



## $(n\text{-Bu}_4\text{N})[\text{Fe}(\text{cbdt})_2]$ : Synthesis, crystal structure and magnetic characterisation of a new $\text{Fe}^{\text{III}}$ bisdithiolene complex

A.C. Cerdeira<sup>a</sup>, D. Simão<sup>a</sup>, I.C. Santos<sup>b</sup>, A. Machado<sup>b</sup>, L.C.J. Pereira<sup>b</sup>, J.C. Waerenborgh<sup>b</sup>, R.T. Henriques<sup>a,c</sup>, M. Almeida<sup>b,\*</sup>

<sup>a</sup> Departamento de Engenharia Química, Instituto Superior Técnico, Av. Rovisco Pais, P-1049-001 Lisboa, Portugal

<sup>b</sup> Departamento Química, Instituto Tecnológico e Nuclear/CFMUL, P-2686-953 Sacavém, Portugal

<sup>c</sup> Instituto de Telecomunicações, Pólo de Lisboa, Instituto Superior Técnico, Av. Rovisco Pais, P-1049-001 Lisboa, Portugal

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### ABSTRACT

The synthesis of the dithiol precursor of the new ligand 4-cyanobenzene-1,2-dithiolate (cbdt) is described. The  $(n\text{-Bu}_4\text{N})[\text{Fe}(\text{cbdt})_2]$  complex, was prepared and characterised by X-ray diffraction, Mössbauer spectroscopy and magnetisation measurements. The crystal structure consists in *cis*  $[\text{Fe}(\text{cbdt})_2]^-$  units dimerised in a *trans* fashion, with Fe in a square pyramidal coordination, the dimers being well isolated from each other by the cations. The magnetic susceptibility shows that the  $[\text{Fe}(\text{cbdt})_2]^-$  units have a  $S = 3/2$  spin configuration.

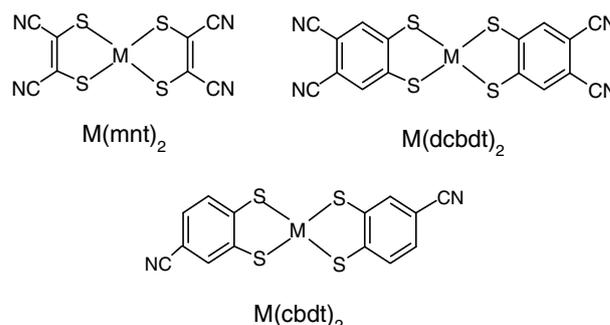
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### 1. Introduction

Transition metal bis(dithiolene) complexes, due to a vivid redox behaviour, diversity of coordination geometries and variable magnetic moments, have deserved increasing attention as key building blocks for preparing conducting and magnetic molecular materials for more than 30 years [1]. Simpler bisdithiolene complexes such as  $\text{M}(\text{mnt})_2^{z-}$  (mnt = maleonitriledithiolate) have provided the basis of compounds with very interesting properties such as magnetic chains in molecular solids also having conducting chains based on other donor species [2], metallic conductivity [3] or molecular ferromagnetism [4]. Such type of bis(dithiolene) complexes, specially if based on extended and delocalised  $\pi$ -ligands, are expected to present a wider range of accessible oxidation states and large solid state interactions, making them particularly promising for conducting materials. Indeed some of these complexes based on thiophene dithiolate ligands were shown to have low oxidation potentials and to be interesting conducting and magnetic building blocks [1e,1g,5].

The large variety of coordination geometries observed in these complexes that can range from tetrahedral to square planar, or dimerised, trimerised [6] and polymeric arrangements of  $[\text{M}(\text{S}_2\text{L})_2]$  units [7] or even more complex cluster units such as

$\text{M}_4(\text{S}_2\text{L})_3$  [8] remains far from being understood in spite of several rationalisation attempts [9]. Among Fe(III) bisdithiolene complexes, the square pyramidal coordination (4+1), due to the formation of dimeric arrangements,  $[\text{Fe}(\text{S}_2\text{L})_2]_2^{2-}$  was for longtime thought to be a rule. However, the first example of an undimerised square planar Fe(III) bisdithiolene was recently reported by us, having the quinoxaline dithiolate as ligand [10]. The electronic structure of the Fe bisdithiolene complexes, the role of the ligands and possible spin states are still topics of discussion in current studies [11].



\* Corresponding author. Tel.: +351 219946171; fax: +351 219941455.

E-mail address: malmeida@itn.pt (M. Almeida).

We have previously reported a series of  $[M(\text{dcbdt})_2]^{z-}$  complexes based on the ligand 4,5-dicyanobenzene-1,2-dithiolate, (dcbdt), with different transition metals  $M = \text{Ni, Cu, Au, Pd, Pt, Fe}$  and  $\text{Co}$ , which were found to exist in a variety of easily accessible oxidation states ( $z = 0.4, 1, 2$ ) [12]. Some of these complexes can exist in a partially oxidised state with  $z = 0.4$  and salts such as  $(n\text{-Bu}_4\text{N})_2 [M(\text{dcbdt})_2]_5$  with  $M = \text{Au}$  and  $\text{Ni}$  were found to be associated with relatively high electrical conductivity in the solid state [13]. The  $\text{Fe(III)}$  complex of this series with  $z = 1$  was found to exist in strongly dimerised geometry, typical of  $\text{Fe(III)}$  but with a rare low spin  $S = 1/2$  configuration [14].

In order to further explore chemical modifications on these ligands we decided to prepare analogous complexes with the so far unreported aromatic monocyno substituted ligand 4-cyanobenzene-1,2-dithiolate. In this paper we describe the preparation of this ligand precursor, the corresponding dithiol (**3**) ( $\text{H}_2\text{cbdt}$ ), and the synthesis and characterisation of the  $[\text{Fe}(\text{cbdt})_2]$  complex.

## 2. Experimental

### 2.1. Synthesis

#### 2.1.1. General

Elemental analyses were performed by the analytical services of ITN –  $^1\text{H}$  and  $^{13}\text{C}$  NMR: Varian (300 MHz),  $\text{DMSO-}d_6$  or acetone as solvent, TMS as internal standard – IR: Perkin–Elmer 1330. Solvents were purified and dried using standard procedures while commercial products were used as received.

#### 2.1.2. 1,2-Bis(*S*-benzylthio)-4-cyanobenzene (**2**)

To a suspension of sodium hydride (2.79 g, 116.3 mmol) in dry DMF (72 ml), benzylthiol (8.67 g, 85 mmol) was added dropwise, under nitrogen and keeping the temperature between 3 and 5 °C. A solution of 3,4-dichlorobenzonitrile (**1**) (6 g, 34.9 mmol) (Aldrich) in DMF (15 ml) was then added in small portions. The reaction mixture was left overnight at room temperature, under nitrogen with stirring. The DMF was removed by distillation under reduced pressure and to the resulting light orange product was added water (30 ml). The aqueous layer was extracted with chloroform ( $3 \times 30$  ml) and the organic layer was separated and washed successively with water ( $3 \times 30$  ml). The organic layer was dried with  $\text{Na}_2\text{SO}_4$ , evaporated and the resulting orange oil was precipitated with MeOH and kept overnight at a temperature below 0 °C. The product was filtered and recrystallised with MeOH to give a pale yellow solid (4.09 g, 11.8 mmol,  $\eta = 34\%$ ). M.p. 69–71 °C;  $^1\text{H}$  NMR (300 MHz, acetone- $d_6$ , 25 °C, TMS):  $\delta = 7.61$  (s, 1H), 7.53 (s, 1H), 7.51 (s, 1H), 7.38–7.26 (m, 10H), 4.36 (s, 2H), 4.32 (s, 2H); IR (KBr pellet):  $\tilde{\nu} = 3060\text{--}3020$  (w, Ar-H), 2920 (w, C–H), 2220 (s,  $\text{C}\equiv\text{N}$ ), 1570 (m,  $\text{C}=\text{C}$ )  $\text{cm}^{-1}$ ; Elemental Anal. Calc. (%) for  $\text{C}_{21}\text{H}_{17}\text{NS}_2$  (345.99): C, 73.00; H, 4.38; N, 4.05; S, 18.56. Found: C, 72.60; H, 5.34; N, 3.94; S, 18.52%.

#### 2.1.3. 4-Cyanobenzene-1,2-dithiol (**3**)

A solution of **2** (1 g, 2.9 mmol) in dry toluene (250 ml) was added dropwise to a suspension of finely powdered anhydrous  $\text{AlCl}_3$  (0.96 g, 7.2 mmol) in dry toluene (20 ml). The mixture was stirred under nitrogen at room temperature for 72 h. Water was added (90 ml) and the organic layer was separated and washed successively with water ( $3 \times 90$  ml) and extracted with 5% aq NaOH ( $3 \times 50$  ml). Upon acidification with 5% aq HCl a greyish solid precipitated that was filtered to give **3** (0.27 g, 1.6 mmol,  $\eta = 80\%$ ). M.p. 64–66 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO-}d_6$ , 25 °C, TMS):  $\delta = 8.16$  (s, 1H), 7.99 (s, 1H), 7.75 (d, 1H), 4.28 (s, 1H), 4.26 (s, 1H); IR (KBr pellet):  $\tilde{\nu} = 3060$  (w, Ar-H), 2540 (m, S–H), 2220

(s,  $\text{C}\equiv\text{N}$ ), 1575 (m,  $\text{C}=\text{C}$ )  $\text{cm}^{-1}$ ; Elemental Anal. Calc. (%) for  $\text{C}_7\text{H}_5\text{NS}_2$  (167.27): C, 50.26; H, 3.02; N, 8.38; S, 38.35. Found: C, 51.53; H, 2.66; N, 7.43; S, 37.60%.

#### 2.1.4. (*n*-Bu<sub>4</sub>N) [Fe(cbdt)<sub>2</sub>] (**4**)

Compound **3** (0.1 g, 0.6 mmol) was dissolved in 15 ml of NaOH aq. (5%). A solution of *n*-Bu<sub>4</sub>NI (0.22 g, 0.6 mmol) in EtOH/H<sub>2</sub>O (1:1) (15 ml) was added, followed by a solution of  $\text{FeCl}_3$  (0.05 g, 0.3 mmol) in the same solvent. The mixture was cooled, filtered and the precipitate was recrystallised from acetone/*i*-BuOH to give **4** as very dark red needles (0.11 g, 0.175 mmol,  $\eta = 30\%$ ). M.p. 267–269 °C; IR (KBr pellet):  $\tilde{\nu} = 2960\text{--}2870$  (m, C–H), 2220 (s,  $\text{C}\equiv\text{N}$ ), 1565–1475–1440 (s,  $\text{C}=\text{C}$ ), 430 (w, S–Fe)  $\text{cm}^{-1}$ ; Elemental Anal. Calc. (%) for  $\text{C}_{30}\text{H}_{42}\text{N}_3\text{FeS}_4$  (628.84): C, 57.30; H, 6.75; N, 6.68; S, 20.39. Found: C, 57.75; H, 6.81; N, 6.51; S, 20.41%.

#### 2.1.5. (Ph<sub>4</sub>P) [Fe(cbdt)<sub>2</sub>] (**5**)

Following a similar procedure as used to **4** but with a solution of  $\text{Ph}_4\text{PBr}$  instead of *n*-Bu<sub>4</sub>NI, **5** was obtained as very dark red crystals (0.08 g, 0.11 mmol,  $\eta = 37\%$ ). M.p. 154–156 °C; IR (KBr pellet):  $\tilde{\nu} = 3055$  (w, Ar-H), 2210 (s,  $\text{C}\equiv\text{N}$ ), 1560 (m,  $\text{C}=\text{C}$ ), 425 (w, S–Fe)  $\text{cm}^{-1}$ ; Elemental Anal. Calc. (%) for  $\text{C}_{38}\text{H}_{26}\text{N}_2\text{FeS}_4\text{P}$  (725.72): C, 62.89; H, 3.61; N, 3.86; S, 17.67. Found: C, 62.73; H, 3.64; N, 3.68; S, 17.49%.

### 2.2. X-ray diffraction

X-ray diffraction experiments were performed with a Bruker AXS APEX CCD detector diffractometer using graphite monochromated Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71073$  Å), in the  $\omega$  and  $\varphi$  scans mode. A semi empirical absorption correction was carried out using SADABS [15]. Data collection, cell refinement and data reduction were done with the SMART and SAINT programs [16]. The structures were solved by direct methods using SIR97 [17] and refined by fullmatrix least-squares methods with the SHELXL97 [18] program using the WINGX software package [19]. Non-hydrogen atoms were refined with anisotropic thermal parameters whereas H-atoms were placed in idealised positions and allowed to refine riding on the parent C atom. Molecular graphics were prepared using ORTEP3 [20]. A summary of the crystal data, structure solution and refinement are given in Table 1. Selected bond lengths and bond angles are also given in Table 2.

### 2.3. Mössbauer Spectroscopy

$^{57}\text{Fe}$  Mössbauer spectra were collected at 300 K and 4 K using a constant acceleration spectrometer and a 50 mCi  $^{57}\text{Co}$  source in Rh matrix. The spectrometer was calibrated against an  $\alpha\text{-Fe}$  foil. The

**Table 1**  
Crystallographic data of  $[(n\text{-Bu})_4\text{N}]_2[\text{Fe}(\text{cbdt})_2]_2$

Crystal system	monoclinic
Space group	$P2_1/c$
Crystal size (mm)	$0.36 \times 0.24 \times 0.06$
<i>a</i> (Å)	14.4219(3)
<i>b</i> (Å)	17.6158(3)
<i>c</i> (Å)	14.9678(3)
$\alpha$ (°)	90
$\beta$ (°)	118.726(4)
$\gamma$ (°)	90
<i>V</i> (Å <sup>3</sup> )	3334.6(5)
<i>Z</i>	4
$\rho_{\text{calc}}$ ( $\text{Mg m}^{-3}$ )	1.252
$\mu$ ( $\text{mm}^{-1}$ )	0.725
<i>S</i> (on $F^2$ )	1.111
$R$ [ $I > 2\sigma(I)$ ], $wR$ ( $F^2$ )	$R_1 = 0.0776$ , $wR_2 = 0.2042$
$wR$ ( $F^2$ )	1.119

**Table 2**  
Selected bond lengths (Å) and angles (°) for  $[(n\text{-Bu}_4\text{N})_2[\text{Fe}(\text{cbdt})_2]]$

Fe(1)–S(3)	2.1919 (17)	S(2)–C(2)	1.733(6)
Fe(1)–S(4)	2.2306 (16)	S(3)–C(8)	1.852(7)
Fe(1)–S(2)	2.2346 (17)	S(4)–C(9)	1.617(8)
Fe(1)–S(1)	2.2372 (15)	C(1)–C(2)	1.397(8)
Fe(1)–S(1a)	2.4734 (13)	C(8)–C(9)	1.371(9)
Fe(1)–Fe(1a)	3.0869(10)	C(14)–N(2)	1.153(10)
S(1)–C(1)	1.773(6)	C(7)–N(1)	1.148(10)
S(3)–Fe(1)–S(4)	90.07(7)	S(2)–Fe(1)–S(1)	89.05(6)
S(3)–Fe(1)–S(2)	158.43(6)	S(3)–Fe(1)–S(1a)	101.78(6)
S(4)–Fe(1)–S(2)	84.00(6)	S(4)–Fe(1)–S(1a)	98.97(5)
S(3)–Fe(1)–S(1)	90.47(7)	S(2)–Fe(1)–S(1a)	99.63(5)
S(4)–Fe(1)–S(1)	162.25(6)	S(1)–Fe(1)–S(1a)	98.28(5)
Fe(1)–S(1)–Fe(1a)	81.72(5)		

a:  $-x, -y+2, -z$ .

4 K spectrum was taken with a liquid-He cryostat. Needle-shaped crystals of  $(n\text{-Bu}_4\text{N})_2 [\text{Fe}(\text{cbdt})_2]$  were packed 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 [21].

#### 2.4. Magnetic susceptibility

Magnetic susceptibility measurements were performed in the range 2–300 K using a longitudinal Faraday system (Oxford Instruments) with a 7 T superconducting magnet using a magnetic field of 5 T and a gradient of 1 T/m. A polycrystalline sample of **4** (25.66 mg) was placed inside a previously calibrated thin wall Teflon bucket. The force was measured with a microbalance (Sartorius S3D-V). Data were corrected for the contributions due to the sample holder and core diamagnetism, estimated from tabulated Pascal constants as  $4.88 \times 10^{-4}$  emu/mol.

### 3. Results and discussion

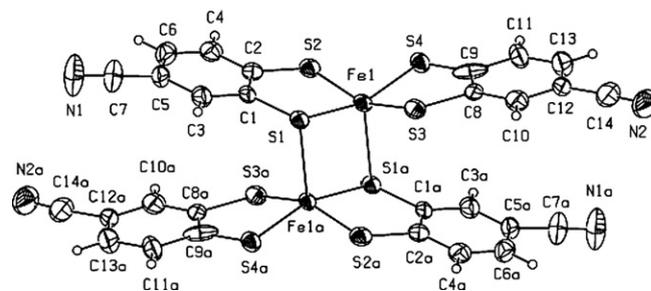
The synthesis of the complex is based on the ligand precursor 4-cyanobenzene-1,2-dithiol (**3**), a new compound which is prepared starting from commercially available 3,4-dichlorobenzonitrile (**1**). The followed synthetic procedure is similar to that previously used for the preparation of the dcbdt ligand [12]. It involves the preparation of the aromatic dibenzylsulphide, 1,2-bis(S-benzylthio)-4-cyanobenzene (**2**), in 34% yield, followed by a mild cleavage with

the assistance of anhydrous aluminium chloride (Scheme 1) to obtain **3** in 80% yield.

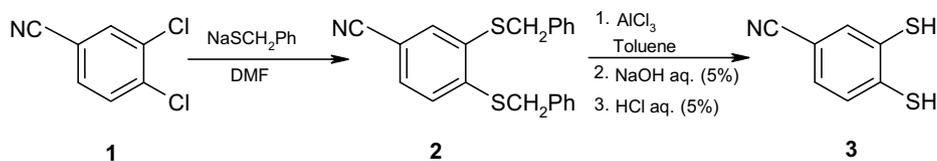
The iron (III) complex with the ligand 4-cyanobenzene-1,2-dithiolate was obtained by the reaction of the dithiol **3** with FeCl<sub>3</sub>, in a hydro-alcoholic solvent mixture, and precipitated in the form of the tetrabutylammonium or tetraphenylphosphonium salts  $(n\text{-Bu}_4\text{N}) [\text{Fe}(\text{cbdt})_2]$  (**4**) and  $(\text{Ph}_4\text{P}) [\text{Fe}(\text{cbdt})_2]$  (**5**) (Scheme 2), following the usual preparation procedure for other bisdithiolene complexes [22,12].

The crystals obtained for compound **4**, enabled the crystal structure determination by X-ray diffraction. An ORTEP view of the complex anions is depicted in Fig. 1, showing the atomic labelling scheme. Selected bond lengths and angles for these compounds are presented in Table 2. The asymmetric unit contains one cation and one  $[\text{Fe}(\text{cbdt})_2]^-$  anion with the CN groups in the cis configuration. The anions present the characteristic dimerisation of Fe(III) bisdithiolenes forming  $[\text{Fe}(\text{cbdt})_2]_2^{2-}$  units with an inversion centre between the two Fe atoms which adopt the usual 4+1 iron coordination geometry. The equatorial Fe–S bonds distances at Fe–S(1) 2.237(14) Å, Fe–S(2) 2.234(17) Å, Fe–S(3) 2.192(17) Å, Fe–S(4) 2.231(15) Å, and the two Fe–S(4a) apical bonds at 2.474(13) Å are typical of Fe(III) dimerised complexes. As shown in Fig. 2 the dimeric anions are well isolated from each other and the only close contacts are S···H and N···H hydrogen bonds with the cations.

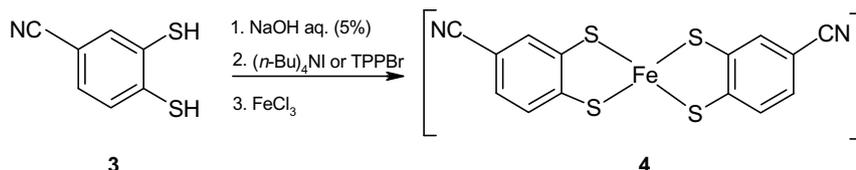
Cyclic voltammetry of  $(n\text{-Bu}_4\text{N}) [\text{Fe}(\text{cbdt})_2]$  in dichloromethane solutions with  $(n\text{-Bu}_4\text{N})\text{PF}_6$  as supporting electrolyte showed that this compound is stable in the range  $-0.5$  to  $0.5$  V versus Ag/AgCl. At these limits complex irreversible oxidation reduction processes take place denoting a possible equilibrium between dimerised and dissociated  $[\text{Fe}(\text{cbdt})_2]$  species in solution.



**Fig. 1.** ORTEP diagrams and atomic numbering scheme of the complex  $[\text{Fe}(\text{cbdt})_2]_2^{2-}$  in **4** with thermal ellipsoids at 40% probability level.



**Scheme 1.**



**Scheme 2.**

**Table 3**

Estimated parameters from the Mössbauer spectra of  $(n\text{-Bu}_4\text{N})_2[\text{Fe}(\text{cbdt})_2]$  taken at 300 and 4 K

T, K	IS, mm/s	QS, mm/s	$\Gamma$ , mm/s
300	0.24	3.05	0.25
4	0.34	3.01	0.26

IS, isomer shift relative to metallic iron at 300 K; QS, quadrupole splitting,  $\Gamma$  = full width at half height. Precision of fitting procedure:  $\pm 0.02$  mm/s for IS, QS and  $\Gamma$ .

The Mössbauer spectra of **4** clearly show two single peaks with narrow line-widths (Fig. 3). They were therefore fitted with one quadrupole doublet. Both peaks have the same width but different areas, which may be attributed to texture effects due to the fact that the principal axis of the needle-shaped crystals tends to lie preferentially in a plane perpendicular to the  $\gamma$ -ray direction. This is further confirmed by the fact that the area ratio did not change with temperature. The estimated parameters are summarised in Table 3. The increase in the isomer shifts, IS, with decreasing temperature may be explained by the second order Doppler shift. The quadrupole splitting, QS, is temperature independent within experimental error.

Within experimental error, the isomer shift (Table 3) is the same of other bisdithiolene complexes at the same temperature, in agreement with  $\text{Fe}^{\text{III}}$  in an almost identical square pyramidal coordination by five sulfur atoms [14,23]. The QS values of the  $[\text{Fe}(\text{dcbdt})_2]$  and  $[\text{Fe}(\text{cbdt})_2]$  compounds are almost identical but significantly larger than those of the  $[\text{Fe}(\text{dmit})_2]$  and  $[\text{Fe}(\text{mnt})_2]$  compounds, respectively. This difference cannot be ascribed to different spin states since these latter compounds were found to have  $S = 3/2$  as well as the title compound (see below) while for  $[\text{Fe}(\text{dcbdt})_2]$  there is evidence for a  $S = 1/2$  state [14].

The paramagnetic susceptibility,  $\chi_P$ , of  $(n\text{-Bu}_4\text{N})_2[\text{Fe}(\text{cbdt})_2]$ , is  $\sim 18 \times 10^{-4}$  emu/mol at room temperature, decreases upon cooling, reaching a minimum of  $6 \times 10^{-4}$  emu/mol between 30 and

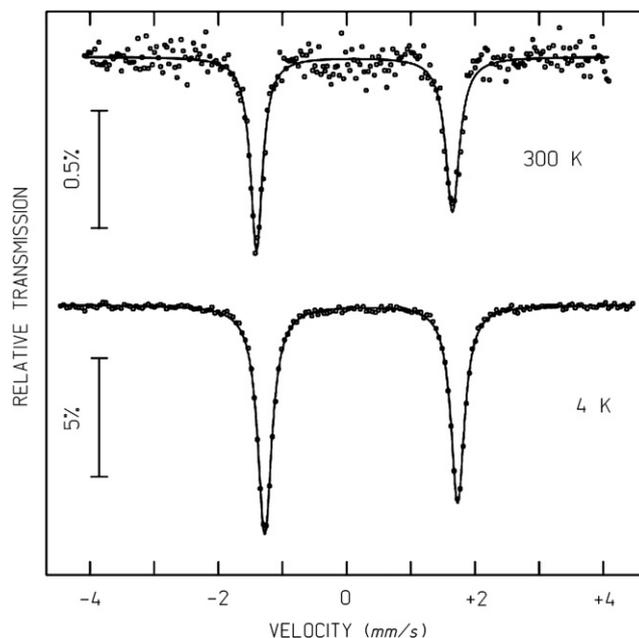
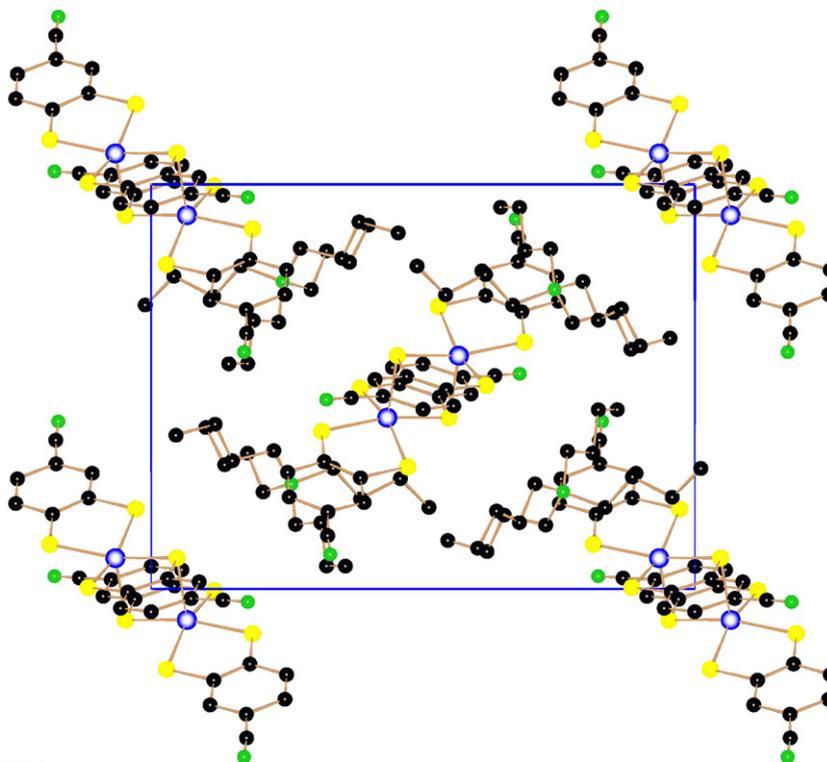


Fig. 3. Mössbauer spectra of  $(n\text{-Bu}_4\text{N})_2 \text{Fe}(\text{cbdt})_2$ .

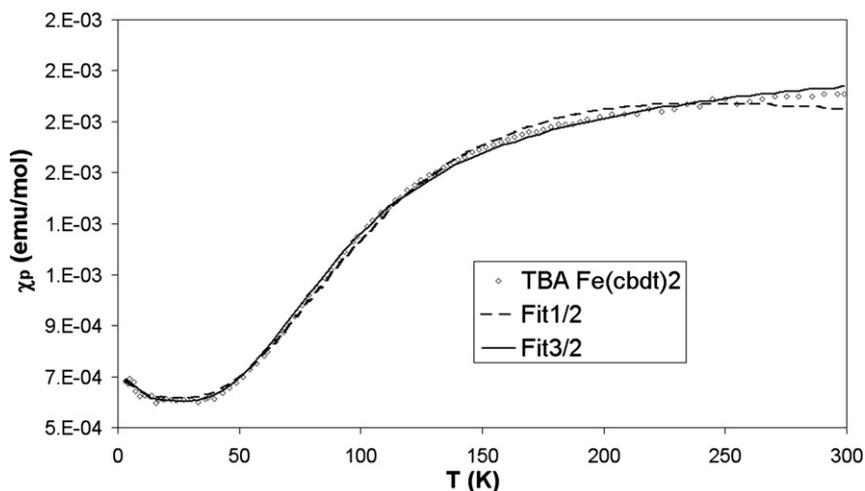
10 K (Fig. 4) and at lower temperatures the magnetic susceptibility shows a small increase as a Curie tail due to impurities. In spite of its paramagnetism, this compound was found to be EPR silent in a X-band spectrometer, as it happens in many of these iron bisdithiolene complexes.

In view of the crystal structure the magnetic behaviour of  $(n\text{-Bu}_4\text{N})_2[\text{Fe}(\text{cbdt})_2]$  is expected to be dominated by the antiferromagnetic intradimer interactions typical of all other known  $\text{Fe}(\text{III})$  bisdithiolene complexes, with exception of a quinoxalinedithiolate



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Fig. 2. Crystal structure of  $[n\text{-Bu}_4\text{N}]_2 \text{Fe}(\text{cbdt})_2$ , **4** viewed along the  $b$  axis.



**Fig. 4.** Paramagnetic susceptibility  $\chi_p$  of  $(n\text{-Bu}_4\text{N})[\text{Fe}(\text{cbdt})_2]$  as a function of the temperature  $T$ . The dashed line is a fit by Eq. (2), considering dimers of  $S = 1/2$  spins and the continuous line a fit by Eq. (1), considering dimers of  $S = 3/2$  spins (see text).

complex that is the only example of a undimerised Fe(III) bisdithiolene complex reported so far [10]. The magnetic susceptibility data of Fig. 4 denotes in addition to this dimer contribution the presence of a significant temperature independent paramagnetism comparable to the one previously found in  $(n\text{-Bu}_4\text{N})_2[\text{Fe}(\text{dcbdt})_2]$  [14]. The latter compound was found to present the  $[\text{Fe}(\text{dcbdt})_2]$  units in a low spin  $S = 1/2$  configuration at variance with almost all other Fe(III) bisdithiolate complexes studied in detail, such as  $\text{Fe}(\text{mnt})_2$ , which present an intermediate spin  $S = 3/2$  spin configurations [23,24].

Therefore, the magnetic susceptibility data of  $(n\text{-Bu}_4\text{N})_2[\text{Fe}(\text{cbdt})_2]$  was tentatively fitted to Eqs. (1) and (2), both considering, besides a possible Curie tail,  $C$ , and a temperature independent term,  $A$ , a contribution of antiferromagnetic coupled  $S = 3/2$  dimers (Eq. (1)) or  $S = 1/2$  dimers (Eq. (2)) [25].

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

$$\chi_p = A + \frac{C}{T} + \frac{2Ng^2\mu_B^2}{kT} \left[ 3 + \exp\left(\frac{-J}{kT}\right) \right]^{-1} \quad (2)$$

Here  $N$  is the Avogadro's number,  $g$  the Landé factor,  $\mu_B$  the Bohr magneton and  $J$  the intradimer antiferromagnetic coupling parameter.

As observed in Fig. 4, Eq. (1) provides a good fit of experimental data with  $A = 5.9 \times 10^{-4}$  emu/mol,  $(Ng^2\mu_B)/k_B = 1.232(8)$  K emu/mol, corresponding to  $g \approx 1.81$ ,  $C = 36(2) \times 10^{-5}$  K emu/mol and  $-J/k_B = 276(1)$  K. The low  $C$  value corresponds to  $\approx 0.1\%$  of  $S = 1/2$  impurities (or  $\approx 0.02\%$  of  $S = 3/2$ ) denoting the high purity of the sample. Eq. (2) with the best parameters  $A = 5.9 \times 10^{-4}$  emu/mol,  $(Ng^2\mu_B)/k_B = 1.94(3)$  K emu/mol, corresponding to  $g \approx 2.28$ ,  $C = 40(8) \times 10^{-5}$  K emu/mol and  $-J/k_B = 333(3)$  K is clearly unable to fit properly the data.

The obtained  $J$  value is comparable to those reported for other iron bisdithiolenes compounds with well isolated Fe(III) bisdithiolene dimers and with virtually identical coordination geometry, such as  $\text{PyH}[\text{Fe}(\text{mnt})_2]^-$  where the susceptibility data was also fitted to a similar Eq. (1) with  $J$  values of 258 K [23].

#### 4. Conclusion

In summary, we synthesised a new aromatic *ortho*-areneedithiol, and the first complex of this ligand with Fe,  $[\text{Fe}(\text{cbdt})_2]^{2-}$ , was prepared and characterised. This new cbdt ligand and the  $\text{Fe}(\text{cbdt})_2$

complex open the way to the preparation of a new family of transition metal complexes, with other metallic elements such as Ni, Au, Pd, Cu, Co which are expected to be reported subsequently and be used as building blocks for new molecular materials.

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#### Appendix A. Supplementary material

CCDC 655941 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.ica.2008.02.068](https://doi.org/10.1016/j.ica.2008.02.068).

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