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## $(n\text{-Bu}_4\text{N})_2[\text{Fe}(\text{dcbdt})_2]_2$ . Synthesis, crystal structure and magnetic characterisation

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### Abstract

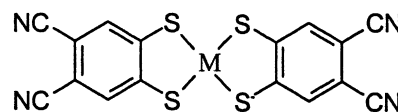
The  $(n\text{-Bu}_4\text{N})_2[\text{Fe}(\text{dcbdt})_2]_2$  complex, where 4,5-dicyanobenzene-1,2-dithiolate (dcbdt), was prepared and characterised by X-ray diffraction, Mössbauer spectroscopy and magnetisation measurements. The crystal structure as determined by single crystal X-ray diffraction is triclinic, space group  $P\bar{1}$  with cell parameters  $a = 9.5660(1) \text{ \AA}$ ,  $b = 13.0200(2) \text{ \AA}$ ,  $c = 16.0850(2) \text{ \AA}$ ,  $\alpha = 67.554^\circ(1)$ ,  $\beta = 86.797^\circ(1)$ ,  $\gamma = 70.523^\circ(1)$ ,  $V = 1738.77(4) \text{ \AA}^3$  and it consists in strongly dimerised  $[\text{Fe}(\text{dcbdt})_2]^-$  units, which are stacked side by side as chains along  $a$ . The magnetic susceptibility shows that the  $[\text{Fe}(\text{dcbdt})_2]^-$  units have a low spin  $S = 1/2$  configuration and, besides a strong intradimer antiferromagnetic interaction, present also a significant interdimer antiferromagnetic interaction mediated by short side contacts.

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**Keywords:** Fe–Bisdithiolene complexes; Magnetic susceptibility; Mössbauer spectroscopy; X-ray crystal structures

### 1. Introduction

The recent synthesis of the extended  $\pi$ -ligand 4,5-dicyanobenzene-1,2-dithiolate, (dcbdt), in our laboratory [1] and of the nickel complexes  $[\text{Ni}(\text{dcbdt})_2]^{2-}$ , opened the way to the preparation of a new family of similar complexes of this ligand, with different transition metals. The extended nature of this ligand stabilises a diversity of oxidation states (e.g.  $z = 1, 2, 0.4$  for  $M = \text{Ni}$ ) and also, depending on the metal  $M$ , different magnetic moments are expected, making such complexes promising building blocks for the preparation of novel molecular materials with interesting electrical and magnetic properties.



$M(\text{dcbdt})_2$

The Ni(III) complex with this ligand in the  $(n\text{-Bu}_4\text{N})_2[\text{Ni}(\text{dcbdt})_2]_2$  salt was found to present a very strong dimerisation, with the metal in a 4+1 square based pyramidal coordination configuration. This coordination is typical of all Fe(III) bisdithiolate complexes reported so far [2] but uncommon on Ni bisdithiolate complexes, which more often appear isolated with a square planar coordination. Fe(III) bisdithiolene monoanionic complexes are paramagnetic species often found in an intermediate spin  $S = 3/2$  configuration and therefore  $\text{Fe}(\text{dcbdt})_2$  complexes appears as new interesting paramagnetic members of this family.

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In this paper we describe the synthesis and the characterization of the corresponding Fe analogue (*n*-Bu<sub>4</sub>N)<sub>2</sub>[Fe(dcbdt)<sub>2</sub>].

## 2. Experimental

### 2.1. Synthesis

4,5-dicyanobenzene-1,2-dithiol (0.32 g, 1.66 mmol), prepared as previously reported, [1] was dissolved in 5 ml of NaOH aq. (5%). A solution of *n*-Bu<sub>4</sub>NBr (0.27 g, 0.84 mmol) in EtOH/H<sub>2</sub>O (1:1) (5 ml) was added, followed by a solution of FeCl<sub>3</sub>·6H<sub>2</sub>O (0.22 g, 0.81 mmol) in the same solvent. The mixture was stirred with immediate formation of a dark brown precipitate that, after 5 min, was filtered and washed with EtOH. The crude material was recrystallised from EtOH to give (*n*-Bu<sub>4</sub>N)<sub>2</sub>[Fe(dcbdt)<sub>2</sub>] as brown platelets (0.379 g, 0.28 mmol, 69%). m.p. > 348 °C; <sup>1</sup>H NMR (300 MHz, [D<sub>6</sub>]DMSO, 25 °C, TMS): δ = 0.94 (s, 12H; CH<sub>3</sub>), 1.30 (m, 8H; CH<sub>2</sub>), 1.57 (m, 8H; CH<sub>2</sub>), 3.16 (m, 8H; CH<sub>2</sub>), 7.70 (s, 4 H; Ar–H); <sup>13</sup>C NMR (300 MHz, [D<sub>6</sub>]DMSO, 25 °C, TMS): δ = 15.93, 19.08, 23.79, 57.48, 112.06, 125.54, 126.88, 136.54; IR (KBr pellet):  $\tilde{\nu}$  = 3060–3040 (w, Ar–H), 2960–2880 (m, C–H), 2220 (s, C≡N), 1500 (m, C=C), 410 (w, S–Fe) cm<sup>-1</sup>; Elemental Anal. Calc. (%) for C<sub>64</sub>H<sub>80</sub>N<sub>10</sub>S<sub>8</sub>Fe<sub>2</sub> (1357.58): C 56.62, H 5.94, N 10.32, S 18.89; Found: C 55.25, H 6.77, N 10.23, S 18.52.

### 2.2. X-ray diffraction

A black prismatic single crystal of the compound was used for data collection on a Nonius Kappa CCD diffractometer equipped with a graphite monochromated Mo K $\alpha$  radiation source ( $\lambda$  = 0.71073 Å). Data collection was performed at room temperature. No absorption correction was performed and the structure was solved by direct methods (SIR97) [3] and refined against  $F^2$  with a full-matrix least-squares algorithm using SHELX-97 [4] and the WINGX (1.64) software package. [5] All non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were added in calculated positions and refined riding on the corresponding C atoms. Collection parameters and crystallographic data are summarised in Table 1.

### 2.3. Mössbauer spectroscopy

<sup>57</sup>Fe Mössbauer spectra were collected at temperatures between 300 and 6 K using a conventional spectrometer and He flow cryostat with a 50 mCi <sup>57</sup>Co source in Rh matrix and a sinusoidal velocity vs. time waveform. The spectrometer was calibrated against an  $\alpha$ -Fe foil. Platelet shaped crystals of (*n*-Bu<sub>4</sub>N)<sub>2</sub>[Fe(dcbdt)<sub>2</sub>] were mixed with perspex powder

Table 1  
Crystallographic data of (*n*-Bu<sub>4</sub>N)<sub>2</sub>[Fe(dcbdt)<sub>2</sub>]

Crystal system	Triclinic
Space group	$P\bar{1}$
<i>a</i> (Å)	9.5660(1)
<i>b</i> (Å)	13.0200(2)
<i>c</i> (Å)	16.0850(2)
$\alpha$ (°)	67.554(1)
$\beta$ (°)	86.797(1)
$\gamma$ (°)	70.523(1)
<i>V</i> (Å <sup>3</sup> )	1738.77(4)
<i>Z</i>	1
$\rho_{\text{calc}}$ (Mg m <sup>-3</sup> )	1.296
$R[I \geq 2\sigma(I)]$	0.0392
$wR(F^2)$	0.1057

and the resulting material was pressed into a perspex holder in order to obtain a disk shaped Mössbauer absorber, containing approximately 5 mg of natural Fe cm<sup>-2</sup>. The spectra were fitted to Lorentzian lines using a non-linear least-squares computer method [6].

### 2.4. Magnetic susceptibility

Magnetic susceptibility measurements in the range 2–300 K were performed using a longitudinal Faraday system (Oxford Instruments) with a 7 T superconducting magnet, under a magnetic field of 5 T and forward and reverse field gradients of 1 T m<sup>-1</sup>. A polycrystalline sample ( $\approx$  10 mg) was placed inside a previously calibrated thin wall Teflon bucket. The force was measured with a microbalance (Sartorius S3D-V). Under these conditions the magnetization was found to be proportional to the applied magnetic field.

## 3. Results and discussion

(*n*-Bu<sub>4</sub>N)<sub>2</sub>[Fe(dcbdt)<sub>2</sub>] was obtained by a procedure similar to that used to obtain the previously reported analogous Ni complex following a standard reaction of the 4,5-dicyanobenzene-1,2-dithiol with FeCl<sub>3</sub> and *n*-Bu<sub>4</sub>NBr, the main difference being that the Fe(III) complex is obtained directly, while the Ni(III) analog was obtained by oxidation of the Ni(II) complex. In fact if an Fe(II) salt were used the Fe(III) complex would be obtained equally just by air oxidation. Cyclic voltammetry of (*n*-Bu<sub>4</sub>N)<sub>2</sub>[Fe(dcbdt)<sub>2</sub>] in acetonitrile solution shows that this compound is very stable in the range –0.20–0.8 V vs. Ag/AgCl with irreversible reduction and oxidation occurring beyond these limits. Preliminary results suggest that, similarly to what has been found for Ni and Au analogues, [1,7,8] the partially oxidised compound (*n*-Bu<sub>4</sub>N)<sub>2</sub>[Fe(dcbdt)<sub>2</sub>]<sub>5</sub> is also obtained by electrochemical oxidation of (*n*-Bu<sub>4</sub>N)<sub>2</sub>[Fe(dcbdt)<sub>2</sub>]. However, due to the reduced solubility of (*n*-

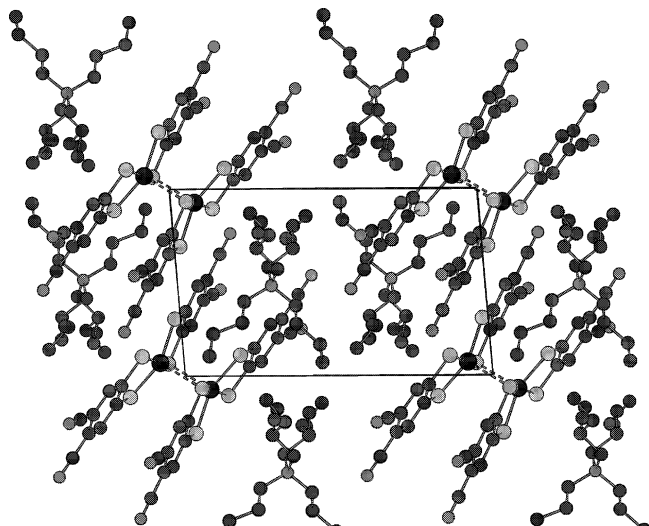


Fig. 1.  $(n\text{-Bu}_4\text{N})_2[\text{Fe}(\text{dcbdt})_2]_2$  crystal structure viewed along  $(0,1,0)$ .

$\text{Bu}_4\text{N})_2[\text{Fe}(\text{dcbdt})_2]_2$  in common solvents, electrochemical oxidation afforded only a fine microcrystalline powder on the electrodes which could not be further characterised besides an elemental analysis with results approximated to this stoichiometry.

The crystal structure of  $(n\text{-Bu}_4\text{N})_2[\text{Fe}(\text{dcbdt})_2]_2$  is identical to that of the Ni analogue, [1] the two compounds being isostructural (see Fig. 1). Iron was found to exhibit the 4+1 square based pyramidal coordination configuration typical of Fe(III) bisdithiolate complexes, due to the strong dimerisation of the  $[\text{Fe}(\text{dcbdt})_2]^-$  units which are related by an inversion center (Fig. 2). Further to the equatorial Fe–S bonds at distances Fe–S(1) 2.2308(5) Å, Fe–S(2) 2.2263(5) Å, Fe–S(3) 2.2215(5) Å, Fe–S(4) 2.2215(5) Å, there are two apical Fe–S(1)\* bonds at 2.4760(5) Å. These distances are comparable to those found in many other dimerised Fe(III) bisdithiolene complexes with ligands as different as *mnt* = maleonitriledithiolate, [9,10] *bdt* = benzo-1,2-dithiolate, [11] *tdas* = 1,2,5-thiadiazole-3,4-dithiolate [12] or *dmit* = 4,5-dimercapto-1,3-dithiol-2-thionate [13] (see Table 2). In spite of the strong nonplanarity of the  $\text{Fe}(\text{dcbdt})_2$  units, with the Fe atom displaced (0.37

Å) from the plane defined by the four basal S atoms, the *dcbdt* ligands remain almost planar with atomic r.m.s. deviations from their average plane smaller than 0.023, and 0.039 Å, and the two ligands make a dihedral angle of  $9.6^\circ$ .

In the tetrabutylammonium cation two of the four *n*-butyl chains show a disorder over two sets of sites which affects only the two last carbon atoms. The other two *n*-butyl chains and the major components of the disordered ones adopt the commonly observed *anti* conformation (torsion angles close to  $180^\circ$ ), while the minor disordered components form torsion angles of  $66.4(11)^\circ$  (*gauche* conformation) and  $89.2(16)^\circ$ .

Along *c* and *b* the dimerised anions and the cations are alternating. However, along *a* the  $[\text{Fe}(\text{dcbdt})_2]_2^{2-}$  dimers are arranged next to each others in chains, with five significant interactions connecting side by side two  $[\text{Fe}(\text{dcbdt})_2]^-$  units of adjacent dimers, namely the hydrogen bonds  $\text{N}(2)\cdots\text{H}(11^*)$  and  $\text{N}(2^*)\cdots\text{H}(11)$  at 2.602 Å and  $158^\circ$ , and  $\text{S}(4^*)\cdots\text{H}(3)$  and  $\text{S}(4)\cdots\text{H}(3^*)$  at 3.249 Å and  $150^\circ$  and a short contact  $\text{S}(2)\cdots\text{S}(2^*)$  at 3.835 Å, (see Fig. 3).

The Mössbauer spectra were fitted with one quadrupole doublet (see Fig. 4). Both peaks have the same width but different areas, which may be attributed to texture effects as the principal axis of the needle shaped crystals lies preferentially in a plane perpendicular to the  $\gamma$ -rays. This is further confirmed by the fact that the area ratio did not change with temperature. The estimated parameters are summarised in Table 3, where they are also compared with those deduced from the Mössbauer spectra of some other Fe(III) bisdithiolene complexes of known structure, [14] including  $(n\text{-Bu}_4\text{N})[\text{Fe}(\text{dmit})_2]$  [13] which was also studied in this work. The increase in the isomer shifts,  $\delta$ , with decreasing temperature may be explained by the second order Doppler shift. The variation of the quadrupole splitting,  $\Delta$ , with temperature is very small. The smooth temperature dependence of  $\delta$  and  $\Delta$  gives no evidence of a spin crossover within the 6–300 K range.

Within experimental error, the isomer shifts of all the bisdithiolene complexes at the same temperature (Table

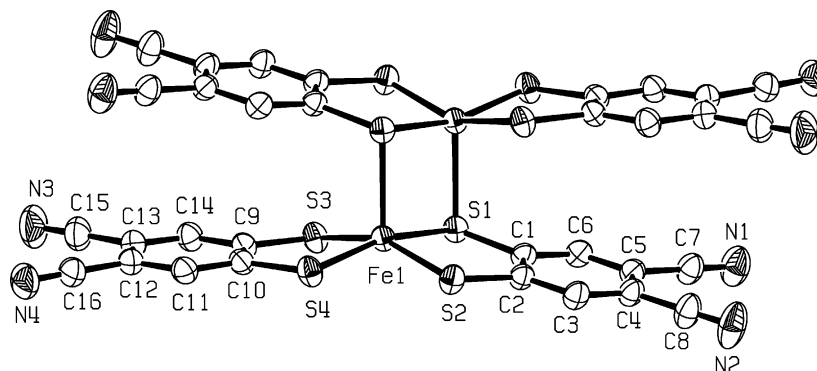


Fig. 2. ORTEP diagram and atomic numbering scheme of the  $[\text{Fe}(\text{dcbdt})_2]_2^{2-}$  dimers.

Table 2  
Fe–S bondlengths in bisdithiolene complexes (Å)

Compound Ref.	(NBu <sub>4</sub> ) <sub>2</sub> [Fe(dcbdt) <sub>2</sub> ] <sub>2</sub> this work	(HPy) <sub>2</sub> [Fe(mnt) <sub>2</sub> ] <sub>2</sub> [10]	(NBu <sub>4</sub> ) <sub>2</sub> [Fe(mnt) <sub>2</sub> ] <sub>2</sub> [9]	(NEt <sub>4</sub> ) <sub>2</sub> [Fe(bdt) <sub>2</sub> ] <sub>2</sub> [11]	(NBu <sub>4</sub> ) <sub>2</sub> [Fe(dmit) <sub>2</sub> ] <sub>2</sub> [13]	(NBu <sub>4</sub> ) <sub>2</sub> [Fe(tdas) <sub>2</sub> ] <sub>2</sub> [12]
Equatorial	2.2215(5)	2.230(4)	2.247	2.214	2.248	2.230
Equatorial	2.2263(5)	2.223(4)	2.177	2.233	2.242	2.235
Equatorial	2.2215(5)	2.218(4)	2.196	2.236	2.238	2.242
Equatorial <sup>a</sup>	2.2308(5)	2.235(4)	2.281	2.241	2.250	2.271
Apical	2.4760(5)	2.493(2)	2.474	2.471	2.478	2.501

<sup>a</sup> Equatorial bond to apical S.

3) are the same, in agreement with Fe(III) in an almost identical square pyramidal coordination by five sulfur atoms. The quadrupole splitting values of the [Fe(dcbdt)<sub>2</sub>] compound is however significantly larger than those of the [Fe(dmit)<sub>2</sub>] and [Fe(mnt)<sub>2</sub>] compounds. The spin of this latter compound was found to be 3/2 [15,16]. The observed differences in the quadrupole splittings may therefore be related to different spin states in the [Fe(mnt)<sub>2</sub>] and [Fe(dcbdt)<sub>2</sub>] as suggested by the magnetic properties (see below).

The paramagnetic susceptibility,  $\chi_P$ , of (*n*-Bu<sub>4</sub>N)<sub>2</sub>[Fe(dcbdt)<sub>2</sub>]<sub>2</sub> as function of temperature, calculated from raw data considering a diamagnetic contribution estimated from tabulated Pascal constants as  $-4.09 \times 10^{-4}$  emu mol<sup>-1</sup> of Fe, is shown in Fig. 5. At room temperature,  $\chi_P$ , amounts to  $1.6 \times 10^{-3}$  emu mol<sup>-1</sup> of Fe, and upon cooling it slightly increases toward a broad maximum around 200 K and then decreases reaching an almost constant value of  $\sim 8.2 \times 10^{-4}$  emu mol<sup>-1</sup> between 50 and 15 K. In spite of its paramagnetism, (*n*-Bu<sub>4</sub>N)<sub>2</sub>[Fe(dcbdt)<sub>2</sub>]<sub>2</sub> was found to be EPR silent at room temperature, as it happens in many of these dimerised metal bisdithiolene complexes.

As in all other Fe(III) bisdithiolate complexes previously studied, the magnetic behavior of (*n*-Bu<sub>4</sub>N)<sub>2</sub>[Fe(dcbdt)<sub>2</sub>]<sub>2</sub> is expected to be dominated by the antiferromagnetic intradimer interactions. However, the data of Fig. 5 denotes in addition to this dimer contribution the presence of a significant temperature independent paramagnetic contribution.

Either low spin  $S = 1/2$  or intermediate spin  $S = 3/2$  spin configurations, have been proposed for Fe(III) bisdithiolate complexes, [2a,17,18] essentially based on the room temperature effective moment values. However a detailed analysis of the magnetic behavior in these complexes was done only in case of Fe(mnt)<sub>2</sub> [10,16], and the results clearly indicated the intermediate spin configuration ( $S = 3/2$ ). In this sense the susceptibility of (*n*-Bu<sub>4</sub>N)<sub>2</sub>[Fe(dcbdt)<sub>2</sub>]<sub>2</sub> was first tentatively fitted to an equation considering, besides a possible Curie tail,  $C$ , and a temperature independent term,  $A$ , a contribution of antiferromagnetic coupled  $S = 3/2$  dimers of the type [19]:

$$\chi = A + \frac{C}{T} + \frac{2Ng^2\mu_B^2}{k(T-\theta)} \frac{e^{\frac{J}{kT}} + 5e^{\frac{3J}{kT}} + 14e^{\frac{6J}{kT}}}{1 + 3e^{\frac{J}{kT}} + 5e^{\frac{3J}{kT}} + 7e^{\frac{6J}{kT}}} \quad (1)$$

where  $N$  is the Avogadro's number,  $g$  the Landé constant,  $\mu_B$  the Bohr magneton and  $\theta$  a molecular field parameter, included to account for the possible interdimer interactions. However, this equation was clearly unsuitable to achieve any reasonable fit to our

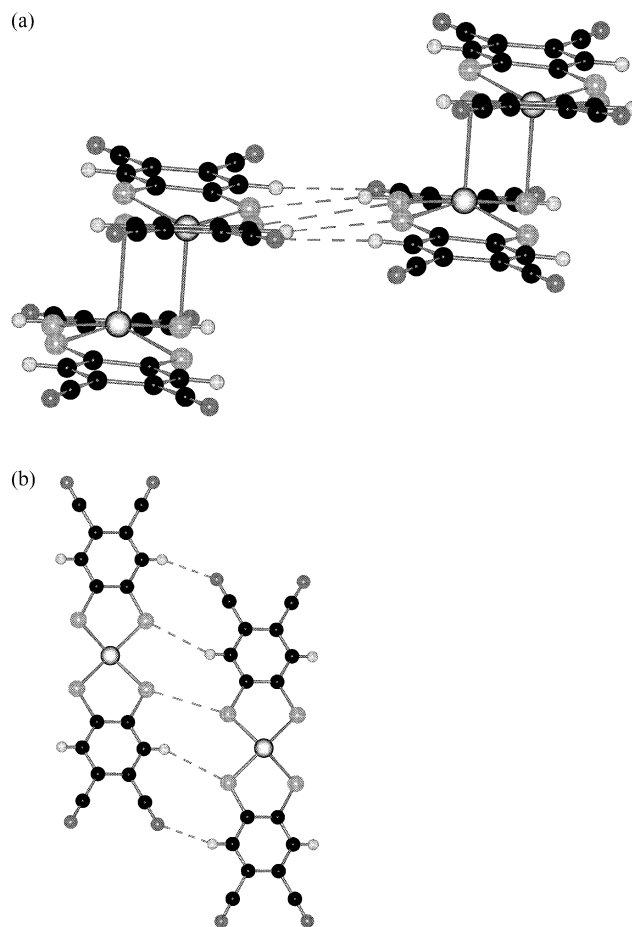


Fig. 3. Chain of [Fe(dcbdt)<sub>2</sub>]<sup>2-</sup> dimers connected along *a* by S...S contacts and N...H and S...H hydrogen bonds. (a) Side view. (b) Detail of two [Fe(dcbdt)<sub>2</sub>]<sup>-</sup> units of adjacent dimers viewed perpendicularly to their average plane with indication of the short contacts connecting them.

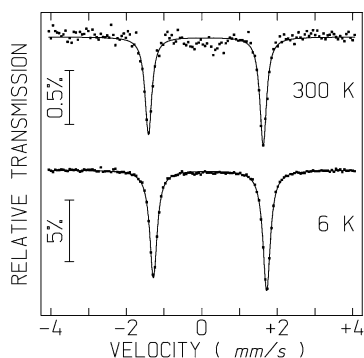


Fig. 4. Mössbauer spectra of  $(n\text{-Bu}_4\text{N})_2[\text{Fe}(\text{dcbdt})_2]_2$ .

data, as seen by the best fit (dotted line in Fig. 5) obtained with  $A = 7.8(2) \times 10^{-4} \text{ emu mol}^{-1}$ ,  $C = 0.00893(36) \text{ emu mol}^{-1} \text{ K}$ ,  $g = 1.61(1)$ ,  $\theta = 31.2(8) \text{ K}$  and  $J = 337(4) \text{ K}$ . Besides the very poor quality of the fit, the positive  $\theta$  values and small  $g$ -value are not realistic.

A much better fit was obtained with the Eq. (2) for, a singlet–triplet model of  $S = 1/2$  dimers [19]:

$$\chi = A + \frac{C}{T} + \frac{2Ng^2\mu_B^2}{k(T - \theta) \left[ 3 + \exp\left(\frac{-J}{kT}\right) \right]} \quad (2)$$

with  $A = 8.30(7) \times 10^{-4} \text{ emu mol}^{-1}$ ,  $\theta = -82(12) \text{ K}$ ,  $C = 0.00798(16) \text{ emu mol}^{-1} \text{ K}$ ,  $g = 1.98(4)$ ,  $J = 286(4) \text{ K}$  (continuous line Fig. 5). This fit is of much better quality and the physical parameters obtained are more realistic, clearly indicating that this compound is in a low spin  $S = 1/2$  configuration at variance with  $S = 3/2$  for  $[\text{Fe}(\text{mnt})_2]_2^{2-}$ . It is also worth refer to the low value

obtained for  $C$ , which corresponds to less than 0.5% of  $S = 1/2$  impurities, indicating the high degree of purity of the sample.

The large  $\theta$  value obtained reflects the crystal structure with dimers far from being well isolated. In fact the side by side interaction of the dimers in the crystal structure, with several short contacts making chains of interacting dimers along  $a$ , suggests that an alternated chain model with the antiferromagnetic interactions  $J$  and  $J'$  may be more realistic than the simple dimer model (Eq. (2)).

Such an alternated Heisenberg chain model has approximate solutions given as a function of  $\alpha = J'/J$  by the Eq. (3)[20].

$$\chi = \frac{Ng^2\beta^2}{kT} \frac{A + Bx + Cx^2}{1 + Dx + Ex^2 + Fx^3} \quad (3)$$

with and  $x = |J|/kT$  the following coefficients valid for  $kT > 0.25 \text{ J}$  and  $0.4 < \alpha \leq 1$ :  $A = 0.25$ ,  $B = -0.068475 + 0.13194\alpha$ ,  $C = 0.0042563 - 0.031670\alpha + 0.12278\alpha^2 - 0.29943\alpha^3 + 0.21814\alpha^4$ ,  $D = 0.035255 + 0.65210\alpha$ ,  $E = -0.00089418 - 0.10209\alpha + 0.87155\alpha^2 - 0.18472\alpha^3$ ,  $F = 0.045230 - 0.0081910\alpha + 0.83234\alpha^2 - 2.6181\alpha^3 + 1.92813\alpha^4$ .

The best fit of this equation with  $g = 2.0$  to our experimental data, considering also a similar temperature independent paramagnetic term with  $A = 7.50 \times 10^{-4} \text{ emu mol}^{-1}$  and a negligible Curie tail,  $C = 0.00066 \text{ emu mol}^{-1} \text{ K}^{-1}$ , gives a line almost perfectly superimposed to that of Eq. (2) (thick solid line in Fig. 5), which was obtained with  $\alpha = 0.414(7)$  and  $J = 362.1(5) \text{ K}$ .

Table 3  
Mössbauer parameters at different temperatures of Fe–bisdithiolen compounds

Absorber	$T$ (K)	$\delta$ (mm s $^{-1}$ )	$\Delta$ (mm s $^{-1}$ )	$\Gamma$ (mm s $^{-1}$ )	Reference
$(n\text{-Bu}_4\text{N}) [\text{Fe}(\text{dcbdt})_2]$	300	0.22	3.04	0.23	this work
	250	0.25	3.04	0.22	this work
	225	0.26	3.03	0.25	this work
	200	0.27	3.03	0.23	this work
	150	0.29	3.01	0.22	this work
	100	0.31	3.01	0.23	this work
	75	0.32	3.01	0.24	this work
	50	0.33	3.00	0.21	this work
	6	0.33	3.00	0.22	this work
$(n\text{-Bu}_4\text{N}) [\text{Fe}(\text{mnt})_2]$	80	0.33	2.68	0.29	[16]
$(\text{Et}_4\text{N}) [\text{Fe}(\text{mnt})_2]$	300	0.24	2.81		[14]
	80	0.33	2.76		[14]
$[\text{Hpy}]_2 [\text{Fe}(\text{mnt})_2]$	300	0.24	2.75	0.24	[10]
	80	0.35	2.69	0.28	[10]
$(\text{Per})_2 [\text{Fe}(\text{mnt})_2]$	300	0.25	2.83	0.26	[16]
	80	0.34	2.79	0.28	[16]
	6	0.36	2.79	0.25	[16]
$(n\text{-Bu}_4\text{N}) [\text{Fe}(\text{dmit})_2]$	80	0.36	2.58	0.29	this work

$\delta$ , isomer shift relative to metallic iron at 300 K;  $\Delta$ , quadrupole splitting;  $\Gamma$ , full width at half height. Precision of fitting procedure:  $\pm 0.01 \text{ mm s}^{-1}$  for  $\delta$ ,  $\Delta$  and  $\Gamma$ .



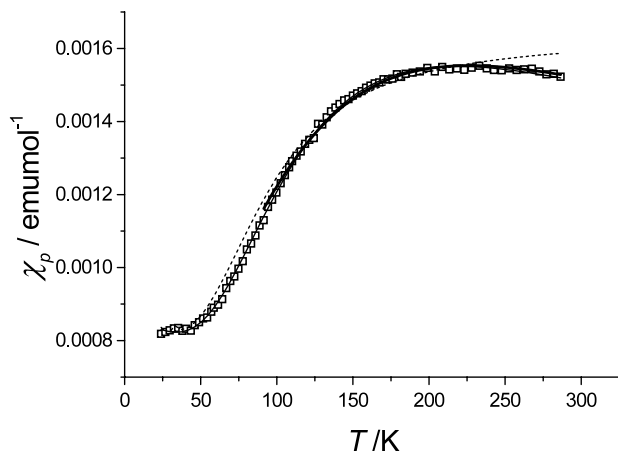


Fig. 5. Paramagnetic susceptibility for  $(n\text{-Bu}_4\text{N})_2[\text{Fe}(\text{dcbdt})_2]_2$  per mole of Fe. The dotted line and solid lines are fits to Eqs. (1)–(3) (see text).

Besides all the uncertainties of the fitting and the neglected effects of a possible temperature dependence of  $J$  and  $J'$ , the large  $\alpha$  value obtained indicates the existence of quite strong interdimer interactions, which is consistent with the large  $\theta$  value obtained from the fit of Eq. (2).

In conclusion, the new compound  $(n\text{-Bu}_4\text{N})_2[\text{Fe}(\text{dcbdt})_2]_2$  was prepared and it presents a strong dimerisation of the  $[\text{Fe}(\text{dcbdt})_2]^-$  units which have a low spin  $S=1/2$  configuration. In this compound besides a strong intradimer antiferromagnetic interaction, there is also a significant interdimer antiferromagnetic interaction, mediated by hydrogen bonds and short  $\text{S}\cdots\text{S}$  contacts.

#### 4. Supplementary material

Further crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 196494. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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