

# Mononuclear and binuclear oxo-bridged iron(III) complexes of *N,N'*-bis(2-pyridylmethyl)ethane-1,2-diamine (bispicen)

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## Abstract

The syntheses and characterization of a series of iron(III) complexes of the ligand *N,N'*-bis(2-pyridylmethyl)ethane-1,2-diamine (bispicen),  $C_{14}H_{18}N_4$  are described. The monomeric complexes [(bispicen)FeCl<sub>2</sub>]ClO<sub>4</sub> (**1**) and the corresponding chloride salt [(bispicen)FeCl<sub>2</sub>]Cl (**1a**) have been isolated and the structure of the perchlorate salt (**1**) has been determined from three-dimensional crystallographic data. The complex crystallizes in space group  $P2_1/c$  of the monoclinic system with four mononuclear species in a cell of dimensions  $a = 7.323(2)$ ,  $b = 14.370(3)$ ,  $c = 18.103(4)$  Å,  $\beta = 90.71(2)^\circ$ . The structure has been refined to a final  $R$  factor of 0.0496 based on 2948 observed independent reflections. The central iron(III) atom is pseudo-octahedrally bonded to the four nitrogen atoms of the ligand and to two *cis* chloride ligands. The  $\mu$ -oxodiron(III) complex {[(bispicen)(Cl)Fe]<sub>2</sub>( $\mu$ -O)}(I<sub>3</sub>)<sub>2</sub> (**2**),  $C_{28}H_{36}Cl_2Fe_2I_6N_8O$ , crystallizes in space group  $P2_1/n$  of the monoclinic system with two binuclear species in a cell of dimensions  $a = 8.570(2)$ ,  $b = 14.756(3)$ ,  $c = 17.083(3)$  Å,  $\beta = 99.68(2)^\circ$ . The structure has been refined to a final  $R$  factor of 0.0417 based on 2272 observed independent reflections. The complex contains a linear Fe–O–Fe unit with Fe–O and Fe···Fe separations of 1.798(1) and 3.596(2) Å, respectively. The  $\mu$ -oxo,  $\mu$ -acetatodiiron(III) complex {[(bispicen)Fe]<sub>2</sub>( $\mu$ -O)( $\mu$ -OAc)}I<sub>3</sub>·2H<sub>2</sub>O (**3**),  $C_{30}H_{43}Fe_2I_3N_8O_5$ , crystallizes in space group  $P\bar{1}$  of the triclinic system with two binuclear species in a cell of dimensions  $a = 10.785(2)$ ,  $b = 12.378(2)$ ,  $c = 15.834(2)$  Å,  $\alpha = 87.060(10)$ ,  $\beta = 87.180(10)$ ,  $\gamma = 70.630(10)^\circ$ . The structure has been refined to a final  $R$  factor of 0.0386 based on 4739 observed independent reflections. The complex contains a bent Fe–O–Fe unit with a bridging Fe–O–Fe angle of 129.8(2)° and associated average Fe–O and Fe···Fe separations of 1.794(1) and 3.248(2) Å, respectively. The Fe–O (acetato) distances are 2.009(3) and 2.040(4) Å. The  $\mu$ -oxo,  $\mu$ -carbonatodiiron(III) complex {[(bispicen)Fe]<sub>2</sub>( $\mu$ -O)( $\mu$ -CO<sub>3</sub>)}I<sub>2</sub>·6H<sub>2</sub>O (**4**),  $C_{29}H_{48}Fe_2I_2N_8O_{10}$ , also crystallizes in space group  $P\bar{1}$  of the triclinic system with two binuclear species in a cell of dimensions  $a = 10.158(2)$ ,  $b = 13.459(2)$ ,  $c = 15.712(3)$  Å,  $\alpha = 73.020(10)$ ,  $\beta = 85.290(10)$ ,  $\gamma = 79.230(10)^\circ$ . The structure has been refined to a final  $R$  factor of 0.0348 based on 4294 observed independent reflections. The structure of the complex cation is very similar to that in **3**, and contains a bent Fe–O–Fe unit with a bridging Fe–O–Fe angle of 129.0(2)° and associated average Fe–O and Fe···Fe separations of 1.796(11) and 3.241(2) Å, respectively. The Fe–O (carbonato) distances are 1.962(4) and 1.963(4) Å. The binuclear complexes exhibit antiferromagnetic interactions with  $J$  values of  $-102.1$ ,  $-118.2$ , and  $-113.6$  cm<sup>-1</sup> for **2**, **3** and **4**, respectively. The electronic spectra are similar to those observed in related species.

## Introduction

Oxo-bridged diiron(III) complexes are of current interest in the field of inorganic chemistry. This is largely due to the discovery of the presence of oxo-bridged diiron centers in a variety of biological systems [1–6]. Recently, the presence of a ( $\mu$ -oxo)bis( $\mu$ -carboxylato)diiron(III) core in methemerythrin [3] and a ( $\mu$ -oxo)( $\mu$ -carboxylato)diiron(III) core in *E. coli* ribonucleotide reductase has been unambiguously demonstrated by X-ray analysis [7]. This has led to the

synthesis and characterization of a large number of diiron complexes [8–12] in an effort to discover model complexes which would mimic the biological systems. Like the biological systems alluded to above, the synthetic complexes fall into two classes, triply bridged [8–11] and doubly bridged [12] complexes. While most of the complexes have been found to exhibit spectral and magnetic properties similar to the biological diiron sites, they do not exhibit redox behavior similar to that of the proteins. Encouraged by our previous results that tetradentate N<sub>4</sub> ligands like *N,N'*-bis(2-pyridylmethyl)ethane-1,2-diamine stabilize different oxidation states of the bis( $\mu$ -oxo)dimanganese core [13], we have

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synthesized and investigated mononuclear and oxo-bridged diiron(III) complexes of *N,N'*-bis(2-pyridylmethyl)ethane-1,2-diamine. A mononuclear iron(III) complex of this ligand has been previously reported and shown to form ( $\mu$ -oxo)diiron(III) complexes in aqueous solution under appropriate pH conditions, but no structural data and only limited spectral and magnetic data are available [14]. In this paper we report the synthesis and physical properties of both mononuclear and binuclear iron(III) complexes of this ligand.

## Experimental

### Synthetic methods

Bispicen·4HCl was synthesized according to literature procedures [15], while all other chemicals were purchased commercially and used as received except tetraethylammonium perchlorate, which was recrystallized twice from boiling water before use. Elemental analyses were performed by Atlantic Microlab, Norcross, GA.

#### $[(\text{Bispicen})\text{FeCl}_2]\text{Cl}$ (**1a**)

To an aqueous solution (40 ml) of bispicen·4HCl (1.940 g, 5 mmol) was added  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (1.350 g, 5 mmol) with stirring. After 10 min sodium acetate (2.040 g, 15 mmol) was added to the yellow solution. The yellow solid that precipitated was filtered off and air dried. The complex was recrystallized from acetonitrile as yellow needles (1.580 g, yield 78%). *Anal.* Calc. for  $\text{C}_{14}\text{H}_{18}\text{Cl}_3\text{FeN}_4$ : C, 39.80; H, 4.77; N, 13.26; Cl, 25.17. Found: C, 39.68; H, 4.80; N, 13.17; Cl, 25.27%.

The perchlorate salt of the complex,  $[(\text{bispicen})\text{FeCl}_2]\text{ClO}_4$  (**1**), was synthesized by the same procedure except that sodium perchlorate (1 g) was added to the solution before the addition of sodium acetate. The complex was recrystallized from acetonitrile as yellow hexagonal prisms (1.800 g, 77%). *Anal.* Calc. for  $\text{C}_{14}\text{H}_{18}\text{Cl}_3\text{FeN}_4\text{O}_4$ : C, 35.89; H, 3.87; N, 11.96; Cl, 22.70. Found: C, 35.92; H, 3.87; N, 12.01; Cl, 22.62%.

#### $\{[(\text{Bispicen})(\text{Cl})\text{Fe}]_2(\mu\text{-O})\}(I_3)_2$ (**2**)

To an aqueous solution (10 ml) of **1a** (0.405 g, 1 mmol) was added potassium iodide (2 g) with stirring. The brown precipitate that formed was filtered off after 10 min and recrystallized from acetonitrile as brown rectangular prisms (0.315 g, 44%). *Anal.* Calc. for  $\text{C}_{28}\text{H}_{36}\text{Cl}_2\text{Fe}_2\text{I}_6\text{N}_8\text{O}$ : C, 23.28; H, 2.51; N, 7.76. Found: C, 23.11; H, 2.47; N, 7.71%.

#### $\{[(\text{Bispicen})\text{Fe}]_2(\mu\text{-O})(\mu\text{-CH}_3\text{COO})\}I_3 \cdot 2\text{H}_2\text{O}$ (**3**) and $\{[(\text{bispicen})\text{Fe}]_2(\mu\text{-O})(\mu\text{-CO}_3)\}I_2 \cdot 6\text{H}_2\text{O}$ (**4**)

These complexes were synthesized by the same procedure as employed for **2** except that the respective bridging anions (sodium acetate or sodium carbonate)

were added prior to the addition of KI. Complex **3** was recrystallized from acetonitrile as green-brown rectangular prisms (0.285 g, 52%). *Anal.* Calc. for **3**,  $\text{C}_{30}\text{H}_{43}\text{Fe}_2\text{I}_3\text{N}_8\text{O}_5$ : C, 33.11; H, 3.98; N, 10.30; I, 34.99. Found: C, 33.14; H, 4.00; N, 10.23; I, 34.80%. Complex **4** was also recrystallized from acetonitrile as green-brown rectangular prisms (0.275 g, 53%). *Anal.* Calc. for **4**,  $\text{C}_{29}\text{H}_{48}\text{Fe}_2\text{I}_2\text{N}_8\text{O}_{10}$ : C, 33.68; H, 4.68; N, 10.83; I, 24.54. Found: C, 33.72; H, 4.68; N, 10.81; I, 24.49%.

### X-ray structure determination

The structures of the complexes **1–4** were determined at room temperature on a Nicolet R3m/V diffractometer equipped with a molybdenum tube [ $\lambda(\text{K}\alpha_1)=0.70926$  Å;  $\lambda(\text{K}\alpha_2)=0.71354$  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 [16].

#### $[(\text{Bispicen})\text{FeCl}_2](\text{ClO}_4)$ (**1**)

The complex crystallizes in the centrosymmetric monoclinic space group  $P2_1/c$  with four mononuclear cations in the unit cell. All hydrogen atoms except the secondary amino hydrogens were placed in calculated positions ( $\text{C-H}=0.96$  Å). All non-hydrogen atoms were refined anisotropically. The final values of the conventional  $R$  factors were  $R=0.0496$ ,  $R_w=0.0801$ , based on 2948 independent reflections with  $I>3\sigma(I)$ . Positional parameters are listed in Table 2.

#### $\{[(\text{Bispicen})(\text{Cl})\text{Fe}]_2(\mu\text{-O})\}(I_3)_2$ (**2**)

The complex crystallizes in the centrosymmetric monoclinic space group  $P2_1/n$  with two binuclear cations in the unit cell. All hydrogen atoms were placed in calculated positions ( $\text{C-H}=0.96$  Å) while all non-hydrogen atoms were refined anisotropically. The final values of the conventional  $R$  factors were;  $R=0.0417$ ,  $R_w=0.0527$  based on 2272 independent reflections with  $I>3\sigma(I)$ . Positional parameters are listed in Table 3.

#### $\{[(\text{Bispicen})\text{Fe}]_2(\mu\text{-O})(\mu\text{-CH}_3\text{COO})\}I_3 \cdot 2\text{H}_2\text{O}$ (**3**)

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 ( $\text{C-H}=0.96$  Å) while all non-hydrogen atoms were refined anisotropically. The final values of the conventional  $R$  factors were  $R=0.0386$ ,  $R_w=0.0525$ , based on 4739 independent reflections with  $I>3\sigma(I)$ . Positional parameters are listed in Table 4.

TABLE 1. Crystallographic data for the complexes 1–4

	1	2	3	4
Formula	C <sub>14</sub> H <sub>18</sub> Cl <sub>3</sub> FeN <sub>4</sub> O <sub>4</sub>	C <sub>28</sub> H <sub>36</sub> Cl <sub>2</sub> Fe <sub>2</sub> I <sub>6</sub> N <sub>8</sub> O	C <sub>30</sub> H <sub>43</sub> Fe <sub>2</sub> I <sub>3</sub> N <sub>8</sub> O <sub>5</sub>	C <sub>29</sub> H <sub>48</sub> Fe <sub>2</sub> I <sub>2</sub> N <sub>8</sub> O <sub>10</sub>
<i>a</i> (Å)	7.323(2)	8.570(2)	10.785(2)	10.158(2)
<i>b</i> (Å)	14.370(3)	14.756(3)	12.378(2)	13.459(2)
<i>c</i> (Å)	18.103(4)	17.083(3)	15.834(2)	15.712(3)
$\alpha$ (°)	90	90	87.060(10)	73.020(10)
$\beta$ (°)	90.71(2)	99.68(2)	87.180(10)	85.290(10)
$\gamma$ (°)	90	90	70.630(10)	79.230(10)
<i>V</i> (Å <sup>3</sup> )	1904.9(7)	2129.5(8)	1990.4(6)	2017.4(6)
<i>Z</i>	4	2	2	2
Formula weight	468.5	1444.6	1088.1	1034.3
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 1̄	<i>P</i> 1̄
<i>T</i> (°C)	22	22	22	22
$\mu$ (mm <sup>-1</sup> )	1.241	5.146	3.076	2.290
NO <sup>a</sup>	4410	3773	5919	5663
NO [ <i>I</i> > 3 $\sigma$ ( <i>I</i> )]	2948	2272	4739	4294
<i>R</i> <sup>b</sup>	0.0496	0.0417	0.0386	0.0348
<i>R</i> <sub>w</sub> <sup>c</sup>	0.0801	0.0527	0.0525	0.0524

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

TABLE 2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement coefficients ( $\text{\AA}^2 \times 10^3$ ) for 1

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub> <sup>a</sup>
Fe(1)	3185(1)	2569(1)	4482(1)	28(1)
N(1)	4081(5)	1724(3)	3588(2)	38(1)
N(2)	1817(5)	1233(3)	4692(2)	35(1)
N(3)	631(5)	2731(3)	3841(2)	34(1)
N(4)	1436(5)	3211(3)	5250(2)	35(1)
Cl(1)	5448(2)	2112(1)	5276(1)	47(1)
Cl(2)	4344(2)	3933(1)	4071(1)	45(1)
C(1)	4910(7)	2047(4)	2983(3)	48(2)
C(2)	5520(8)	1449(5)	2439(3)	67(2)
C(3)	5301(9)	519(6)	2533(4)	86(3)
C(4)	4433(8)	164(5)	3145(4)	71(2)
C(5)	3840(6)	799(3)	3674(3)	45(1)
C(6)	2888(7)	486(3)	4356(3)	49(2)
C(7)	-100(6)	1277(3)	4446(3)	40(1)
C(8)	-245(6)	1818(3)	3735(3)	40(1)
C(9)	-542(6)	3422(3)	4184(3)	43(1)
C(10)	-133(6)	3563(3)	4992(3)	37(1)
C(11)	-1291(7)	4064(3)	5438(3)	50(2)
C(12)	-807(8)	4208(4)	6166(3)	61(2)
C(13)	804(9)	3842(4)	6439(3)	59(2)
C(14)	1883(8)	3343(4)	5962(3)	49(2)
Cl(3)	370(2)	1153(1)	6957(1)	58(1)
O(1)	1757(5)	1589(3)	7306(2)	97(2)
O(2)	176(8)	281(2)	7218(3)	112(3)
O(3)	625(10)	1134(4)	6228(1)	205(6)
O(4)	-1194(5)	1630(4)	7096(5)	211(7)

<sup>a</sup>Equivalent isotropic *U* defined as one third of the trace of the orthogonalized *U*<sub>*ij*</sub> tensor.

### {[(*Bispicen*)Fe]<sub>2</sub>( $\mu$ -O)( $\mu$ -CO<sub>3</sub>)]<sub>2</sub>·6H<sub>2</sub>O (4)}

The complex crystallizes in the triclinic space group *P*1̄ with two dinuclear cations in the unit cell. All hydrogen atoms were placed at calculated positions

TABLE 3. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement coefficients ( $\text{\AA}^2 \times 10^3$ ) for 2

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub> <sup>a</sup>
Fe(1)	5349(1)	337(1)	11026(1)	35(1)
O(1)	5000	0	10000	42(3)
Cl(1)	2957(3)	1061(2)	11114(2)	53(1)
N(1)	6583(8)	1618(5)	10880(4)	37(2)
N(2)	7882(8)	-5(5)	11208(5)	42(3)
N(3)	6032(9)	442(5)	12346(4)	48(3)
N(4)	4777(8)	-957(5)	11518(4)	42(3)
C(1)	6047(11)	2455(6)	10929(5)	45(3)
C(2)	6827(12)	3207(6)	10747(6)	52(4)
C(3)	8289(12)	3081(7)	10500(6)	57(4)
C(4)	8881(11)	2242(7)	10472(6)	54(4)
C(5)	8015(10)	1509(6)	10663(5)	40(3)
C(6)	8543(10)	529(6)	10623(6)	42(3)
C(7)	8639(11)	231(7)	12032(6)	56(4)
C(8)	7578(14)	1(8)	12609(6)	63(4)
C(9)	4847(13)	-65(7)	12704(6)	56(4)
C(10)	4478(11)	-953(7)	12262(6)	49(4)
C(11)	3963(13)	-1708(8)	12611(6)	60(4)
C(12)	3726(13)	-2489(8)	12190(7)	63(4)
C(13)	4079(13)	-2533(7)	11432(7)	62(4)
C(14)	4589(12)	-1749(7)	11122(6)	52(4)
I(1)	7846(1)	-3610(1)	10376(1)	59(1)
I(2)	9116(1)	-2358(1)	11676(1)	81(1)
I(3)	6739(1)	-4834(1)	9092(1)	73(1)

<sup>a</sup>Equivalent isotropic *U* defined as one third of the trace of the orthogonalized *U*<sub>*ij*</sub> tensor.

(C–H = 0.96 Å) while the non-hydrogens were refined anisotropically. The final values of the conventional *R* factors were, *R* = 0.0348, *R*<sub>w</sub> = 0.0524, based on 4294 independent reflections with *I* > 3 $\sigma$ (*I*). Positional parameters are given in Table 5.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}^a$
Fe(1)	1573(1)	6823(1)	7996(1)	51(1)
N(1)	1231(5)	7294(4)	9336(3)	59(2)
N(2)	2594(5)	5281(4)	8714(3)	64(2)
N(3)	137(5)	5891(4)	7992(3)	62(2)
N(4)	1923(5)	5973(4)	6814(3)	60(2)
O(1)	2870(3)	7421(3)	7809(2)	53(1)
O(2)	13(3)	8191(3)	7693(3)	62(2)
Fe(2)	2809(1)	8803(1)	7374(1)	51(1)
N(5)	2942(5)	8450(4)	6060(3)	59(2)
N(6)	4898(4)	8438(5)	7107(3)	65(2)
N(7)	2835(5)	10553(4)	6977(3)	64(2)
N(8)	3025(4)	9513(4)	8534(3)	56(2)
O(3)	821(3)	9591(3)	7369(3)	63(2)
C(1)	318(6)	8195(6)	9663(4)	72(3)
C(2)	292(8)	8478(7)	10492(5)	86(3)
C(3)	1233(9)	7797(8)	11001(5)	95(4)
C(4)	2160(8)	6861(7)	10688(4)	86(3)
C(5)	2165(6)	6626(5)	9840(4)	63(2)
C(6)	3190(6)	5638(5)	9423(4)	72(3)
C(7)	1632(7)	4707(5)	9031(4)	75(3)
C(8)	758(7)	4695(6)	8324(5)	82(3)
C(9)	-225(6)	5904(6)	7115(4)	73(3)
C(10)	981(6)	5610(5)	6559(4)	66(2)
C(11)	1127(8)	5005(7)	5810(5)	92(4)
C(12)	2281(9)	4785(8)	5339(5)	101(4)
C(13)	3227(9)	5194(7)	5607(5)	96(4)
C(14)	3040(6)	5750(6)	6357(4)	74(3)
C(15)	1925(6)	8617(6)	5558(4)	68(2)
C(16)	2077(8)	8356(6)	4717(4)	80(3)
C(17)	3337(9)	7922(7)	4375(4)	91(4)
C(18)	4390(7)	7765(6)	4875(4)	79(3)
C(19)	4174(6)	8023(5)	5734(4)	62(2)
C(20)	5276(6)	7766(6)	6334(4)	72(2)
C(21)	5209(6)	9509(6)	7056(4)	75(3)
C(22)	4146(6)	10463(6)	6603(4)	73(3)
C(23)	2463(7)	11293(5)	7712(4)	70(2)
C(24)	2874(6)	10640(5)	8530(4)	62(2)
C(25)	3029(6)	11156(6)	9253(5)	74(3)
C(26)	3337(7)	10511(6)	9995(4)	78(3)
C(27)	3498(6)	9357(6)	9998(4)	71(3)
C(28)	3351(5)	8884(5)	9260(3)	59(2)
C(29)	-114(5)	9202(5)	7480(3)	51(2)
C(30)	-1460(6)	10015(6)	7334(5)	76(3)
I(1)	8500(1)	8147(1)	5069(1)	79(1)
I(2)	3209(1)	3314(1)	1255(1)	76(1)
I(3)	4895(1)	7088(1)	2102(1)	75(1)
O(1W)	3156(7)	5259(6)	2982(4)	121(3)
O(2W)	575(7)	7071(7)	3139(4)	135(4)

<sup>a</sup>Equivalent isotropic *U* defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

### Physical measurements

Electronic absorption spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer in acetonitrile solvent. Magnetic susceptibility measurements were performed by the Faraday method on equipment described elsewhere [17]. The molar susceptibilities were corrected for ligand diamagnetism using Pascal's

TABLE 5. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement coefficients ( $\text{\AA}^2 \times 10^3$ ) for **4**

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}^a$
Fe(1)	2628(1)	6765(1)	7965(1)	26(1)
O(1)	2143(3)	8143(3)	7902(2)	29(1)
O(2)	4527(4)	6720(3)	7599(3)	39(1)
N(1)	2779(4)	6126(3)	9390(3)	30(2)
N(2)	2972(5)	5033(3)	8161(3)	35(2)
N(3)	549(5)	6452(3)	8186(3)	36(2)
N(4)	2032(5)	6864(3)	6649(3)	37(2)
Fe(2)	3174(1)	9131(1)	7719(1)	27(1)
N(5)	2851(5)	9879(3)	6323(3)	37(2)
N(7)	1515(5)	10272(3)	8032(3)	34(2)
N(6)	4166(5)	10571(3)	7428(3)	39(2)
N(8)	3524(4)	9010(3)	9075(3)	28(2)
O(3)	4953(4)	8336(3)	7543(3)	35(1)
C(1)	2406(6)	6687(5)	9959(4)	38(2)
C(2)	2478(6)	6248(5)	10878(4)	45(3)
C(3)	2941(7)	5177(5)	11197(4)	49(3)
C(4)	3291(7)	4595(5)	10625(4)	47(2)
C(5)	3209(6)	5073(4)	9710(4)	39(2)
C(6)	3574(6)	4475(5)	9032(4)	44(2)
C(7)	1702(6)	4718(4)	8061(4)	40(2)
C(8)	555(6)	5297(5)	8476(5)	50(3)
C(9)	-160(6)	7021(5)	7355(4)	48(3)
C(10)	698(7)	6979(5)	6548(4)	43(2)
C(11)	170(9)	7073(5)	5723(5)	62(3)
C(12)	1026(12)	7043(7)	5018(5)	82(4)
C(13)	2357(12)	6922(7)	5122(5)	82(4)
C(14)	2860(8)	6828(5)	5951(4)	53(3)
C(15)	2047(7)	9558(5)	5856(4)	45(2)
C(16)	1950(8)	9972(5)	4948(4)	58(3)
C(17)	2668(9)	10770(6)	4517(5)	63(3)
C(18)	3469(8)	11104(5)	4991(4)	54(3)
C(19)	3544(7)	10640(4)	5903(4)	42(2)
C(20)	4458(7)	10949(5)	6450(4)	47(2)
C(21)	3273(7)	11347(5)	7806(5)	48(3)
C(22)	1818(7)	11363(4)	7668(4)	44(2)
C(23)	1238(6)	9955(4)	9007(4)	35(2)
C(24)	2484(6)	9414(4)	9528(4)	33(2)
C(25)	2521(6)	9312(5)	10434(4)	40(2)
C(26)	3652(7)	8771(5)	10883(4)	44(2)
C(27)	4742(7)	8357(5)	10413(4)	43(2)
C(28)	4631(6)	8498(4)	9531(4)	37(2)
C(29)	5334(6)	7399(4)	7400(3)	30(2)
O(4)	6477(4)	7189(3)	7084(3)	47(2)
I(1)	1320(1)	2250(1)	248(1)	43(1)
I(2)	5159(1)	3793(1)	6773(1)	72(1)
O(1W)	2943(5)	688(3)	2229(3)	57(2)
O(2W)	-887(5)	10514(4)	6990(3)	67(2)
O(3W)	1576(7)	7534(5)	2639(4)	86(3)
O(4W)	309(7)	5814(5)	3345(4)	94(3)
O(5W)	-2153(7)	6232(6)	4309(4)	108(3)
O(6W)	2723(6)	4268(4)	3809(4)	75(2)

<sup>a</sup>Equivalent isotropic *U* defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

constants. 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.

## Results and discussion

### Synthesis

The complex  $[(\text{bispicen})\text{FeCl}_2]\text{Cl}$  (**1a**) was synthesized by mixing the hydrochloride salt of the ligand and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in water and adding less than sufficient sodium acetate (3:1,  $\text{NaOAc}:\text{bispicen} \cdot 4\text{HCl}$ ). The complex precipitated as a yellow solid. Previously [14], the complex **1a** has been synthesized by mixing the free ligand and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in methanol and was reported as a green solid. The green solid is presumably due to partial hydrolysis of **1a**. Hydrolysis of **1a** in aqueous solution and addition of KI lead to the formation of the oxo-bridged diiron(III) complex **2**. In the presence of the bridging anions ( $\text{CH}_3\text{COO}^-$  or  $\text{CO}_3^{2-}$ ) hydrolysis leads to the formation of the dibridged complexes **3** and **4**. Complexes were precipitated as iodide or triiodide salts, and were recrystallized from acetonitrile.

### Description of the structures

#### *Cis- $\alpha$ -dichloro*[*N,N'*-bis(2-pyridylmethyl)ethane-1,2-diamine]iron(III) perchlorate (**1**)

The structure of this mononuclear iron(III) complex consists of *cis- $\alpha$* - $[(\text{bispicen})\text{FeCl}_2]^+$  cations and perchlorate anions. A view of the cation is shown in Fig. 1. Principal bond distances and angles are listed in Table 6.

The geometry about the iron atom is roughly octahedral, with axial ligation provided by the pyridine groups and equatorial ligation by the amine nitrogen atoms and the chloride ligands. As can be seen in

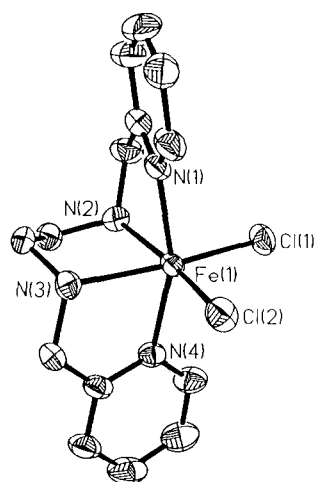


Fig. 1. View of the  $[(\text{bispicen})\text{Fe}(\text{Cl})_2]^+$  cation in the crystals of the perchlorate salt **1**. In this and following figures, some carbon atoms are unlabeled and all hydrogen atoms are omitted for clarity.

TABLE 6. Selected bond lengths (Å) and angles (°) for **1**

Bond lengths			
Fe(1)–N(1)	2.132(4)	Fe(1)–N(2)	2.200(4)
Fe(1)–N(3)	2.201(4)	Fe(1)–N(4)	2.114(4)
Fe(1)–Cl(1)	2.278(1)	Fe(1)–Cl(2)	2.266(1)
Bond angles			
N(1)–Fe(1)–N(2)	77.3(1)	N(1)–Fe(1)–N(3)	85.9(1)
N(2)–Fe(1)–N(3)	78.4(1)	N(1)–Fe(1)–N(4)	160.4(1)
N(2)–Fe(1)–N(4)	89.2(1)	N(3)–Fe(1)–N(4)	77.4(1)
N(1)–Fe(1)–Cl(1)	95.0(1)	N(2)–Fe(1)–Cl(1)	88.2(1)
N(3)–Fe(1)–Cl(1)	166.0(1)	N(4)–Fe(1)–Cl(1)	98.8(1)
N(1)–Fe(1)–Cl(2)	97.1(1)	N(2)–Fe(1)–Cl(2)	170.0(1)
N(3)–Fe(1)–Cl(2)	93.1(1)	N(4)–Fe(1)–Cl(2)	94.1(1)
Cl(1)–Fe(1)–Cl(2)	100.6(1)		

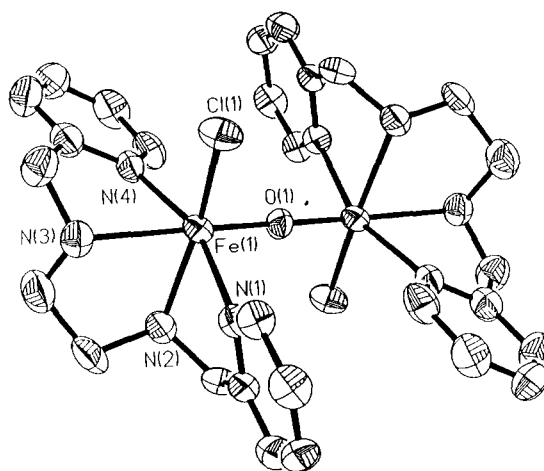


Fig. 2. View of the  $\{[(\text{bispicen})(\text{Cl})\text{Fe}]_2(\mu\text{-O})\}^{2+}$  cation in the crystals of the triiodide salt **2**.

Fig. 1, the isomer is the *cis- $\alpha$* -dichloro species. The Cl(1)–Fe–Cl(2) bond angle is  $100.6(1)^\circ$ , the Fe–Cl bond lengths are 2.278(1) and 2.266(1) Å and the Fe–N bond lengths are 2.132(4), 2.200(4), 2.201(4) and 2.114(4) Å. These values fall within the ranges observed for other high spin iron(III) complexes [18–21].

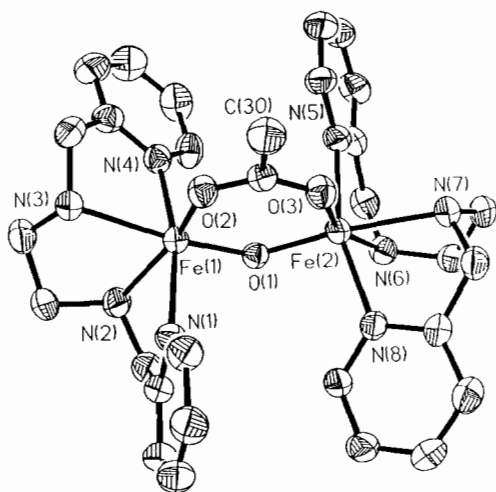
#### $\{[(\text{Bispicen})(\text{Cl})\text{Fe}]_2(\mu\text{-O})\}(\text{I}_3)_2$

The structure of the complex consists of  $\{[(\text{bispicen})(\text{Cl})\text{Fe}]_2(\mu\text{-O})\}^{2+}$  cations and  $\text{I}_3^-$  anions. A view of the cation is given in Fig. 2. Principal bond distances and angles are listed in Table 7.

The geometry about each iron center is roughly octahedral with the axial ligation provided by the pyridine groups and the equatorial ligation provided by the amine nitrogens, chloride ligand and the bridging oxygen atom. The bridging oxygen atom O(1) lies on a crystallographic inversion center which relates one half of the binuclear cation to the other. The Fe–O–Fe angle is constrained to  $180^\circ$  by symmetry and the Fe–Fe

TABLE 7 Selected bond lengths (Å) and angles (°) for 2

Bond lengths			
Fe(1)–O(1)	1.798(1)	Fe(1)–Cl(1)	2.339(3)
Fe(1)–N(1)	2.201(7)	Fe(1)–N(2)	2.200(7)
Fe(1)–N(3)	2.237(7)	Fe(1)–N(4)	2.176(8)
O(1)–Fe(1A)	1.798(1)	I(1)–I(2)	2.952(1)
I(1)–I(3)	2.877(1)		
Bond angles			
O(1)–Fe(1)–Cl(1)	100.7(1)	O(1)–Fe(1)–N(1)	97.5(2)
Cl(1)–Fe(1)–N(1)	93.3(2)	O(1)–Fe(1)–N(2)	94.2(2)
Cl(1)–Fe(1)–N(2)	161.9(2)	N(1)–Fe(1)–N(2)	74.4(3)
O(1)–Fe(1)–N(3)	166.9(2)	Cl(1)–Fe(1)–N(3)	89.3(2)
N(1)–Fe(1)–N(3)	90.3(3)	N(2)–Fe(1)–N(3)	77.8(3)
O(1)–Fe(1)–N(4)	97.1(2)	Cl(1)–Fe(1)–N(4)	96.8(2)
N(1)–Fe(1)–N(4)	160.3(2)	N(2)–Fe(1)–N(4)	91.4(3)
N(3)–Fe(1)–N(4)	73.1(3)	Fe(1)–O(1)–Fe(1A)	180
I(2)–I(1)–I(3)	177.6(1)		

Fig. 3. View of the  $\{[(\text{bispicen})\text{Fe}]_2(\mu\text{-O})(\mu\text{-OAc})\}^{3+}$  cation in the crystal of the iodide salt 3

distance is 3.596 Å. The Fe–N and Fe–O distances fall in the range normally observed for binuclear iron(III) complexes with a single oxygen bridge [21].

The  $\text{I}_3^-$  ion is slightly non-linear, the I(2)–I(1)–I(3) angle being 177.6(1)°. The corresponding bond lengths are 2.877(1) and 2.952(1) Å; all of these metrical parameters are consistent with earlier observations of this anion [22].

#### $\{[(\text{Bispicen})\text{Fe}]_2(\mu\text{-O})(\mu\text{-CH}_3\text{COO})\}_3 \cdot 2\text{H}_2\text{O}$ (3)

The structure of the complex consists of  $\{[(\text{bispicen})\text{Fe}]_2(\mu\text{-O})(\mu\text{-CH}_3\text{COO})\}^{3+}$  cations, iodide ions and water molecules. A view of the cation is given in Fig. 3. Principal bond distances and angles are listed in Table 8.

The geometry about each iron(III) center is again roughly octahedral, with axial ligation provided by the pyridine groups and equatorial ligation by the amine

TABLE 8 Selected bond lengths (Å) and angles (°) for 3

Bond lengths			
Fe(1)–N(1)	2.210(5)	Fe(1)–N(2)	2.157(4)
Fe(1)–N(3)	2.217(6)	Fe(1)–N(4)	2.150(5)
Fe(1)–O(1)	1.794(4)	Fe(1)–O(2)	2.009(3)
Fe(2)–O(1)	1.793(4)	Fe(2)–N(5)	2.136(5)
Fe(2)–N(6)	2.170(5)	Fe(2)–N(7)	2.232(5)
Fe(2)–N(8)	2.131(5)	Fe(2)–O(3)	2.040(4)
Bond angles			
N(1)–Fe(1)–N(2)	74.7(2)	N(1)–Fe(1)–N(3)	96.6(2)
N(2)–Fe(1)–N(3)	79.2(2)	N(1)–Fe(1)–N(4)	166.5(2)
N(2)–Fe(1)–N(4)	93.5(2)	N(3)–Fe(1)–N(4)	74.3(2)
N(1)–Fe(1)–O(1)	94.5(2)	N(2)–Fe(1)–O(1)	100.3(2)
N(3)–Fe(1)–O(1)	168.3(2)	N(4)–Fe(1)–O(1)	94.2(2)
N(1)–Fe(1)–O(2)	89.2(2)	N(2)–Fe(1)–O(2)	154.8(2)
N(3)–Fe(1)–O(2)	83.6(2)	N(4)–Fe(1)–O(2)	99.5(2)
O(1)–Fe(1)–O(2)	100.2(2)	Fe(1)–O(1)–Fe(2)	129.8(2)
O(1)–Fe(2)–N(5)	99.0(2)	O(1)–Fe(2)–N(6)	98.3(2)
N(5)–Fe(2)–N(6)	79.1(2)	O(1)–Fe(2)–N(7)	173.1(2)
N(5)–Fe(2)–N(7)	87.1(2)	N(6)–Fe(2)–N(7)	79.8(2)
O(1)–Fe(2)–N(8)	96.8(2)	N(5)–Fe(2)–N(8)	161.2(2)
N(6)–Fe(2)–N(8)	88.6(2)	N(7)–Fe(2)–N(8)	76.6(2)
O(1)–Fe(2)–O(3)	99.7(2)	N(5)–Fe(2)–O(3)	93.2(2)
N(6)–Fe(2)–O(3)	161.4(2)	N(7)–Fe(2)–O(3)	82.9(2)
N(8)–Fe(2)–O(3)	94.1(2)		

nitrogens and bridging oxo and acetato groups. Although the complex could be expected to have two-fold symmetry about the Fe–O–Fe unit, bisecting the bridging acetato group, such symmetry is not observed; hence, the  $(\mu\text{-oxo})(\mu\text{-acetato})$ diiron(III) core contains two crystallographically independent iron centers. The Fe–O–Fe bond angle is 129.8(2)° and the Fe···Fe separation is 3.248 Å. The structural features are comparable to those of the analogous diiron(III) complex of tris(2-pyridylmethyl)amine [12b].

#### $\{[(\text{Bispicen})\text{Fe}]_2(\mu\text{-O})(\mu\text{-CO}_3)\}_2 \cdot 6\text{H}_2\text{O}$ (4)

The structure of this complex consists of  $\{[(\text{bispicen})\text{Fe}]_2(\mu\text{-O})(\mu\text{-CO}_3)\}^{2+}$  cations, iodide anions and water molecules. A view of the cation is given in Fig. 4. The principal bond distances and angles are listed in Table 9.

The structure of the cation is very similar to that of the cation in 3. 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 carbonate groups. The Fe–O–Fe angle is 129.0(2)° and the Fe···Fe separation is 3.241 Å. 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. This complex also

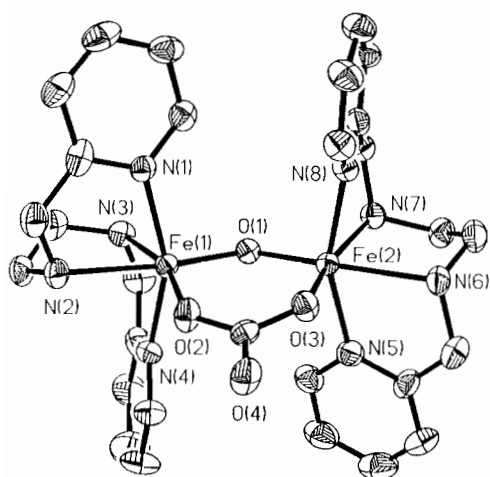


Fig. 4. View of the  $\{[(\text{bispicen})\text{Fe}]_2(\mu\text{-O})(\mu\text{-CO}_3)\}^{2+}$  cation in the crystals of the iodide salt **4**.

TABLE 9. Selected bond lengths (Å) and angles (°) for **4**

Bond lengths			
Fe(1)–O(1)	1.803(4)	Fe(1)–O(2)	1.962(4)
Fe(1)–N(1)	2.159(4)	Fe(1)–N(2)	2.224(5)
Fe(1)–N(3)	2.210(5)	Fe(1)–N(4)	2.162(5)
Fe(2)–O(1)	1.788(4)	Fe(2)–N(5)	2.154(4)
Fe(2)–N(7)	2.186(4)	Fe(2)–N(6)	2.262(5)
Fe(2)–N(8)	2.142(5)	Fe(2)–O(3)	1.963(4)
Bond angles			
O(1)–Fe(1)–O(2)	100.3(2)	O(1)–Fe(1)–N(1)	99.0(2)
O(2)–Fe(1)–N(1)	100.9(2)	O(1)–Fe(1)–N(2)	172.0(2)
O(2)–Fe(1)–N(2)	87.2(2)	N(1)–Fe(1)–N(2)	76.9(2)
O(1)–Fe(1)–N(3)	93.8(2)	O(2)–Fe(1)–N(3)	163.4(2)
N(1)–Fe(1)–N(3)	85.2(2)	N(2)–Fe(1)–N(3)	79.1(2)
O(1)–Fe(1)–N(4)	97.5(2)	O(2)–Fe(1)–N(4)	92.9(2)
N(1)–Fe(1)–N(4)	156.1(2)	N(2)–Fe(1)–N(4)	84.5(2)
N(3)–Fe(1)–N(4)	76.6(2)	Fe(1)–O(1)–Fe(2)	129.0(2)
O(1)–Fe(2)–N(5)	99.3(2)	O(1)–Fe(2)–N(7)	92.3(2)
N(5)–Fe(2)–N(7)	89.2(2)	O(1)–Fe(2)–N(6)	170.7(2)
N(5)–Fe(2)–N(6)	76.3(2)	N(7)–Fe(2)–N(6)	79.4(2)
O(1)–Fe(2)–N(8)	99.3(2)	N(5)–Fe(2)–N(8)	157.6(2)
N(7)–Fe(2)–N(8)	77.7(2)	N(6)–Fe(2)–N(8)	83.4(2)
O(1)–Fe(2)–O(3)	101.6(2)	N(5)–Fe(2)–O(3)	95.1(2)
N(7)–Fe(2)–O(3)	164.5(2)	N(6)–Fe(2)–O(3)	87.1(2)
N(8)–Fe(2)–O(3)	93.3(2)		

exhibits structural features similar to the analogous diiron complex of tris(2-pyridylmethyl)amine [12c].

#### Electronic absorption spectra

Complexes **3** and **4** exhibit rich electronic spectral features in the 300–550 nm region, whereas **1** and **2** exhibit only a single band at 355 nm. **3** and **4** exhibit a weak band at 660 and 667 nm, respectively. The spectral data for complexes **3** and **4** are consistent with those of similar ( $\mu\text{-oxo}$ )diiron(III) complexes [8, 12b] and can be assigned to  ${}^6A_1 \rightarrow ({}^4E, {}^4A_1)$  and oxo LMCT

transitions. The electronic spectra are summarized in Table 10. Absence of any electronic spectral bands in the 400–500 nm region observed for the linear Fe–O–Fe complex **2** clearly confirms the conclusion, based on the spectroscopic features of other  $\mu\text{-oxo}$ diiron(III) complexes, that these spectral features are associated with the presence of a bent Fe–O–Fe unit [12c]. The spectra of **3** and **4** also reveal striking similarities to those of azidomethemerythrin [23].

#### Magnetic susceptibility

The temperature dependence of the magnetic susceptibility of powdered samples of the mononuclear complex **1** and the binuclear complexes **2**, **3** and **4** were measured in the range 4–296 K. The monomeric complex **1** exhibits a magnetic moment of approximately  $6.05 \mu_B$  at room temperature, which declines slightly to a value of  $5.80 \mu_B$  at 5 K. This result is consistent with the expected value of  $\sqrt{35}$  for a high spin  $d^5$  iron(III) species. As is shown in Fig. 5, for the  $\mu\text{-O}, \mu\text{-CO}_3$  complex **4**, the effective magnetic moment at room temperature is approximately  $2.63 \mu_B$ , declining mono-

TABLE 10. Electronic spectral data for **1–4**

Complex	$\lambda_{\text{max}}$ (nm)	$\epsilon$ ( $\text{mM}^{-1} \text{cm}^{-1}$ )
<b>1</b>	355	(3.8)
<b>2</b>	355	(14.66)
<b>3</b>	330	(9.55)
	365	(sh)
	456	(sh)
	502	(sh)
	660	(0.13)
<b>4</b>	422	(1.11)
	477	(sh)
	492	(sh)
	529	(0.12)
	667	(0.06)

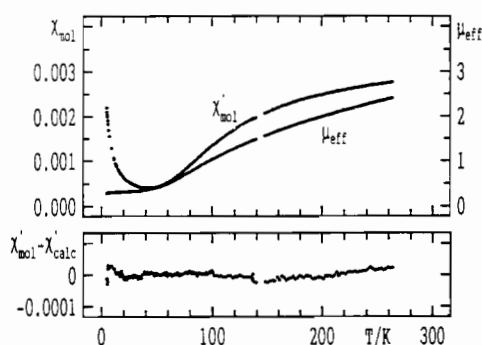


Fig. 5. Magnetic susceptibility (left scale) and effective magnetic moment (right scale) for the complex  $\{[(\text{bispicen})\text{Fe}]_2(\mu\text{-O})(\mu\text{-CO}_3)\}I_2 \cdot 6H_2O$  (**4**). The lower curve shows the fit of the susceptibility data to the values calculated using the parameters  $g=2.073$ ,  $2J=-227.3 \text{ cm}^{-1}$ .

TABLE 11 Structural and magnetic properties for doubly-bridged iron(III) complexes of the type  $[\text{Fe}_2(\text{L})_2(\mu\text{-O})(\mu\text{-X})]^n+$ 

L	X	$\phi$ ( $^\circ$ ) <sup>a</sup>	Fe–O (Å)	Fe··Fe (Å)	$-J$ ( $\text{cm}^{-1}$ )	Ref
bispicen	OAc <sup>-</sup>	129.8	1.794	3.248	118.2	this work
TMPA <sup>b</sup>	OAc <sup>-</sup>	129.7	1.790	3.243	114.3	12b
TMPA <sup>b</sup>	OBz <sup>-</sup>	129.2	1.795	3.241	118.6	12c
HDP <sup>c</sup>	OBz <sup>-</sup>	128.3	1.79	3.218		12a
TMPA <sup>b</sup>	MaleateH <sup>-</sup>	131.0	1.794	3.261	119.9	12c
bispicen	CO <sub>3</sub> <sup>2-</sup>	129.0	1.796	3.241	113.6	this work
TMPA <sup>b</sup>	CO <sub>3</sub> <sup>2-</sup>	125.4	1.800	3.196	108.4	12c

<sup>a</sup>Fe–O–Fe bridging angle. <sup>b</sup>Tris(2-pyridylmethyl)amine. <sup>c</sup>*N*-(*o*-Hydroxybenzyl)-*N,N*-bis(2-pyridylmethyl)amine

tonically to a value of  $0.28 \mu_B$  at 4.5 K. These properties are consistent with the existence of a singlet ground state in the complex. The properties of the other binuclear complexes, **2** and **3**, are qualitatively similar to those shown in Fig. 5.

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

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

by minimization of the function

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

within the framework of regression analysis. The term  $C/T$  accounts for the presence of small quantities of (presumably monomeric) paramagnetic impurities, while  $K$  accounts for temperature independent paramagnetism (TIP) and for any minor deviations in the 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

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

where we have assumed that the  $g$  values for the two iron atoms are identical, 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  $\mu$ -oxo complex **2**, the fitting leads to a value of  $2J = -204.4(2) \text{ cm}^{-1}$  with  $g = 1.987(1)$ ,  $K = 3.35 \times 10^{-4}$ , and impurities equivalent to 1.24% of monomeric iron(III); this observed  $J$  value of  $-102.1 \text{ cm}^{-1}$  for **2** is comparable to those of  $-103.0$  and  $-107.0$  recently reported in analogous, linear  $\mu$ -oxodiiron(III) complexes [24, 25]. For the  $\mu$ -O,  $\mu$ -OAc complex **3** the corresponding values are  $2J = -236.4(2) \text{ cm}^{-1}$ ,  $g = 2.048(1)$ ,

$K = 1.98 \times 10^{-4}$ , and 0.29% monomeric iron(III), and for the  $\mu$ -O,  $\mu$ -CO<sub>3</sub> complex **4** they are  $2J = -227.3(2) \text{ cm}^{-1}$ ,  $g = 2.073(2)$ ,  $K = 1.27 \times 10^{-4}$  and 0.23% monomer. These  $J$  values of  $-118.2$  and  $-113.6 \text{ cm}^{-1}$  are very similar to the values of  $-114.3$  and  $-108.4 \text{ cm}^{-1}$ , respectively, reported for the analogous complexes with TMPA in place of bispicen [12b, 12c].

The complexes **2**, **3** and **4** provide examples of  $\mu$ -oxodiiron(III) complexes with both single (**2**) and double (**3**, **4**) bridges, and with Fe–O–Fe bond angles ( $\phi$ ) in the broad range of 129.0 to 180°, and  $J$  values in the narrow range of  $-102.1$  to  $-118.2 \text{ cm}^{-1}$ ; hence, the present observations support the earlier conclusion of Que and co-workers [12c] that there is no obvious correlation between  $J$  and either  $\phi$  or any other structural feature in complexes of this type. The magnetic and structural parameters of the doubly bridged binuclear complexes are compared with those of analogous complexes in Table 11.

### Electrochemistry

The cyclic voltammogram of **1** consists of a quasi-reversible redox couple at  $+0.09 \text{ V}$  (versus Ag/AgCl in acetonitrile) corresponding to the Fe(III)/Fe(II) process [26]. The cyclic voltammograms of complexes **2**, **3** and **4** exhibit a single irreversible cathodic wave in the region  $-0.6$  to  $-0.8 \text{ V}$ . The marked difference between the electrochemical properties observed for the monomeric complex **1** and the set of ( $\mu$ -oxo)-diiron(III) complexes **2–4** reveals the dominant influence of the oxo-bridging unit on the redox properties of the diiron(III) complexes. On the other hand, the close similarity of the redox properties of **2–4** with each other indicates that the presence of additional bridging groups does not considerably influence their redox properties.

### Supplementary material

Tables S1–S4 (hydrogen atom parameters for complexes **1**, **2**, **3**, **4**), S5–S8 (anisotropic thermal parameters for complexes **1**, **2**, **3**, **4**) and S9–S12 (listings of observed



and calculated structure amplitudes for complexes 1, 2, 3, 4) are available from D.J.H. on request.

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