso} of the resprective carbon atoms. The localization of the H atoms bound to O atoms of the three water molecules was not possible. These atoms were omitted from the refinement. Crystallographic data and details of the structure analyses are given in Table 44, positional parameters, isotropic equivalent parameters for the non-H atoms in Table 45, anisotropic displacement parameters for the non-H atoms in Table 46 and selected bond lengths and angles in Table 47.

Table 44 Crystallographic data and details of the structure determination $[As(C_6H_5)_4]_2(C_3S_6O_3)\cdot 3H_2O$.

Formula	$As_2C_{53}H_{46}O_6S_6$
Lattice constants	a =12.6953(8)Å, α =75.542(4)°
	b =13.1833(9)Å, β =69.941(3)°
	c =17.6888(8)Å, γ =71.247(3)°
Volume of unit cell	2600.75 $Å^3$
Number of formula units	Z = 2
Density (calc.)	$\rho = 1.424$ g · cm^{-3}
Absorption coefficient	$\mu = 15.7$ cm^{-1}
Crystal system, space group	Triclinic, $P\bar{1}$ (№ 2)
Diffractometer	Nonius kappa-CCD
Radiation, wave length	Mo-Kα, λ = 0.7107 Å
Temperature of measurement	T = 293 K
Range of data collection	$2\theta < 52.97^{\circ}$
Number of data collected	17152
Number of independent reflections, R_{merge}	8682, 18.25%
Number of refined parameters	706
Ratio reflections/parameters	12.3
R (|F|) for all reflections	26.33%
R (|F|) for 2616 reflections with $F_0 > 4\sigma(F_0)$	5.61 %
$wR(F^2)$	15.71 %
Largest electron density difference peak and hole	+0.66 / -0.27 e /$Å^3$

Table 45 Positional parameters, equivalent isotropic parameters U_{eq} /Å^2 for the non-H atoms in the structure of $[As(C_6H_5)_4]_2[C_3S_6O_3]\cdot 3\ H_2O$.

Atom	**x**	**y**	**z**	**U_{eq}**
As1	0.18147(8)	0.64564(8)	0.45832(5)	0.058(3)
As2	0.31113(8)	1.24276(8)	0.00154(5)	0.058(3)
S1	0.4812(3)	1.1685(3)	0.2804(2)	0.128(1)
S2	0.7043(2)	1.2201(2)	0.31314(14)	0.076(8)
S3	0.6822(3)	1.4878(3)	0.2749(2)	0.127(1)
S4	0.4104(3)	1.3936(4)	0.2230(2)	0.132(1)
S5	0.4866(3)	1.5134(3)	0.2172(2)	0.130(1)
S6	0.8333(2)	1.1686(3)	0.2059(2)	0.082(9)
O1	0.7744(6)	1.1795(7)	0.1451(4)	0.111(2)
O2	0.9116(5)	1.2371(6)	0.1785(4)	0.094(2)
O3	0.8821(7)	1.0569(6)	0.2369(5)	0.133(3)
O4	0.8249(8)	0.9436(7)	0.3886(5)	0.157(4)
O5	0.5872(8)	1.0013(7)	0.4273(5)	0.140(3)
O6	-0.0061(9)	-0.0008(8)	0.4246(6)	0.183(4)
C1	0.5115(9)	1.2868(9)	0.2627(6)	0.086(3)
C2	0.5985(9)	1.3178(9)	0.2735(5)	0.069(3)
C3	0.5967(9)	1.428(1)	0.2578(5)	0.091(3)
C4	0.1292(7)	0.6545(9)	0.3669(4)	0.058(2)
C5	0.2835(7)	0.7365(8)	0.4261(5)	0.060(2)
C6	0.2573(8)	0.4992(7)	0.4890(5)	0.056(2)
C7	0.0540(8)	0.6898(7)	0.5485(5)	0.062(2)
C8	0.2885(8)	1.1387(7)	0.0976(5)	0.062(2)
C9	0.2070(7)	1.3808(7)	0.0205(5)	0.054(2)
C10	0.2926(7)	1.1899(9)	-0.0817(5)	0.063(2)
C11	0.4642(7)	1.2595(7)	-0.0273(5)	0.060(2)
C12	0.0809(9)	0.7540(9)	0.3301(6)	0.065(3)
C13	0.2310(9)	1.474(1)	-0.0294(6)	0.071(3)
C14	0.2583(9)	1.265(1)	-0.1476(7)	0.080(3)
C15	0.052(1)	0.673(1)	0.2359(7)	0.094(4)
C16	0.0333(9)	1.491(1)	0.0952(6)	0.077(3)
C17	0.252(1)	0.9926(9)	0.2363(7)	0.081(3)
C18	0.270(1)	1.114(2)	-0.2067(9)	0.098(4)
C19	-0.129(1)	0.752(1)	0.6803(8)	0.102(4)
C20	0.487(1)	1.315(1)	0.0190(6)	0.097(4)

Table 45 continued

C21	0.597(1)	1.326(1)	0.0046(8)	0.114(5)
C22	0.439(1)	0.860(1)	0.3749(7)	0.083(4)
C23	0.5521(8)	1.2105(9)	-0.0871(6)	0.082(3)
C24	0.1896(11)	0.429(1)	0.5379(7)	0.092(3)
C25	0.6629(9)	1.218(1)	-0.1032(8)	0.102(4)
C26	0.3139(9)	1.081(1)	-0.0810(6)	0.086(4)
C27	0.3731(9)	1.0963(9)	0.1384(6)	0.072(3)
C28	0.055(1)	1.582(1)	0.0480(7)	0.076(3)
C29	-0.056(1)	0.727(1)	0.5413(6)	0.079(3)
C30	0.169(1)	1.031(1)	0.1977(8)	0.087(3)
C31	0.1072(8)	1.3872(9)	0.0857(5)	0.066(3)
C32	0.349(1)	0.879(1)	0.4399(8)	0.088(4)
C33	0.041(1)	0.766(1)	0.2650(7)	0.079(3)
C34	0.2703(9)	0.817(1)	0.4666(6)	0.080(3)
C35	0.1863(9)	1.1052(9)	0.1274(6)	0.068(3)
C36	0.380(1)	0.718(1)	0.3571(6)	0.082(3)
C37	0.248(1)	1.223(1)	-0.2089(7)	0.097(4)
C38	0.353(1)	1.024(1)	0.2071(7)	0.088(4)
C39	-0.019(1)	0.716(1)	0.6880(6)	0.094(4)
C40	0.156(1)	1.573(1)	-0.0173(7)	0.091(3)
C41	0.1400(8)	0.5619(9)	0.3388(6)	0.071(3)
C42	0.241(1)	0.323(1)	0.5565(9)	0.099(4)
C43	0.099(1)	0.576(1)	0.2724(8)	0.085(4)
C44	-0.1490(9)	0.757(1)	0.6092(8)	0.098(4)
C45	0.373(1)	0.460(1)	0.4607(7)	0.098(4)
C46	0.459(1)	0.781(1)	0.3334(8)	0.081(3)
C47	0.423(1)	0.350(1)	0.4798(8)	0.114(5)
C48	0.075(1)	0.681(1)	0.6232(6)	0.088(4)
C49	0.300(1)	1.044(1)	-0.142(1)	0.095(4)
C50	0.353(2)	0.282(1)	0.5264(9)	0.108(4)
C51	0.685(1)	1.275(1)	-0.0599(9)	0.115(5)

Table 46 Anisotropic displacement parameters U_{ij} /Å^2 for the non-H atoms in the structure of $[As(C_6H_5)_4]_2[C_3S_6O_3]\cdot 3\ H_2O$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{12}**	**U_{13}**	**U_{23}**
As1	0.0523(6)	0.0628(7)	0.0579(6)	-0.0164(5)	-0.0119(4)	-0.0154(5)
As2	0.0506(6)	0.0644(7)	0.0573(6)	-0.0150(5)	-0.0120(4)	-0.0138(5)
S1	0.081(2)	0.147(4)	0.183(3)	-0.035(2)	-0.026(2)	-0.080(3)
S2	0.076(2)	0.070(2)	0.077(2)	-0.017(2)	-0.023(1)	-0.009(1)
S3	0.134(3)	0.078(2)	0.157(3)	-0.039(2)	-0.023(2)	-0.017(2)
S4	0.092(2)	0.175(4)	0.120(2)	0.036(2)	-0.050(2)	-0.075(3)
S5	0.130(3)	0.107(3)	0.080(2)	0.043(2)	-0.018(2)	-0.010(2)
S6	0.056(2)	0.076(2)	0.105(2)	-0.013(2)	-0.011(1)	-0.016(2)
O1	0.087(5)	0.141(7)	0.102(5)	-0.028(5)	-0.025(4)	-0.043(5)
O2	0.077(5)	0.107(6)	0.104(5)	-0.053(5)	-0.009(4)	-0.007(4)
O3	0.105(6)	0.079(6)	0.144(6)	0.002(5)	-0.009(5)	-0.001(5)
O4	0.156(8)	0.120(8)	0.144(7)	-0.0006(1)	-0.032(6)	-0.011(6)
O5	0.174(8)	0.116(7)	0.165(7)	-0.069(7)	-0.058(6)	-0.015(6)
O6	0.181(9)	0.118(8)	0.175(8)	-0.019(7)	-0.008(7)	-0.045(6)
C1	0.061(7)	0.095(9)	0.083(1)	-0.0006(1)	-0.014(5)	-0.036(6)
C2	0.074(7)	0.072(8)	0.065(6)	-0.010(6)	-0.016(5)	-0.032(6)
C3	0.082(8)	0.086(9)	0.072(7)	-0.007(7)	-0.012(5)	-0.025(6)
C4	0.064(6)	0.064(7)	0.039(5)	-0.023(6)	-0.013(4)	-0.013(5)
C5	0.044(5)	0.063(7)	0.069(6)	-0.015(5)	-0.012(5)	-0.017(5)
C6	0.062(6)	0.053(6)	0.055(5)	-0.005(5)	-0.026(5)	-0.011(5)
C7	0.050(6)	0.058(7)	0.068(6)	-0.013(5)	-0.005(5)	-0.022(5)
C8	0.062(6)	0.050(6)	0.058(5)	-0.015(5)	-0.006(5)	-0.012(5)
C9	0.047(5)	0.050(6)	0.047(5)	-0.008(4)	-0.009(4)	-0.016(5)
C10	0.051(6)	0.070(8)	0.062(6)	-0.019(5)	-0.012(5)	-0.031(6)
C11	0.030(5)	0.063(7)	0.074(6)	-0.012(5)	-0.009(4)	-0.011(5)
C12	0.075(7)	0.057(8)	0.072(7)	-0.024(6)	-0.025(6)	-0.007(6)
C13	0.074(7)	0.069(7)	0.059(6)	-0.024(7)	-0.014(5)	-0.004(6)
C14	0.075(7)	0.098(7)	0.074(7)	-0.045(8)	-0.007(6)	-0.032(8)
C15	0.072(8)	0.127(9)	0.071(8)	-0.019(8)	-0.017(6)	-0.033(9)
C16	0.051(6)	0.102(9)	0.062(7)	-0.003(7)	-0.016(5)	-0.026(7)
C17	0.074(8)	0.061(8)	0.091(8)	-0.007(7)	-0.013(7)	-0.005(6)
C18	0.090(9)	0.141(9)	0.087(9)	-0.054(9)	-0.024(7)	-0.034(9)
C19	0.089(9)	0.104(9)	0.087(9)	-0.029(8)	0.009(8)	-0.036(8)
C20	0.073(8)	0.131(9)	0.086(8)	-0.048(8)	0.004(6)	-0.054(7)
C20	0.073(8)	0.131(9)	0.086(8)	-0.048(8)	0.004(6)	-0.054(7)

Table 46 continued

C21	0.073(8)	0.175(9)	0.134(9)	-0.067(9)	-0.0004(7)	-0.083(9)
C22	0.084(9)	0.091(9)	0.073(8)	-0.046(7)	-0.021(7)	0.021(7)
C23	0.050(6)	0.091(9)	0.097(8)	-0.027(6)	-0.007(6)	-0.038(6)
C24	0.089(8)	0.063(9)	0.111(9)	-0.032(8)	-0.040(7)	0.007(7)
C25	0.050(8)	0.133(9)	0.126(9)	-0.026(7)	-0.008(6)	-0.051(9)
C26	0.076(7)	0.102(9)	0.085(8)	-0.013(7)	-0.023(6)	-0.053(7)
C27	0.068(7)	0.073(8)	0.063(7)	-0.024(6)	-0.015(6)	-0.002(6)
C28	0.080(8)	0.068(9)	0.076(7)	-0.015(6)	-0.024(7)	-0.012(7)
C29	0.067(7)	0.104(9)	0.074(7)	-0.024(7)	-0.010(7)	-0.030(7)
C30	0.060(8)	0.069(8)	0.120(9)	-0.023(7)	-0.011(7)	-0.020(7)
C31	0.058(6)	0.066(8)	0.056(6)	-0.017(6)	-0.0008(9)	-0.019(5)
C32	0.106(9)	0.080(9)	0.094(9)	-0.049(8)	-0.043(8)	-0.006(7)
C33	0.096(9)	0.069(9)	0.085(8)	-0.017(7)	-0.036(7)	-0.018(7)
C34	0.068(7)	0.095(9)	0.068(7)	-0.020(7)	-0.017(5)	-0.027(6)
C35	0.065(7)	0.064(8)	0.076(7)	-0.013(6)	-0.02358	-0.009(6)
C36	0.081(7)	0.089(9)	0.083(8)	-0.035(7)	-0.010(6)	-0.027(6)
C37	0.074(8)	0.150(9)	0.078(9)	-0.052(9)	-0.016(6)	-0.016(9)
C38	0.086(9)	0.083(9)	0.100(9)	-0.035(8)	-0.031(7)	0.013(7)
C39	0.118(9)	0.113(9)	0.049(6)	-0.046(9)	-0.020(7)	-0.024(6)
C40	0.117(9)	0.055(9)	0.080(8)	-0.043(8)	-0.030(8)	0.002(6)
C41	0.059(6)	0.072(8)	0.078(7)	-0.008(6)	-0.026(5)	-0.023(6)
C42	0.104(9)	0.074(9)	0.142(9)	-0.027(9)	-0.080(9)	0.008(9)
C43	0.077(8)	0.094(9)	0.097(9)	-0.021(8)	-0.026(7)	-0.044(8)
C44	0.063(7)	0.118(9)	0.094(9)	-0.011(8)	-0.008(8)	-0.032(8)
C45	0.096(9)	0.062(9)	0.092(8)	0.023(7)	-0.017(7)	-0.007(6)
C46	0.067(7)	0.076(9)	0.104(9)	-0.019(7)	-0.013(6)	-0.015(8)
C47	0.097(9)	0.091(9)	0.100(9)	0.017(9)	-0.011(8)	-0.018(8)
C48	0.095(8)	0.124(9)	0.056(6)	-0.045(8)	-0.014(7)	-0.030(6)
C49	0.081(8)	0.100(9)	0.117(9)	-0.019(8)	-0.001(8)	-0.066(9)
C50	0.148(9)	0.055(9)	0.107(9)	0.003(9)	-0.074(9)	-0.005(8)
C51	0.049(7)	0.159(9)	0.134(9)	-0.035(9)	-0.015(8)	-0.027(9)

Table 47 Selected bond lengths / Å and angles / ° for $[As(C_6H_5)_4]_2(C_3S_6O_3)\cdot 3H_2O$.

As(1)–C(4)	1.919 (2)	As(2)–C(8)	1.895 (5)
As(1)–C(5)	1.895 (3)	As(2)–C(9)	1.902 (4)
As(1)–C(6)	1.885 (4)	As(2)–C(10)	1.887 (2)
As(1)–C(7)	1.876 (4)	As(2)–C(11)	1.905 (2)
C(1)–C(2)	1.381 (1)	S(1)–C(1)	1.650 (2)
C(2)–C(3)	1.422 (1)	S(2)–C(2)	1.734 (4)
C(1)–S(4)	1.753(4)	S(3)–C(3)	1.658 (2)
C(3)–S(5)	1.734 (4)	S(4)–S(5)	2.061 (2)
S(6)–O(1)	1.452 (2)	S(2)–S(6)	2.132 (5)
S(6)–O(2)	1.433 (2)	S(6)–O(3)	1.449 (3)
C(4)–As(1)–C(5)	107.09 (1)	C(8)–As(2)–C(9)	110.82 (1)
C(5)–As(1)–C(6)	111.64 (1)	C(9)–As(2)–C(10)	112.29 (1)
C(6)–As(1)–C(7)	108.08 (1)	C(10)–As(2)–C(11)	110.07 (1)
C(1)–S(4)–S(5)	95.70 (1)	C(3)–S(5)–S(4)	96.18 (1)
C(1)–C(2)–C(3)	119.58(1)	C(2)–S(2)–S(6)	102.86(1)
S(2)–S(6)–O(2)	108.24(1)	S(2)–S(6)–O(3)	100.99(1)
O(1)–S(6)–O(2)	110.58(1)	S(2)–S(6)–O(1)	107.94(1)

3.5.1.6 Discussion the structure of $[As(C_6H_5)_4]_2(C_3S_6O_3)\cdot 3H_2O$

The structure of this compound consists of discrete $(C_3S_6O_3)^{2-}$ ions, $[As(C_6H_5)_4]^+$ ions, and three water molecules which are linked by electrostatic forces, hydrogen bonds, and Van der Waals interactions (Figure 44). The C_3S_5 fragment (without SO_3 group) is essentially planar. The C(1)−S(4) and C(3)−S(5) distances are almost identical with 1.753(4) and 1.734(4) Å, respectively. The disulfide bond S(4)−S(5) is 2.061(2) Å and the two carbon-carbon bonds C(1)−C(2) and C(2)−C(3) are 1.381(1) and 1.422(1) Å, respectively. An SO_3 group connected to $(C_3S_5)^{2-}$ ring through S(2) with S(2)−S(6) bond length of 2.132(5) Å and S(6)−O bond length average 1.45 Å. The planar C_3S_5 fragment is bound with the central sulfur atom S(2) to a pyramidal SO_3 group. The S(2)−S(6) bond is 2.132(5) Å long and the S(6)−O bonds are of average 1.45 Å. The SO_3 group is not coplanar with the C_3S_5 fragment. The angle at S(2) is C(2)−S(2)−S(6) 102.86(1)° and the two torsion angles C(1)−C(2)−S(2)−S(6) and C(3)−C(2)−S(2)−S(6) are 89.20(1)° and -93.60(1)° respectively. The coordination environment for S(6) is an equilateral triangle based tetrahedron with O(1), O(2) and O(3) atoms in the base and all O−O−O angles deviate only by maximally 1° from 60°.

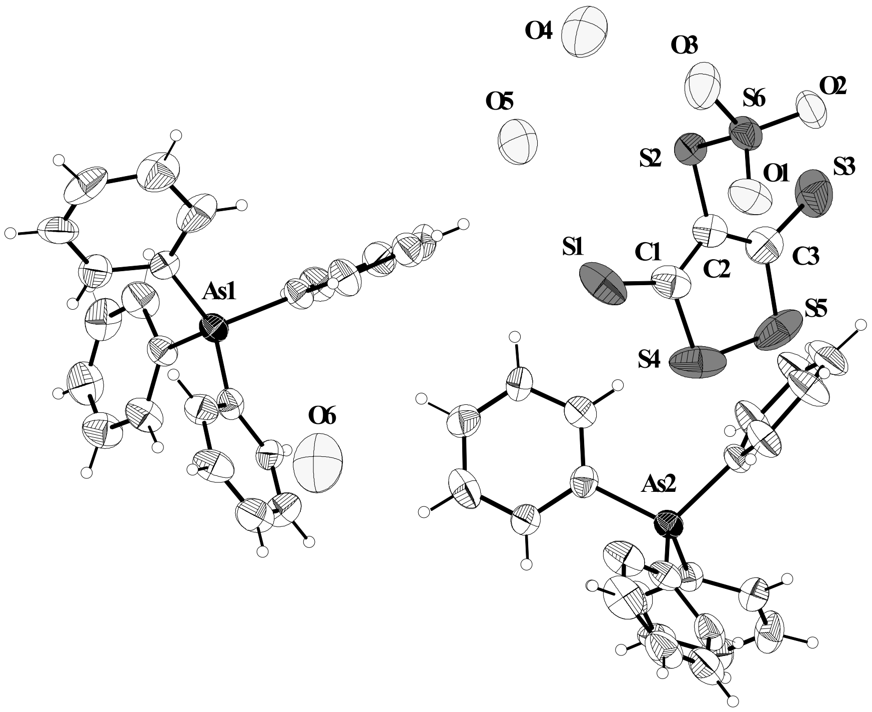


Figure 44 The ions in the structure of $[As(C_6H_5)_4]_2(C_3S_6O_3)\cdot 3H_2O$. Thermal ellipsoids are drawn to include a probability density of 50%.

The two crystallographically independent $[As(C_6H_5)_4]^+$ ions do not show unusual parameters, in which the As−C bond length average for both As1 and As2 is 1.898 Å. C−C bond length within the phenyl rings vary from 1.319(2) to 1.422(2) Å, C–As–C angles ranging from 107.09(1)^o to 112.29(1)^o. In the unit cell the bulky cations and the anions are packed in a way that every $(C_3S_6O_3)^{2-}$ ion completely surrounded by $[As(C_6H_5)_4]^+$ ions (Figures 45 and 46).

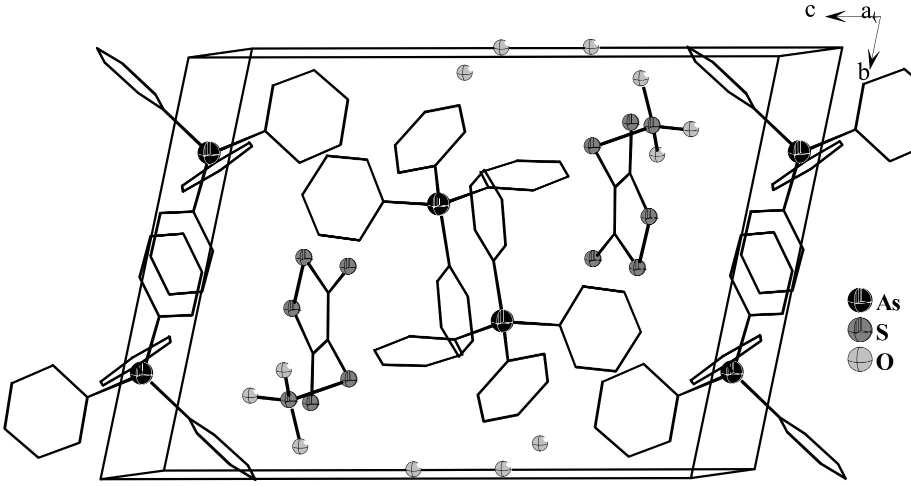


Figure 45 The unit cell of $[As(C_6H_5)_4]_2(C_3S_6O_3)\cdot 3H_2O$ in a view along the *a*-axis, hydrogen atoms were omitted for clarity.

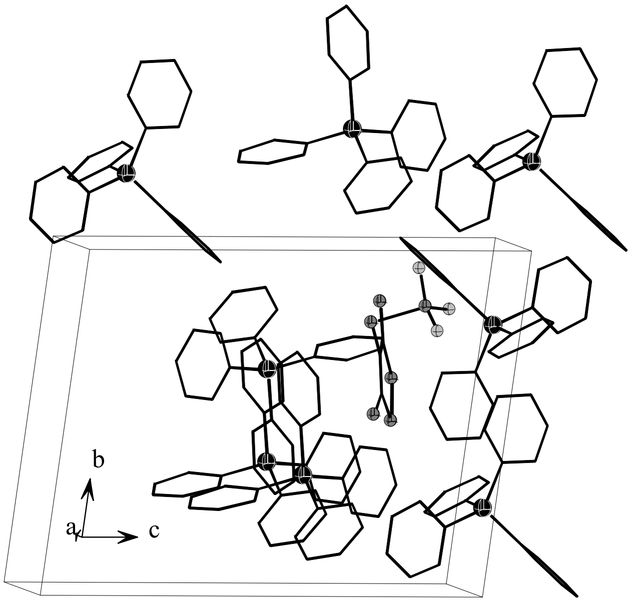


Figure 46 A part of the unit cell of $[As(C_6H_5)_4]_2(C_3S_6O_3)\cdot 3H_2O$ showing the coordination of the $(C_3S_6O_3)^{2-}$ by surrounding $[As(C_6H_5)_4]^+$ cations .

3.5.2 Tetraphenylarsonium Salts Prepared under Exclusion of Air

3.5.2.1 Structure Determination of $[As(C_6H_5)_4](C_3S_4H)$

The crystals of this compound are sensitive towards the air and were therefore sealed in glass capillaries. The diffraction quality of the crystals towards X-rays was checked by preliminary precession exposures, which showed the monoclinic symmetry. Data were collected at ambient temperature using a Nonius kappa-CCD diffractometer equipped with Mo-Kα radiation (λ=0.7107 Å). The space group could be derived from the data set as monoclinic, $P\ 1\ 2_1/n\ 1$ (№ 14). A structure model was obtained by direct method [38] and refined against F^2 with anisotropic displacement parameters for all non-hydrogen atoms [39]. The H atom attached to the C_3S_4 fragment was identified in a difference Fourier synthesis. It was included as individual atom with free positional and isotropic displacement parameters in the refinement. Hydrogen atoms attached to the carbon atoms of the phenyl rings were located in idealized, calculated positions and refined in a riding model with B_{iso} fixed to 1.2 B_{iso} of the resprective carbon atoms. Crystallographic data and details of the structure analyses are given in Table 48, positional parameters, isotropic equivalent parameters for the non-H atoms in Table 49, anisotropic displacement parameters for the non-H atoms in Table 50 and selected bond lengths and angles in Table 51.

Table 48 Crystallographic data and details of the structure determination $[As(C_6H_5)_4](C_3S_4H)$.

Formula	$AsC_{27}H_{21}S_4$
Lattice constants	a = 11.1684(4) Å
	b = 14.3466(5) Å, β= 95.435(2)°
	c = 15.8470(5) Å
Volume of unit cell	2527.73 $Å^3$
Number of formula units	Z = 4
Density (calc.)	$\rho = 1.442\ g \cdot cm^{-3}$
Absorption coefficient	$\mu = 16.9\ cm^{-1}$
Crystal system, space group	Monoclinic, $P\ 2_1/n$ (№14)
Diffractometer	Nonius kappa-CCD
Radiation, wave length	Mo-Kα, λ = 0.7107 Å
Temperature of measurement	T = 293 K
Range of data collection	2θ < 52.12°
Number of data collected	9968
Number of independent reflections, R_{merge}	4823, 4.28%
Number of refined parameters	353
Ratio reflections/parameters	13.7
R (|F|) for all reflections	9.58%
R (|F|) for 2625 reflections with $F_0 > 4\sigma(F_0)$	3.92 %
$wR(F^2)$	10.39 %
Largest electron density difference peak and hole	+0.28 / -0.44 e /$Å^3$

Table 49 Positional parameters, equivalent isotropic parameters U_{eq} /Å^2 for the non-H atoms and displacement isotropic parameters for H atom in the structure of [As(C_6H_5)$_4$](C_3S_4H).

Atom	**x**	**y**	**z**	**U_{eq}**
As1	0.55701(3)	-0.00406(3)	0.20221(2)	0.0500(1)
S1	-0.13044(11)	-0.27691(9)	0.12495(7)	0.0787(3)
S2	0.08337(12)	-0.16578(12)	0.12648(9)	0.0995(5)
S3	0.04752(19)	-0.03373(14)	0.37817(14)	0.1434(8)
S4	0.15086(14)	-0.07433(12)	0.21945(13)	0.1210(6)
C1	-0.0402(3)	-0.1984(3)	0.1777(3)	0.062(1)
C2	-0.0499(4)	-0.1563(3)	0.2551(3)	0.070(1)
C3	0.0360(4)	-0.0924(3)	0.2874(3)	0.088(1)
C4	0.5864(4)	-0.0400(3)	0.3176(2)	0.0571(9)
C5	0.7008(3)	0.0384(3)	0.1584(2)	0.0525(9)
C6	0.5018(3)	-0.1135(3)	0.1420(2)	0.0533(9)
C7	0.4352(3)	0.0885(3)	0.1870(2)	0.0526(9)
C8	0.6961(4)	-0.0207(3)	0.3627(3)	0.070(1)
C9	0.4304(5)	-0.2733(4)	0.0570(3)	0.082(1)
C10	0.6224(7)	-0.0960(4)	0.4844(3)	0.093(2)
C11	0.8568(5)	0.1524(5)	0.1557(4)	0.101(2)
C12	0.5700(4)	-0.1941(3)	0.1527(3)	0.068(1)
C13	0.9103(5)	0.0990(5)	0.0985(4)	0.090(2)
C14	0.8600(4)	0.0172(4)	0.0705(3)	0.081(1)
C15	0.7111(6)	-0.0480(4)	0.4472(4)	0.096(2)
C16	0.3249(6)	0.1969(4)	0.0947(4)	0.094(2)
C17	0.5164(6)	-0.1142(4)	0.4384(3)	0.090(2)
C18	0.3589(4)	0.1058(3)	0.2475(3)	0.065(1)
C19	0.7556(4)	-0.0148(3)	0.1000(3)	0.066(1)
C20	0.4977(4)	-0.0868(3)	0.3557(3)	0.071(1)
C21	0.3973(4)	-0.1135(3)	0.0876(3)	0.064(1)
C22	0.5338(5)	-0.2734(4)	0.1100(4)	0.084(1)
C23	0.2655(5)	0.1681(4)	0.2309(4)	0.087(2)
C24	0.7517(5)	0.1212(4)	0.1858(3)	0.080(1)
C25	0.3625(4)	-0.1941(4)	0.0454(3)	0.074(1)
C26	0.4188(5)	0.1349(4)	0.1098(3)	0.080(1)
C27	0.2476(5)	0.2115(4)	0.1551(4)	0.087(1)
H1	-0.123(4)	-0.174(3)	0.293(3)	0.078(1)

Table 50 Anisotropic displacement parameters U_{ij} /Å^2 for the non-H atoms in the structure of $[As(C_6H_5)_4](C_3S_4H)$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{12}**	**U_{13}**	**U_{23}**
As1	0.0509(2)	0.0522(2)	0.0471(2)	-0.0001(2)	0.0050(1)	0.0035(2)
S1	0.0820(6)	0.0879(9)	0.0667(7)	-0.0038(7)	0.0093(6)	-0.0124(6)
S2	0.0775(8)	0.118(1)	0.107(1)	-0.0066(8)	0.0271(7)	0.0256(9)
S3	0.155(1)	0.110(1)	0.153(2)	-0.005(1)	-0.047(1)	-0.055(1)
S4	0.0843(9)	0.102(1)	0.174(2)	-0.0235(9)	-0.0041(9)	0.023(1)
C1	0.054(2)	0.061(2)	0.071(3)	0.003(2)	0.008(2)	0.012(2)
C2	0.070(3)	0.066(3)	0.074(3)	-0.006(2)	-0.0010(2)	-0.004(2)
C3	0.085(3)	0.059(3)	0.114(4)	0.002(3)	-0.017(3)	-0.0003
C4	0.066(2)	0.053(2)	0.052(2)	0.002(2)	0.004(2)	0.003(2)
C5	0.057(2)	0.055(2)	0.046(2)	-0.002(2)	0.006(2)	0.004(2)
C6	0.050(2)	0.054(2)	0.056(2)	-0.005(2)	0.005(2)	0.003(2)
C7	0.050(2)	0.052(2)	0.056(2)	-0.003(2)	0.005(2)	-0.002(2)
C8	0.075(3)	0.064(3)	0.067(3)	0.002(2)	-0.012(2)	0.009(2)
C9	0.087(4)	0.066(3)	0.094(3)	-0.016(3)	0.011(3)	-0.017(3)
C10	0.144(5)	0.076(4)	0.058(3)	0.027(4)	0.0001(9)	0.004(3)
C11	0.102(4)	0.113(5)	0.091(4)	-0.050(4)	0.022(3)	-0.015(3)
C12	0.065(3)	0.056(3)	0.081(3)	0.001(2)	-0.010(2)	-0.000(2)
C13	0.060(3)	0.124(5)	0.088(4)	-0.022(3)	0.015(2)	0.007(3)
C14	0.069(3)	0.095(4)	0.085(3)	0.008(3)	0.029(2)	0.004(3)
C15	0.114(5)	0.078(4)	0.087(4)	0.013(3)	-0.040(3)	-0.008(3)
C16	0.113(4)	0.084(4)	0.084(3)	0.031(3)	-0.001(3)	0.014(3)
C17	0.126(5)	0.081(4)	0.066(3)	0.005(3)	0.026(3)	0.018(3)
C18	0.062(2)	0.073(3)	0.061(2)	0.007(2)	0.012(2)	-0.007(2)
C19	0.073(3)	0.057(3)	0.069(2)	0.006(2)	0.020(2)	0.004(2)
C20	0.079(3)	0.076(3)	0.057(2)	-0.005(2)	0.008(2)	0.009(2)
C21	0.057(2)	0.070(3)	0.063(2)	-0.001(2)	0.001(2)	-0.004(2)
C22	0.078(3)	0.054(3)	0.118(4)	0.001(2)	-0.007(3)	-0.003(3)
C23	0.071(3)	0.097(4)	0.097(4)	0.013(3)	0.024(3)	-0.015(3)
C24	0.084(3)	0.082(3)	0.077(3)	-0.026(3)	0.025(2)	-0.018(2)
C25	0.060(3)	0.093(4)	0.067(3)	-0.014(3)	-0.004(2)	-0.013(3)
C26	0.089(3)	0.084(3)	0.067(3)	0.024(3)	0.016(2)	0.017(2)
C27	0.077(3)	0.080(4)	0.103(4)	0.023(3)	-0.007(3)	-0.007(3)

Table 51 Selected bond lengths / Å and angles / ° for $[As(C_6H_5)_4](C_3S_4H)$.

As(1)–C(4)	1.898 (4)	C(1)–S(2)	1.730(4)
As(1)–C(5)	1.909 (4)	C(3)–S(4)	1.770(6)
As(1)–C(6)	1.909 (4)	S(1)–C(1)	1.680(4)
As(1)–C(7)	1.900 (4)	S(3)–C(3)	1.661(6)
C(1)–C(2)	1.381(6)	C(2)–H(1)	1.087(1)
C(2)–C(3)	1.389(6)	S(2)–S(4)	2.062(3)
C(4)–As(1)–C(5)	111.3 (2)	C(3)–S(4)–S(2)	96.01(0)
C(5)–As(1)–C(6)	108.9 (2)	C(3)–C(2)–H(1)	118.81(1)
C(6)–As(1)–C(7)	108.5 (2)	C(2)–C(1)–S(1)	129.87(1)
C(1)–S(2)–S(4)	95.22(1)	C(1)–C(2)–C(3)	120.46(1)

3.5.2.2 Discussion the structure of $[As(C_6H_5)_4](C_3S_4H)$

The structure of this compound consists of discrete $(C_3S_4H)^-$ anions and $[As(C_6H_5)_4]^+$ cations as shown by the thermal ellipsoid diagram in (Figure 47). The anionic unit can be derived from a $(C_3S_5)^{2-}$ anion, in which a C−S bond cleavage had occurred and the substitution of the central sulfur atom by a hydrogen atom. As expected, the $(C_3S_4H)^-$ ligand is fairly close to planarity and deviates by less than one degree and the hydrogen atom deviates maximum by 2.5^o from the plane of the C_3S_4 ring as evident from torsional angles. The C−C two bonds lengths are almost equal with an average 1.385 Å which is in between single and double bond. C2−H1 bond is 1.09 Å. S1−C1 and S3−C3 nearly have the same length of 1.68 and 1.66 Å, respectively. C1−S2 and C3−S4 bond lengths are 1.73 and 1.77 Å respectively. The value of S2−S4 bond length is 2.06 Å as expected for a S−S single bond.

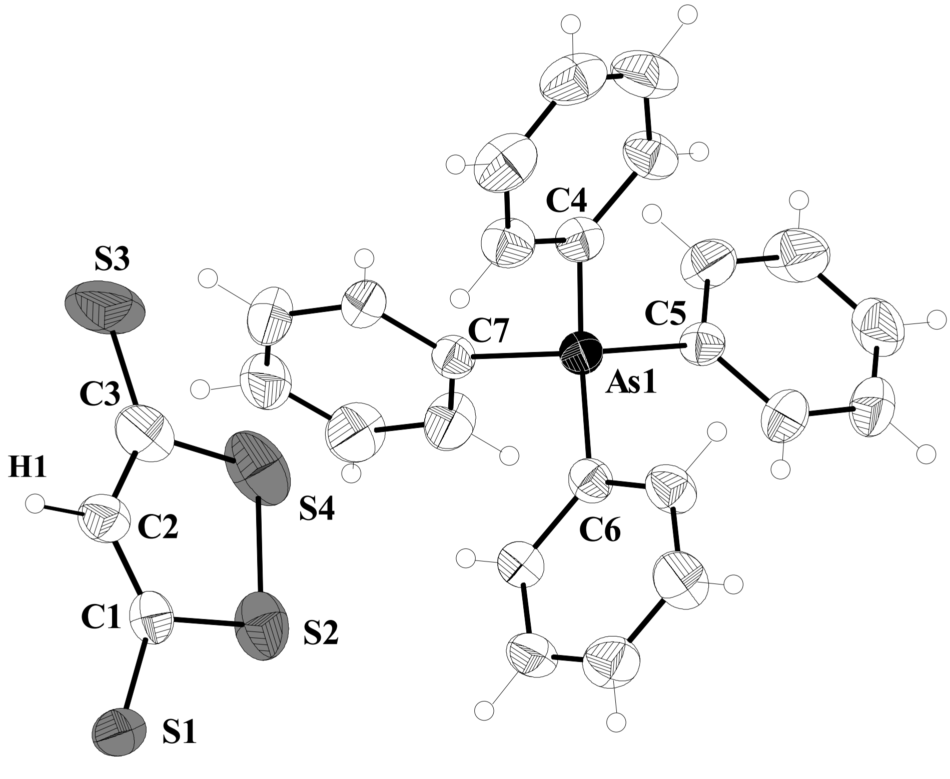


Figure 47 The structure of $[As(C_6H_5)_4](C_3S_4H)$. Thermal ellipsoids are drawn to include a probability density of 50%.

The cation structure is unexceptional, and the intratomic dimensions obtained here do not differ significantly from the corresponding details reported for this ion in other crystallographic studies. The deviation from a regular tetrahedral structure around the arsenic atoms are small, the C−As−C bond angles ranging from 106.03(1) to 111.25(1)°, the As−C bond length average is 1.904 Å, and the C−C phenyl rings bond lengths ranging from 1.35 to 1.39 Å. The $[As\ (C_6H_5)_4]^+$ complexes and the $(C_3S_4H)^-$anions are connected via a three-dimensional net of C−H···S bridges (Figure 49). These bridges connect the $[As\ (C_6H_5)_4]^+$ complexes to a one-dimensional strand along the *c*-axis. Each $[As\ (C_6H_5)_4]^+$ is connected with two neighbored $(C_3S_4H)^-$ ions. Hydrogen bridges with H·····A < r(A) + 2.0 Å of 2.81(2) Å for H(24)·····S(1) and 2.97(3) Å for H(15)·····S(3) are observed [42].

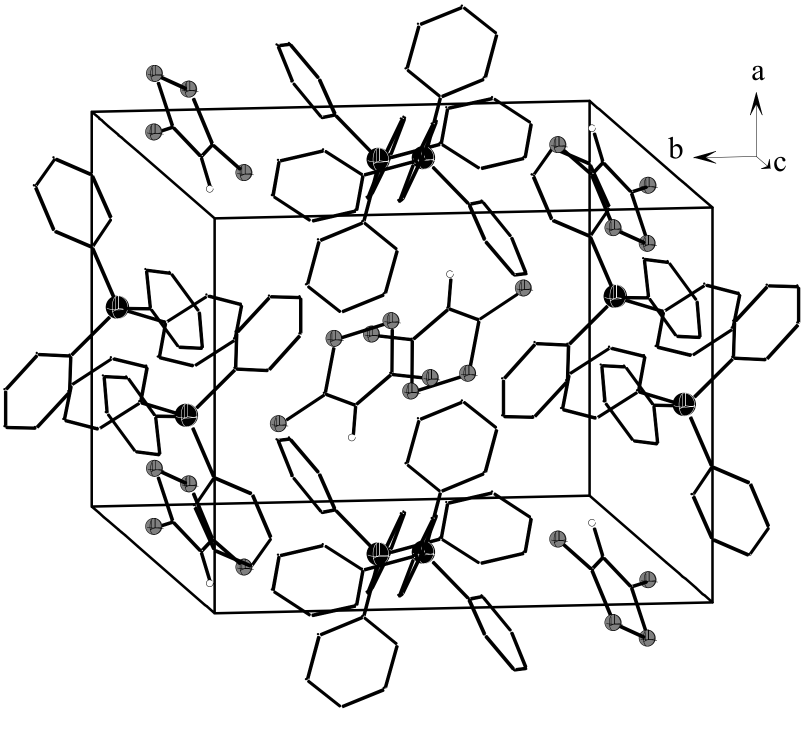


Figure 48 The unit cell of $[As(C_6H_5)_4](C_3S_4H)$ in a view inclined to the *c*-axis.

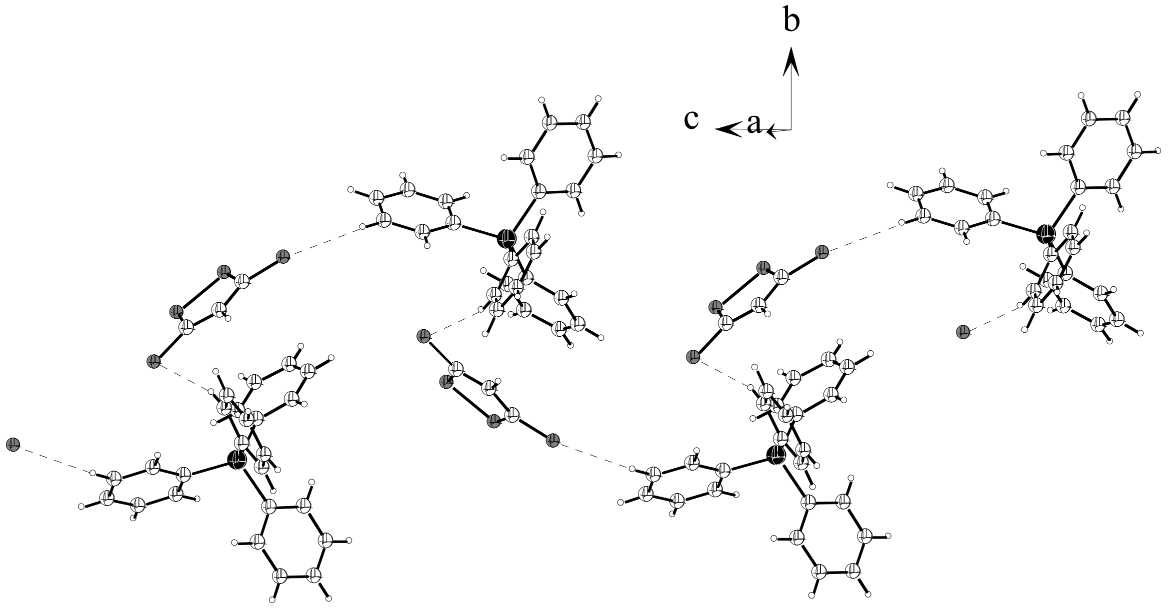
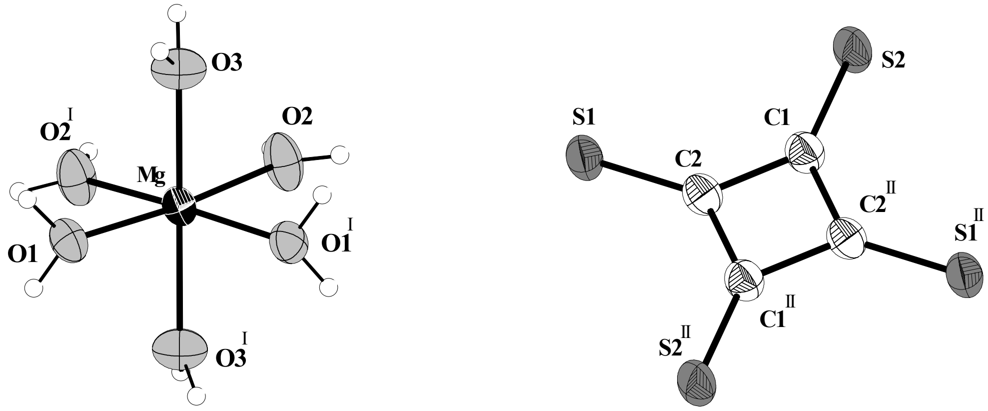


Figure 49 The interconnection of the $[As(C_6H_5)_4]^+$ cations and the $(C_3S_4H)^-$ anions to chains by H···S bridges.

3.6 Conclusion

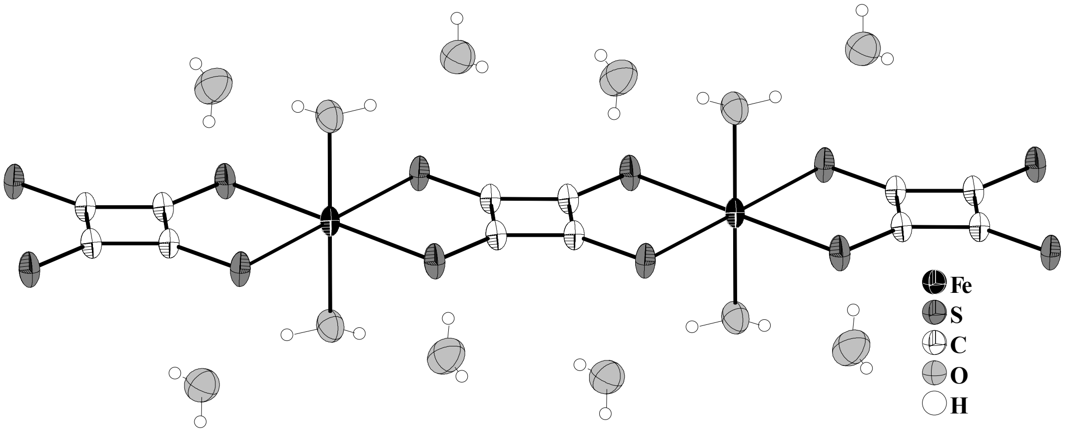
In contrast to the well known squarate ion $(C_4O_4)^{2-}$, the analogue tetrathiosquarate $(C_4S_4)^{2-}$ is less explored. Especially only a few salt like compounds or coordination complexes were characterized. Tetrathiosquarate $(C_4S_4)^{2-}$ forms water soluble compounds of salt like character with the earth alkaline ions from Mg^{2+} to Ba^{2+}. While Ca^{2+} and Sr^{2+} yield almost isotypic tetrahydrates $M(C_4S_4)\cdot 4\ H_2O$, Mg^{2+} and Ba^{2+} show a different behaviour. For Mg^{2+} the formation of the discrete octahedral complex ions $[Mg(H_2O)_6]^{2+}$ is observed. Ba^{2+} forms a double salt $Ba_4K_2(C_4S_4)_5\cdot 16\ H_2O$ under inclusion of the potassium ions for the starting compound $K_2(C_4S_4)\cdot H_2O$. $Ba_4K_2(C_4S_4)_5\cdot 16\ H_2O$ is the least soluble of the series.



The ions in the structure of $[Mg(H_2O)_6](C_4S_4)$.

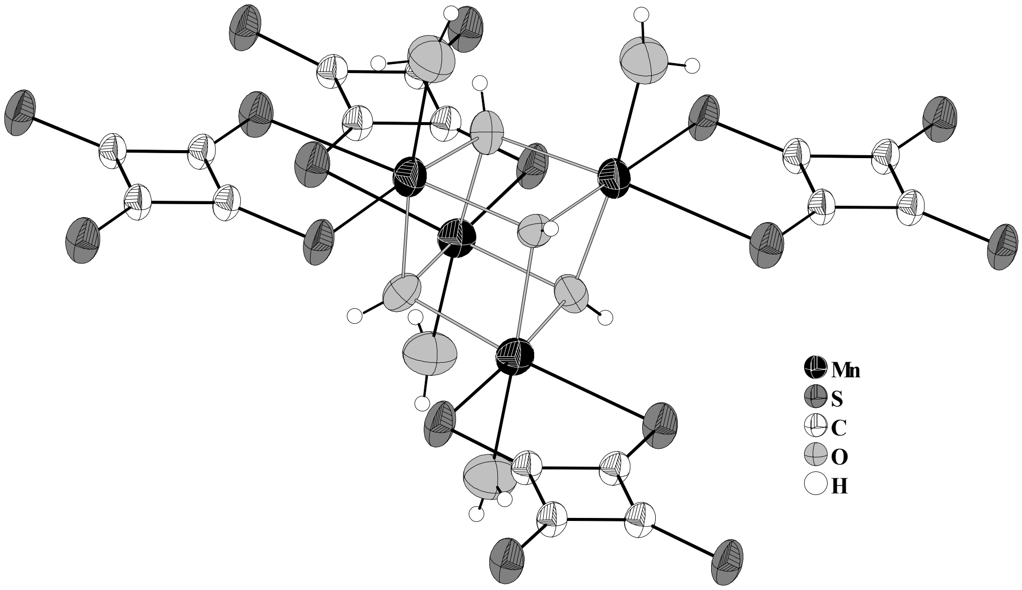
The Ca^{2+}, Sr^{2+}, and Ba^{2+} containing salts show high coordination numbers for the earth alkaline ions, which are linked by bridging H_2O molecules and bridging tetrathiosquarate ions to one dimensional strands for Ca^{2+} and Sr^{2+} or to a three dimensional network for $Ba_4K_2(C_4S_4)_5\cdot 16\ H_2O$. In all structures, the $(C_4S_4)^{2-}$ ions almost fulfil D_{4h} symmetry despite small derivations from the ideal symmetry are generally observed caused by the coordination to the cations. Tetrathiosquarate $(C_4S_4)^{2-}$ forms water soluble compounds of salt like character also with Mn^{2+} and Fe^{2+} ions. In both structures, water molecules are present as ligands and fill the coordination environment of the cations to octahedra. In the iron(II) salt

$[Fe(H_2O)_2](C_4S_4)\cdot 4H_2O$, the Fe^{2+} ions are coordinated by two H_2O ligands and linked by bridging tetrathiosquarate ions to a one-dimensional strand.



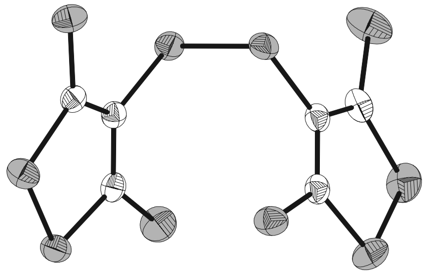
Section of the structure of $[Fe(H_2O)_2](C_4S_4)\cdot 4H_2O$.

The four uncoordinated H_2O molecules bridge the strands together through O–H···S and O–H···O hydrogen bonds. The Mn(II) salt $[Mn_4(OH)_4(H_2O)_4](C_4S_4)_2$ is made up of cube-shaped complexes $[Mn(OH)_4(H_2O)_4]^{4+}$, which are connected by tetrathiosquarate ions to a two-dimensional network, in which O–H···S and O–H···O bridging bonds connect the layers to a three-dimensional structure.

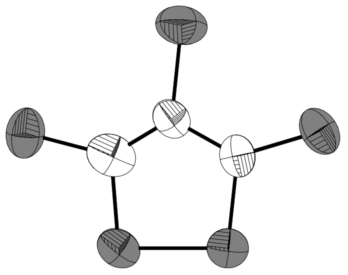


Section of the structure of $[Mn_4(OH)_4(H_2O)_4](C_4S_4)_2$.

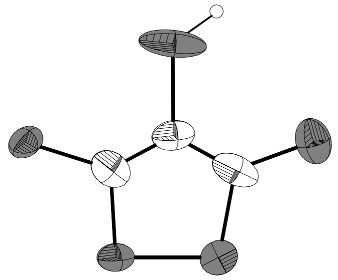
β-$(C_3S_5)^{2-}$ turned out to be quite sensitive to oxidation, giving at room temperature in aqueous solution the $(C_6S_{10})^{2-}$ ion, which was isolated using Ca^{2+} and Sr^{2+} as $[Ca(H_2O)_7](C_6S_{10})$ and $[Sr(H_2O)_8](C_6S_{10})\cdot H_2O$. $(C_6S_{10})^{2-}$ ions are isostructural in both structure as evident of the bond lengths and torsion angles which indicates that both ions are in the most stable conformation in both structures. To further study the hydrolysis and oxidation processes, aqueous solutions of the potassium salt of β-$(C_3S_5)^{2-}$ were brought to crystallization using tetraphenylarsonium chloride, $[As(C_6H_5)_4]Cl$. By this method, several hydrolysis and oxidation products of β-$(C_3S_5)^{2-}$ could be trapped as the respective $[As(C_6H_5)_4]^+$ salts. Under air, crystals of $[As(C_6H_5)_4]_2(C_3S_5)\cdot 2H_2O$ could be isolated. The structure of this compound contains planar, discrete β-$(C_3S_5)^{2-}$ ions, which are not coordinated or derivatized. Crystals of $[As(C_6H_5)_4](HC_3S_5)$, containing the monoprotonated form of $(C_3S_5)^{2-}$ were found. $[As(C_6H_5)_4]_2(C_3S_6O_3)\cdot 3H_2O$ is the third isolated compound formed under air. The new $(C_3S_6O_3)^{2-}$ ion is built of a planar C_3S_5 moiety with a pyramidal SO_3 group attached to the outer S atom of the C_3S_5 group. Under exclusion of air $[As(C_6H_5)_4](C_3S_4H)$ crystals were formed within few days. The anionic unit derives from $(C_3S_5)^{2-}$ by a C−S bond cleavage and the substitution of the sulfur atom by a hydrogen atom under formation of a new C−H bond.



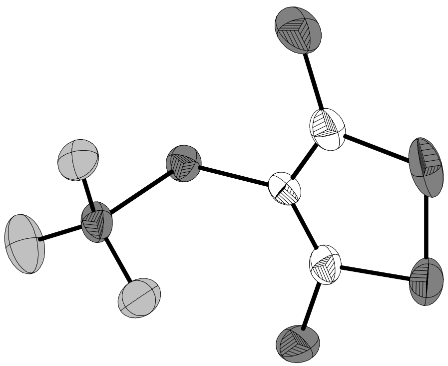
$(C_6S_{10})^{2-}$



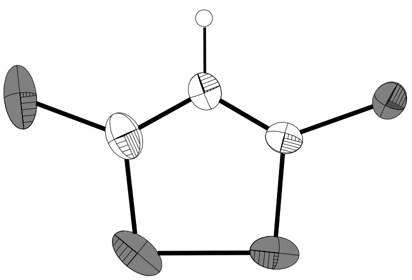
β-$(C_3S_5)^{2-}$



$(HC_3S_5)^{1-}$



$(C_3S_6O_3)^{2-}$



$(C_3S_4)^{1-}$

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