Synthesis and properties of a binuclear (μ-oxo) diiron(III) complex containing a tripodal polybenzimidazole ligand

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Abstract

Several iron(III) complexes of the polybenzimidazole ligand tris((benzimidazol-2-yl)methyl)amine(ntb) have been synthesized and characterized. The μ-oxo bridged dinuclear complex, $[Fe_2O(ntb)_2Cl_2](PF_6)_2 \cdot 4THF$, has been isolated and structurally characterized by X-ray crystallography. The complex crystallizes in the triclinic space group $P\bar{1}$ with one complex molecule per unit cell. The cell dimensions are $a = 13.758(3)$, $b = 13.913(2)$, $c = 11.526(1)$ Å, $\alpha = 110.52(1)$, $\beta = 90.56(2)$, $\gamma = 60.65(2)°$ and $V = 1765.2$ Å^3. The structure refined to a final agreement factor (R) of 0.057 using 5092 reflections with $I > 3\sigma(I)$. The complex is a centrosymmetric dimer and the coordination environment around each iron(III) center is pseudooctahedral. One benzimidazole pendant is bonded *trans* to the bridging oxo group, while the other benzimidazole pendants, the tertiary amine nitrogen atom and Cl$^-$ ion are bonded *cis* to the oxo ligand. The Fe–O–Fe bridging angle is 180°, as required by the crystallographically imposed center of symmetry. The Fe–Fe separation is 3.610(1) Å. A mononuclear form of complex **1**, $[Fe(ntb)Cl_2](PF_6)_{0.5}(Cl)_{0.5}$ (**2**), has been prepared and shown to form **1** in aqueous ethanol solutions containing NEt$_4$Cl. Compounds **1** and **2** can be used to prepare compound **3** which contains a μ-oxo-μ-acetato bridged core structure, $[Fe_2O(ntb)_2(OAc)](ClO_4)_3$. Compound **3** was recrystallized from an acetonitrile solution containing THF. The dinuclear complex **1** exhibits antiferromagnetic exchange with a *J* value of -100 cm^{-1}. The room temperature solution effective magnetic moments for compounds **1** ($\mu_{eff} = 2.0$) and **3** ($\mu_{eff} = 1.85$ BM) are consistent with antiferromagnetically coupled diiron(III) complexes and indicate that the μ-oxo bridged structure is retained in solution. The room temperature effective magnetic moment of compound **2** is 5.9 BM. The electronic spectra of compounds **1**–**3** are similar to those observed for related complexes. The cyclic voltammetry of compound **1** indicates that the dinuclear complex can stabilize redox levels higher than $+3$. Compound **2** exhibits a single one electron redox process at $E_{1/2} = 0.468$ V NHE. The proton NMR spectra of compounds **1** and **3** confirm the stability of the μ-oxo bridged structures in solution. Inequivalent benzimidazole NH proton signals are observed for compounds **1** and **3**, consistent with the X-ray crystal structure of **1**.

Introduction

Oxo bridged diiron(III) complexes containing imidazole ligands are of interest as analogues of the active sites of non-heme iron proteins [1]. Hemerythrin [2] is the protypical member of a class of non-heme iron proteins that contain oxo bridged structures. Other members of this group include ribonucleotide reductase [3], purple acid phosphatases [4] and methane monooxygenase [5]. The structures of methemerythrin [6] and the oxidized form of ribonucleotide reductase [3a] from *Escherichia coli* have been reported recently to contain (μ-oxo) bis(μ-carboxylato) and (μ-oxo)-(μ-carboxylato) bridged core structures, respectively,

and histidine imidazole as a ligand. In an attempt to model the structure and physical properties of these biological systems, a large number of oxo bridged diiron complexes containing nitrogen donor ligands have been prepared and characterized [1], but only a limited number of these complexes contain imidazole ligands [7].

More recent efforts in modeling the structure and reactivity of diiron protein active sites have focused on the mechanism of O$_2$ binding in hemerythrin. Both deoxyHr and metHr are known to contain an open coordination site on one of the iron centers that readily binds small anion ligands [2]. In addition, the azide ligand in N$_3$metHr is labile and known to exchange with other anion ligands [2c]. Dioxygen, on the other hand, is known to react with the diferrous center of

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deoxyHr resulting in a bound hydroperoxide ion stabilized by intramolecular hydrogen bonding involving the bridging oxo group (oxyHr) [6a, 8].

In an attempt to prepare oxo-bridged diiron complexes with labile coordination sites, we have prepared a new (μ-oxo) diiron(III) complex containing a tripodal benzimidazole ligand, tris((benzimidazol-2-yl)methyl)amine (ntb) [9]. In this paper we report the synthesis crystal structure and physical properties of [Fe$_2$O(ntb)$_2$-Cl$_2$](PF$_6$)$_2$·4THF (1). In addition, we have prepared and characterized a monomeric form of the ntb tripodal ligand, [Fe(ntb)Cl$_2$](PF$_6$)$_{0.5}$(Cl)$_{0.5}$.

Experimental

Reagents and synthetic methods

((C$_2$H$_5$)$_4$N)$_2$[Fe$_2$OCl$_6$] [10] and tris((benzimidazol-2-yl)methyl)amine (ntb) [9] were prepared as previously reported. All other reagents were used as received. Elemental analyses were performed by Midwest Microlab, LTD, Indianapolis, IN.

[Fe$_2$O(ntb)$_2$Cl$_2$](PF$_6$)$_2$·4THF (1)

Method A. To 15 ml of acetonitrile were added ntb (0.311 g, 0.763 mmol) and KPF$_6$ (0.707 g, 3.84 mmol). Solid FeCl$_3$·6H$_2$O (0.207 g, 0.766 mmol) was added with stirring and the resulting orange solution was filtered to remove precipitated salts. Sodium acetate (0.0321 g, 0.391 mmol) was added and the solution was stirred for 18 h. The solution was then evaporated to dryness and the residue dissolved in 3 ml of acetonitrile to which 50 ml of THF were added. The solution was filtered and allowed to sit at -40 °C for three days giving 0.147 g of [Fe$_2$O(ntb)$_2$Cl$_2$](PF$_6$)$_2$ (29.6%) as the dihydrate. Slow vapor diffusion of an acetonitrile solution of the complex containing THF gave crystals of 1 as the THF solvate which were suitable for X-ray crystal structure determination. *Anal.* Calc. for Fe$_2$C$_{48}$H$_{42}$N$_{14}$P$_2$Cl$_2$F$_{12}$O·2H$_2$O: C, 43.04; H, 3.46; N, 14.64. Found: C, 43.44; H, 3.21; N, 14.30%.

Method B. To ((C$_2$H$_5$)$_4$N)$_2$[Fe$_2$OCl$_6$] (0.442 g, 0.736 mmol) in 5 ml of acetonitrile was added ntb (0.607 g, 1.49 mmol) followed by KPF$_6$ (1.145 g, 6.219 mmol). The mixture was stirred for 1 h and filtered giving a dark red solution. The solution was layered with 20 ml of THF and stored in a refrigerator at -40 °C for 3 days giving orange microcrystals of the desired complex (0.447 g, 46.6%).

[Fe(ntb)Cl$_2$](PF$_6$)$_{0.5}$Cl$_{0.5}$ (2)

The ligand ntb (0.329 g, 0.808 mmol) and NH$_4$PF$_6$ (0.714 g, 4.38 mmol) were dissolved in 15 ml of ethanol. A solution of FeCl$_3$·6H$_2$O (0.220 g, 0.814 mmol) in 10 ml of ethanol was added slowly with stirring. The deep red solution was carefully filtered and the filtrate stirred for an additional 10 min giving a dark orange precipitate. Elemental analysis suggests the presence of 0.5 Cl$^-$ and 0.5 PF$_6^-$ counterions per cation. *Anal.* Calc. for FeC$_{24}$H$_{21}$N$_7$P$_{0.5}$Cl$_{2.5}$F$_3$: C, 46.2; H, 3.4; N, 15.7. Found: C, 46.5; H, 3.7; N, 15.3%.

[Fe$_2$O(CH$_3$CO$_2$)(ntb)$_2$](ClO$_4$)$_3$·THF·2H$_2$O (3)

To a stirred slurry of ntb (0.662 g, 1.62 mmol) and sodium acetate (0.135 g, 1.65 mmol) in 10 ml of acetonitrile was added solid Fe(ClO$_4$)$_3$·xH$_2$O (0.606 g, 1.62 mmol). The resulting green solution was stirred for 2 h after which a white solid was filtered off. The filtrate was layered with 30 ml of THF and after sitting for 24 h a mass of dark green crystals was isolated (0.624 g, 63.3%). Recrystallization was accomplished by vapor diffusion of an acetonitrile solution with THF. *Anal.* Calc. for Fe$_2$C$_{54}$H$_{57}$N$_{14}$O$_{17}$Cl$_3$: C, 46.06; H, 4.08; N, 13.93. Found: C, 46.33; H, 3.81; N, 13.63%.

X-ray structure determination

The structure of compound 1 was determined at room temperature on an Enraf-Nonius CAD4 diffractometer using molybdenum radiation and a graphite monochromator. A summary of the crystal data and experimental parameters are listed in Table 1. X-ray grade crystals were grown by slow vapor diffusion of an acetonitrile solution containing 1 and THF. Compound 1 crystallizes in the triclinic space group $P\bar{1}$ which was confirmed using the program TRACER [11] and the successful solution of the structure. A suitable crystal was chosen for data collection and coated with

TABLE 1. Crystallographic data for complex 1

Formula	C$_{56}$H$_{58}$Fe$_2$F$_{12}$N$_{14}$O$_3$Cl$_2$P$_2$
Formula weight	1447.71
Space group	$P\bar{1}$
a (Å)	13.758(3)
b (Å)	13.913(2)
c (Å)	11 526(1)
α (°)	110.52(1)
β (°)	90.56(2)
γ (°)	60.65(2)
V (Å^3)	1765 2
Z	1
D_{calc} (g cm^{-3})	1 36
T (°C)	23(1)
R	0 057
R_w	0 062
μ (cm^{-1})	6 10
No. unique reflections	6196
No. observed reflections	5092 ($I > 3\sigma(I)$)
No. variables	449
GOF	1 01
Max. Δ/σ	0 20
Highest peak (e Å^3)	0 47(7)

epoxy then sealed in a capillary. The data were collected using the ω–2θ scan technique and corrected for Lorentz and polarization effects as well as for absorption effects (ψ scans). The unique iron atom was located using Patterson techniques and refinement of the structure was performed using least-squares methods associated with the SDP/VAX [11] program package. The PF_6^- counterion and both THF solvate molecules were found to be disordered. The former was modeled using a single P atom and 18 F atoms giving three PF_6^- groups having occupancies of 0.45, 0.30 and 0.25. The latter groups were modeled with four THF units (for each) with occupancies ranging from 0.2 to 0.3. Scattering factors were taken from Cromer and Waber [12] and anomalous dispersion effects were included in F_c [13]. All hydrogen atoms were placed in calculated positions (C–H = 1.00 Å, B_{iso} = 1.2 B of the bonded atom) and included in the final cycle as fixed contributions. The final convergence factors were $R = 0.057$ and $R_w = 0.062$ based on 5092 reflections with $I > 3\sigma(I)$. Selected bond distances and angles associated with the cation are given in Table 2. See also 'Supplementary material'.

Physical measurements

Electronic spectral data were recorded on a Shimadzu model 160 spectrophotometer in acetonitrile. ^1H NMR spectra were obtained on a Varian XL300 MHz spectrometer. Magnetic susceptibility measurements were performed using a variable temperature superconducting magnetometer by Quantum Design MPMS operating at 0.5 T in the range 2–300 K. A powdered sample of compound 1 (11 to 45 mg) was placed in a kelf bucket that had been calibrated independently. Diamagnetic corrections were evaluated using Pascal's constants. The data were processed and the quantity minimized was $\Sigma(Y_{exp} - Y_{cal})^2$, with $X - Y$ and $Y = XT$. The quality of the fit was estimated through the statistical index R, where N is the number of measurements. R values are listed in Table SIX ('Supplementary material').

$$R = \frac{\Sigma(Y_{expt} - Y_{cal})^2}{N\Sigma(Y_{expt})^2}$$

Cyclic voltammograms were recorded using a PARC model 174 universal programmer and model 175 potentiostat/galvanostat. All electrochemical measurements were performed in an inert atmosphere glove box using degassed acetonitrile solutions containing 0.1 M tetrabutyl ammonium perchlorate (TBAP) as a supporting electrolyte. A platinum wire was used as the working electrode. The counter and reference electrodes were a platinum coil and Ag/AgCl, respectively.

Results and discussion

Synthesis

The tetradentate tripodal ligand tris((benzimidazole-2-yl)methyl)amine (ntb) reacts with $Fe(ClO_4)_3$ in the presence of sodium acetate to form a doubly bridged (μ-oxo)(μ-acetate)diiron(III) complex via the now familiar self-assembly method [14]. We have found that ntb also reacts with $FeCl_3 \cdot 6H_2O$ and $((C_2H_5)_4N)_2$-$[Fe_2OCl_6]$ to give a linear bridged μ-oxo diiron(III) complex. The presence of sodium acetate appears to be necessary for the formation of the oxo bridge when using $FeCl_3$ as the metal source. In the absence of a base, such as sodium acetate, only the mononuclear $Fe(ntb)Cl_2^+$ cation (2) is isolated. Hydrolysis of 2 leads to the formation of compound 1 in the presence of $NaPF_6$ and NEt_4Cl in aqueous ethanol. However, in the presence of sodium acetate and $NaPF_6$, the hydrolysis of 2 yields a green precipitate which analyzes for the doubly bridged compound, $[Fe_2O(ntb)_2(O_2CCH_3)]$ $(PF_6)_3$ (3).

Interestingly, the addition of excess NEt_4Cl to an aqueous ethanol solution of 3 results in the formation of compound 1. The lability of the carboxylate bridge of $[Fe_2O(ntb)_2(O_2CCH_3)]^{3+}$ is not surprising because it has been shown previously that bridging carboxylate ligands of (μ-oxo)bis(μ-carboxylato)diiron(III) complexes readily exchange with phosphate ligands and other anions [15]. Indeed, chemistry very similar to that observed for compound 1 has been reported for $Fe_2O(tacn)_2(O_2CCH_3)_2)](PF_6)_2$ in aqueous solutions containing NaN_3 or NaNCS [16]. In these cases, both bridging acetate ligands are displaced resulting in the formation of singly bridged μ-oxo complexes $[Fe_2O(tacn)_2X_4]$ (where $X = N_3^-$ or NCS^-). Interestingly, when tacn is replaced with Me_3tacn only mononuclear $FeLX_3$ complexes are isolated. As with Me_3tacn, steric interactions may also play a role in the lability of the acetate bridge of compound 3.

Displacement of the carboxylate bridge in 3 by Cl^- to give a linear μ-oxo bridged compound, such as 1,

TABLE 2. Selected bond lengths (Å) and angles (°) for 1

Fe–Fe	3.610(1)	Fe–N2	2.093(4)
Fe–Cl	2.293(1)	Fe–N4	2.249(5)
Fe–O1	1.8050(9)	Fe–N6	2.094(4)
Fe–N1	2.360(4)		
Fe–O1–Fe	180	O1–Fe–N4	165 2(1)
Cl–Fe–O1	102.63(7)	O1–Fe–N6	90.6(1)
Cl–Fe–N1	167.3(1)	N1–Fe–N2	75.3(1)
Cl–Fe–N2	104.0(2)	N1–Fe–N4	75.3(1)
Cl–Fe–N4	92.0(1)	N1–Fe–N6	75.6(1)
Cl–Fe–N6	104.15(9)	N2–Fe–N4	87.4(2)
O1–Fe–N1	90 1(1)	N2–Fe–N6	150.8(1)
O1–Fe–N2	90.7(1)	N4–Fe–N6	84.0(2)

is not likely to be biologically relevant to the chemistry reported for hemerythrin because the triply bridged core structures of deoxyHr and metHr are known to remain unaltered in the presence of simple anions, such as N_3^-, Cl^-, OH^-, NCS^- and HO_2^- [2c]. On the other hand, purple acid phosphatase is thought to contain a bridging carboxylate anion that is displaced or ruptured in reactions with phosphoesters and O_2 [4]. Therefore, linear or bent μ-oxo diiron(III) core structures may be important intermediates in the chemistry of some non-heme iron proteins.

Description of crystal structure of compound 1

The structure of compound **1** consists of the $[Fe_2O(ntb)_2Cl_2]^{2+}$ cation, four tetrahydrofuran solvate molecules and two PF_6^- counteranions. The complex crystallizes in the triclinic space group $P\bar{1}$. A view of the centrosymmetric cation is shown in Fig. 1. Selected bond lengths and angles of the cation coordination sphere are given in Table 2.

The bridging oxo group (O1) lies on a crystallographic center of symmetry that relates both halves of the molecule. The Fe–O1 bond length is 1.8050(9) Å while the Fe1–O1–Fe2 bond angle is 180° and the Fe–Fe separation is determined to be 3.610(1) Å. The remaining five coordination sites on the iron centers are occupied by the tetradentate ntb ligand nitrogen atoms and a chloride ion giving a distorted octahedral geometry. The amine nitrogen atom (N1) of the ntb ligand bonds cis to the bridging oxo group and trans to the chloride ion, and has a bond length of 2.360(4) Å. Two of the benzimidazole moieties bond cis to the oxo group (N2 (2.093(4) Å) and N6 (2.094(4) Å), while the third benzimidazole donor (N4) bonds trans to the oxo group at a distance of 2.249(5) Å.

In general, the benzimidazole pendants are bonded more strongly to the iron center than to the amine

nitrogen atoms because they are good π donors. The benzimidazole ligand bonded trans to the bridging oxo ligand, however, has a longer Fe–N bond distance due to the trans influence of the oxo group. A similar trans influence is observed for the imidazole ligands that are bonded trans to the bridging oxo group in N_3metHr [6].

The trans orientation of the benzimidazole donor in compound **1**, relative to the oxo group, was not anticipated, since it seemed more logical that the weaker and hence longer Fe–N1 amine bond would better accommodate the trans influence exerted by the oxo bridging ligand. It seems then that the coordination geometry of the ntb ligand relative to the oxo group is controlled in part by interligand steric interactions between opposing ntb ligands. Similar interligand repulsion effects in iron oxo complexes of the tpa tripodal ligand were reported to result in the formation of unsymmetric μ-oxo diiron(III) complexes [17]. In this case, the interligand steric interaction between pyridine pendants is relieved by the unsymmetric orientation of the tpa ligands relative to the oxo bridge. A structure similar to complex **1** has been reported for the diiron(III) complex of 2-[bis((benzimidazol-2-yl)methyl)amino]-ethanol (bbimae) [18]. As with compound **1**, the oxo bridged complex of bbimae is centrosymmetric with an Fe–O–Fe angle of 180°. The amine nitrogen atoms and benzimidazole ligands bond cis to the bridging oxo group while the hydroxyethyl oxygen atom bonds trans to the bridge. The benzimidazole pendants are stacked parallel to their symmetry related counterparts about the inversion center. A similar stacking arrangement of the benzimidazole ligands is observed for compound **1**, which relieves any interligand steric interactions. The closest interatomic separation between benzimidazole ligands in compound **1** is 2.93 Å (between H6 and H9B).

Electronic spectra

Complexes **1** and **2** exhibit intense charge-transfer transitions in the 300–420 nm region. For compound **1**, only two intense transitions centered at 300 nm ($\epsilon = 4500$ M^{-1} cm^{-1} Fe^{-1}) and 401 nm ($\epsilon = 3630$ M^{-1} cm^{-1} Fe^{-1}) are observed and have been assigned to oxo → Fe(III) charge-transfer transitions. The spectrum of compound **2** is qualitatively similar to **1** with transitions centered at 302 nm ($\epsilon = 2140$ M^{-1} cm^{-1}) and 405 nm ($\epsilon = 1770$ M^{-1} cm^{-1}). The similarity in appearance of the solution spectra of both complexes **1** and **2** initially suggested that either compound **2** hydrolyzes readily to compound **1** or that compound **1** decomposes to compound **2** in acetonitrile solutions. However, solution magnetic susceptibility measurements on both compounds show that they are stable in acetonitrile (vide infra). Interestingly, the electronic spec-
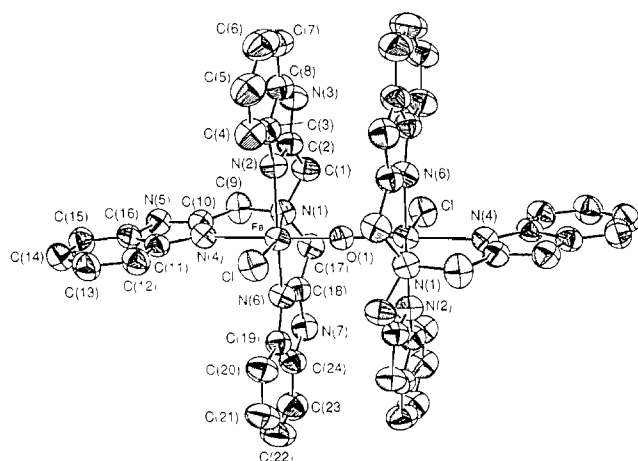

Fig. 1. ORTEP plot of $[Fe_2O(ntb)_2Cl_2]^{2+}$ Hydrogen atoms omitted for clarity

trum of $[Fe(HB(Pz)_3)Cl_3]^-$ is very similar to the spectra of compounds 1 and 2 displaying only two transitions at 291 nm ($\epsilon = 4800$ M^{-1} cm^{-1}) and 394 nm ($\epsilon = 6400$ M^{-1} cm^{-1}) that are thought to arise from Cl$^-$ → Fe(III) charge-transfer transitions [19]. The electronic spectrum of 3 displays an absorption maximum at 368 nm ($\epsilon = 4340$ M^{-1} cm^{-1} Fe^{-1}) with a shoulder at 331 nm ($\epsilon = 3800$ M^{-1} cm^{-1} Fe^{-1}) corresponding to oxo → Fe^{III} charge-transfer transitions. In addition there is a shoulder at 480 nm ($\epsilon = 320$ M^{-1} cm^{-1} Fe^{-1}) possibly arising from an oxo → Fe^{III}, $^6A_1$ → (^4A, ^4E) d-d transition, or $CH_3CO_2^-$ → Fe^{III} charge-transfer transition. A broad band is observed at 601 nm ($\epsilon = 91$ M^{-1} cm^{-1} Fe^{-1}) that is assigned to the $^6A_1$ → $^4T_2(^4G)$ transition.

Magnetic susceptibility

Solution magnetic susceptibility measurements were conducted on compounds 1-3 in acetonitrile at 295 K using the Evans method [20]. For compounds 1 and 3 the effective magnetic moments were determined to be equal to 2.0 and 1.85 BM/Fe, respectively, indicative of antiferromagnetically coupled diiron(III) complexes. Compound 2, on the other hand, has an effective magnetic moment of 5.9 BM which is normal for a mononuclear high spin Fe(III) complex. Solid state variable temperature magnetic susceptibility studies have been performed on compound 1. The temperature dependence of the magnetic susceptibility data of compound 1 is best described by the isotropic exchange Hamiltonian, $H = -2JS_1 \cdot S_2$ for two interacting spins with $S = 5/2$. The magnetic data were fit using the expression below:

$$X_{calc} = P \frac{35N\beta}{3kT} + (1-P) \frac{Ng^2\beta^2}{KT} \times (2 \exp(2x)$$

$$+ 10 \exp(6x) + 28 \exp(12x) + 60 \exp(20x)$$

$$+ 110 \exp(30x))(1 + 3 \exp(2x) + 5 \exp(6x)$$

$$+ 7 \exp(12x) + 9 \exp(20x) + 11 \exp(30x))^{-1}$$

$$+ TIP \tag{1}$$

Equation(1) was modified to account for temperature independent paramagnetism (*TIP*) and a small percentage (*P*) of paramagnetic impurity. When the temperature is decreased, the moment decreases to about 0.7 BM at temperatures lower than 50 K, where it plateaus due to the presence of a small amount of an uncoupled Curie-behaved contaminant. This is consistent with the $S = 0$ state being the ground state. The best fit of the experimental data gives a J value of -100 cm^{-1} and $g = 1.87$ with *TIP* equal to 202×10^{-6} cm^3 mol^{-1} and P equal to 1.48×10^{-2}.

Examination of the literature shows that mono-bridged μ-oxo diiron(III) complexes exhibit exchange interactions in the range -65 to -191 cm^{-1} [21] (Table 3). Complexes of planar macrocycles (e.g. porphyrins) are generally in the high range of exchange values while complexes containing less rigid structures fall around -90 cm^{-1}.

The J value determined for 1 is in the range of values reported for structurally similar compounds [18, 21, 22], but smaller than the values reported for (μ-oxo)diiron(III) porphyrin complexes [23, 24]. The Fe-Fe distance of 3.610(1) Å is too large to result in the antiferromagnetic exchange interaction from direct Fe-Fe overlap. Instead, the magnetic interaction arises from the so-called superexchange pathways. For a (μ-oxo)diiron(III) complex the exchange pathway most favored is through π bonds formed from the Fe d_{xz} and oxo p_x orbitals or through σ bonds formed from the overlap of the Fe d_{z^2} and oxo p_z orbitals [18, 21]. The most favored exchange pathway for bent Fe-O-Fe systems is the π pathway while the σ pathway is favored relative to the π pathway for linear Fe-O-Fe systems. For bent systems the overlap between the p_x orbital of the oxo group and the d_{xz} orbital of the Fe(III) ion increases relative to linear systems. Conversely, the overlap of the p_z orbital of the oxo group and the d_{z^2} orbital of the Fe(III) ion increases in the linear systems relative to the bent systems. Because there are two types of exchange pathways with one greater in linear systems and one greater in bent systems, there is no real correlation between the Fe-O-Fe angle and the value of J for (μ-oxo) diiron(III) complexes, as reported by others [22].

TABLE 3 Comparison of core dimensions and magnetic data for linear (μ-oxo) diiron(III) complexes

	Fe-Fe (Å)	Fe-O (Å)	$-J$ (cm^{-1})	Ref
$[Fe_2O(ntb)_2Cl_2]^{2+}$	3 610(1)	1.8050(9)	100	this work
$[Fe_2O(bbimae)_2Cl_2]^{2+}$	3.563(1)	1.7816(7)	103	18
$[Fe_2O(bbimae)_2NCS_2]^{2+}$	3.559(1)	1.7795(8)	95-105	18
$[Fe_2O(tpa)_2Cl_2]^{2+}$	3.580(1)	1.790(1)	109.7	22
$[Fe(TPP)]_2O$	3.518(1)	1.759(1)	187	24
$[Fe(TPC)]_2O$	3 510(5)	1.747(5)	191	23
		1 763(5)		

One factor which may influence *J*, however, is the Fe–O distance. For the porphyrin complexes [Fe(TPC)]₂O (Fe–O–Fe = 180°) and [Fe(TPP)]₂O (Fe–O–Fe = 180°) large *J* values of −191 and −186 cm⁻¹, respectively, have been reported [23, 24]. These complexes both have very short Fe–O bond distances of about 1.75 Å. The linear complexes [Fe(tpa)Cl]₂O [22] and [Fe(bbimae)]₂O [18] have *J* values of −110 and −103 cm⁻¹, respectively. The Fe–O bond lengths [22b] of these complexes are more like those of complex 1 (1.805 Å) with distances of 1.790 and 1.782 Å, respectively (Table 3). The weaker exchange interaction in complexes that possess linear oxo bridges may be related to the fact that the crossed $d_{z^2} - d_{xz}$ interaction emphasized in bent bridged oxo complexes is no longer operative.

¹H NMR spectroscopy

In order to elucidate the solution structure of complex 1 further, the ¹H NMR spectra of [Fe₂O(ntb)₂(O₂CCH₃)]³⁺ (3) and compound 1 were recorded in CD₃CN. The ¹H NMR spectra of both compounds are shown in Fig. 2. The spectrum of complex 1 appears to be less complicated than that of

[Fe₂O(ntb)₂(O₂CCH₃)]³⁺. The simplicity of the spectrum of 1 is attributed to the presence of the inversion center. In general, there are sharp resonances between 6 and 8 ppm and between 10 and 13 ppm in the spectrum of 1 that are assigned to H6 and H7, respectively, of the phenyl rings of the benzimidazole pendants. There appears to be a series of broad resonances, some buried, between 8 and 15 ppm which is probably due to the H8 protons of the phenyl rings. The spectrum of compound 3 shows a broad resonance at 10 ppm which does not correspond to a peak in the spectrum of compound 1. This resonance is assigned to the methyl protons of the bridging acetate group. The spectra of both compounds 1 and 3 display resonances that are associated with D₂O exchangeable protons. These signals are located between 16 and 20 ppm for compound 1 and 15 and 18 ppm for 3, and are assigned to the N–H protons of the benzimidazole moieties. The presence of two N–H resonances in the spectrum of compound 1 in a 2:1 ratio offers proof that the solid state structure of the complex is retained in solution. Compound 3, on the other hand, possesses three resonances associated with N–H exchangeable protons at 17, 18 and 19 ppm. A very broad resonance is also observed at 30 and 27 ppm for compounds 3 and 1, respectively. These signals are probably due to either H9 protons (benzimidazole) or methylene protons of the ntb ligand.

It should be noted that there are three plausible structures for [Fe₂O(ntb)₂(O₂CCH₃)]³⁺: (i) both ntb ligands occupy positions about the iron centers with the amine nitrogen atom *trans* to the oxo group, (ii) the amine nitrogen atom of one ntb ligand is bonded *trans* to the oxo, while the other amine is bonded *cis* to the oxo bridge, or (iii) the amine nitrogen atoms of both ntb ligands bond *cis* to the oxo group. Case (i) has been observed for a polyimidazole ligand containing 2-substituted 1-methylimidazole pendants, such as tris((1-methylimidazol-2-yl)methyl)amine (tmima) [25]. Case (ii) has been observed for ligands containing pyridine pendants, e.g., tpa [17, 22] Finally case (iii) includes compound 1 and a tpa complex containing a bridging phthalate group [22]. Of the three possibilities, cases (i) and (ii) should produce the most interligand steric interactions for the ntb ligand. Therefore it is probable that [Fe₂O(ntb)₂(O₂CCH₃)]³⁺ adopts a structure described in case (iii). In this configuration there are minimal interligand steric interactions The inequivalence of the benzimidazole NH protons in the NMR spectrum of compound 3 supports this conclusion.

Fig 2 ¹H NMR spectra of compounds 1 (a) and 3 (b) in CD₃CN referenced to external TMS.

Electrochemistry

Cyclic voltammograms of complexes 1 and 2 were obtained in acetonitrile solutions containing TBAP as the supporting electrolyte (see 'Supplementary mate-
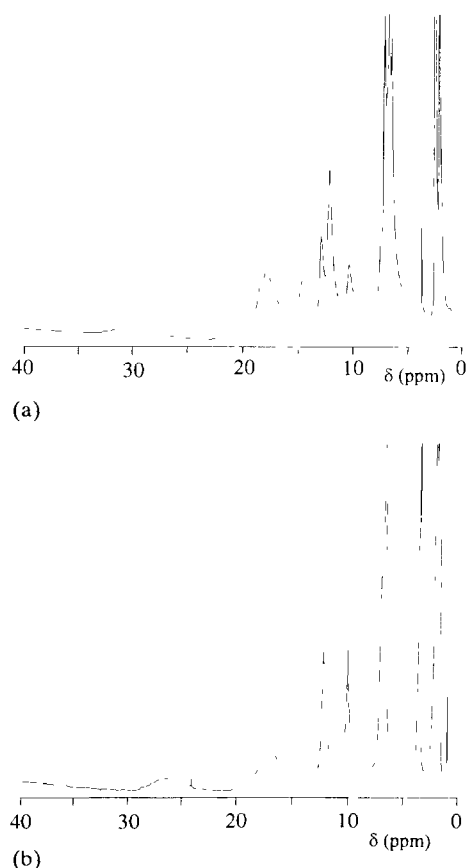
rial'). Compound **1** exhibits an irreversible reduction at -0.18 V NHE (not shown) and a coupled oxidation-reduction wave at 0.74 and 0.42 V, respectively. The $E_{1/2}$ value for this process is 0.58 V, however, ΔE is 0.32 V. The redox process therefore by definition is irreversible [26]. Based on the work of others [27, 28], the wave at -0.18 V is probably due to either a one-electron or two-electron reduction of the compound. Assuming that compound **1** exists as an $Fe_2(III,III)$ dimer at 0 V NHE, the redox process centered at 0.58 V would potentially correspond to the $Fe_2(III,III) \leftrightarrow Fe_2(III,IV)$ process, assuming that one electron has been transferred.

Compound **2** displays an oxidation wave at 0.525 V NHE and a coupled reduction step at 0.411 V. For this process $E_{1/2}=0.468$ V and $\Delta E=0.114$ V. Although ΔE is greater than the value of $0.059/n$ V (for $n=1$) associated with a reversible electrochemical process, the i_a/i_c ratios at various scan rates are approximately unity. Furthermore, the plots of i_a and i_c versus the square root of the scan rate are linear. Therefore this redox process is at the very least quasi-reversible, and corresponds to the one electron $Fe(III) \leftrightarrow Fe(II)$ redox couple.

We have reevaluated the electrochemistry of $[Fe_2O(ntb)_2(O_2CCH_3)]^{3+}$ reported previously by Nishida *et al.* [7b] and verify their findings. $[Fe_2O(ntb)_2(O_2CCH_3)]^{3+}$ shows an irreversible reduction wave at 0.06 V and an irreversible oxidation wave at 0.64 V NHE. These results are qualitatively similar to those observed for compound **1** with one exception, no reduction wave coupled to the oxidation process at 0.64 V is detected. The wave at 0.06 V presumably is due to the $Fe_2(III,III) \rightarrow Fe_2(II,III)$ reduction, while the wave at 0.64 V is tentatively assigned to the $Fe_2(III,III) \rightarrow Fe_2(III,IV)$ oxidation.

Electrochemical studies performed on $[Fe(TPP)]_2O$ and $[Fe(salen)]_2O$ show that these complexes may be oxidized to the $Fe_2(III,IV)$ mixed valence state having $E_{1/2}$ values for the redox process less than 1.4 V [29, 30]. In fact, the diiron(III) TPP and salen complexes have been chemically oxidized and the corresponding mixed valence complexes isolated. These mixed valence complexes have $S=1/2$ ground states and show single line EPR signals at $g=2$ [30]. Attempts to chemically oxidize compound **1** have failed to produce a species displaying an EPR signal near $g=2$.

Conclusions

In this study, a new linear (μ-oxo) bridged diiron(III) complex (**1**) has been prepared and characterized by several physical methods. The crystal structure of **1** shows that the complex is a centrosymmetric dimer and has benzimidazole pendants associated with the tripod polybenzimidazole ligand bonded *trans* to the oxo bridge. The other benzimidazole pendants bond *cis* to the bridging oxo group and are paired about the center of symmetry. The iron centers in **1** are strongly coupled antiferromagnetically resulting in a reasonably well-resolved ^1H NMR spectrum of the complex. The ^1H spectrum of **1** differs from the spectrum of the related oxo-iron complex, $[Fe_2O(ntb)(O_2CCH_3)]^{3+}$ (**3**), in the number of benzimidazole NH protons detected. The data support the presence of a bent oxo bridge in **3** and a linear bridge in **1**. The acetate bridge in **3** was found to be easily displaced by Cl^- in aqueous ethanol. Under such conditions, compound **1** was afforded in high yields. Finally, the electrochemical properties of **1** have been evaluated by cyclic voltammetry, and the data suggest that an $Fe^{III}Fe^{IV}$ form of the complex is generated upon oxidation at 0.74 V (NHE).

Supplementary material

Tables of the atomic positional parameters and isotropic thermal parameters, anisotropic thermal parameters, selected bond lengths and angles, H atom parameters, bond distances and angles for anions and solvate molecules, magnetic susceptibility data (36 pages), and figures showing the plot of the variable temperature magnetic data and cyclic voltammograms (2 pages) are available from the authors on request.

Acknowledgements

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