



**HAL**  
open science

## Transition Metal Tetrathiosquarates: One-Dimensional Linking in the Fe(II) salt $\text{FeC}_4\text{S}_4 \times 6 \text{H}_2\text{O}$

Johannes Beck, Robert Glaum, Paul Kögerler, Manfred Speldrich, Younis Ben-Amer

► **To cite this version:**

Johannes Beck, Robert Glaum, Paul Kögerler, Manfred Speldrich, Younis Ben-Amer. Transition Metal Tetrathiosquarates: One-Dimensional Linking in the Fe(II) salt  $\text{FeC}_4\text{S}_4 \times 6 \text{H}_2\text{O}$ . *Journal of Inorganic and General Chemistry / Zeitschrift für anorganische und allgemeine Chemie*, 2009, 635 (12), pp.1991. 10.1002/zaac.200900189 . hal-00498925

**HAL Id: hal-00498925**

**<https://hal.science/hal-00498925>**

Submitted on 9 Jul 2010

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



**Transition Metal Tetrathiosquarates: One-Dimensional Linking in the Fe(II) salt FeC<sub>4</sub>S<sub>4</sub>·6 H<sub>2</sub>O**

Journal:	<i>Zeitschrift für Anorganische und Allgemeine Chemie</i>
Manuscript ID:	zaac.200900189
Wiley - Manuscript type:	Article
Date Submitted by the Author:	31-Mar-2009
Complete List of Authors:	Beck, Johannes; University of Bonn, Inorganic Chemistry Glaum, Robert; University of Bonn, Inorganic Chemistry Kögerler, Paul; RWTH Aachen, Inorganic Chemistry Speldrich, Manfred; RWTH Aachen, Inorganic Chemistry Ben-Amer, Younis; University of Bonn, Inorganic Chemistry
Keywords:	tetrathiosquarate, cyclobutene-1,2-dithione-3,4-dithiolate(2-), iron(II), optical spectrum, magnetism



1  
2  
3  
4  
5  
6  
7 **Transition Metal Tetrathiosquarates: One-Dimensional Linking**  
8 **in the Fe(II) salt  $\text{FeC}_4\text{S}_4 \cdot 6 \text{H}_2\text{O}$**   
9

10  
11  
12  
13  
14  
15 **Johannes Beck**\*<sup>[a]</sup>, **Robert Glaum**<sup>[a]</sup>, **Paul Kögerler**<sup>[b]</sup>, **Manfred Speldrich**<sup>[b]</sup> and **Younis**  
16 **Ben-Amer**<sup>[a]</sup>  
17

18  
19  
20  
21  
22  
23  
24 Bei der Redaktion eingegangen am.....  
25  
26  
27  
28  
29  
30  
31

32 *Dedicated to Professor Martin Jansen on the Occasion of his 65<sup>th</sup> Birthday*  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47

---

48  
49 \*Prof. Dr. J. Beck

50 e-mail: j.beck@uni-bonn.de

51  
52  
53 [a] Universität Bonn, Institut für Anorganische Chemie

54 Gerhard-Domagk-Str. 1, D-53121 Bonn

55  
56 [b] RWTH Aachen University, Institut für Anorganische Chemie

57 Landoltweg 1, D-52074 Aachen  
58  
59  
60

1  
2  
3  
4  
5  
6 **Abstract.** The addition of a solution of tetrathiosquarate using  $\text{K}_2\text{C}_4\text{S}_4 \cdot \text{H}_2\text{O}$  to an aqueous  
7 solution of Fe(II) chloride yields mainly an insoluble, brown-black, amorphous material, but  
8 from the filtrate the Fe(II) salt  $\text{FeC}_4\text{S}_4 \cdot 6\text{H}_2\text{O}$  can be isolated as dark red crystals in low overall  
9 yield. The crystal structure determination shows the presence of  $\text{C}_4\text{S}_4^{2-}$  ions, which act each  
10 as bidentate chelating ligands towards two  $\text{Fe}^{2+}$  ions forming linear one-dimensional chains  
11  $[\text{Fe}(\text{H}_2\text{O})_2(\text{C}_4\text{S}_4)]_n$  with two aqua ligands coordinated in trans positions of the octahedral  
12  $\text{FeS}_4(\text{OH}_2)_2$  coordination polyhedron. Additional water molecules link the chains via  $\text{O}-\text{H}\cdots\text{O}$   
13 bridges to a three dimensional network. The  $\text{C}_4\text{S}_4^{2-}$  ions are planar but show substantial  
14 distortion from ideal  $D_{4h}$  symmetry caused by the chelating coordination. The infrared and  
15 Raman spectra show bands typical for the molecular building units. The single-crystal vis/nir  
16 absorption spectrum of  $\text{FeC}_4\text{S}_4 \cdot 6\text{H}_2\text{O}$  reveals a weak absorption around  $\tilde{\nu} = 6100 \text{ cm}^{-1}$  which  
17 is assigned to the transition  ${}^5\text{T}_{2g} \rightarrow {}^5\text{E}_g$ . Above  $14000 \text{ cm}^{-1}$  the spectrum is completely dark,  
18 in agreement with the deep red colour of the compound. The magnetic properties of  
19  $\text{FeC}_4\text{S}_4 \cdot 6\text{H}_2\text{O}$  show the expected single-ion effects for high-spin Fe(II) centers in a  
20 tetragonally distorted coordination environment and antiferromagnetic coupling within the  
21 coordination polymer. The quantitative analysis results of the susceptibility data concur with  
22 the ligand field parameters estimated from optical spectroscopy studies.  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57

58 **Keywords:** tetrathiosquarate; cyclobutene-1,2-dithione-3,4-dithiolate(2-); iron(II); optical  
59 spectrum; magnetism.  
60

## Introduction

In contrast to the well known anion of squaric acid, the squarate ion  $C_4O_4^{2-}$ , the sulfur bearing analogue tetrathiosquarate  $C_4S_4^{2-}$  is less explored.  $C_4S_4^{2-}$  was firstly prepared by *Seitz et al.* The potassium salt  $K_2C_4S_4 \cdot H_2O$  is a well water soluble compound of intensive yellow colour containing the square-planar  $C_4S_4^{2-}$  ion [1]. Up to now 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 isotopic tetrahydrates  $MC_4S_4 \cdot 4H_2O$ ,  $Mg^{2+}$  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 [2].  $Ba^{2+}$  forms a double salt  $BaK_2(C_4S_4)_5 \cdot 16H_2O$  under inclusion of the potassium ions from the starting compound  $K_2C_4S_4 \cdot H_2O$ .  $Ba_4K_2(C_4S_4)_5 \cdot 16H_2O$  is the least soluble of the series [3]. 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  $Ba_4K_2(C_4S_4)_5 \cdot 16H_2O$ . 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.

The behaviour of  $C_4S_4^{2-}$  against transition metal ions in aqueous solution is substantially different. Generally, insoluble, amorphous, deeply coloured precipitations are formed [4]. The semiconducting poly(nickel tetrathiosquarate)  $[K_{0.15}(NiC_4S_4)]_n$  was subject of a structural study using LAXS and EXAFS spectroscopy revealing a polymeric band structure with bidentate  $C_4S_4$  groups [5] and of theoretical considerations [6, 7]

Transition metal complexes of  $C_4S_4^{2-}$  are known mainly from the work of *W. Beck et al.* Most of them are complexes of the type  $[L_nM(C_4S_4)ML_n]^x$  ( $x = 0$ ,  $ML_n = Mn(CO)_4$ ,  $Rh(CO)_2$ ;  $PMePh_2Au$  [8],  $(PPh_3)_2M$  with  $M = Cu, Ag$ ;  $x = 2-$ ,  $ML_n = M(CO)_4$  with  $M = Cr, Mo, W$ ) [9]. In these complexes,  $C_4S_4^{2-}$  acts as bridging ligand between two metal atoms. A unique example of a complex with a chelating and terminal ligand function is  $[(C_4S_4)Ni(py)_2(C_4S_4)]^{2-}$  [10]. It is significant that all these complexes contain besides tetrathiosquarate additional ligands, which obviously prevent the formation of insoluble polymers.

1  
2  
3 We found now that Fe(II) ions do not quantitatively precipitate with tetrathiosquarate, but  
4 allow for the isolation of the crystalline compound  $\text{FeC}_4\text{S}_4 \cdot 6\text{H}_2\text{O}$ , the first of this kind of a  
5 transition metal ion obtained from aqueous solution.  
6  
7  
8  
9

## 10 11 12 13 **Experimental**

14  
15  
16 The starting material  $\text{K}_2\text{C}_4\text{S}_4 \cdot \text{H}_2\text{O}$  was obtained by the procedure described in [1].  
17  
18

19  
20 IR spectra in the region  $400 - 4000 \text{ cm}^{-1}$  were recorded with a Burker Vector 22 spectrometer.  
21 Spectra of the solid samples were obtained as KBr pellets.  
22  
23

24  
25 The single crystal electronic absorption spectra of  $\text{FeC}_4\text{S}_4 \cdot 6\text{H}_2\text{O}$  was measured at 293 K in the  
26 nir/vis ( $5800 - 25000 \text{ cm}^{-1}$ , step-width  $\Delta\lambda(\text{vis}) = 1 \text{ nm}$ ,  $\Delta\lambda(\text{nir}) = 2 \text{ nm}$ ) using a strongly  
27 modified CARY 17 microcrystal spectrophotometer (Spectra Services, ANU Canberra,  
28 Australia). Details of the spectrometer have already been described in literature [11, 12]. A  
29 needle-shaped, dark red crystal with dimensions  $0.3 \times 0.04 \times 0.04 \text{ mm}^3$  was selected for the  
30 investigation. The reference intensity was measured using a pinhole instead of the crystal  
31 mounted on an aperture.  
32  
33  
34  
35  
36  
37  
38

39  
40 The magnetic susceptibility of a polycrystalline sample of  $\text{FeC}_4\text{S}_4 \cdot 6\text{H}_2\text{O}$  was measured using  
41 SQUID magnetometry (MPMS-5XL, Quantum Design) in the temperature range 2 – 300 K at  
42 an applied field of 0.1 Tesla. The susceptibility data were corrected for the sample holder  
43 (PTFE tube) and for diamagnetic/TIP contributions ( $\chi_{\text{dia}}(\text{FeC}_4\text{S}_4 \cdot 6\text{H}_2\text{O}) = -154 \times 10^{-11} \text{ m}^3$   
44  $\text{mol}^{-1}$ ) calculated from tabulated values.  
45  
46  
47  
48  
49

50  
51 *FeC<sub>4</sub>S<sub>4</sub> · 6 H<sub>2</sub>O*: An aqueous solution of 0.235 g (1 mmol)  $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$  in 10 ml water was  
52 added to an aqueous solution of 0.272 g (1 mmol)  $\text{K}_2\text{C}_4\text{S}_4 \cdot \text{H}_2\text{O}$  in 10 ml water. A brown  
53 precipitate is formed immediately. The solution was filtered and the resulting brownish-  
54 yellow filtrate was left standing open abandoned to slow evaporation at room temperature.  
55 Within two days, dark red, needle shaped crystals of  $\text{FeC}_4\text{S}_4 \cdot 6\text{H}_2\text{O}$  precipitate. The yield  
56 based on the amount of  $\text{FeCl}_2 \cdot 6\text{H}_2\text{O} / \text{K}_2\text{C}_4\text{S}_4 \cdot \text{H}_2\text{O}$  did not exceed 5 %. Several runs of this  
57 procedure were necessary to obtain sufficient material serving as samples for the  
58 spectroscopic and physical measurements.  
59  
60

## Crystal Structure Analyses

The crystals of the title 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 triclinic symmetry. Data were collected at ambient temperature using a Bruker-Nonius kappa-CCD diffractometer equipped with Mo-K $\alpha$  radiation. The space group could be derived from the data set as triclinic  $P\bar{1}$  (No. 2). A structure model was obtained by direct method [13] and refined against  $F^2$  with anisotropic displacement parameters for all non-hydrogen atoms [14]. The refinement confirmed the centrosymmetry of the structure. The H atoms were all identified in a difference Fourier synthesis. They were refined with the geometrical restraint of the same O–H distances within 0.01 Å. H(11) and H(12), attached to the oxygen atoms of the coordinating aqua ligands, were refined with free isotropic displacement parameters, whereas these parameters were fixed for all other H atoms to  $B_{iso} = 1.2 B_{iso}$  of the attached O atoms. Crystallographic data and details of the structure analysis are given in Table 1, positional parameters and equivalent isotropic parameters for the non-H atoms and isotropic displacement for H atoms in Table 2, and selected bond lengths and angles in Table 3.

Further information on the crystal structure analyses have been deposited with the Cambridge Crystallographic Data Centre. CCDC nnnnnn contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

## Results and Discussion

### *Synthesis*

As already known, all transition metal ions form in aqueous solution dark-coloured precipitations with  $C_4S_4^{2-}$ . The solubility of the precipitated materials is generally very low, so the intensively yellow coloured solution of  $K_2C_4S_4$  is completely decolourised on addition of transition metal ions. We observed now, that the filtrate of the precipitation reaction with  $Fe^{2+}$  is still of brownish-yellow colour, even in the presence of a slight excess of  $Fe^{2+}$ . Slow

1  
2  
3 evaporation of the filtrate gives rise to the crystallisation of dark-red crystals of  
4  $\text{FeC}_4\text{S}_4 \cdot 6\text{H}_2\text{O}$ . The yield of the reaction is inherently very low and did not exceed 5 %.  
5  
6  
7

### 9 *Crystal structure of $\text{FeC}_4\text{S}_4 \cdot 6\text{H}_2\text{O}$*

10 The structure of  $\text{FeC}_4\text{S}_4 \cdot 6\text{H}_2\text{O}$  is built of one-dimensional polymeric strands.  
11 Tetrathiosquarate ions act as bridging ligands between  $\text{Fe}^{2+}$  ions making up the linear chain  
12  $-\text{Fe}-\text{C}_4\text{S}_4-\text{Fe}-\text{C}_4\text{S}_4-$ . The six-coordinate iron atom is located on a crystallographic centre of  
13 symmetry and is coordinated by two bidentate tetrathiosquarate anions occupying the  
14 equatorial positions and by two water molecules occupying the axial positions (Figure 1). The  
15  $\text{FeS}_4$  unit is planar as required by symmetry. The  $\text{O}-\text{Fe}-\text{O}$  linear unit is positioned normal to  
16 the  $\text{FeS}_4$  plane. The  $\text{Fe}-\text{O}$  bond length is 2.129(2) Å, while the respective  $\text{Fe}-\text{S}$  bonds to S(1)  
17 and S(2) amount almost identical to 2.5595(5) and 2.5519(5) Å, respectively (Table 3). The  
18 angles in the octahedral coordination environment around Fe are  $180^\circ$  and near to  $90^\circ$ ,  
19 differing maximally by  $\pm 2.7^\circ$ . The anions are located at a centre of symmetry giving them  
20 strictly planar molecular shape. The two independent C–C bonds are equal within standard  
21 deviations and amount to 1.462(3) Å, the two independent C–S bonds of 1.648(2) and  
22 1.649(2) Å also do not differ significantly. The S...S distances in the outer perimeter of the  
23  $\text{C}_4\text{S}_4^{2-}$  ion show, however, significant deviations from the ideal square  $D_{4h}$  symmetry. The  
24 short S(1)...S(2) and S(1)<sup>II</sup>...S(2)<sup>II</sup> distances of 3.5986(5) Å are observed between the  
25 coordinating S atoms, which are attached to the same Fe atom. The S(1)...S(2)<sup>II</sup> and  
26 S(1)<sup>II</sup>...S(2) distances in the direction of the chain are substantially longer (3.9733(5) Å). This  
27 is accompanied by two largely differing C–C–S angles (Table 3). The tetrathiosquarate ions is  
28 thus strongly deformed to a rectangular shape by the chelating coordination to the Fe atoms.  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45

46 In the unit cell, the  $[\text{Fe}(\text{H}_2\text{O})_2(\text{C}_4\text{S}_4)_{2/2}]_n$  chains are running along the *c*-axis (Figure 2). All  
47 chains are identical by translational symmetry and within the chains the  $\text{C}_4\text{S}_4$  groups are  
48 identical by translation, so all  $\text{C}_4\text{S}_4$  groups in the structure are arranged parallel to each other.  
49 The structure contains four additional water molecules per formula unit. These water  
50 molecules are located between the  $[\text{Fe}(\text{H}_2\text{O})_2(\text{C}_4\text{S}_4)_{2/2}]_n$  chains and connect them via  $\text{O}-\text{H}\cdots\text{O}$   
51 and  $\text{O}-\text{H}\cdots\text{S}$  bridges to a three-dimensional net (Figure 3). Hydrogen bridges with  $\text{H}\cdots\text{A} < r(\text{A})$   
52 + 2.0 Å are observed [15]. The  $\text{O}\cdots\text{H}$  distances are in the range from 2.02 to 2.30 Å with the  
53 respective  $\text{O}\cdots\text{O}$  distances from 2.74 to 3.04 Å. The water molecules at O(2) connect  
54 neighboured Fe centres via eight-membered rings consisting of two  $\text{H}_2\text{O}(1)$  and two  $\text{H}_2\text{O}(2)$   
55 molecules along the *b*-axis. The  $\text{O}(3)\cdots\text{S}(2)$  distance is 3.338 Å, which amounts the sum of  
56  
57  
58  
59  
60



van der Waals radii (3.32 Å [16]), the respective O–H...S bridge amounts 2.68 Å. The O–H...S bridges in the structure of FeC<sub>4</sub>S<sub>4</sub>·6H<sub>2</sub>O are weaker than those found in the structures of CaC<sub>4</sub>S<sub>4</sub>·4H<sub>2</sub>O [2] where H...S distances of 2.492 Å were found and even weaker than those in Ba<sub>4</sub>K<sub>2</sub>(C<sub>4</sub>S<sub>4</sub>)<sub>5</sub>·16H<sub>2</sub>O with H...S distances beginning with 2.328 Å [3].

### Vibrational Spectroscopy

The IR spectrum of FeC<sub>4</sub>S<sub>4</sub>·6H<sub>2</sub>O shows close similarities to those of the earth alkaline tetrathiosquarates [2, 3]. Most of the observed absorption bands (606m, 745m, 788s, 873w, 1021sh, 1186vs, 1220vs, 1375w, 1618s, 1763w, 3474w, 3591w /cm<sup>-1</sup>) arise from the normal modes of the C<sub>4</sub>S<sub>4</sub><sup>2-</sup> ion with D<sub>4h</sub> symmetry [17]. The strong band at 1618 cm<sup>-1</sup> can be attributed to bending fundamental of coordinated H<sub>2</sub>O, which is for example observed at 1580 cm<sup>-1</sup> for K<sub>2</sub>[FeCl<sub>5</sub>(H<sub>2</sub>O)] [18]. We did not succeed in recording a Raman spectrum of FeC<sub>4</sub>S<sub>4</sub>·6H<sub>2</sub>O due to strong fluorescence occurring on irradiation with Nd:YAG laser (1064 nm), even at low laser powers.

### Electronic Absorption Spectroscopy

The single-crystal UV/vis/nir absorption spectrum of FeC<sub>4</sub>S<sub>4</sub>·6H<sub>2</sub>O reveals a weak absorption around  $\tilde{\nu} = 6100 \text{ cm}^{-1}$ , which we assign to the transition  ${}^5T_{2g} \rightarrow {}^5E_g$  of the [Fe(H<sub>2</sub>O)<sub>2</sub>(C<sub>4</sub>S<sub>4</sub>)<sub>2</sub>] chromophore. Above 14000 cm<sup>-1</sup> the spectrum is completely dark, in agreement with the deep red colour of the compound. Fig. 4 shows the spectrum depicted as the absorbance  $A = -\log(I_{\text{crystal}}/I_{\text{reference}})$  versus the wavenumber  $\tilde{\nu}$ . The nir/vis electronic absorption spectrum reveals a rather low ligand-field splitting for the chromophore [Fe(H<sub>2</sub>O)<sub>2</sub>(C<sub>4</sub>S<sub>4</sub>)<sub>2</sub>] with  $\Delta_o = 6100 \text{ cm}^{-1}$ . It is also somewhat surprising, that the coordination of iron(II) by two chelating tetrathiosquarate ligands and two water molecules does not lead to a splitting of the  ${}^5T_{2g} \rightarrow {}^5E_g$  transition. While we can not completely exclude further absorption below 5800 cm<sup>-1</sup>, below the spectrometer limit, this does not appear very likely to us. For the hexa-aquo Fe(II) complex [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>,  $\Delta_o = 9400 \text{ cm}^{-1}$  is reported [19]. The homoleptic complex of the tetramethyl-dithiooxamide with iron(II) shows octahedral coordination and  $\Delta_o = 6800 \text{ cm}^{-1}$  [20]. It is the only well documented example for Fe<sup>2+</sup> ions octahedrally coordinated by sulfur ligands. Similar ligand-field splittings are, however, observed for hexa-thiocyanate complexes [21]. Above 14000 cm<sup>-1</sup> the spectrum is completely dark, in agreement with the deep red

colour of the compound. The absorption in this spectral region is attributed to metal-ligand charge transfer and to intra-ligand electronic transitions.

## Magnetism

The magnetic low-field susceptibility of  $\text{FeC}_4\text{S}_4\cdot 6\text{H}_2\text{O}$  as a function of temperature (2.0 – 300 K) is shown in Figure 5, represented by effective magnetic moment  $\mu_{\text{eff}} = 797.74 (\chi_{\text{m}} T)^{1/2}$  (SI units). The effective magnetic moment of the title compound at 290 K is 4.77 per Fe(II) ion, slightly lower than the spin-only value of  $4.90 \mu_{\text{B}}$  for a high-spin  $d^6$  system. Note that the magnetism of high-spin Fe(II) complexes (free ion ground term  $^5D$ ) implies a significant temperature dependence of  $\mu_{\text{eff}}$  due to first-order orbital contributions according to the  $^5T_2(D)$  ground state [22].

The observed magnetic properties were analyzed with CONDON using the complete basis set (full d manifolds, i.e. 210 functions for Fe(II) ( $3d^6$ )) as a function of the applied field  $B$ . These factors are necessary to yield reliable information on the magnetic dipole orientation with respect to the local symmetry elements. CONDON takes into account the following single-ion effects: interelectronic repulsion, spin-orbit coupling, ligand field effects and the applied field [23]. Therefore, modeling the magnetic properties requires the ligand-field effect, spin-orbit coupling, and exchange coupling all to be taken into account. The values for the spin-orbit coupling parameter ( $\zeta = 340 \text{ cm}^{-1}$ ) and Racah parameters ( $B = 720 \text{ cm}^{-1}$ ,  $C = 4B$ ) were chosen on the basis of the optical spectra [24, 25] and used as constants in the following calculations. The exchange interactions between the spin-2 centers within the chain are considered in the molecular field approximation

$$\chi_{\text{m}}^{-1} = \chi_{\text{m}}^{-1}(B, C, \zeta, B_q^k) - \lambda_{\text{MF}}, \quad (1)$$

where  $\chi_{\text{m}}$  represents the single-ion susceptibility and  $\lambda_{\text{mf}}$  the molecular field parameter. The effective magnetic moment exhibits a significant temperature dependence, resulting in a decay from 4.77 at room temperature to 3.0 at 20 K. To reproduce this monotonous decrease in  $\mu_{\text{eff}}$  we need to accommodate both (antiferromagnetic) exchange coupling between nearest neighbor spin centers as well as ligand field effects with respect to the tetragonally distorted octahedral coordination environments of the Fe centers in  $\text{FeC}_4\text{S}_4\cdot 6\text{H}_2\text{O}$  ( $D_{4h}$ ). To this effect a ligand field operator with reference to the fourfold rotation axis for the angular part of the wave function was adopted [26, 27]:

$$H_{\text{LF}}^{\text{tet}} = B_0^2 \sum_{i=1}^N C_0^2(i) + B_0^4 \sum_{i=1}^N C_0^4(i) + B_4^4 \sum_{i=1}^N (C_4^4(i) + C_{-4}^4(i)) \quad (2)$$

In cubic systems the ligand field parameter  $B_0^2$  is zero and a fixed relation between  $B_4^4 = \sqrt{5/14} B_0^4$  exist, so that only the coefficient  $B_0^4$  remains an essential fitting parameter (all ligand field parameters stated in Wybourne notation [27]). The crystallographic structure shows that the coordination polyhedron is very strongly compressed so that a negative value for  $B_0^2$  is predicted by the point charge electrostatic model (PCEM). A least-squares fit for calculated and experimental values of  $\chi_m$  for the temperature range between 15 – 290 K (for which the molecular field model is valid), yields  $\lambda_{\text{MF}} = -5.89 \times 10^6 \text{ mol cm}^{-3}$ ,  $B_0^2 = -41000 \text{ cm}^{-1}$ ,  $B_0^4 = 13200 \text{ cm}^{-1}$ ,  $B_4^4 = 5900 \text{ cm}^{-1}$  ( $SQ = 0.6 \%$ ; blue graph in Fig. 5).

As expected, the negative molecular field parameter  $\lambda_{\text{MF}}$  indicating antiferromagnetic coupling, mediated by the tetrathiosquarate linkers, is essential for a good fit. Note that the ligand field parameters obtained here correspond well with the LFOS from the UV/VIS data ( $Dq \approx 600 \text{ cm}^{-1}$ ).

## Conclusions

Tetrathiosquarate  $\text{C}_4\text{S}_4^{2-}$  forms a slightly water soluble complex compound of salt like character with  $\text{Fe}^{2+}$  ions and allows for the isolation of dark red  $\text{FeC}_4\text{S}_4 \cdot 6\text{H}_2\text{O}$ . The crystal structure, consisting of 1-D polymeric bands  $-\text{Fe}(\text{OH}_2)_2-\text{C}_4\text{S}_4-$ , confirms the structure models that had been set up earlier for the amorphous polymeric transition metal tetrathiosquarates, precipitated from aqueous solution. The Fe(II) ion exhibits a tetragonally distorted  $\text{FeO}_2\text{S}_4$  coordination with low ligand-field splitting and high-spin configuration. An antiferromagnetic exchange coupling between the Fe(II) ions is present, mediated by the tetrathiosquarate linkers.

## Acknowledgement

The support of this work within the *Collaborative Research Area* 813 (Sonderforschungsbereich 813) of the *Deutsche Forschungsgemeinschaft* “Chemistry at Spin Centres” is gratefully acknowledged. We thank G. Dittmann for her dedicated help with the synthesis of  $\text{K}_2\text{C}_4\text{S}_4 \cdot \text{H}_2\text{O}$  and J. Daniels for the collection of the diffraction data.

**Table 1** Crystallographic data and details of the structure determination for FeC<sub>4</sub>S<sub>4</sub>·6H<sub>2</sub>O

Compound	<b>FeC<sub>4</sub>S<sub>4</sub>·6H<sub>2</sub>O</b>
Formula	C <sub>4</sub> H <sub>12</sub> FeO <sub>6</sub> S <sub>4</sub>
Formula weight	340.23
Crystal system	triclinic
Space group	<i>P</i> $\bar{1}$
<i>Z</i>	1
<i>a</i> / Å	6.3345(3)
<i>b</i> / Å	7.2894(4)
<i>c</i> / Å	7.6016(4)
$\alpha$ / °	72.329(3)
$\beta$ / °	73.234(3)
$\gamma$ / °	81.405(3)
<i>V</i> / Å <sup>3</sup>	319.49(3)
Density (calc.) / g·cm <sup>-3</sup>	1.768
$\mu$ / cm <sup>-1</sup>	18.4
Diffractometer	Bruker-Nonius kappaCCD
Radiation	Mo-K $\alpha$ , $\lambda$ =0.7107 Å
Temperature / K	293
Range of data collection / °	2 $\theta$ < 55.05
Index ranges	-8 ≤ <i>h</i> ≤ 8 -9 ≤ <i>k</i> ≤ 9 -9 ≤ <i>l</i> ≤ 9
Reflections collected	2872
Independent reflections, <i>R</i> <sub>merg</sub>	1474, 0.020
No. of data / parameters	1474 / 91
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.048
<i>wR</i> ( <i>F</i> <sup>2</sup> )	0.0726
<i>R</i> ( <i> F </i> ) for [ <i>n</i> ] <i>F</i> <sub>0</sub> > 4 $\sigma$ ( <i>F</i> <sub>0</sub> )	0.0292 [1214]
<i>R</i> ( <i> F </i> ) for all data	0.0407
Largest difference peak and hole / e·Å <sup>-3</sup>	+0.64 / -0.34

**Table 2** Positional coordinates and equivalent isotropic displacement parameters  $U_{eq} / \text{\AA}^2$  for the non-H atoms in the structure of  $\text{FeC}_4\text{S}_4 \cdot 6\text{H}_2\text{O}$ . H atoms were refined with isotropic displacement parameters. Standard deviations refer to the last significant digit.

Atom	x	y	z	$U_{eq}$
Fe	0	0	0	0.0243(2)
S(1)	0.27921(8)	-0.10705(8)	0.20307(7)	0.0300(2)
S(2)	0.27340(8)	-0.11709(8)	-0.27003(7)	0.0292(2)
C(1)	0.1131(3)	-0.0442(3)	0.3895(3)	0.0248(4)
C(2)	0.1106(3)	-0.0489(3)	-0.4163(3)	0.0247(4)
O(1)	0.1098(3)	0.2846(2)	-0.1137(3)	0.0342(3)
O(2)	0.7186(3)	-0.4431(3)	-0.1061(3)	0.0464(5)
O(3)	0.6660(4)	-0.3806(3)	0.4955(3)	0.0530(5)
H(11)	0.172(5)	0.311(4)	-0.053(4)	0.07(1)
H(12)	0.171(5)	0.315(4)	-0.216(3)	0.07(1)
H(21)	0.709(5)	-0.409(4)	-0.206(3)	0.056
H(22)	0.798(4)	-0.530(3)	-0.101(4)	0.056
H(31)	0.599(5)	-0.283(3)	0.502(5)	0.064
H(32)	0.592(5)	-0.462(4)	0.539(4)	0.064

**Table 3** Selected bond lengths / Å and angles / ° in the structure of  $\text{FeC}_4\text{S}_4 \cdot 6\text{H}_2\text{O}$ . For symmetry operations see legend of Fig. 1.

Fe – O(1)	2.129(2)	C(1) – S(1)	1.648(2)
Fe – S(1)	2.5595(5)	C(2) – S(2)	1.649(2)
Fe – S(2)	2.5519(5)	C(1) – C(2)	1.462(3)
		C(1) – C(2) <sup>II</sup>	1.462(3)
S(1) – Fe – S(2)	89.50(2)	S(1) – Fe – S(2) <sup>I</sup>	90.50(2)
S(1) – Fe – O(1)	87.79(5)	S(1) – Fe – O(1) <sup>I</sup>	92.21(5)
S(2) – Fe – O(1)	92.71(5)	S(2) – Fe – O(1) <sup>I</sup>	87.29(5)
C(1) – C(2) – C(1) <sup>II</sup>	90.1(2)	C(2) – C(1) <sup>II</sup> – C(2) <sup>II</sup>	89.9(2)
C(2) – C(1) – S(1)	130.5(2)	C(2) <sup>II</sup> – C(1) – S(1)	139.6(2)
C(1) – C(2) – S(2)	130.3(2)	C(1) <sup>II</sup> – C(2) – S(2)	139.7(2)

## References

- 1  
2  
3  
4  
5  
6  
7  
8 [1] R. Allmann, T. Debaerdemaeker, K. Mann, R. Matusch, R. Schmiedel,  
9 G. Seitz, *Chem. Ber.* **1976**, *109*, 2215.  
10  
11 [2] J. Beck, Y. Ben-Amer, *Z. Anorg. Allg. Chem.* **2007**, *633*, 435.  
12  
13 [3] J. Beck, Y. Ben-Amer, *Z. Anorg. Allg. Chem.* **2008**, *634*, 1522.  
14  
15 [4] F. Götzfried, W. Beck, A. Lerf, A. Sebald, *Angew. Chem.* **1979**, *91*, 499.  
16  
17 [5] T. Vogt, C. Faulmann, R. Soules, P. Lecante, A. Mosset, P. Castan, P.  
18 Cassoux, J. Galy, *J. Amer. Chem. Soc.* **1988**, *110*, 1833.  
19  
20 [6] M. C. Böhm, *Phys. Status Solidi* **1984**, *121*, 255.  
21  
22 [7] S. Alvarez, R. Vicente, R. Hoffmann, *J. Amer. Chem. Soc.* **1985**, *107*,  
23 6253.  
24  
25 [8] P. G. Jones, G. M. Sheldrick, A. Fügner, F. Götzfried, W. Beck, *Chem.*  
26 *Ber.* **1981**, *114*, 1413.  
27  
28 [9] W. Beck, F. Götzfried, R. Grenz, G. Urban, *Chem. Ber.* **1985**, *118*, 4179.  
29  
30 [10] W. Beck, F. Götzfried, R. Grenz, U. Nagel, *Chem. Ber.* **1986**, *119*, 1217.  
31  
32 [11] E. Krausz, *Aust. J. Chem.* **1993**, *46*, 1041.  
33  
34 [12] E. Krausz, *AOS News* **1998**, *12*, 21.  
35  
36 [13] G. M. Sheldrick, *SHELXS-97, Program for Crystal Structure Solution*,  
37 University of Göttingen, Germany, **1997**.  
38  
39 [14] G. M. Sheldrick, *SHELXL-93, Program for Crystal Structure Refinement*,  
40 University of Göttingen, Germany, **1993**.  
41  
42 [15] Y. Elerman, H. Füss, W. Joswig, *Acta Crystallogr.* **1982**, *B38*, 1799.  
43  
44 [16] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441.  
45  
46 [17] H. Torii, M. Tasumi, I. M. Bell, R. J. H. Clark, *Chem. Phys.* **1997**, *216*,  
47 67.  
48  
49 [18] M. Falk, C.-H. Huang, O. Knop, *Canad. J. Chem.* **1975**, *53*, 51.  
50  
51 [19] F. A. Cotton, M. D. Meyers, *J. Am. Chem. Soc.* **1960**, *82*, 5023.  
52  
53 [20] G. Peyronel, G. C. Pellacani, A. Pignedoli, G. Benetti, *Inorg. Chim. Acta*  
54 **1971**, *5*, 263.  
55  
56 [21] A. B. P. Lever, *Inorganic Electronic Spectroscopy*, 2<sup>nd</sup> ed. Elsevier,  
57 Amsterdam, **1984**.  
58  
59 [22] F.E. Mabbs, D.J. Machin, *Magnetism and Transition Metal Complexes*,  
60

- 1  
2  
3 Chapman and Hall, London **1973**, p.90.  
4  
5 [23] H. Schilder, H. Lueken, *J. Magn. Magn. Mater.* **2004**, 281, 17.  
6  
7 [24] J.S. Griffith, *The Theory of Transition-Metal Ions*, Cambridge University  
8 Press, London **1971**.  
9  
10 [25] H. L. Schläfer, G. Gliemann, *Einführung in die Ligandenfeldtheorie*,  
11 Akad. Verlagsgesellschaft, Frankfurt **1967**.  
12  
13  
14 [26] C. Görller-Walrand, K. Binnemans, Rationalization of crystal-field  
15 parametrization, in: K.A. Gschneidner, Jr., L. Eyring (eds.), *Handbook on*  
16 *the Physics and Chemistry of Rare Earths*, vol. 23, ch.155, p.121,  
17 Elsevier, Amsterdam **1996**.  
18  
19  
20  
21 [27] B.G. Wybourne, *Spectroscopic Properties of Rare Earths*, Wiley, New  
22 York, London, Sydney **1965**.  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60



## Legends for Figures

**Fig. 1** A section of the  $[\text{Fe}(\text{H}_2\text{O})_2(\text{C}_4\text{S}_4)]_n$  chain in the structure of  $\text{FeC}_4\text{S}_4 \cdot 6\text{H}_2\text{O}$ . Thermal ellipsoids are drawn to include a probability density of 70%. Symmetry operations:  $\text{I} = -x, -y, -z$ ;  $\text{II} = -x, -y, -1 - z$ .

**Fig. 2** The unit cell of  $\text{FeC}_4\text{S}_4 \cdot 6\text{H}_2\text{O}$  in a perspective view along the  $c$ -axis. Atoms are drawn as spheres of arbitrary radii. The coordination of the  $\text{Fe}^{2+}$  ions is shown as massive octahedra.

**Fig. 3** The unit cell of  $\text{FeC}_4\text{S}_4 \cdot 6\text{H}_2\text{O}$  in a perspective view along the  $a$ -axis. Fe, C, S, and H atoms are drawn as spheres of arbitrary radii, oxygen atoms are drawn as ellipsoids scaled to include a probability density of 50 %. Short  $\text{O}-\text{H}\cdots\text{O}$  and  $\text{O}-\text{H}\cdots\text{S}$  bridges are drawn as fragmented bonds.

**Fig. 4** Single-crystal electronic absorption spectrum of  $\text{FeC}_4\text{S}_4 \cdot 6\text{H}_2\text{O}$ .

**Fig. 5** Temperature dependence of  $\mu_{\text{eff}}$  of  $\text{FeC}_4\text{S}_4 \cdot 6\text{H}_2\text{O}$  at 0.1 Tesla (circles: experimental data, best least squares fit to employed model: blue line). The red graph represents a simulation of the single-ion effects without exchange coupling interactions (see text).

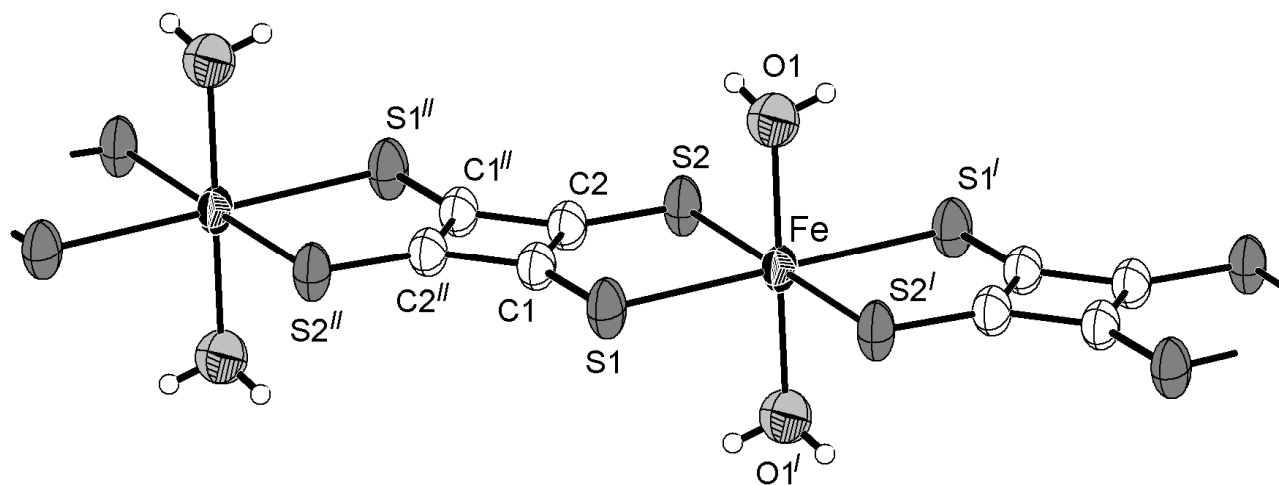


Fig. 1

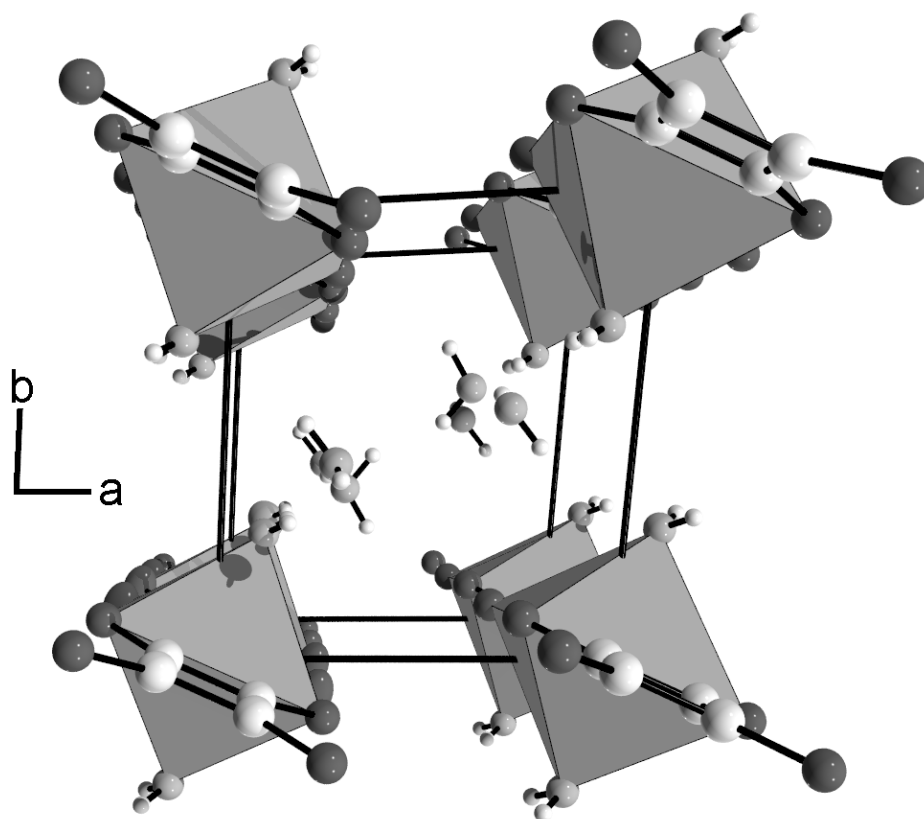


Fig. 2

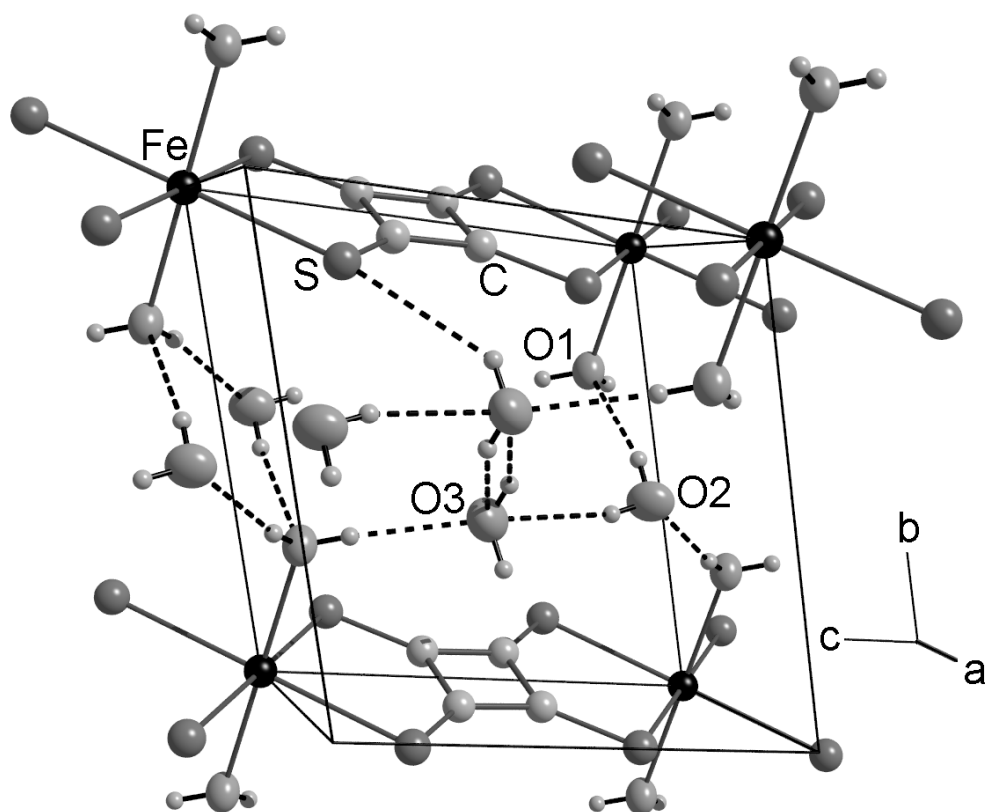


Fig. 3

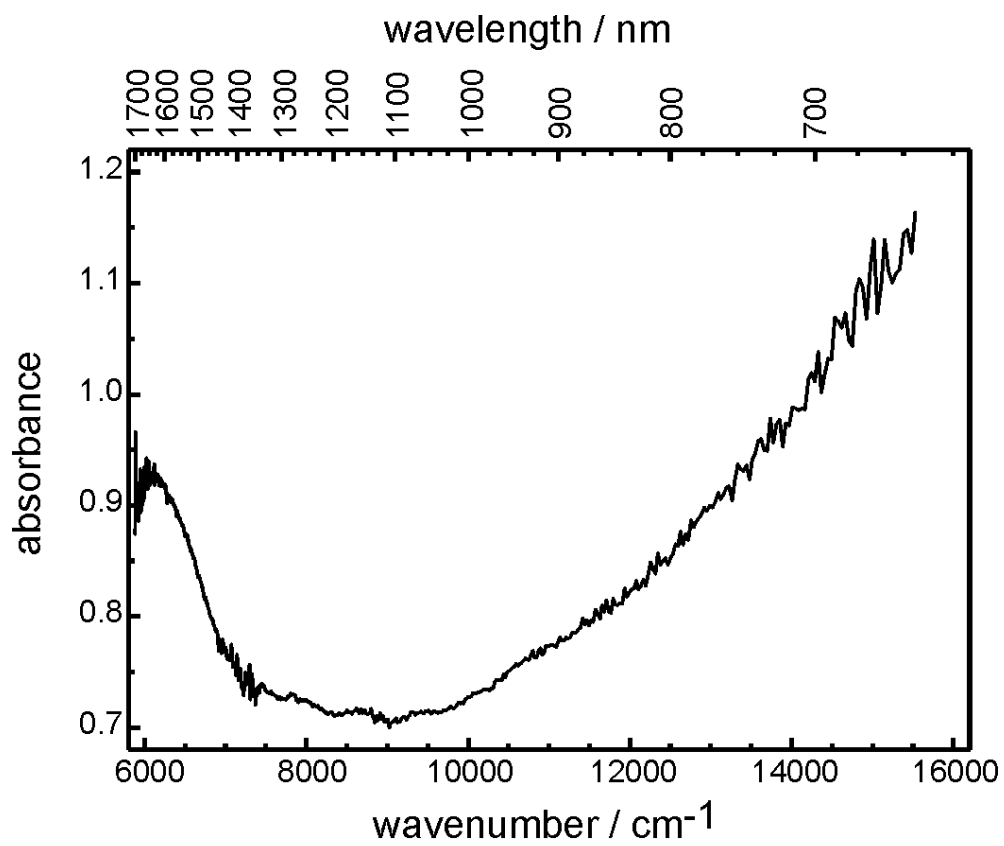
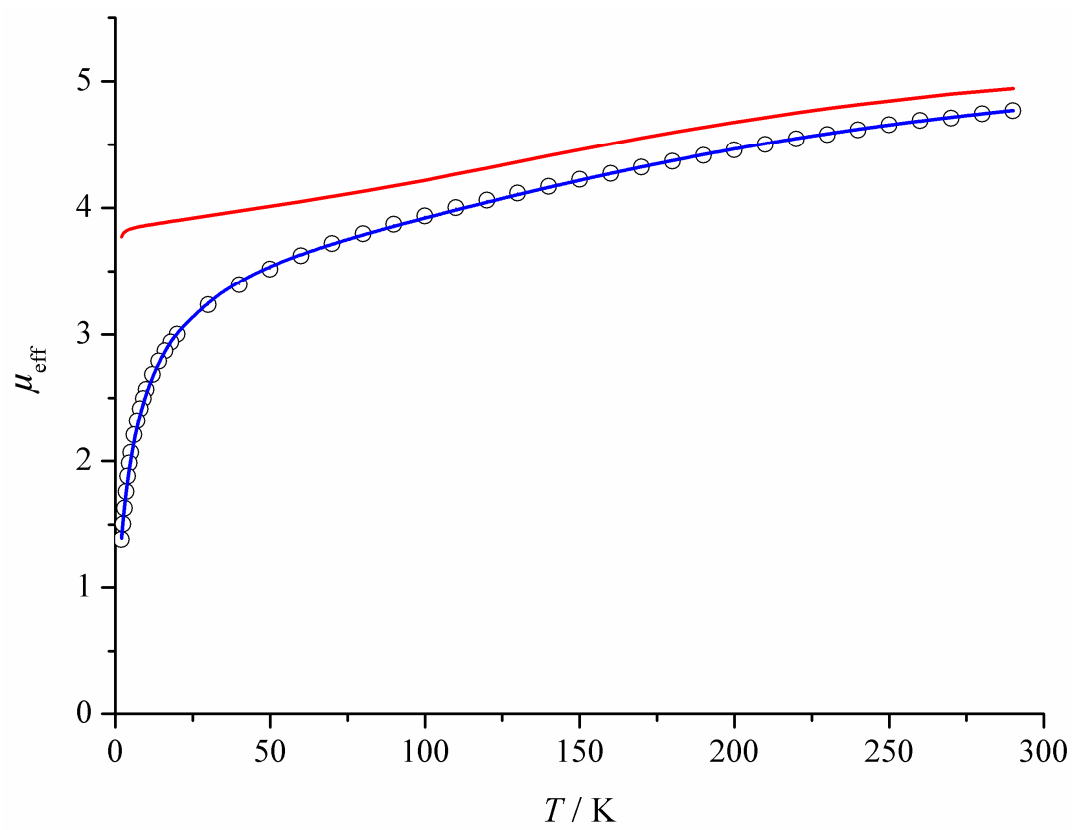


Fig. 4

**Fig. 5**