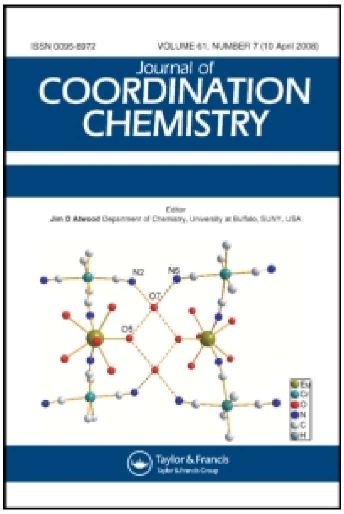

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, Crystal Structure and Magnetochemistry of a Novel Trinuclear Iron Complex [Fe 3 O(ClC 6 H 4 CO 2) 6 (H 2 O) 2.5 (C 2 H 5 OH) 0.5]ClO 4 ·0.5H 2 O

Yan Bing[a]; Chen Zhi-Da[a]
[a] State Key Laboratory of Rare Earth Material Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing, China

To cite this Article Bing, Yan and Zhi-Da, Chen(2002) 'Synthesis, Crystal Structure and Magnetochemistry of a Novel Trinuclear Iron Complex [Fe 3 O(ClC 6 H 4 CO 2) 6 (H 2 O) 2.5 (C 2 H 5 OH) 0.5]ClO 4 ·0.5H 2 O', Journal of Coordination Chemistry, 55: 2, 241 — 249

To link to this Article: DOI: 10.1080/00958970211881

URL: http://dx.doi.org/10.1080/00958970211881

J. Coord. Chem., 2002, Vol. 55(2), pp. 241 – 249

SYNTHESIS, CRYSTAL STRUCTURE AND MAGNETOCHEMISTRY OF A NOVEL TRINUCLEAR IRON COMPLEX $[Fe_3O(ClC_6H_4CO_2)_6(H_2O)_{2.5}(C_2H_5OH)_{0.5}]ClO_4 \cdot 0.5H_2O$

YAN BING[a,b] and CHEN ZHI-DA[a,b,]*

[a]*State Key Laboratory of Rare Earth Material Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing, 100871, China;* [b]*The University of Hong Kong Joint Laboratory of Rare Earth Material and Bioinorganic Chemistry, Peking University, Beijing, 100871, China*

(Received 22 August 2000)

A novel trinuclear iron complex was synthesized in ethanol solution, $[Fe_3O(ClC_6H_4CO_2)_6(H_2O)_{2.5}(C_2H_5OH)_{0.5}]ClO_4 \cdot 0.5H_2O$. The title complex crystallizes in the tetragonal system, space group P_{4_1}, with unit cell dimensions: $a = 12.356(2)$, $c = 42.315(14)$ Å, $V = 6460.3$ (19) Å^3, $Dx = 1330$ Mg m^{-3}, $Z = 4$. $F(000) = 2608$ and was refined to $R1 = 0.066$ and b axile. Variable temperature magnetic susceptibilities indicate weak antiferromagnetic coupling between Fe(III) centres through the carboxylate bridge.

Keywords: Trinuclear iron complex; Crystal structure; Magnetochemistry; *Para*-chloro benzoic acid

INTRODUCTION

The biological role of polynuclear oxo-. hydroxo-, and alkoxo-bridged iron systems has become the subject of considerable interest over the last few years [1 – 3]. Active sites in some metalloproteins systems such as hemerythrin [4, 5], methane monooxygenase [6, 7], and ribonucleotide reductase [8, 9] may contain diiron cores, where the iron site can cycle from

---

*Corresponding author.

ISSN: 0095-8972 © 2002 Taylor & Francis Ltd DOI: 10.1080/00958970290002171

Fe_2^{II} to Fe_2^{III}. It is very surprising that remarkably similar structures can exhibit varied functions in these proteins. Studies of the synthesis of model complexes to model the iron proteins have been extensive and suggest how important a role they play in biological systems. In the present work. a novel trinuclear complex. $[Fe_3O(ClC_6H_4CO_2)_6(H_2O)_{2.5}(C_2H_5OH)_{0.5}]ClO_4 \cdot 0.5H_2O$, has been synthesized in ethanol, and its structure has been determined. The magnetochemical properties of the complex have been investigated.

EXPERIMENTAL

Physical Measurements

Elemental analyses (C, H, N) were carried out using an Elementar Cario EL instrument. Infrared spectroscopy (KBr pellets) was performed using a Nicolet 7199B spectrophotometer in the range 4000 ~ 400 cm^{-1}. Variable-temperature magnetic susceptibilities (1.8 ~ 300 K) were measured with a MagLab-2000 magnetometer; all data were corrected for diamagnetism of constituent atoms with Pascal's constants.

TABLE I Crystal data and structure refinement details for the title complex

Identification code	$[Fe_3O(ClC_6H_4CO_2)_6(H_2O)_3(C_2H_5OH)_{0.5}]ClO_4 \cdot 0.5H_2O$
Empirical formula	$C_{43}H_{33}Cl_7Fe_3O_{20.50}$
Formula weight	1293.39
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Tetragonal
Space group	$P4_1$
Unit cell dimensions	$a = 12.356(2)$ Å $c = 42.315(8)$ Å
Volume	6460.3(19) Å^3
Z	4
Calculated density	1.330 Mg m^{-3}
Absorption coefficient	1.015 mm^{-1}
$F(000)$	2608
Crystal size	0.45 × 0.40 × 0.40 mm
θ range for data collection	2.33 to 25.00°
Reflections collected	6218
Reflections unique	5676
$R(int)$	0.1263
Absorption correction	Psi
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5676/12/429
Goodness-of-fit on F^2	1.043
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.066$, $wR_2 = 0.147$
Absolute structure parameter	0.17(4)
Largest diff. peak and hole	0.447 and −0.405 e.Å^{-3}

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\times 10^3$ Å^2) for the complex

Atoms	*x/a*	*v/b*	*z/c*	*U(eq)*
Fe(1)	2953(2)	3285(2)	1375	44(1)
Fe(2)	4182(2)	3335(2)	2063(1)	50(1)
Fe(3)	1773(2)	2204(2)	2001(1)	50(1)
Cl(1)	905(8)	−2917(5)	659(2)	173(4)
Cl(2)	−3494(5)	5960(8)	1276(2)	188(4)
Cl(3)	9574(5)	1786(8)	889(3)	185(4)
Cl(4)	4521(5)	10072(3)	1553(2)	125(2)
Cl(5)	5232(6)	−2926(5)	2935(2)	148(3)
Cl(6)	671(6)	6748(7)	3523(2)	153(3)
O	2976(7)	2921(7)	1822(2)	44(2)
O(1)	2876(9)	3601(8)	904(3)	60(3)
C(l)	2780(3)	4590(2)	744(10)	105(14)
C(2)	3860(3)	4920(4)	618(11)	109(14)
O(2)	5517(9)	3784(9)	2351(3)	78(3)
O(3)	482(9)	1385(8)	2218(3)	66(3)
O(11)	2397(7)	1860(7)	1243(2)	50(3)
O(12)	1629(9)	1142(8)	1658(3)	67(3)
O(21)	660(7)	3165(9)	1816(3)	68(3)
O(22)	1444(8)	3873(8)	1393(3)	60(3)
O(31)	5267(8)	2768(8)	1765(3)	70(3)
O(32)	4470(8)	2830(7)	1304(2)	54(3)
O(41)	4324(8)	4843(8)	1910(3)	67(3)
O(42)	3450(7)	4809(8)	1430(2)	51(3)
O(51)	4339(8)	1945(8)	2299(3)	69(3)
O(52)	2716(8)	1131(7)	2241(3)	61(3)
O(61)	1689(8)	3132(8)	2393(3)	61(3)
O(62)	3271(9)	4003(8)	2429(3)	74(3)
C(10)	1942(11)	1084(11)	1383(4)	43(3)
C(11)	1708(11)	101(11)	1197(4)	46(4)
C(12)	1185(16)	−719(17)	1349(6)	100(6)
C(13)	864(15)	−1673(15)	1170(5)	81(5)
C(14)	1146(17)	−1745(16)	878(5)	91(6)
C(15)	1741(15)	−927(16)	718(5)	86(6)
C(16)	1986(11)	9(11)	883(4)	50(4)
C(20)	671(14)	3795(13)	1574(5)	56(4)
C(21)	−369(14)	4312(14)	1499(4)	69(5)
C(22)	−417(15)	4982(16)	1236(5)	84(6)
C(23)	−1409(19)	5461(18)	1139(6)	104(7)
C(24)	−2251(18)	5321(18)	1364(6)	109(7)
C(25)	−2230(16)	4741(16)	1642(5)	92(6)
C(26)	−1251(15)	4210(15)	1726(5)	79(5)
C(30)	5284(12)	2674(11)	1454(4)	41(4)
C(31)	6334(11)	2354(10)	1334(4)	44(4)
C(32)	7143(13)	2032(13)	1504(4)	64(5)
C(33)	8213(14)	1773(14)	1388(5)	79(5)
C(34)	8341(18)	1950(18)	1090(6)	102(7)
C(35)	7517(16)	2240(15)	866(5)	82(6)
C(36)	6495(16)	2443(15)	1010(5)	82(6)
C(40)	3935(12)	5298(12)	1659(4)	49(4)
C(41)	4090(10)	6481(10)	1625(3)	38(3)
C(42)	3716(12)	7027(12)	1368(4)	58(4)
C(43)	3863(13)	8176(14)	1340(5)	70(5)
C(44)	4351(14)	8627(14)	1584(5)	72(5)

TABLE II (Continued)

Atoms	*x/a*	*v/b*	*z/c*	*U(eq)*
C(45)	4728(13)	8190(13)	1844(4)	63(4)
C(46)	4595(14)	7040(13)	1872(4)	68(5)
C(50)	3679(14)	1112(13)	2324(4)	60(4)
C(51)	4068(11)	143(11)	2477(3)	47(4)
C(52)	5140(14)	118(15)	2573(4)	73(5)
C(53)	5520(17)	−872(18)	2743(5)	104(7)
C(54)	4786(16)	−1748(15)	2748(5)	81(6)
C(55)	3760(15)	−1716(15)	2632(4)	77(5)
C(56)	3422(13)	−786(14)	2486(4)	71(5)
C(60)	2293(14)	3869(13)	2510(4)	53(4)
C(61)	1913(12)	4498(13)	2757(4)	58(4)
C(62)	2609(15)	5306(14)	2885(4)	77(5)
C(63)	2180(17)	6096(16)	3134(5)	88(6)
C(64)	1140(19)	5907(19)	3210(5)	106(7)
C(65)	435(15)	5143(16)	3098(5)	85(6)
C(66)	851(17)	4475(17)	2852(5)	93(6)
Cl(7)	7985(4)	2403(7)	2647(2)	124(2)
O(71)	9127(9)	2442(17)	2606(5)	174(8)
O(72)	7370(2)	2440(2)	2362(4)	243(11)
O(73)	7790(2)	3234(17)	2880(5)	231(11)
O(74)	7630(2)	1506(17)	2841(6)	253
O(4)	390(2)	−650(2)	2407(7)	119(10)

Synthesis of $[Fe_3O(ClC_6H_4CO_2)_6(H_2O)_{2.5}(C_2H_5OH)_{0.5}]ClO_4 \cdot 0.5H_2O$

A stirred solution of $FeCl_3 \cdot 6H_2O$ (0.70 g, 2.58 mmol) in EtOH (20 cm^3) was treated with solid sodium *para*-chlorobenzoate (0.93 g, 5.20 mmol). After stirring for 15 mins, the solution changed colour from orange to brown and then $NaClO_4 \cdot H_2O$ (0.365 g, 2.6 mmol) was added. The resulting green-brown slurry was stirred overnight at ambient temperature. After filtration, the red-brown filtrate was left to stand at room temperature. After about one month, deep orange, single crystals suitable for X-ray crystal structure determination were obtained. *Anal.*, Calc. for $C_{43}H_{33}Cl_7Fe_3O_{20.50}$ (%): C, 39.90; H, 2.55; Cl, 19.21. Found: C, 40.34; H, 2.50; N, 18.92. IR spectrum: 3412 cm^{-1} (m), 1595 cm^{-1} (s), 1560 cm^{-1} (m), 1414 cm^{-1} (s), 1283 cm^{-1} (w), 1174 cm^{-1} (w), 1121 cm^{-1} (m), 1108 cm^{-1} (w), 1089 cm^{-1} (w), 1015 cm^{-1} (w), 856 cm^{-1} (w), 773 cm^{-1} (m), 688 cm^{-1} (w). 636 cm^{-1} (w), 553 cm^{-1} (m). 416 cm^{-1} (w).

X-ray Crystallography

Diffraction experiments for a light brown crystal with dimensions $0.45 \times 0.40 \times 0.40$ mm were performed with graphite-monochromated $MoK\alpha$ radiation on a Enraf-Nodius CAD4 four-circle diffractometer. Some 6218 intensity data were collected in the range $2.33 \leq \theta \leq 25.00°$ of which 5676 were unique using the $\omega-2\theta$ scan mode. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods. Hydrogen atoms were added geometrically and were not refined. The final *R* and *Rw* values were 0.066 and 0.147, respectively. All calculations were performed on a 586PC computer using SHELXS-97 and SHELXL-97. A summary of crystallographic data and additional data collection parameters is given in Table I. Final atomic coordinates and equivalent isotropic displacement parameters are listed in Table II.

RESULTS AND DISCUSSION

Description of the Structure

Thc crystal structure of the title complex consists of monomeric $[Fe_3O(ClC_6H_4CO_2)_6(H_2O)_3(C_2H_5OH)_{0.5}]^+$ cations and perchlorate anions. Figure 1 shows the structure of the complex. The Fe coordination geometry is a slightly distorted octahedron consisting of the central oxygen atom, four oxygen atoms from bridging *para*-chloro benzoate groups and one oxygen atom from solvent molecules (H_2O or ethanol). The overall structure is thus the common basic carboxylate type seen for many other non-mixed valence trinuclear Fe or Mn complexes. It is noteworthy that there is little difference between the three Fe atoms. Fe(2) and Fe(3) atom show the same coordination situation, while Fe(1) is slightly different. The coordinated O atom from solvent molecules for Fe(1) is shared by H_2O and an ethanol molecule. In the unit cell of the complex, for one half of complex molecular unit, the coordinated O atom from solvent for Fe(1) is provided by one H_2O molecule, the same as for Fe(2) and Fe(3); for the other half, the coordinated O atom for Fe(1) is provided by one ethanol molecule. The average Fe–O–Fe angle is 120°. Besides the central O–Fe average distance of 1.903 Å, the average values for the other five Fe(1, 2, 3)–O bond distances are as follows; Fe(1)–O, 1.996(10) Å; Fe(2)–O, 2.031(11) Å; Fe(3)–O, 2.020(10) Å. The bond angles central O–Fe–O from carboxylate group are all nearly 90°, while the bond angles central O–Fe–O from the terminal solvent molecules are all nearly 180°. The average O–Fe–O (carboxylate group) angles are 94.4(4)° (O–Fe(1)–O (carboxylate)), 96.3(4)° (O–Fe(2)–O (carboxylate)) and 95.1(4)° (O–Fe(3)–O (carboxylate)), respectively. Bond angles central O–Fe–O from the terminal solvent

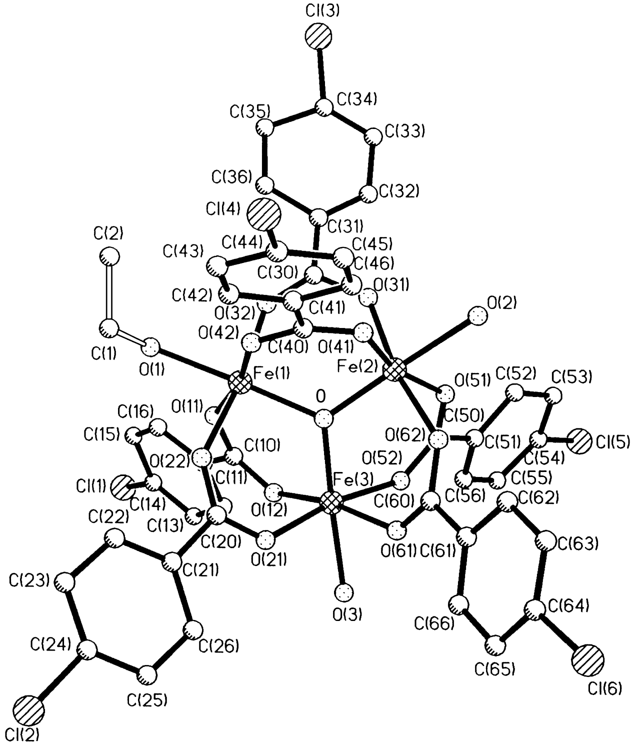

FIGURE 1 Crystal structure of $[Fe_3O(ClC_6H_4CO_2)_6(H_2O)_3(C_2H_5OH)_{0.5}]ClO_4 \cdot 0.5H_2O$ showing atom numbering scheme.

molecules are 177.0(4)° (O–Fe(1)–O(1)), 178.0(4)° (O–Fe(2)–O(1)) and 177.4(4)° (O–Fe(3)–O(1)), respectively. Table III gives other selected bond lengths and angles for the complex. There exists uncoordinated H_2O molecules between adjacent complex molecular units. Perchlorate ions form hydrogen bonds O·····H·····O with O atoms of terminal coordinated solvent molecules. Table IV gives possible hydrogen bonding dimensions in the complex.

Magetochemistry

Temperature-dependent molar susceptibility measurements of a crystal line sample complex were carried out in the temperature range 1.8 ~ 300 K. Results are shown in Figure 2 in the form of a $\chi_m T$ *versus* T plot. Values of $\chi_m T$ decrease from 3.78 cm^3 K mol^{-1} at 285 K to 031 cm^3 K mol^{-1} at 1.8 K. This indicates antiferromagnetic coupling between Fe(III) centers. If it is

TABLE III Selected bond lengths [Å] and angles [°] for the title complex

Fe(1)–O	1.943(10)	Cl(2)–C(24)	1.77(2)
Fe(1)–O(11)	1.970(9)	Cl(3)–C(34)	1.76(2)
Fe(1)–O(32)	1.980(10)	Cl(4)–C(44)	1.802(18)
Fe(1)–O(42)	1.995(10)	Cl(5)–C(54)	1.746(19)
Fe(1)–O(22)	2.003(11)	Cl(6)–C(64)	1.78(2)
Fe(1)–O(1)	2.033(11)	O(1)–C(1)	1.401(11)
Fe(2)–O	1.878(9)	C(1)–C(2)	1.496(11)
Fe(2)–O(31)	1.969(12)	O(11)–C(10)	1.259(16)
Fe(2)–O(41)	1.980(11)	O(12)–C(10)	1.229(18)
Fe(2)–O(51)	1.997(10)	O(21)–C(20)	1.288(19)
Fe(2)–O(62)	2.084(12)	O(22)–C(20)	1.227(18)
Fe(2)–O(2)	2.123(11)	O(31)–C(30)	1.322(17)
Fe(3)–O	1.889(9)	O(32)–C(30)	1.206(16)
Fe(3)–O(12)	1.964(10)	O(41)–C(40)	1.295(18)
Fe(3)–O(21)	1.979(11)	O(42)–C(40)	1.287(18)
Fe(3)–O(52)	2.037(10)	O(51)–C(50)	1.317(18)
Fe(3)–O(61)	2.020(11)	O(52)–C(50)	1.240(18)
Fe(3)–O(3)	2.100(10)	O(61)–C(60)	1.277(18)
Cl(1)–C(14)	1.75(2)	O(62)–C(60)	1.266(17)
O–Fe(1)–O(11)	94.2(4)	O–Fe(3)–O(21)	96.1(4)
O–Fe(1)–O(32)	94.0(4)	O(12)–Fe(3)–O(21)	92.6(5)
O(11)–Fe(1)–O(32)	91.9(4)	O–Fe(3)–O(52)	93.2(4)
O–Fe(1)–O(42)	95.8(4)	O(12)–Fe(3)–O(52)	89.2(5)
O(11)–Fe(1)–O(42)	169.8(4)	O(21)–Fe(3)–O(52)	170.3(5)
O(32)–Fe(1)–O(42)	89.7(4)	O–Fe(3)–O(61)	96.0(4)
O–Fe(1)–O(22)	93.5(4)	O(12)–Fe(3)–O(61)	168.9(4)
O(11)–Fe(1)–O(22)	90.6(4)	O(21)–Fe(3)–O(61)	87.0(4)
O(32)–Fe(1)–O(22)	171.9(4)	O(52)–Fe(3)–O(61)	89.4(4)
O(42)–Fe(1)–O(22)	86.5(4)	O–Fe(3)–O(3)	177.4(4)
O–Fe(1)–O(1)	177.0(4)	O(12)–Fe(3)–O(3)	86.1(4)
O(11)–Fe(1)–O(1)	83.0(4)	O(21)–Fe(3)–O(3)	86.2(4)
O(32)–Fe(1)–O(1)	87.1(4)	O(52)–Fe(3)–O(3)	84.4(4)
O(42)–Fe(1)–O(1)	87.0(4)	O(61)–Fe(3)–O(3)	82.8(4)
O(22)–Fe(1)–O(1)	85.6(4)	Fe(2)–O–Fe(3)	122.3(5)
O–Fe(2)–O(31)	95.4(4)	Fe(2)–O–Fe(1)	118.5(4)
O–Fe(2)–O(41)	98.5(4)	Fe(3)–O–Fe(1)	119.2(4)
O(31)–Fe(2)–O(41)	93.7(4)	C(1)–O(1)–Fe(1)	130(2)
O–Fe(2)–O(51)	96.6(4)	O(1)–C(1)–C(2)	109(3)
O(31)–Fe(2)–O(51)	87.0(5)	C(10)–O(11)–Fe(1)	134.7(10)
O(41)–Fe(2)–O(51)	164.7(5)	C(10)–O(12)–Fe(3)	135.3(9)
O–Fe(2)–O(62)	94.8(4)	C(20)–O(21)–Fe(3)	132.1(10)
O(31)–Fe(2)–O(62)	169.8(5)	C(20)–O(22)–Fe(1)	136.0(11)
O(41)–Fe(2)–O(62)	85.3(4)	C(30)–O(31)–Fe(2)	132.8(10)
O(51)–Fe(2)–O(62)	91.3(5)	C(30)–O(32)–Fe(1)	139.0(10)
O–Fe(2)–O(2)	178.0(4)	C(40)–O(41)–Fe(2)	130.1(10)
O(31)–Fe(2)–O(2)	86.0(5)	C(40)–O(42)–Fe(1)	132.4(10)
O(41)–Fe(2)–O(2)	82.7(4)	C(50)–O(51)–Fe(2)	130.6(10)
O(51)–Fe(2)–O(2)	82.1(5)	C(50)–O(52)–Fe(3)	134.5(10)
O(62)–Fe(2)–O(2)	83.8(4)	C(60)–O(61)–Fe(3)	133.8(10)
O–Fe(3)–O(12)	95.1(4)	C(60)–O(62)–Fe(2)	131.6(10)

assumed that the three Fe(III) ions are equivalent, a theoretical expression for the molar magnetic susceptibility can be derived by using the Kambe vector-coupling method and the Van Vleck equation. Details of the

TABLE IV Possible hydrogen bonds distances [Å] and angles [°] for the title complex

O1 O73(#1)	2.840	O2 O72	2.832
Fel O1 O73(#1)	130.0	Fe2 O2 O72	119.0
O3 O71(#2)	2.686	O3 O4	2.638
Fe3 O3 O71(#2)	120.5	Fe3 O3 O4	128.7

Symmetry operations: #1 = y, $1-x$, $-0.25+z$; #2 = $-1+x$, y, z.

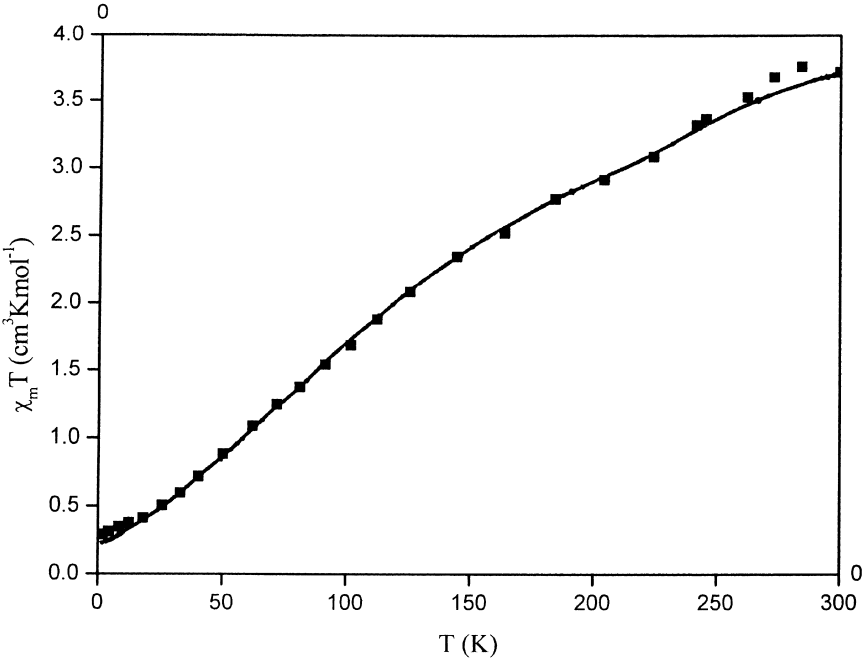

FIGURE 2 Temperature dependence of magnetic susceptibility for the title complex, experimental (◆) and calculated (—) data.

expression have been described in the literature [10]. The best fitting parameters for the complex are $J = -10.44\,\mathrm{cm}^{-1}$, $g = 1.98$, and $R = 2.8 \times 10^{-5}$, where R is the agreement factor defined as $R = \{\Sigma[(\chi_m T)_{obs}(i) - (\chi_m T)_{calcd}(i)]^2 / \Sigma[(\chi_m T)_{obs}(i)]^2\}$. The negative value of J also indicates weak antiferromagnetic coupling through the carboxylate group.

Supplementary Material

H atom positions. anisotropic thermal parameters and lists of observed and calculated structures are available from the authors on request.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (29831010, 20023005). the State Key Project for Fundamental Research in China (G1998061306) and the China Postdoctoral Science Foundation.

References

[1] S. J. Lippard, *Angew. Chem., Int. Ed. Engl.* **27**, 344 (1988).
[2] M. K. Donald, *Chem. Rev.* **90**, 585 (1990).
[3] M. Konno and M. M. Kido, *Bull. Chem. Soc. Jpn.* **64**, 339 (1991).
[4] P. C. Wilkins and R. G. Wilkins, *Coord. Chem. Rev.* **79**, 195 (1987).
[5] S. Sheriff, W. A. Hendrichkson and J. L. Smith, *J. Mol. Biol.* **197**, 273 (1987).
[6] B. G. Fox, K. K. Surerus, E. Munck and J. D. Lipscomb, *J. Biol. Chem.* **263**, 10553 (1988).
[7] A. Ericson, B. Hedman, K. O. Hodgson, J. Green, H. Dalton, J. G. Bentsen, R. H. Gbeer and S. J. Lippard, *J. Am. Chem. Soc.* **110**, 2330 (1988).
[8] P. Nordlund, B. M. Sjoberg and H. Eklund, *Nature* **345**, 593 (1990).
[9] B. A. Averill, J. C. Davis, S. Brum, T. Zirino, J. Sanderts-Loehr, T. M. Loehr, J. T. Sage and P. G. Debrunner, *J. Am. Chem. Soc.* **109**, 3670 (1987).
[10] S. Menage, S. E. Vitols, P. Bergerat, E. Godjvi, O. Kahn, T. J. Girerd, M. Guillot, X. Soluns and T. Calvet, *Inorg. Chem.* **30**, 2666 (1991).