Inorganica Chimica Acta, *216* (1994) 21–29

Binuclear oxo-bridged iron(III) complexes of *N,N'*-bis(2-pyridylmethyl)ethane-1,2-diamine (bispicen) and related ligands

Navamoney Arulsamy, Patricia A. Goodson and Derek J. Hodgson*
Department of Chemistry, University of Wyoming, Laramie, WY 82071 (USA)

Jørgen Glerup* and Kirsten Michelsen*
Chemistry Laboratory I, H C Ørsted Institute, Universitetsparken 5, DK-2100 Copenhagen Ø (Denmark)

(Received June 15, 1993)

Abstract

The syntheses and characterization of a series of binuclear iron(III) complexes of the ligands *N,N'*-bis(2-pyridylmethyl)ethane-1,2-diamine (bispicen), $C_{14}H_{18}N_4$, *N,N'*-bis(2-pyridylmethyl)propane-1,3-diamine (bispictn), $C_{15}H_{20}N_4$, and *N,N'*-bis(2-pyridylmethyl)-*N,N'*-bis(methyl)-1,2-ethanediamine, $C_{16}H_{22}N_4$, are described. The μ-oxo,μ-carbonatodiiron(III) complex $\{[(\text{bispictn})\text{Fe}]_2(\mu\text{-O})(\mu\text{-CO}_3)\}(\text{ClO}_4)_2 \cdot 3H_2O$, $C_{31}H_{46}Cl_2Fe_2N_8O_{15}$ (**1**) crystallizes in space group $P\bar{1}$ of the triclinic system with two binuclear species in a cell of dimensions $a = 12.552(3)$, $b = 12.980(3)$, $c = 15.016(3)$ Å, $\alpha = 88.49(3)$, $\beta = 68.57(3)$, $\gamma = 64.56(3)°$. The tetradentate ligand binds the iron center in *cis-β* fashion. The structure has been refined to a final *R* factor of 0.0531 based on 2624 observed independent reflections. The complex contains a bent Fe–O–Fe unit with a bridging Fe–O–Fe angle of 129.7(3)° and associated average Fe–O and Fe···Fe separations of 1.803(7) and 3.264(2) Å, respectively. The Fe–O (carbonato) distances are 1.960(5) and 1.968(5) Å. The complex $\{[(\text{bispicMe}_2\text{en})\text{Fe}]_2(\mu\text{-O})(\mu\text{-CO}_3)\}(\text{ClO}_4)_2 \cdot 2H_2O$, $C_{33}H_{48}Cl_2Fe_2N_8O_{14}$ (**2**) crystallizes in space group *C2/c* of the monoclinic system with eight binuclear species in a cell of dimensions $a = 19.580(4)$, $b = 13.442(3)$, $c = 32.727(7)$ Å, $\beta = 94.07(3)°$. The structure has been refined to a final *R* factor of 0.0634 based on 3279 observed independent reflections. The ligand binds the iron centers in *cis-α* fashion. The structure of the complex cation contains a bent Fe–O–Fe unit with a bridging Fe–O–Fe angle of 125.5(3)° and associated average Fe–O and Fe···Fe separations of 1.810(18) and 3.220(2) Å, respectively. The Fe–O (carbonato) distances are 1.930(6) and 1.925(7) Å. The novel μ-oxo,μ-sulfatodiiron(III) complex $\{[(\text{bispicMe}_2\text{en})\text{Fe}]_2(\mu\text{-O})(\mu\text{-SO}_4)\}(\text{ClO}_4)_2 \cdot 2H_2O$, $C_{32}H_{48}Cl_2Fe_2N_8O_{15}S$ (**4**) crystallizes in space group *Pbca* of the orthorhombic system with eight binuclear species in a cell of dimensions $a = 16.049(3)$, $b = 16.875(3)$, $c = 31.325(6)$ Å. The structure has been refined to a final *R* factor of 0.0682 based on 1776 observed independent reflections. The ligand binds the iron centers in *cis-α* fashion. The structure of the complex cation contains a bent Fe–O–Fe unit with a bridging Fe–O–Fe angle of 132.4(5)° and associated average Fe–O and Fe···Fe separations of 1.806(4) and 3.306(2) Å, respectively. The Fe–O (sulfato) distances are 1.980(11) and 1.981(11) Å. Cyclic voltammograms of the complexes reveal an irreversible reduction at c. −0.70 V versus Ag/AgCl reference electrode for **1**, **3** and **4** and a quasi-reversible reduction for **2** at −0.585 V corresponding to the $\text{Fe}_2(\text{III/III}) \leftrightarrow \text{Fe}_2(\text{II/III})$ redox process.

Key words: Crystal structures; Iron complexes; Oxo complexes; Polydentate ligand complexes; Amine complexes

Introduction

The intimate involvement of (μ-oxo)diiron core-containing metalloproteins such as methemerythrin, hemerythrin, *E. coli* ribonucleotide reductase and purple acid phosphatase in various biological functions is well established [1–4]. In the last decade, a large number of (μ-oxo)diiron(III) complexes, also containing one or two additional carboxylato bridges, have been synthesized as models for the biological systems [5–10]. These complexes are interesting not only from a purely chemical point of view but also from a biochemical point of view. The studies have shown that the diiron(III) complexes display substantial antiferromagnetism attributable to super-exchange coupling of $S = 5/2$ ferric ions via the bridges similar to the biological systems. Most of them also exhibit electronic absorption spectra comparable to those of the enzymes. Electrochemical reversibility is also a desired feature for a good model complex as it is well known that hemerythrin undergoes

---

*Authors to whom correspondence should be addressed

SSDI 0020-1693(93)03705-F

a reversible Fe_2(III/III)↔Fe_2(II/II) redox process during the oxygen transport process. Unlike the biological systems, most of the (μ-oxo)diiron(III/III) complexes exhibit only irreversible reduction except $\{[(Me_3TACN)Fe]_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2\}(PF_6)_2$, (where Me_3TACN = 1,4,7-trimethyl-1,4,7-triazacyclononane), which exhibits a quasi-reversible one-electron reduction corresponding to the Fe_2(III/III)↔Fe_2(II/III) redox process [6b]. In order to further understand the chemical and physical properties of (μ-oxo)diiron(III) core-containing complexes, we have synthesized a series of new such complexes and investigated their spectral, magnetic and electrochemical properties. In addition to the synthesis and characterization of μ-carboxylato complexes, we report here the first doubly-bridged complexes of this type to contain the μ-sulfato bridging ligand.

Experimental

Syntheses

Caution. The compounds described were isolated as perchlorate salts and should be handled as potentially explosive compounds.

Ligands

The preparations of the tetrahydrochlorides of *N*,*N*′-bis(2-pyridylmethyl)-1,2-ethanediamine (bispicen), *N*,*N*′-bis(2-pyridylmethyl)-1,3-propanediamine (bispictn) and *N*,*N*′-bis(2-pyridylmethyl)-*N*,*N*′-bis(methyl)-1,2-ethanediamine ($bispicMe_2en$) have been described before [11–13].

Complexes

μ-Carbonato-μ-oxobis[N,N′-bis(2-pyridylmethyl)-1,3-propanediamine]diiron(III,III) perchlorate trihydrate, $[(bispictn)Fe^{III}(O)(CO_3)Fe^{III}(bispictn)](ClO_4)_2\cdot 3H_2O$, (1). In a small conical flask, bispictn·4HCl·$2H_2O$ (133 mg, 0.30 mmol) was dissolved in water (3 ml). The solution was neutralized with a solution of sodium carbonate (2 M, ~0.5 ml). Nitrogen was bubbled through the solution for 5 min. Then an aqueous solution of iron(II) sulfate heptahydrate (83 mg, 0.30 mmol in 1 ml) was added. The nitrogen flow was continued for another 5 min, a solution of sodium perchlorate (1 M, 2 ml) was added to the yellow–green solution, and the flask was left in open air until the next day, when dark green crystals had separated. They were filtered and washed with a solution of sodium perchlorate (1 M) and with ethanol (96%). Yield 98 mg (69%). *Anal.* Calc. for $[Fe_2(C_{15}H_{20}N_4)_2OCO_3](ClO_4)_2\cdot 3H_2O$: C, 39.05; N, 11.75; H, 4.86; Cl, 7.45. Found: C, 39.14; N, 11.84; H, 4.63; Cl, 7.58%. The content of crystal water could vary. Large crystals were obtainable when the solution was oxidized more slowly (through a small inlet tube or a loose stopper).

μ-Carbonato-μ-oxobis[N,N′-bis(2-pyridylmethyl)-N,N′-bis(methyl)-1,2-ethanediamine]diiron(III,III) perchlorate trihydrate, $[(bispicMe_2en)Fe^{III}(O)(CO_3)Fe^{III}(bispicMe_2en)](ClO_4)_2\cdot 2H_2O$ (2). This compound was obtained by the same procedure as **1** except that $bispicMe_2en$·4HCl (125 mg, 0.30 mmol) was used instead of bispictn·4HCl·$2H_2O$. Yield 96 mg (65%). *Anal.* Calc. for $[Fe_2(C_{16}H_{22}N_4)_2OCO_3](ClO_4)_2\cdot 3H_2O$: C, 41.11; N, 11.62; H, 5.07; Cl, 7.36. Found: C, 40.61; N, 11.43; H, 5.14; Cl, 7.25%. The content of crystal water could vary.

μ-Sulfato-μ-oxobis[N,N′-bis(2-pyridylmethyl)-1,2-ethaneanediamine]diiron(III,III) perchlorate monohydrate, $[(bispicen)Fe^{III}(O)(SO_4)Fe^{III}(bispicen)](ClO_4)_2\cdot H_2O$ (3). This dark, yellow–green complex was obtained by exactly the same procedure as **1** except that bispictn·4HCl·$2H_2O$ was replaced by bispicen·4HCl·$2H_2O$ (127 mg, 0.30 mmol) and sodium carbonate was replaced by sodium hydroxide (2 M, ~0.5 ml). Yield 109 mg (79%). *Anal.* Calc. for $[Fe_2(C_{14}H_{18}N_4)_2OSO_4](ClO_4)_2\cdot H_2O$: C, 36.35; N, 12.10; H, 4.14; Cl, 7.77; S, 3.46. Found: C, 37.32; N, 12.10; H, 4.11; Cl, 7.58; S, 3.80%. The content of crystal water could vary.

μ-Sulfato-μ-oxobis[N,N′-bis(2-pyridylmethyl)-N,N′-bis(methyl)-1,2-ethanediamine]diiron(III,III) perchlorate dihydrate, $[(bispicMe_2en)Fe^{III}(O)(SO_4)Fe^{III}(bispicMe_2en)](ClO_4)_2\ 2H_2O$ (4). Flaky, yellow–green crystals were obtained by the same procedure as **3** except that $bispicMe_2en$·4HCl (125 mg, 0.30 mmol) was used instead of bispicen·4HCl·$2H_2O$. Yield 85 mg (57%). *Anal.* Calc. for $[Fe_2(C_{16}H_{22}N_4)_2OSO_4](ClO_4)_2\cdot 2H_2O$: C, 38.46; N, 11.21; H, 4.84; Cl. 7 09; S, 3.21. Found: C. 38.34; N, 11.05; H, 4.87; Cl, 7.31; S, 3 21%. The content of crystal water could vary.

Analyses

The microanalytical laboratory of the H.C. Ørsted Institute carried out the carbon, nitrogen, hydrogen and halogen analyses by standard methods.

Spectroscopy

Electronic spectra were recorded on a Cary model 118 spectrophotometer. The compounds were dissolved in water and acetonitrile.

Magnetochemistry

Magnetic susceptibility of powdered samples were measured by the Faraday method in the temperature range 4–300 K at a field strength of 1.3 T. The magnetic field was calibrated with Hg[Co(NCS)$_4$]. A detailed description of the instrumentation has been published elsewhere [14]. The molar susceptibilities were corrected for ligand diamagnetism using Pascal's constants.

Electrochemistry

Cyclic voltammograms were recorded on a BAS 100A electrochemical analyzer in acetonitrile, using a glassy-carbon working electrode, a Pt-wire auxiliary electrode and an Ag/AgCl reference electrode. Solutions were approximately 1 mM with 0.1 M tetraethylammonium perchlorate (TEAP) as supporting electrolyte.

X-ray structure determination

The structures of the complexes **1**, **2** and **4** were determined at room temperature on a Nicolet R3m/V diffractometer equipped with a molybdenum tube ($\lambda(K\alpha_1) = 0.70926$ Å; $\lambda(K\alpha_2) = 0.71354$ Å) and a graphite monochromator. Crystal data and experimental parameters are presented in Table 1. The data were corrected for Lorentz–polarization effects and absorption. The structures were solved by direct methods or Patterson techniques and refined by least-squares techniques; the programs used were from the SHELXTL system [15].

{[(Bispictn)Fe]$_2$(μ-O)(μ-CO$_3$)}(ClO$_4$)$_2$·3H$_2$O (1). The complex crystallizes in the triclinic space group $P\bar{1}$ with two binuclear cations in the unit cell. All hydrogen atoms were placed in calculated positions (C–H = 0.96 Å), while all non-hydrogen atoms were refined anisotropically. The final values of the conventional R factors were $R = 0.0531$, $R_w = 0.0717$, based on 2624 independent reflections with $I > 3\sigma(I)$. Positional parameters are listed in Table 2.

{[(BispicMe$_2$en)Fe]$_2$(μ-O)(μ-CO$_3$)}(ClO$_4$)$_2$·2H$_2$O (2). The complex crystallizes in the monoclinic space group $C2/c$ with eight binuclear cations in the unit cell. All hydrogen atoms were placed in calculated positions while the non-hydrogen atoms were refined anisotropically. The final values of the conventional R factors were, $R = 0.0634$, $R_w = 0.0844$, based on 3279 independent reflections with $I > 3\sigma(I)$. Positional parameters are given in Table 3.

{[(BispicMe$_2$en)Fe]$_2$(μ-O)(μ-SO$_4$)}(ClO$_4$)$_2$·2H$_2$O (4). The complex crystallizes in the orthorhombic space group $Pbca$ with eight binuclear cations in the unit cell. All hydrogen atoms were placed in calculated positions, and because of the paucity of data only Fe, Cl, S and O atoms were refined anisotropically while the other non-hydrogen atoms (C, N) were refined isotropically. The final values of the conventional R factors were, $R = 0.0682$, $R_w = 0.0687$, based on 1776 independent reflections with $I > 3\sigma(I)$. Positional parameters are given in Table 4.

Results and discussion

Syntheses

The (μ-oxo)(μ-carbonato)diiron(III) complexes **1** and **2** and the (μ-oxo)(μ-sulfato)diiron(III) complexes **3** and **4** were synthesized as perchlorate salts as described in 'Experimental'. The crystals obtained from the reaction mixture were analytically pure and of them the crystals of **1**, **2** and **4** were suitable for X-ray analysis. Hence, the structures of **1**, **2** and **4** could be determined by X-ray crystallography. Elemental analysis together with

TABLE 1. Crystallographic data for the complexes **1**, **2** and **4**

	1	**2**	**4**
Formula	$C_{31}H_{46}Cl_2Fe_2N_8O_{15}$	$C_{33}H_{48}Cl_2Fe_2N_8O_{14}$	$C_{32}H_{48}Cl_2Fe_2N_8O_{15}S$
a (Å)	12 552(3)	19.580(4)	16.049(3)
b (Å)	12 980(3)	13.442(3)	16.875(3)
c (Å)	15 016(3)	32 727(7)	31.325(6)
α (°)	88.49(3)	90	90
β (°)	68 57(3)	94 07(3)	90
γ (°)	64 56(3)	90	90
V (Å^3)	2031(4)	8592(3)	8484(3)
Z	2	8	8
Formula weight	953.4	963.4	999 4
Space group	$P\bar{1}$	$C2/c$	$Pbca$
T (°C)	22	22	22
μ (mm^{-1})	0.922	0.871	0.935
NO^a	3784	5620	5541
NO ($I > 3\sigma(I)$)	2624	3279	1776
R^b	0.0531	0.0634	0.0682
$R_w{}^c$	0.0717	0.0844	0.0687

[a] NO = no. of observed reflections. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$

TABLE 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for 1

	x	y	z	U_{eq}[a]
Fe(1)	1152(1)	92(1)	2650(1)	38(1)
O(1)	2314(5)	−1351(4)	2636(3)	43(3)
O(2)	−280(5)	233(4)	3838(4)	42(3)
N(1)	351(7)	−364(5)	1766(5)	42(4)
N(2)	2377(6)	81(6)	1165(4)	45(4)
N(3)	1867(7)	1021(6)	3233(5)	47(4)
N(4)	−71(7)	1993(6)	2548(5)	44(4)
Fe(2)	2096(1)	−2441(1)	3339(1)	42(1)
O(3)	293(5)	−1558(5)	4234(4)	46(3)
N(5)	1547(9)	−3225(6)	2434(5)	51(5)
N(6)	3909(7)	−3867(6)	2358(5)	55(4)
N(7)	2975(7)	−2210(6)	4265(5)	49(4)
N(8)	2131(7)	−3856(6)	4288(5)	51(4)
C(1)	−821(10)	−331(7)	2058(7)	52(5)
C(2)	−1181(10)	−786(8)	1481(8)	57(6)
C(3)	−294(13)	−1328(8)	551(9)	73(8)
C(4)	910(11)	−1348(8)	239(7)	61(6)
C(5)	1198(9)	−847(7)	841(6)	49(6)
C(6)	2457(9)	−839(8)	552(6)	53(5)
C(7)	3676(10)	−111(9)	1021(7)	70(6)
C(8)	3646(10)	826(10)	1643(7)	75(7)
C(9)	3274(9)	677(9)	2714(7)	66(6)
C(10)	1086(10)	2290(8)	3413(7)	62(6)
C(11)	299(9)	2714(8)	2790(6)	49(5)
C(12)	−49(11)	3808(8)	2531(8)	74(7)
C(13)	−833(11)	4162(9)	2040(8)	76(7)
C(14)	−1295(10)	3446(9)	1853(7)	62(6)
C(15)	−881(9)	2377(8)	2096(6)	55(6)
C(16)	340(11)	−3044(8)	2610(7)	56(6)
C(17)	47(12)	−3517(9)	1980(9)	72(7)
C(18)	1035(19)	−4205(12)	1153(11)	98(11)
C(19)	2267(15)	−4427(9)	965(8)	85(8)
C(20)	2519(11)	−3895(8)	1610(7)	59(6)
C(21)	3795(10)	−4016(8)	1445(7)	67(6)
C(22)	5058(10)	−3708(9)	2189(7)	76(6)
C(23)	5266(9)	−3590(9)	3101(8)	80(6)
C(24)	4330(10)	−2409(9)	3740(8)	72(6)
C(25)	2803(9)	−2828(8)	5110(6)	63(5)
C(26)	2626(9)	−3873(8)	4835(7)	56(5)
C(27)	2876(11)	−4747(10)	5466(8)	80(7)
C(28)	2614(13)	−5627(11)	5350(8)	97(8)
C(29)	2069(12)	−5620(10)	4693(9)	92(8)
C(30)	1854(10)	−4731(9)	4184(7)	70(7)
C(31)	−558(8)	−489(8)	4360(6)	35(5)
O(4)	−1671(5)	−170(5)	5001(4)	45(3)
Cl(1)	2655(2)	2614(2)	9462(2)	61(1)
O(5)	3404(10)	1807(11)	8638(9)	184(8)
O(6)	3445(8)	2864(7)	9803(5)	97(5)
O(7)	1946(11)	2216(1)	10156(8)	158(10)
O(8)	1848(11)	3602(8)	9246(8)	160(8)
Cl(2)	5526(4)	2931(3)	2220(4)	130(3)
O(9)	5375(15)	3673(12)	2954(10)	202(12)
O(10)	6133(14)	3242(11)	1312(11)	230(11)
O(11)	6170(15)	1810(10)	2176(11)	259(12)
O(12)	4292(16)	3219(16)	2354(13)	250(14)
O(1W)	7090(13)	8671(15)	4615(10)	233(13)
O(2W)	5266(16)	1038(18)	4059(13)	273(17)
O(3W)	6828(31)	8164(37)	3211(16)	543(50)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

TABLE 3 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for **2**

	x	y	z	U_{eq}[a]
Fe(1)	8796(1)	1313(1)	3773(1)	34(1)
O(1)	9018(3)	141(4)	3553(2)	37(2)
O(2)	8481(3)	926(4)	4295(2)	44(2)
N(1)	7760(4)	1410(6)	3490(3)	45(3)
N(2)	8903(4)	2178(6)	3204(3)	46(3)
N(3)	8753(4)	2913(6)	4010(3)	45(3)
N(4)	9803(4)	1657(6)	4042(3)	47(3)
Fe(2)	8867(1)	−1080(1)	3772(1)	33(1)
O(3)	8434(3)	−759(4)	4265(2)	42(2)
N(5)	9854(4)	−1215(5)	4107(3)	41(3)
N(6)	9509(4)	−1941(6)	3355(3)	45(3)
N(7)	8570(4)	−2670(5)	3921(3)	43(3)
N(8)	7927(4)	−1392(5)	3412(2)	38(3)
C(1)	7185(5)	1218(7)	3670(3)	48(4)
C(2)	6554(6)	1217(9)	3476(4)	66(5)
C(3)	6506(6)	1455(10)	3074(5)	81(6)
C(4)	7088(7)	1670(8)	2880(4)	72(5)
C(5)	7724(6)	1611(7)	3097(3)	52(4)
C(6)	8379(5)	1768(8)	2910(3)	56(4)
C(7)	8750(6)	3253(7)	3269(3)	55(4)
C(8)	9034(6)	3548(8)	3698(3)	62(5)
C(9)	9199(6)	2930(7)	4397(3)	55(4)
C(10)	9841(5)	2346(7)	4342(3)	47(4)
C(11)	10444(7)	2525(9)	4573(4)	70(5)
C(12)	11007(7)	1977(11)	4512(4)	78(6)
C(13)	10979(6)	1277(9)	4203(4)	66(5)
C(14)	10371(5)	1107(9)	3971(3)	55(4)
C(15)	9594(6)	2079(9)	3057(3)	75(5)
C(16)	8054(5)	3294(7)	4098(3)	56(4)
C(17)	9971(5)	−1084(7)	4515(3)	49(4)
C(18)	10627(6)	−1088(8)	4697(4)	60(4)
C(19)	11166(6)	−1270(8)	4468(5)	69(5)
C(20)	11047(6)	−1436(8)	4053(4)	64(5)
C(21)	10376(5)	−1406(7)	3879(3)	48(4)
C(22)	10207(5)	−1537(8)	3429(3)	58(4)
C(23)	9490(6)	−3000(7)	3478(4)	61(5)
C(24)	8799(6)	−3279(7)	3571(4)	62(5)
C(25)	7819(5)	−2655(7)	3926(3)	53(4)
C(26)	7507(5)	−2059(7)	3568(3)	44(4)
C(27)	6842(6)	−2206(8)	3397(4)	62(5)
C(28)	6600(6)	−1658(8)	3064(3)	56(4)
C(29)	7032(6)	−975(8)	2898(3)	59(4)
C(30)	7683(6)	−858(8)	3082(3)	51(4)
C(31)	9284(6)	−1785(9)	2917(3)	67(5)
C(32)	8862(6)	−3034(8)	4317(3)	63(4)
C(33)	8289(4)	80(7)	4444(3)	36(3)
O(4)	7991(4)	61(5)	4765(2)	63(3)
Cl(1)	6846(2)	4959(2)	3105(1)	65(1)
O(5)	6834(7)	3958(8)	3039(5)	179(8)
O(6)	7317(6)	5488(10)	2911(4)	152(6)
O(7)	6233(6)	5360(11)	3048(7)	242(12)
O(8)	6995(11)	5125(12)	3512(4)	231(11)
Cl(2)	4441(4)	388(6)	434(3)	81(3)
O(9)	4353(7)	1310(9)	460(5)	66(6)
O(10)	4812(17)	120(16)	770(9)	164(15)
O(11)	4834(36)	86(40)	138(13)	266(36)
O(12)	3859(19)	−96(21)	371(19)	304(33)
Cl(3)	5000	22(4)	2500	118(3)
O(13)	5000	968(9)	2500	123(7)
O(14)	5740(11)	−47(12)	2376(6)	235(8)
O(15)	4767(10)	−230(12)	2025(6)	218(7)
O(16)	5000	−823(23)	2500	228(11)
O(1W)	2858(5)	1708(8)	180(3)	115(5)
O(2W)	2744(5)	8431(9)	66(4)	142(6)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

TABLE 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for **4**

	x	y	z	U_{eq}[a]
Fe(1)	603(2)	7019(2)	3396(1)	28(1)
Fe(2)	−802(1)	7078(2)	4166(1)	27(1)
N(1)	723(9)	5766(8)	3323(5)	36(4)
N(2)	283(9)	6779(8)	2720(4)	33(4)
N(3)	1862(8)	7260(9)	3077(5)	38(4)
N(4)	681(10)	8277(8)	3320(4)	34(4)
N(5)	−961(8)	5798(9)	4230(5)	29(4)
N(6)	−1415(8)	6892(9)	4805(5)	37(4)
N(7)	−2130(8)	7321(8)	4000(4)	25(4)
N(8)	−904(9)	8347(9)	4243(5)	32(4)
O(1)	−433(6)	7049(7)	3623(3)	26(4)
O(2)	1279(6)	6956(8)	3923(3)	38(5)
O(3)	263(6)	7060(8)	4487(3)	37(5)
O(4)	1662(7)	6644(9)	4631(4)	54(6)
O(5)	1397(7)	7989(9)	4435(4)	66(6)
S(1)	1174(3)	7171(3)	4381(2)	28(2)
C(11)	1092(10)	5259(11)	3600(6)	37(5)
C(12)	1090(11)	4433(11)	3554(6)	41(6)
C(13)	629(12)	4134(13)	3212(6)	53(6)
C(14)	216(12)	4638(12)	2942(6)	47(6)
C(15)	281(11)	5446(11)	2996(6)	34(5)
C(16)	−174(11)	6013(10)	2721(6)	39(5)
C(17)	1053(11)	6742(12)	2467(6)	47(6)
C(18)	−290(12)	7376(12)	2531(6)	60(7)
C(21)	29(12)	8769(11)	3328(6)	44(6)
C(22)	109(11)	9590(11)	3353(6)	39(5)
C(23)	925(12)	9873(13)	3355(6)	53(6)
C(24)	1585(13)	9393(13)	3321(6)	55(7)
C(25)	1473(12)	8572(12)	3296(6)	37(6)
C(26)	2157(10)	8015(12)	3272(6)	43(5)
C(27)	1662(11)	7354(11)	2619(6)	48(6)
C(28)	2485(11)	6614(11)	3142(6)	52(6)
C(31)	−927(11)	5294(12)	3915(6)	46(6)
C(32)	−927(12)	4470(12)	3985(7)	53(7)
C(33)	−960(11)	4216(13)	4407(7)	55(6)
C(34)	−1018(10)	4725(12)	4732(6)	43(6)
C(35)	−978(11)	5529(11)	4639(6)	32(5)
C(36)	−1047(12)	6169(11)	4970(6)	53(6)
C(37)	−2319(10)	6761(11)	4711(5)	38(6)
C(38)	−1303(11)	7535(11)	5124(6)	52(6)
C(41)	−354(12)	8815(12)	4442(6)	46(6)
C(42)	−478(12)	9647(12)	4459(6)	48(6)
C(43)	−1141(13)	9967(14)	4260(7)	69(8)
C(44)	−1722(11)	9493(11)	4059(6)	40(6)
C(45)	−1576(11)	8680(11)	4036(6)	34(5)
C(46)	−2116(10)	8120(10)	3790(6)	38(5)
C(47)	−2634(10)	7352(10)	4401(6)	38(6)
C(48)	−2458(10)	6737(10)	3698(6)	44(6)
Cl(1)	60(4)	2031(4)	3818(2)	61(3)
O(6)	−251(15)	1487(14)	3529(7)	178(14)
O(7)	−398(14)	2650(12)	3790(12)	300(25)
O(8)	839(11)	2253(15)	3738(6)	162(12)
O(9)	0(19)	1670(19)	4180(7)	282(21)
Cl(2)	2491(6)	4675(5)	2173(2)	71(3)
O(10)	2457(21)	4990(18)	2527(8)	291(22)
O(11)	1990(21)	4073(26)	2135(13)	306(29)
O(12)	3186(16)	4314(22)	2098(12)	289(26)
O(13)	2218(30)	5142(21)	1912(9)	324(29)
O(1W)	6959(10)	821(10)	722(6)	121(9)
O(2W)	7529(9)	4245(11)	709(5)	111(9)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

spectral and magnetic data are consistent with the (μ-oxo)(μ-sulfato)diiron(III) structure for **3**.

Description of the structures

{[(Bispictn)Fe]$_2$(μ-O)(μ-CO$_3$)}(ClO$_4$)$_2$·3H$_2$O (1)

The structure of the complex consists of {[(bispictn)Fe]$_2$(μ-O)(μ-CO$_3$)}$^{2+}$ cations, perchlorate ions and water molecules. A view of the cation is given in Fig. 1. Principal bond distances and angles are listed in Table 5.

The geometry about each iron(III) center is roughly octahedral, with the ligand binding the iron centers in *cis*-β fashion and oxo and carbonato groups bridging them. It is noteworthy that the ligand binds the chrom-

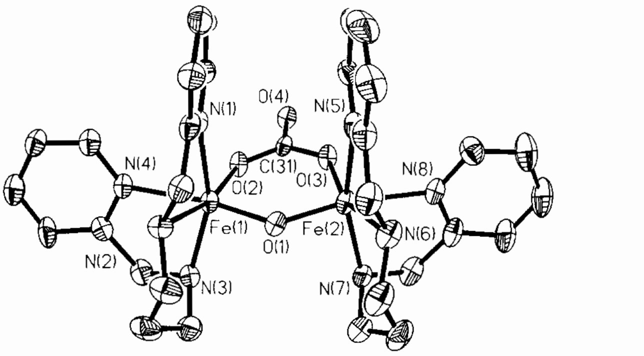

Fig. 1. View of the {[(bispictn)Fe]$_2$(μ-O)(μ-CO$_3$)}$^{2+}$ cation in the crystal of the perchlorate salt **1**.

TABLE 5. Selected bond lengths (Å) and bond angles (°) for **1**

Bond lengths (Å)			
Fe(1)–O(1)	1 808(5)	Fe(1)–O(2)	1.960(5)
Fe(1)–N(1)	2.156(10)	Fe(1)–N(2)	2.193(6)
Fe(1)–N(3)	2.142(10)	Fe(1)–N(4)	2.317(6)
Fe(1)–Fe(2)	3.264(2)	Fe(2)–O(1)	1.798(6)
Fe(2)–O(3)	1.968(5)	Fe(2)–N(5)	2.173(11)
Fe(2)–N(6)	2.202(6)	Fe(2)–N(7)	2 161(10)
Fe(2)–N(8)	2.290(8)		
Bond angles (°)			
O(1)–Fe(1)–O(2)	99.2(2)	O(1)–Fe(1)–N(1)	97 7(3)
O(2)–Fe(1)–N(1)	91.5(3)	O(1)–Fe(1)–N(2)	90 3(2)
O(2)–Fe(1)–N(2)	165.3(3)	N(1)–Fe(1)–N(2)	76 0(3)
O(1)–Fe(1)–N(3)	97.7(3)	O(2)–Fe(1)–N(3)	98.5(3)
N(1)–Fe(1)–N(3)	160.0(3)	N(2)–Fe(1)–N(3)	91 3(3)
O(1)–Fe(1)–N(4)	171 3(3)	O(2)–Fe(1)–N(4)	88 4(2)
N(1)–Fe(1)–N(4)	86.3(3)	N(2)–Fe(1)–N(4)	83 2(2)
N(3)–Fe(1)–N(4)	76.8(3)	Fe(1)–O(1)–Fe(2)	129 7(3)
O(1)–Fe(2)–O(3)	100 3(2)	O(1)–Fe(2)–N(5)	99 2(3)
O(3)–Fe(2)–N(5)	91.0(3)	O(3)–Fe(2)–N(6)	94 4(2)
O(3)–Fe(2)–N(6)	161.4(3)	N(5)–Fe(2)–N(6)	75.3(3)
O(1)–Fe(2)–N(7)	94.2(3)	O(3)–Fe(2)–N(7)	97.9(3)
N(5)–Fe(2)–N(7)	162.4(3)	N(6)–Fe(2)–N(7)	92 3(3)
O(1)–Fe(2)–N(8)	169.6(3)	O(3)–Fe(2)–N(8)	85 7(2)
N(5)–Fe(2)–N(8)	89.1(3)	N(6)–Fe(2)–N(8)	81.7(2)
N(7)–Fe(2)–N(8)	76.5(3)		

ium(III) centers in $\{[(\text{bispictn})\text{Cr}]_2(\mu\text{-OH})_2\}^{4+}$ also in the *cis-β* form [12] whereas in $\{[(\text{bispictn})\text{Mn}]_2(\mu\text{-O})_2\}^{3+}$ in the *cis-α* form [16]. Although the complex could be expected to have two-fold symmetry about the Fe–O–Fe unit, bisecting the bridging carbonato group, such geometry is not observed; hence, the (μ-oxo)(μ-carbonato)diiron(III) core contains two crystallographically independent iron centers. However, the bond distances and angles associated with the two iron centers do not differ considerably. The axial Fe–N (pyridyl) and Fe–N (secondary amino) bonds are shorter than the respective equatorial bonds demonstrating *trans* influence of the bridging oxo and carbonato ligands. The Fe–O–Fe bond angle is 129.7(3)° and the Fe···Fe separation is 3.264(2) Å. The structural features are comparable to those of the analagous diiron(III) complexes of tris(2-pyridylmethyl)amine (tmpa) [6b] and *N,N'*-bis(2-pyridylmethyl)ethane-1,2-diamine (bispicen) [10] The perchlorate ions are approximately tetrahedral with Cl–O distances in the range 1.354(13)–1.441(15) Å and the O–Cl–O bond angles in the range 102.7(11)–110.3(13)° similar to other perchlorate complexes [17].

$\{[(\text{BispicMe}_2\text{en})\text{Fe}]_2(\mu\text{-O})(\mu\text{-CO}_3)\}(\text{ClO}_4)_2\cdot 2H_2O$ (2)

The structure of this complex consists of $\{[(\text{bispicMe}_2\text{en})\text{Fe}](\mu\text{-O})(\mu\text{-CO}_3)\}^{2+}$ cations, perchlorate anions and water molecules. A view of the cation is given in Fig. 2. The principal bond distances and angles are listed in Table 6

The structure of the cation also contains the μ-oxo,μ-carbonatodiiron(III) core The geometry about each iron is roughly octahedral, with axial ligation provided by the pyridine groups and the equatorial ligation by the amine nitrogens and bridging oxo and carbonato groups. The ligand binds the iron centers in the *cis-α* form as does the closely related ligand bispicen in the analogous $\{[(\text{bispicen})\text{Fe}]_2(\mu\text{-O})(\mu\text{-CO}_3)\}^{2+}$ cation [10]. The Fe–O–Fe angle is 125.5(3)° and the Fe···Fe separation is 3.220(2) Å. The Fe–O–Fe angle and Fe···Fe separations are somewhat shorter than those of 125.9° and 3.241(2) Å in $\{[(\text{bispicen})\text{Fe}]_2(\mu\text{-O})(\mu\text{-CO}_3)\}^{2+}$ but are very close to those of 125 4° and 3.196 Å, respectively, in $\{[(\text{tmpa})\text{Fe}]_2(\mu\text{-O})(\mu\text{-CO}_3)\}^{2+}$ [6b, 10]. This complex could also be expected to have two-fold symmetry about the Fe–O–Fe unit bisecting the bridging carbonate, but here again the iron centers are crystallographically independent. The metrical parameters at the two iron centers are not statistically different, however. The *trans* influence of the bridging oxo and carbonato ligands is evident from the observed shorter axial Fe–N bonds in comparison to the equatorial Fe–N bonds. The N-methyl groups are disposed *trans* with respect to the rectangular plane defined by the coordinating oxo group, carbonato oxygen and the tertiary amino nitrogens. The asymmetric unit contains two perchlorate ions in general positions and another perchlorate ion on the two-fold axis together with the complex cation. One of the perchlorates in the general positions was refined with a site occupancy factor of 0.5. The perchlorate on the two-fold axis was highly disorded and could be refined with a total of six oxygens

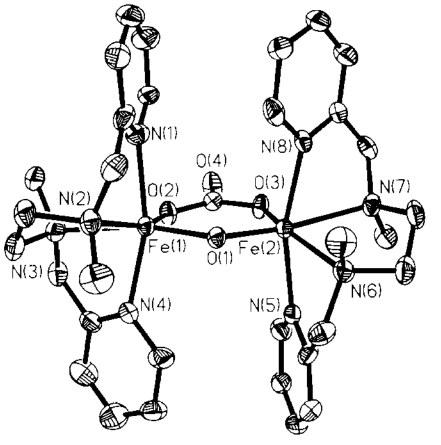

Fig 2 View of the $\{[(\text{bispicMe}_2\text{en})\text{Fe}]_2(\mu\text{-O})(\mu\text{-CO}_3)\}^{2+}$ cation in the crystals of the perchlorate salt **2**

TABLE 6 Selected bond lengths (Å) and bond angles (°) for **2**

Bond lengths (Å)			
Fe(1)–O(1)	1.798(6)	Fe(1)–O(2)	1.930(6)
Fe(1)–N(1)	2.173(8)	Fe(1)–N(2)	2.217(8)
Fe(1)–N(3)	2.289(8)	Fe(1)–N(4)	2.154(8)
Fe(1)–Fe(2)	3.220(2)	Fe(2)–O(1)	1.823(6)
Fe(2)–O(3)	1.925(7)	Fe(2)–N(5)	2.162(8)
Fe(2)–N(6)	2.242(8)	Fe(2)–N(7)	2.277(8)
Fe(2)–N(8)	2.154(8)		
Bond angles (°)			
O(1)–Fe(1)–O(2)	102.7(3)	O(1)–Fe(1)–N(1)	97.3(3)
O(2)–Fe(1)–N(1)	92.7(3)	O(1)–Fe(1)–N(2)	94.8(3)
O(2)–Fe(1)–N(2)	160.2(3)	N(1)–Fe(1)–N(2)	75.6(3)
O(1)–Fe(1)–N(3)	166.9(3)	O(2)–Fe(1)–N(3)	86.1(3)
N(1)–Fe(1)–N(3)	91.9(3)	N(2)–Fe(1)–N(3)	78.4(3)
O(1)–Fe(1)–N(4)	96.4(3)	O(2)–Fe(1)–N(4)	92.1(3)
N(1)–Fe(1)–N(4)	164.2(3)	N(2)–Fe(1)–N(4)	95.3(3)
N(3)–Fe(1)–N(4)	73.4(3)	Fe(1)–O(1)–Fe(2)	125.5(3)
O(1)–Fe(2)–O(3)	102.8(3)	O(1)–Fe(2)–N(5)	96.4(3)
O(3)–Fe(2)–N(5)	91.3(3)	O(1)–Fe(2)–N(6)	96.4(3)
O(3)–Fe(2)–N(6)	157.7(3)	N(5)–Fe(2)–N(6)	75.3(3)
O(1)–Fe(2)–N(7)	168.6(3)	O(3)–Fe(2)–N(7)	84.0(3)
N(5)–Fe(2)–N(7)	92.5(3)	N(6)–Fe(2)–N(7)	79.0(3)
O(1)–Fe(2)–N(8)	96.7(3)	O(3)–Fe(2)–N(8)	95.3(3)
N(5)–Fe(2)–N(8)	163.7(3)	N(6)–Fe(2)–N(8)	93.5(3)
N(7)–Fe(2)–N(8)	73.4(3)		

$\{[(\text{BispicMe}_2\text{en})\text{Fe}]_2(\mu\text{-O})(\mu\text{-SO}_4)\}(\text{ClO}_4)_2\cdot 2H_2O$ (4)

The structure of this complex consists of $\{[(\text{bispicMe}_2\text{en})\text{Fe}]_2(\mu\text{-O})(\mu\text{-SO}_4)\}^{2+}$ cations, perchlorate anions and water molecules. A view of the cation is given in Fig. 3. The principal bond distances and angles are listed in Table 7.

The structure of the cation is substantially similar to that of **2** above, but the complex contains a μ-sulfato group in place of the μ-carbonato The geometry about each iron is again roughly octahedral, with axial ligation provided by the pyridine groups and the equatorial ligation by the amine nitrogens and bridging oxo and carbonato groups. As in complex **2**, the ligand binds the iron centers in the *cis-α* form. The Fe–O–Fe angle of 132.4(5)° is more open in the μ-sulfato complex than in the μ-carbonato complexes **1** and **2** above, and the Fe···Fe separation of 3 306(2) Å is larger than in those complexes; both of these observations result from the longer bridging S–O bonds in the SO_4 group of 1.488(12) and 1.511(11) Å relative to the C–O distances of 1.302(11) and 1.311(11) Å in **2**. With these exceptions, the structure of the cation in **4** is substantially similar to that in **2**, including the observation of shorter axial Fe–N bonds than equatorial Fe–N bonds.

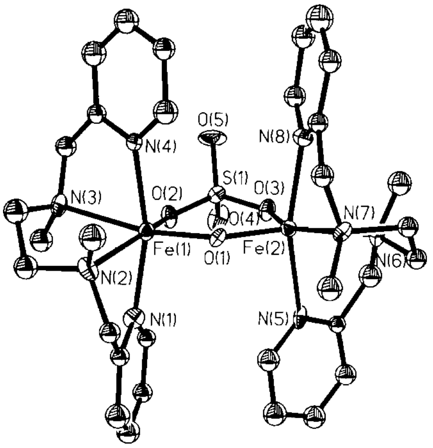

Fig 3. View of the $\{[(\text{bispicMe}_2\text{en})\text{Fe}]_2(\mu\text{-O})(\mu\text{-SO}_4)\}^{2+}$ cation in the crystals of the perchlorate salt **4**.

TABLE 7. Selected bond lengths (Å) and bond angles (°) for **4**

Bond lengths (Å)			
Fe(1)–N(1)	2.135(14)	Fe(1)–N(2)	2.214(14)
Fe(1)–N(3)	2 290(14)	Fe(1)–N(4)	2.141(14)
Fe(1)–O(1)	1.810(9)	Fe(1)–O(2)	1.980(11)
Fe(2)–N(5)	2 185(15)	Fe(2)–N(6)	2.251(14)
Fe(2)–N(7)	2.232(13)	Fe(2)–N(8)	2.161(15)
Fe(2)–O(1)	1.803(9)	Fe(2)–O(3)	1.982(10)
Fe(1)–Fe(2)	3.306		
Bond angles (°)			
N(1)–Fe(1)–N(2)	74.8(5)	N(1)–Fe(1)–N(3)	92.9(5)
N(2)–Fe(1)–N(3)	79 7(5)	N(1)–Fe(1)–N(4)	164.9(6)
N(2)–Fe(1)–N(4)	95 1(5)	N(3)–Fe(1)–N(4)	74.0(6)
N(1)–Fe(1)–O(1)	98 7(6)	N(2)–Fe(1)–O(1)	99.7(5)
N(3)–Fe(1)–O(1)	167.8(6)	N(4)–Fe(1)–O(1)	94.0(6)
N(1)–Fe(1)–O(2)	89 3(6)	N(2)–Fe(1)–O(2)	156.2(5)
N(3)–Fe(1)–O(2)	83.7(5)	N(4)–Fe(1)–O(2)	96.5(6)
O(1)–Fe(1)–O(2)	100.1(4)	N(5)–Fe(2)–N(6)	74.3(6)
N(5)–Fe(2)–N(7)	95.2(5)	N(6)–Fe(2)–N(7)	79.4(5)
N(5)–Fe(2)–N(8)	163.9(5)	N(6)–Fe(2)–N(8)	90.4(6)
N(7)–Fe(2)–N(8)	76 8(5)	N(5)–Fe(2)–O(1)	95.6(6)
N(6)–Fe(2)–O(1)	168.1(5)	N(7)–Fe(2)–O(1)	95.6(5)
N(8)–Fe(2)–O(1)	99.0(6)	N(5)–Fe(2)–O(3)	92.3(5)
N(6)–Fe(2)–O(3)	85 7(5)	N(7)–Fe(2)–O(3)	160.8(5)
N(8)–Fe(2)–O(3)	91.4(6)	O(1)–Fe(2)–O(3)	101.2(4)

Electronic spectroscopy

As is shown for the $(\mu\text{-O})(\mu\text{-CO}_3)$ complexes **1** and **2** in Fig. 4 and for the $(\mu\text{-O})(\mu\text{-SO}_4)$ complexes **3** and **4** in Fig. 5, the complexes exhibit relatively rich spectral features in the region 300–550 nm; this result is in contrast to that observed for singly-bridged, linear μ-oxodiiron(III) complexes, which exhibit only a single band (near 355 nm) in this region [10]. The electronic spectra for the complexes are summarized in Table 8.

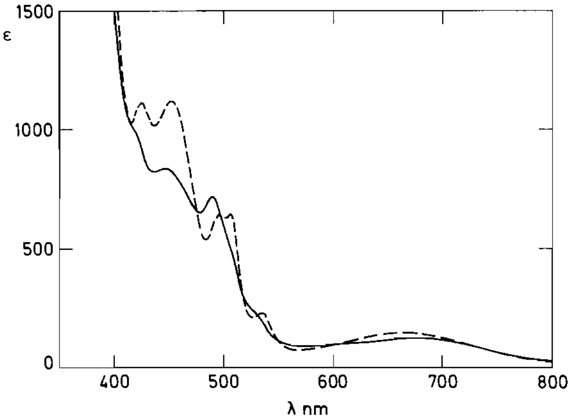

Fig. 4 The electronic spectra (visible region) in water of $\{[(\text{bispictn})\text{Fe}]_2(\mu\text{-O})(\mu\text{-CO}_3)\}(\text{ClO}_4)_2\ 3\text{H}_2\text{O}$ (**1**) (——) and $\{[(\text{bispicMe}_2\text{en})\text{Fe}]_2(\mu\text{-O})(\mu\text{-CO}_3)\}(\text{ClO}_4)_2\ 3\text{H}_2\text{O}$ (**2**) (– – –)

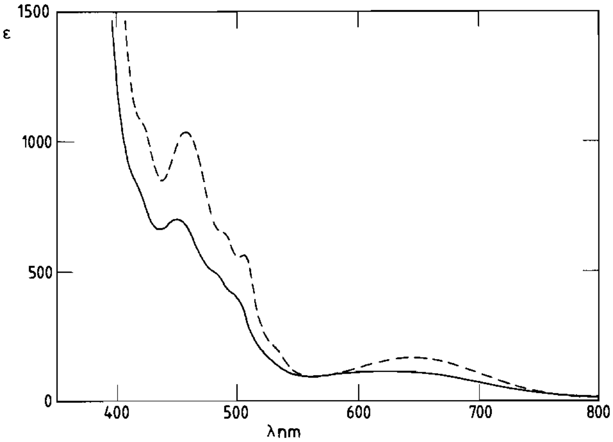

Fig. 5. The electronic spectra (visible region) in water of $\{[(\text{bispicen})\text{Fe}]_2(\mu\text{-O})(\mu\text{-SO}_4)\}(\text{ClO}_4)_2\ \text{H}_2\text{O}$ (**3**) (——) and $\{[(\text{bispicMe}_2\text{en})\text{Fe}]_2(\mu\text{-O})(\mu\text{-SO}_4)\}(\text{ClO}_4)_2\ 2\text{H}_2\text{O}$ (**4**) (– – –).

TABLE 8 Electronic absorption spectra of the complexes

Complex	Ligand	λ (nm) (ϵ (M^{-1} cm^{-1}))
(μ-Oxo)(μ-carbonato) complexes		
1^a	bispictn	657 (167), 605 (sh 154), 525 (sh 317), 492 (762), 440 (sh 920), 420 (1131), 360 (sh 5713), 315 (8726), 246 (20091)
1^b	bispictn	677 (123), 610 (sh 99), 530 (sh 225), 491 (718), 447 (838), 420 (sh 979), 360 (sh 4132), 318 (6570), 265 (sh 15050), 255 (17938)
2^a	bispicMe$_2$en	656 (143), 580 (sh 92), 536 (254), 506 (664), 455 (sh 946), 430 (1189), 360 (sh 5725), 320 (sh 7315), 274 (23188)
2^b	bispicMe$_2$en	667 (143), 580 (sh 76), 536 (226), 507 (647), 497 (642), 453 (1124), 426 (1114), 360 (sh 6778), 337 (8384), 285 (sh 8973), 247 (24258)
(μ-Oxo)(μ-sulfato) complexes		
3^a	bispicen	635 (138), 520 (sh 203), 498 (sh 479), 487 (523), 442 (sh 808), 420 (994), 365 (sh 5388), 328 (9050), 245 (20581)
3^b	bispicen	627 (112), 520 (sh 188), 495 (sh 420), 475 (sh 520), 450 (704), 415 (sh 853), 360 (sh 4593), 315 (8617), 275 (sh 12264), 252 (20031)
4^a	bispicMe$_2$en	635 (166), 530 (199), 503 (472), 493 (504), 454 (984), 426 (1164), 365 (sh 6569), 320 (11097), 248 (23288)
4^b	bispicMe$_2$en	647 (166), 530 (sh 212), 506 (563), 490 (sh 648), 457 (1040), 420 (sh 1080), 362 (sh 7119), 333 (10481), 275 (sh 11845), 251 (23247)

[a] In acetonitrile [b] In water

As might be anticipated, the electronic spectra of these doubly-bridged iron(III) complexes are very similar to that of azidomethemerythrin [18].

Electrochemistry

The cyclic voltammograms of **1** and **4** consist of an irreversible reduction peak at −0.735 and −0.665 V, respectively, versus an Ag/AgCl reference electrode in acetonitrile solvent revealing an irreversible reduction process. The complex **2** also exhibits an irreversible reduction peak at −0.660 V at lower scan rates (<100 mV/s), however at scan rates higher than 100 mV/s, an oxidation peak is also observed with a peak-to-peak separation of *c.* 150 mV corresponding to the quasi-reversible $Fe_2(III/III) \leftrightarrow Fe_2(II/III)$ redox process. The quasi-reversible redox behaviour exhibited by **2** is in contrast to that of **1** and the closely related $\{[(bispicen)Fe]_2(\mu\text{-}O)(\mu\text{-}CO_3)\}I_2 \cdot 6H_2O$ [10]; it is, however, comparable to that of the oxo-bridged diiron(III) complex $\{[(Me_3TACN)Fe]_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2\}(PF_6)_2$, (where Me_3TACN = 1,4,7-trimethyl-1,4,7-triazacyclononane), which exhibits a quasi-reversible redox couple in the same potential range (−0.374 V versus saturated calomel electrode) [6b].

Magnetic properties

The temperature dependence of the magnetic susceptibility of powdered samples of the binuclear complexes **2** and **4** was measured in the range 4–296 K. As shown in Fig. 6, for the μ-O,μ-SO_4 complex **4**, the effective magnetic moment at room temperature is approximately 2.8 μ_B, declining monotonically to a value of 0.6 μ_B at 4 K. These properties are consistent with the existence of a singlet ground state in the complex. The properties of complex **2** are qualitatively similar to those shown in Fig. 6.

The temperature dependence of the magnetic susceptibility was approximated by the expression

$$\chi_{\mathrm{mol,\,exp}} \simeq \chi_{\mathrm{mol,\,calc}} = -\frac{N}{H}\,\frac{\sum_i \frac{\partial E_i}{\partial H}\exp(-E_i/kT)}{\sum_i \exp(-E_i/kT)} + K + C/T$$

by minimization of the function within the framework of regression analysis. The term *C*/*T* accounts for the presence of small quantities of (presumably monomeric) paramagnetic impurities,

$$\sum_T \frac{[\chi'_{\mathrm{mol,\,exp}}(T) - \chi'_{\mathrm{mol,\,calc}}(T)]^2}{\sigma^2(\chi') + \left(\frac{\partial\chi}{\partial T}\right)^2 \sigma^2(T)}$$

while *K* accounts for temperature independent paramagnetism (*TIP*) and for any minor deviations in the

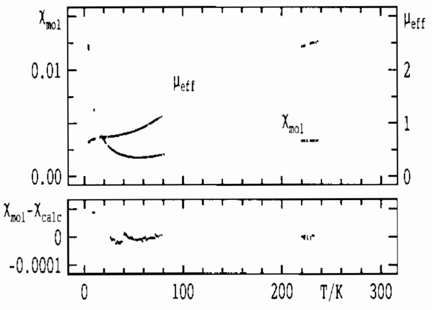

Fig. 6 Magnetic susceptibility (left scale) and effective magnetic moment (right scale) for the complex $\{[(bispicMe_2en)Fe]_2(\mu\text{-}O)(\mu\text{-}SO_4)\}(ClO_4)_2\ 2H_2O$ (**4**) The lower curve shows the fit of the susceptibility data to the values calculated using the parameters g = 2 020, $2J$ = −210 4 cm^{-1}

corrections for the diamagnetism of the atoms. The energies E_i of the various components of the ground-state manifold were obtained using the Hamiltonian operator

$$\mathscr{H} = -2J(\hat{S}_1\ \hat{S}_2)+g_1\beta\hat{S}_1\ \hat{H}+g_2\beta\hat{S}_2\ \hat{H}$$

where we have assumed that the g values for the two iron atoms are identical and isotropic, i.e. we have set $g_1 = g_2$. Since we have two $S=5/2$ centers in the complexes, the Heisenberg term $-2J(\hat{S}_1 \cdot \hat{S}_2)$ in the Hamiltonian gives rise to states with $S=0$, 1, 2, 3, 4, 5, with energies of 0, $-2J$, $-6J$, $-12J$, $-20J$ and $-30J$, respectively. For the μ-oxo,μ-SO_4 complex **4**, the fitting leads to a value of $2J = -210.4(9)$ cm^{-1} with $g = 2.020(5)$, $K = 5.49 \times 10^{-4}$, and impurities equivalent to 1.35% of monomeric iron(III). For the μ-O,μ-CO_3 complex **2** the corresponding values are $2J = -222.8(8)$ cm^{-1}, $g = 2.074(5)$, $K = 2.6 \times 10^{-6}$ and 0.3% monomer. These J values of -105.2 and -111.4 cm^{-1} are very similar to the value of -113.6 cm^{-1} reported for the analogous μ-O, μ-CO_3 complex with bispicen in place of Me$_2$bispicen [10], and to values in the range -108 to -118 cm^{-1} reported for other similar doubly-bridged iron(III) complexes [9].

Supplementary material

Tables S1, S2 and S3 (hydrogen atom parameters for complexes **1**, **2** and **4**); S4, S5 and S6 (anisotropic thermal parameters for complexes **1**, **2** and **4**); S7, S8 and S9 (listings of observed and calculated structure amplitudes for complexes **1**, **2** and **4**) are available from D.J.H. on request

Acknowledgements

This work was supported by the National Science Foundation through Grant No. CHE-9007607 (to D.J.H.) and by the Scientific Affairs Division, North Atlantic Treaty Organization (NATO) through Grant No. CRG 910277 (to D.J.H., K.M. and J.G.).

References

1 (a) R G Wilkins and P.C. Harrington, *Adv Inorg Biochem*, *5* (1983) 51; (b) R E Stenkamp, L C Sieker, L H Jensen and J Sanders-Loehr, *Nature (London)*, *291* (1981) 263, (c) R.E. Stenkamp, L.C. Sieker and L H Jensen, *J Am Chem Soc*, *106* (1984) 618.

2 S. Sheriff, W A Hendrickson and J L Smith, *J Mol Biol*, *197* (1987) 273

3 (a) P Reichard and A Ehrenberg, *Science (Washington, DC)*, *221* (1983) 514, (b) D -M Sjoberg and A Graslund, *Adv Inorg Biochem*, *5* (1983) 87.

4 B C Anatanaitis and P Aisen, *Adv Inorg Biochem*, *5* (1983) 111

5 W H. Armstrong, A. Spool, G C Papaefthymiou, R.B. Frankel and S J Lippard, *J Am Chem Soc*, *106* (1984) 3653

6 (a) K. Wieghardt, K. Pohl and W Gebert, *Angew. Chem., Int Ed Engl*, *22* (1983) 727, (b) J R Hartman, R.L. Rardin, P Chaudhuri, K Pohl, K Wieghardt, B Nuber, J. Weiss, G C. Papaefthymiou, R.B. Frankel and S J Lippard, *J Am Chem Soc*, *109* (1987) 7387

7 H Toftlund, K S. Murray, P R Zwack, L F. Taylor and O P Anderson, *J. Chem Soc, Chem Commun*, (1986) 191

8 P. Gomez-Romero, N Casan-Pastor, A Ben-Hussain and G B Jameson, *J. Am Chem Soc*, *110* (1988) 1988

9 (a) S Yan, L. Que, Jr , L F Taylor and O P. Anderson, *J Am Chem Soc*, *110* (1988) 5222, (b) R E Norman, S Yan, L Que, Jr , G Backes, J Ling, J Sanders-Loehr, J H Zhang and C J. O'Connor, *J. Am Chem Soc*, *112* (1990) 1554; (c) R.E Norman, R C. Holz, S. Menage and L Que, Jr , *Inorg Chem*, *29* (1990) 4629.

10 N. Arulsamy, D J Hodgson and J Glerup, *Inorg Chim Acta*, *209* (1993) 61

11 K Michelsen, *Acta Chem Scand, Ser A*, *31* (1977) 429

12 H.R. Fischer, S J Hodgson, K Michelsen and E. Pedersen, *Inorg Chim Acta*, *88* (1984) 143

13 J. Glerup, P.A. Goodson, A Hazell, D J Hodgson, C.J. McKenzie, K Michelsen, U Rychlewska and H. Toftlund, submitted for publication; H Toftlund, E Pedersen and S. Yde-Andersen, *Acta Chem Scand Ser A*, *38* (1984) 693

14 E Pedersen, *Acta Chem Scand*, *26* (1972) 333, J Josephsen and E. Pedersen, *Inorg Chem*, *16* (1977) 2534

15 G M. Sheldrick, *SHELXTL-Plus Crystallographic System*, Version 2, Nicolet XRD Corp.; Madison, WI, 1987.

16 P.A. Goodson, J. Glerup, D J Hodgson, K Michelsen and E Pedersen, *Inorg Chem*, *30* (1991) 4909

17 J Glerup, P.A Goodson, D J Hodgson, K Michelsen, K M Nielsen and H Weihe, *Inorg Chem*, *31* (1992) 4611, M S Haddad, S R Wilson, D J Hodgson and D N. Hendrickson, *J Am Chem Soc*, *103* (1981) 384, and refs. therein.

18 K Garbett, D W. Darnell, I M. Klotz and R.J P Williams, *Arch Biochem Biophys*, *103* (1969) 419