Inorg. Chem. **1994,** *33,* 3127-3134 **3127**

Synthesis and Reactivity of (μ-Oxo)diiron(III) Complexes of Tris(2-pyridylmethyl)amine. X-ray Crystal Structures of $[tpa(OH)FeOFe(H_2O)tpa](ClO_4)_3$ and $[tpa(Cl)FeOFe(Cl)tpa](ClO_4)_2$

Alan Hazell,[†] Kenneth B. Jensen,[‡] Christine J. McKenzie,[*,‡] and Hans Toftlund[*,‡]

Departments of Chemistry, University of Aarhus, DK-8000 Arhus, Denmark, and Odense University, DK-5230 Odense M, Denmark

Received September 8, 1993[⊗]

Five new (μ-oxo)diiron(III) complexes of the capping tetradentate ligand tris(2-pyridylmethyl)amine (tpa) have been prepared. The diaquo complex $[tpa(H_2O)FeOFe(H_2O)tpa](ClO_4)_4$ (**1**) and its conjugate base $[tpa(OH)FeOFe(H_2O)tpa](ClO_4)_3$ (**2**) serve as useful starting materials for the preparation of other (μ-oxo)-bridged diiron(III) complexes of tpa containing either terminal ligands or an auxiliary bridging group. For example, the terminal water ligands of **1** can be replaced by chloro ligands to give monobridged $[tpa(Cl)FeOFe(Cl)tpa](ClO_4)_2$ (**3**) or by sulfato to give dibridged $[(tpa)FeO(SO_4)Fe(tpa)](ClO_4)_2$ (**4**). Complex **2** shows unusual reactivity; **2** is capable of promoting the hydrolysis of acetonitrile to give a (μ-acetamidato-*N,O*)-bridged complex, $[(tpa)FeO(CH_3CONH)Fe(tpa)](ClO_4)_3$ (**5**). Complexes **1**–**5** show strong antiferromagnetic exchange coupling. The electronic absorption and resonance Raman spectra show distinctions between the mono- and dibridged systems, with **2** defining a borderline case. An X-ray structural analysis of $[tpa(OH)FeOFe(H_2O)tpa](ClO_4)_3$ (**2**) shows it to be monoclinic, space group $P2_1/c$, with $a = 12.092(2)$ Å, $b = 17.740(4)$ Å, $c = 20.633(3)$ Å, and $\beta = 104.148(8)°$ and with 4 formula units in the unit cell. The structure refined to a final R value of 0.054 for 2904 reflections. The coordinated water and hydroxide groups are linked by an intramolecular hydrogen bond, O···O = 2.419(10) Å. The Fe atoms are linked by a μ-oxo bridge; however, in contrast to those of other structurally characterized (μ-oxo)diiron(III) complexes, the two Fe–(μ-O) distances, 1.780(6) and 1.839(6) Å, are significantly different. The Fe–O–Fe angle is 138.9(4)°, and the Fe···Fe distance is 3.389(2) Å. An X-ray structural analysis of $[tpa(Cl)FeOFe(Cl)tpa](ClO_4)_2$ (**3**) shows it to be monoclinic, space group $C2/c$, with $a = 16.308(2)$ Å, $b = 17.178(3)$ Å, $c = 16.575(2)$ Å, and $\beta = 111.807(7)°$ and with 4 formula units per cell. The structure refined to a final R value of 0.061 for 1946 reflections. The cation has 2-fold symmetry with the bridging oxygen atom on the 2-fold axis: Fe–(μ-O) = 1.785(1) Å, Fe–O–Fe = 174.7(5)°, and Fe···Fe = 3.565(2) Å.

Introduction

Oxo-bridged iron(III) complexes have received much attention in recent years.[1] From about 1983 a renewed activity, driven largely by the endeavor to understand the chemistry of diiron sites in the non-heme proteins hemerythrin, ribonucleotide reductase, methane monooxidase, and the purple acid phosphatases, has been apparent in the literature.[1] Several model compounds for the (μ-oxo)bis(μ-carboxylato)diiron(III) active site of methemerythrin have been reported.[1,2] A recent structural analysis of the B2 subunit of *Escherichia coli* ribunucleotide reductase reveals an active site consisting of two iron centers connected by one oxide and one carboxylate group.[3] The other non-heme iron proteins are less well characterized than hemerythrin and ribonucleotide reductase, but their active sites all seem to have some common structural features.

Complexes capable of acting as functional models for the diiron non-heme proteins must have either a free coordination site or a ligand which can be replaced easily by an incoming substrate molecule. The present work reports on the results of our search for model compounds having these features. The nonbridging donor atoms of the complexes reported here are provided by the tetradentate tripodal ligand tris(2-pyridylmethyl)amine (tpa), which has served as a good substitute for the arrangement of the histidine groups anchoring the metal centers in many metalloproteins.

Monomeric tpa complexes have been reported with Cu(II),[4] Fe(II),[5] Na(I),[6] and Ru(II).[7] Geometries based on trigonal bipyramids, octahedra, and rhombohedra are represented among these complexes. There are also numerous examples of dinuclear transition metal complexes containing tpa as a capping ligand. Apart from a monobridged μ-peroxo[8] and a μ-carbonato[9] Cu(II) complex, all the reported dinuclear systems contain either μ-hydroxo or μ-oxo bridges. Chart 1 illustrates possible geometries for mono- and dibridged μ-oxo dinuclear tpa complexes. Structure **IV** has been found for $[tpa(NCS)CrOCr(NCS)tpa](ClO_4)_2$[10] and $[tpaOVOVOtpa](ClO_4)_2$.[11] For this structure only the *trans* rotamer was isolated. The other possible rotamers are less likely to be stable due to severe repulsion between the pyridine groups bound to the adjacent metal ions. Structure **VI** has been found for $[(tpa)Mn(\mu\text{-}O)_2Mn(tpa)]_2(S_2O_6)_3$[12] and $[(tpa)Fe(\mu\text{-}O)(\mu\text{-}RCO_2)Fe(tpa)](ClO_4)_3$,[13] (X = O and RCO_2, respectively). A bis(μ-hydroxo)-bridged complex, related to structure **VI** (where X = OH and the μ-O is protonated), was found for [(tpa)Cr-

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[†] University of Aarhus.

[‡] Odense University.

[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1994.

(1) (a) Kurtz, D. M., Jr. *Chem. Rev.* **1990,** *90,* 585. (b) Lippard, S. J. *Angew. Chem., Int. Ed. Engl.* **1988,** *27,* 344. (c) Que, L., Jr.; True, A. E. *Prog. Inorg. Chem.* **1990,** *38,* 97. (d) Murray, K. S. *Coord. Chem. Rev.* **1974,** *12,* 1.

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

(3) Norlund, P.; Sjöberg, B.-M.; Eklund, H. *Nature* **1990,** *345,* 593.

(4) (a) Garcia, M. C.; Karlin, K. D.; Holwerda, A. *J. Inorg. Biochem.* **1987,** *30,* 167. (b) Nishida, Y.; Takahashi, K. *Inorg. Chem.* **1988,** *27,* 1406.

(5) Højland, F.; Toftlund, H.; Yde-Andersen, S. *Acta Chem. Scand., Ser. A* **1983,** *37,* 251.

(6) Toftlund, H.; Ishiguro, S. *Inorg. Chem.* **1989,** *28,* 2236.

(7) Towle, D. K.; Bostford, C. A.; Hodgson, D. J. *Inorg. Chim. Acta* **1988,** *141,* 167.

(8) Jacobson, R. R.; Tyeklar, Z.; Farooq, A.; Karlin, K. D.; Liu, S.; Zubieta, J. *J. Am. Chem. Soc.* **1988,** *110,* 3690.

(9) Tyeklar, Z.; Paul, P. P.; Jacobson, R. R.; Farooq, A.; Karlin, K. D.; Zubieta, J. *J. Am. Chem. Soc.* **1989,** *111,* 388.

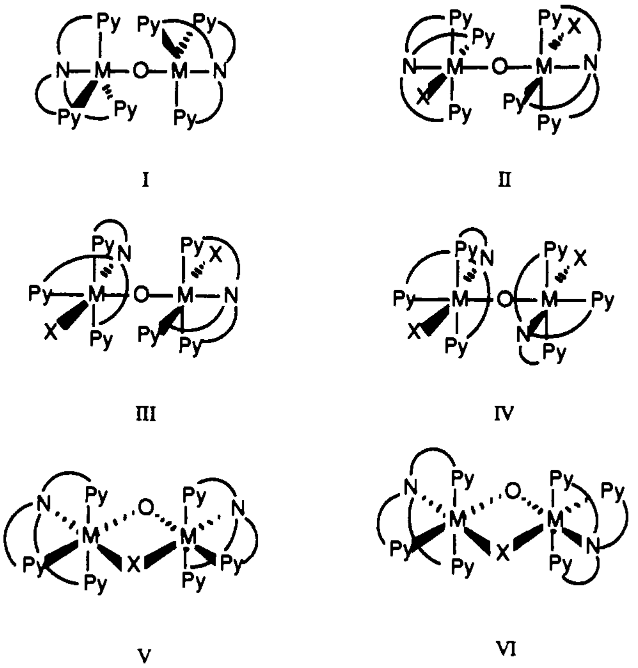
(10) Gafford, B. G.; Holwerda, R. A.; Schugar, H. J.; Potenza, J. A. *Inorg. Chem.* **1988,** *27,* 1126.

(11) Toftlund, H.; Larsen, S.; Murray, K. S. *Inorg. Chem.* **1991,** *30,* 3964.

(12) Oki, A. R.; Glerup, J.; Hodgson, D. J. *Inorg. Chem.* **1990,** *29,* 2435.

0020-1669/94/1333-3127$04.50/0

Chart 1



$(\mu\text{-OH})_2Cr(tpa)](ClO_4)_3$.[14] None of the other structures in Chart 1 have been found up to now.

Experimental Section

Physical Measurements. IR spectra were measured as KBr disks using a Hitachi 270–30 IR spectrometer. UV–visible absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer. Elemental analysis were carried out at the microanalytical laboratory of the H. C. Ørsted Institute, Copenhagen. Tris(2-pyridylmethyl)amine (tpa) was prepared by the method described by Højland *et al.*[5] Compounds dried in vacuum at room temperature. *Caution! Although no problems were encountered in the preparations of the following complexes as perchlorate salts, suitable care should be taken when handling such potentially hazardous compounds.*

Syntheses. (μ-Oxo)diaquobis[tris(2-pyridylmethyl)amine]diiron(III) Perchlorate, $[(tpa)(H_2O)FeOFe(H_2O)(tpa)](ClO_4)_4$ (1). A solution of tpa·$3HClO_4$ (0.207 g, 0.35 mmol) and triethylamine (0.124 g, 1.20 mmol) dissolved in methanol (7 mL) was added to $Fe(ClO_4)_3\cdot 6H_2O$ (0.191 g, 0.41 mmol) dissolved in methanol:water (1:1, 6 mL). Red platelike crystals of $[tpa(H_2O)FeOFe(H_2O)tpa](ClO_4)_4$ grew over several weeks. These were collected and washed with methanol (0.130 g, 32%). Anal. Calcd for $[tpa(H_2O)FeOFe(H_2O)tpa](ClO_4)_4\cdot 2H_2O$, $C_{36}H_{44}Cl_4Fe_2N_8O_{21}$: C, 36.70; H, 3.76; N, 9.51; Cl, 12.03%. Found: C, 36.72; H, 3.81; N, 9.13; Cl, 11.44%.

(Aquo-2κ*O*)(hydroxo-1κ*O*)(μ-oxo)(bis[tris(2-pyridylmethyl)amine]-1κ⁴*N*¹,*N*²,*N*³,*N*⁴;2κ⁴*N*¹,*N*²,*N*³,*N*⁴)diiron(III) Perchlorate, $[(tpa)(OH)FeOFe(H_2O)(tpa)](ClO_4)_3$ (2). A solution of tpa·$3HClO_4$ (0.216 g, 0.36 mmol) and triethylamine (0.081 g, 0.80 mmol) dissolved in methanol (7 mL) was added to $Fe(ClO_4)_3\cdot 6H_2O$ (0.181 g, 0.39 mmol) dissolved in water (3 mL) to produce a red solution. A second portion of triethylamine (0.081 g, 0.80 mmol) in methanol (2 mL) was added slowly. The solution changed to a green color. Green crystals of $[tpa(OH)FeOFe(H_2O)tpa](ClO_4)_3$ were deposited over a few hours. These were collected and washed with methanol (0.113 g, 30%). Anal. Calcd for $[tpa(OH)FeOFe(H_2O)tpa](ClO_4)_3$, $C_{36}H_{39}Cl_3Fe_2N_8O_{15}$: C, 41.50; H, 3.77; N, 10.76; Cl, 10.21. Found: C, 41.25; H, 3.80; N,10.64; Cl, 10.28%.

Table 1. Crystallographic Data and Details of Data Collection and Structure Analyses for $[tpa(OH)FeOFe(H_2O)tpa](ClO_4)_3$ (**2**) and $[tpa(Cl)FeOFe(Cl)tpa](ClO_4)_2$ (**3**)

	2	**3**
chem formula	$C_{36}H_{39}N_8O_{15}Cl_3Fe_2$	$C_{36}H_{36}N_8O_9Cl_4Fe_2$
fw	1041.8	978.2
space group	$P2_1/c$	$C2/c$
a, Å	12.092(2)	16.308(2)
b, Å	17.740(4)	17.178(3)
c, Å	20.633(3)	16.575(2)
β, deg	104.148(8)	111.807(7)
V, Å^3	4292(1)	4311(1)
Z	4	4
T, K	294	294
λ(Mo Kα), Å	0.710 73	0.710 73
ρ_{calc}, g cm^{-3}	1.612	1.507
μ(Mo Kα), cm^{-1}	9.38	9.80
transm coeff	0.802–0.885	0.715–0.964
unique data	7536	4226
significant data[a]	2904	1946
variables	588	340
$R(F_o)$,[b] $R_w(F_o)$[c]	0.054, 0.063	0.061, 0.075

[a] $I/\sigma(I) > 3.0$. [b] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w^{-1} = [\sigma_{cs}(F^2) + 1.03F^2]^{1/2} - |F|$.

(μ-Oxo)dichlorobis[tris(2-pyridylmethyl)amine]diiron(III) Perchlorate, $[(tpa)(Cl)FeOFe(Cl)(tpa)](ClO_4)_2$ (3). A solution of tpa·$3HClO_4$ (0.516 g, 0.87 mmol) and tetrabutylammonium hydroxide (20% in water, 2 mL) dissolved in ethanol (20 mL) was added to $FeCl_2\cdot 4H_2O$ (0.178 g, 0.90 mmol) dissolved in water (10 mL) to produce a red solution. Brown needles of the product crystallized after several days standing in air. These were collected and washed with methanol (0.16 g, 18%). Anal. Calcd for $[tpa(Cl)FeOFe(Cl)tpa](ClO_4)_2$, $C_{36}H_{36}Cl_4Fe_2N_8O_9$: C, 44.20; H, 3.71; N, 11.45; Cl, 14.49. Found: C, 43.25; H, 3.64; N, 11.29; Cl, 14.26%.

(μ-Oxo)(μ-sulfato-*O*,*O*′)bis[tris(2-pyridylmethyl)amine]diiron(III) Perchlorate, $[(tpa)FeO(SO_4)Fe(tpa)](ClO_4)_2$ (4). A solution of tpa·$3HClO_4$ (0.204 g, 0.345 mmol) and triethylamine (0.118 g,1.17 mmol) dissolved in warm methanol (5 mL) was added to a solution of $Fe(ClO_4)_3\cdot 6H_2O$ (0.166 g, 0.36 mmol) in methanol (5 mL). A solution of $Na_2SO_4\cdot 10H_2O$ (0.071 g, 0.22 mmol) in water (2 mL) was added. The solution changed to a green color, and green crystals of $[tpaFeO(SO_4)Fetpa](ClO_4)_2$ began precipitating within seconds. These were collected and washed with methanol (0.157 g, 45%). The complex was recrystallized in acetonitrile. Anal. Calcd for $[tpaFeO(SO_4)Fetpa](ClO_4)_2$, $C_{36}H_{36}Cl_2Fe_2N_8O_{13}S$: C, 43.09; H, 3.62; N, 11.17. Found: C, 43.55; H, 3.68; N, 11.46%.

(μ-Oxo)(μ-acetamidato-1κ*N*:2κ*O*)(bis[tris(2-pyridylmethyl)amine]-1κ⁴*N*¹,*N*²,*N*³,*N*⁴;2κ⁴*N*¹,*N*²,*N*³,*N*⁴)diiron(III) Perchlorate, $[(tpa)FeO(CH_3CONH)Fe(tpa)](ClO_4)_3$ (5). $[tpa(OH)FeOFe(H_2O)tpa](ClO_4)_3$ was dissolved is acetonitrile with warming; after several days of standing, brown crystals of the product were deposited. This method is not completely reproducible; only on one occasion was $[tpaFeO(CH_3CONH)Fetpa](ClO_4)_3$, completely free of the starting material, $[tpa(OH)FeOFe(H_2O)tpa](ClO_4)_3$, isolated. Anal. Calcd for $[(tpa)FeO(CH_3CONH)Fe(tpa)](ClO_4)_3\cdot H_2O$, $C_{38}H_{42}Cl_3Fe_2N_9O_{14}$: C, 42.14; H, 3.90; N, 11.64. Found: C, 42.18; H, 3.74; N, 11.54%.

Magnetic Studies. Magnetic susceptibility measurements were performed by the Faraday method in the temperature range 4–300 K at a field strength of 1.3 T using instrumentation described elsewhere.[15] The molar susceptibilities were corrected for ligand diamagnetism using Pascal's constants.

Resonance Raman. Raman spectra were recorded on a Jarrell-Ash Czerny-Turner scanning spectrometer. The samples were prepared as disks containing 300 mg of KBr, 20 mg of the complex, and 20 mg of K_2SO_4 for use as internal standard (referenced to $\nu_1(SO_4^{2-})$). The spectra of the samples were recorded at three excitation wavelengths, 457.9, 487.9, and 514.5 nm.

X-ray Crystallography. Single crystals of **2** and **3** were mounted on a Huber 4-circle diffractometer. Cell dimensions were determined from reflections measured at $\pm 2\theta$ and high and low χ. Intensities were measured at room temperature; two standard reflections were monitored every 50 reflections. Crystal data are given in Table 1.

Data were corrected for background, Lorentz, and polarization effects

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(13) (a) Norman, R. E.; Holz, R. C.; Ménage, S.; O'Connor, C. J.; Zhang, J. H.; Que, L., Jr. *Inorg. Chem.* **1990**, *29*, 4629. (b) Norman, R. E.; Yan, S.; Que, L., Jr.; Backes, G.; Ling, L.; Sanders-Loehr, J.; Zhang, J. H.; O'Connor, C. J. *J. Am. Chem. Soc.* **1990**, *112*, 1554. (c) Yan, S.; Cox, D. D.; Pearse, L. L.; Juarez-Garcia, C.; Que, L., Jr.; Zhang, J. H.; O'Connor, C. J. *Inorg. Chem.* **1989**, *28*, 2507. (d) Yan, S.; Que, L., Jr.; Taylor, L. F.; Anderson, O. P. *J. Am. Chem. Soc.* **1988**, *110*, 5222–5224.

(14) Hodgson, D. J.; Zeitlow, M. H.; Pedersen, E.; Toftlund, H. *Inorg. Chim. Acta* **1988**, *149*, 111.

(15) (a) Pedersen, E. *Acta Chem. Scand.* **1972**, *26*, 333. (b) Josephsen, J.; Pedersen, E. *Inorg. Chem.* **1977**, *16*, 2534.

and for absorption. The structures were determined using SHELX86[16] and from subsequent difference electron density maps and were refined by the least-squares minimization of $\sum w(|F_o| - |F_c|)^2$ using a modification of ORFLS.[17]

All the non-hydrogen atoms of complex **2** were refined with anisotropic thermal parameters. The hydrogen atoms of tpa were kept fixed at calculated positions, and a common isotropic thermal parameter was refined. Hydrogen atoms on the coordinated water were clearly distinguished, and both coordinates and temperature factors were refined. A difference map showed two possible sites for the hydroxyl hydrogen atom, which was kept fixed with half-occupancy at these sites. Fractional atomic coordinates are listed in Table 2; selected bond distances and angles in Table 3.

All the non-hydrogen atoms of complex **3** were refined with anisotropic thermal parameters. Hydrogen atom positions were located from a difference synthesis and were refined with isotropic thermal parameters. Fractional atomic coordinates are listed in Table 4; selected bond distances and angles in Table 5.

Results and Discussion

Synthesis of the Diaquo (μ-oxo)diiron(III) Complex and its Deprotonated Derivative. The (μ-oxo)diiron(III) complexes of tpa incorporating two terminal water ligands, $[tpa(H_2O)FeOFe(H_2O)tpa](ClO_4)_4$ (**1**), and its singly deprotonated, basic counterpart, $[tpa(OH)FeOFe(H_2O)tpa](ClO_4)_3$ (**2**), were synthesized by hydrolysis of $[Fe(tpa)(H_2O)_2]^{3+}$ in a triethylamine/triethylammonium buffer. The isolation of pure samples of **1**, as red crystals, and of **2**, as green crystals, depends on a subtle pH difference. The crystal structure of **2** has been solved, *vide infra*, and shows the *cis* aquo and hydroxo ligands to be strongly hydrogen bonded. We have recently characterized a diaquo complex closely analogous to **1** with another tripodal tetradentate capping ligand ($[bpp(H_2O)FeOFe(H_2O)bpp](ClO_4)_2$ (bpp = 3-[bis(2-pyridylmethyl)amino]propionate)).[18] The physical properties of $[bpp(H_2O)FeOFe(H_2O)bpp](ClO_4)_2$ and **1** are very similar, and thus **1** is anticipated to contain a nearly linear oxo bridge as in one of the arrangements **II**, **III**, or **IV** in Chart 1.

Substitution Reactions. One of our main objectives in this work has been to prepare diiron complexes containing labile ligands, and accordingly our initial experiments involved testing the versatility of the aquo and hydroxo ligands in complexes **1** and **2** in undergoing replacement reactions. Drüeke *et al.*[19] have proposed an aquo–hydroxo intermediate, in a reaction mechanism for the replacement of bridging carboxylates for bridging phosphates, in diiron complexes of the tridentate capping ligand 1,4,7-trimethyl-1,4,7-triazacyclononane. However the crucial aquo–hydroxo intermediate was not isolated in these studies.[19] Complex **2** is closely related to this proposed intermediate (apart from the fact that **2** lacks a supporting (μ-acetato)-bridge, i.e. the core is dibridged, (μ-O)(μ-H_3O_2), and not tribridged, (μ-O)(μ-CH_3CO_2)(μ-H_3O_2)).

Table 2. Atomic Coordinates and Equivalent Isotropic Temperature Factors (Å^2) for $[tpa(OH)FeOFe(H_2O)tpa](ClO_4)_3$ (**2**)

	x	y	z	U(eq)[a]
Fe(1)	0.79495(11)	0.21956(10)	0.73838(6)	0.043(1)
Fe(2)	0.52204(11)	0.22939(9)	0.64585(7)	0.045(1)
O(1)	0.6714(5)	0.1988(4)	0.6738(3)	0.046(4)
O(2)	0.7099(7)	0.2910(5)	0.7868(4)	0.064(6)
O(3)	0.5325(6)	0.3137(4)	0.7049(3)	0.059(5)
N(10)	0.9582(6)	0.2477(5)	0.8152(4)	0.049(6)
N(11)	0.8678(7)	0.3132(5)	0.6985(4)	0.052(6)
C(12)	0.8301(9)	0.3352(8)	0.6331(5)	0.062(8)
C(13)	0.8707(10)	0.4000(9)	0.6108(6)	0.072(9)
C(14)	0.9477(11)	0.4440(8)	0.6542(8)	0.078(10)
C(15)	0.9878(10)	0.4193(8)	0.7189(6)	0.071(9)
C(16)	0.9459(9)	0.3549(7)	0.7407(6)	0.055(7)
C(17)	0.9749(9)	0.3292(7)	0.8116(5)	0.059(8)
N(21)	0.9149(6)	0.1487(5)	0.7075(3)	0.042(5)
C(22)	0.8876(8)	0.1006(6)	0.6558(4)	0.049(7)
C(23)	0.9654(10)	0.0548(7)	0.6366(5)	0.060(8)
C(24)	1.0777(11)	0.0586(8)	0.6731(6)	0.072(9)
C(25)	1.1069(8)	0.1074(8)	0.7259(6)	0.067(8)
C(26)	1.0240(8)	0.1508(6)	0.7422(5)	0.048(7)
C(27)	1.0548(8)	0.2069(6)	0.7991(5)	0.056(7)
N(31)	0.8024(6)	0.1379(5)	0.8159(4)	0.046(5)
C(32)	0.7411(8)	0.0737(7)	0.8079(5)	0.051(7)
C(33)	0.7532(10)	0.0214(7)	0.8583(6)	0.061(8)
C(34)	0.8303(10)	0.0347(8)	0.9193(6)	0.065(8)
C(35)	0.8916(9)	0.1002(7)	0.9265(5)	0.056(7)
C(36)	0.8776(8)	0.1512(6)	0.8737(5)	0.044(6)
C(37)	0.9420(8)	0.2243(7)	0.8812(4)	0.054(7)
N(40)	0.4731(6)	0.1407(5)	0.5701(4)	0.045(5)
N(41)	0.5461(6)	0.2809(6)	0.5572(4)	0.048(5)
C(42)	0.5562(9)	0.3536(8)	0.5470(6)	0.063(8)
C(43)	0.5858(9)	0.3816(7)	0.4910(7)	0.070(9)
C(44)	0.6021(10)	0.3314(10)	0.4425(7)	0.078(10)
C(45)	0.5898(9)	0.2574(9)	0.4526(6)	0.074(9)
C(46)	0.5630(8)	0.2306(8)	0.5100(5)	0.056(7)
C(47)	0.5536(8)	0.1499(7)	0.5284(5)	0.054(7)
N(51)	0.3321(6)	0.2417(5)	0.6099(4)	0.044(5)
C(52)	0.2660(9)	0.2850(7)	0.6382(5)	0.059(7)
C(53)	0.1471(9)	0.2795(8)	0.6205(6)	0.075(9)
C(54)	0.0973(9)	0.2275(9)	0.5755(6)	0.075(9)
C(55)	0.1631(8)	0.1833(7)	0.5469(5)	0.057(7)
C(56)	0.2808(8)	0.1918(6)	0.5641(5)	0.046(6)
C(57)	0.3533(8)	0.1501(7)	0.5279(5)	0.055(7)
N(61)	0.4674(6)	0.1416(5)	0.7008(4)	0.045(5)
C(62)	0.4447(9)	0.1488(8)	0.7617(6)	0.067(9)
C(63)	0.4125(10)	0.0883(10)	0.7942(6)	0.075(10)
C(64)	0.3980(11)	0.0206(10)	0.7631(9)	0.092(12)
C(65)	0.4204(10)	0.0119(8)	0.7022(7)	0.074(10)
C(66)	0.4540(8)	0.0741(7)	0.6720(5)	0.051(7)
C(67)	0.4890(9)	0.0680(7)	0.6074(6)	0.061(8)
Cl(1)	0.8189(2)	0.0921(2)	0.4579(1)	0.061(2)
O(4)	0.7531(8)	0.1061(6)	0.3923(4)	0.132(8)
O(5)	0.8229(8)	0.1598(6)	0.4963(5)	0.107(8)
O(6)	0.7683(9)	0.0361(6)	0.4884(5)	0.122(8)
O(7)	0.9306(7)	0.0764(6)	0.4570(4)	0.117(8)
Cl(2)	0.2633(2)	0.1024(2)	0.9584(1)	0.061(2)
O(8)	0.1469(7)	0.0910(6)	0.9496(5)	0.121(8)
O(9)	0.3192(8)	0.0846(6)	1.0239(5)	0.132(9)
O(10)	0.2934(8)	0.1755(6)	0.9420(5)	0.116(8)
O(11)	0.3005(10)	0.0499(7)	0.9185(7)	0.165(12)
Cl(3)	0.3266(3)	0.1171(2)	0.3221(2)	0.073(2)
O(12)	0.4229(12)	0.1188(10)	0.3663(7)	0.249(16)
O(13)	0.2686(13)	0.1761(10)	0.3102(10)	0.270(20)
O(14)	0.3508(15)	0.0890(9)	0.2650(6)	0.218(16)
O(15)	0.2758(14)	0.0617(12)	0.3434(11)	0.285(23)
H(1)	0.722(7)	0.319(5)	0.807(4)	0.00(1)
H(2)	0.623(5)	0.314(3)	0.759(3)	0.00(1)

[a] $U(\mathrm{eq}) = {}^1/_3 \sum_i \sum_j U_{ij} a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j$.

Complexes **1** and **2**, in which the basic unit, $[(tpa)FeOFe(tpa)]^{4+}$, is already preformed, proved suitable as starting materials for the preparation of a series of (μ-oxo)diiron(III) complexes of tpa containing either two terminal acido groups or a bridging oxo acido group. The water ligands of **1** can be substituted by chloride ions or by the bridging groups, acetate, diphenyl phosphate, and sulfate. Reactions, in which the terminal waters of **1** are replaced by a bridging group can be verified by UV–vis spectroscopy; bands characteristic for dibridged diiron(III) complexes containing a bent μ-oxo group appear in the spectra on substitution. The previously reported complexes, $[(tpa)FeO(CH_3CO_2)Fe(tpa)](ClO_4)_3$ and $[(tpa)FeO(O_2P(OC_6H_5)_2)Fe(tpa)](ClO_4)_3$,[13b] are formed when 1 equiv of the sodium salts of acetate and diphenyl phosphate, respectively, are added to solutions of **1** in acetonitrile/water. Their quantitative formation is verified by the comparison of extinction coefficients with those reported[13b] and by isolation. Two new complexes were prepared in this fashion, the unsupported (μ-oxo)-bridged complex with terminal chloride ligands, $[tpa(Cl)FeOFe(Cl)tpa](ClO_4)_2$ (**3**) and the dibridged (μ-oxo)(μ-sulfato)-bridged complex, $[(tpa)FeO(SO_4)Fe(tpa)](ClO_4)_2$ (**4**).

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(16) Sheldrick, G. SHELX86: Program for the solution of crystal structures. University of Göttingen, Germany, 1986.

(17) Busing, W. R.; Martin, K. O.; Levy, H. A. ORFLS. Report ORNL-TM-305; Oak Ridge National Laboratory: Oak Ridge, TN, 1962.

(18) Hazell, A.; Jensen, K. B.; McKenzie, C. J.; Toftlund, H. *J. Chem. Soc., Dalton Trans.* **1993**, 3249.

(19) Drüeke, S.; Wieghardt, K.; Nuber, B.; Weiss, J.; Fleischauer, H.-P.; Gehring, S.; Haase, W. *J. Am. Chem. Soc.* **1989**, *111*, 8622.

Table 3. Selected Bond Distances (Å) and Angles (deg) for [tpa(OH)FeOFe(H_2O)tpa](ClO_4)$_3$ (**2**)

	Bond Distances		
Fe(1)–Fe(2)	3.389(2)	Fe(2)–O(1)	1.839(6)
Fe(1)–O(1)	1.780(6)	Fe(2)–O(3)	1.913(7)
Fe(1)–O(2)	2.040(9)	Fe(2)–N(40)	2.194(8)
Fe(1)–N(10)	2.264(8)	Fe(2)–N(41)	2.128(9)
Fe(1)–N(11)	2.137(9)	Fe(2)–N(51)	2.245(7)
Fe(1)–N(21)	2.132(8)	Fe(2)–N(61)	2.124(9)
Fe(1)–N(31)	2.144(8)		
	Angles		
Fe(1)–O(1)–Fe(2)	138.9(4)	O(1)–Fe(2)–O(3)	97.1(3)
O(1)–Fe(1)–O(2)	93.6(3)	O(1)–Fe(2)–N(40)	94.9(3)
O(1)–Fe(1)–N(10)	176.2(3)	O(1)–Fe(2)–N(41)	93.8(3)
O(1)–Fe(1)–N(11)	102.8(3)	O(1)–Fe(2)–N(51)	168.4(3)
O(1)–Fe(1)–N(21)	99.3(3)	O(1)–Fe(2)–N(61)	91.5(3)
O(1)–Fe(1)–N(31)	107.0(3)	O(3)–Fe(2)–N(40)	168.0(3)
O(2)–Fe(1)–N(10)	88.7(3)	O(3)–Fe(2)–N(41)	102.1(4)
O(2)–Fe(1)–N(11)	90.6(4)	O(3)–Fe(2)–N(51)	92.1(3)
O(2)–Fe(1)–N(21)	166.9(3)	O(3)–Fe(2)–N(61)	102.4(3)
O(2)–Fe(1)–N(31)	89.4(4)	N(40)–Fe(2)–N(41)	77.8(3)
N(10)–Fe(1)–N(11)	74.2(3)	N(40)–Fe(2)–N(51)	76.0(3)
N(10)–Fe(1)–N(21)	78.4(3)	N(40)–Fe(2)–N(61)	77.8(3)
N(10)–Fe(1)–N(31)	75.9(3)	N(41)–Fe(2)–N(51)	91.0(3)
N(11)–Fe(1)–N(21)	88.2(3)	N(41)–Fe(2)–N(61)	154.1(3)
N(11)–Fe(1)–N(31)	150.1(3)	N(51)–Fe(2)–N(61)	79.7(3)
N(21)–Fe(1)–N(31)	85.3(3)		

Complexes 3 and 4 were prepared also *via* the one-pot syntheses given in the Experimental Section. The X-ray crystal structure of the linear (μ-oxo)-bridged complex 3 has been determined and is described below. The structure of the cation in 3 has been alluded to earlier as one of the cations in the double salt {[Fe(tpa)Cl_2]$_2$[(tpa)(Cl)FeOFe(Cl)(tpa)]}(ClO_4)$_4$.[13a] However, the full details of this stuctural determination are not yet published.

Hydrolysis of Acetronitrile. Complex **2** shows an unusual reactivity toward acetonitrile. The elemental analysis of a brown-green crystalline product isolated from the attempted recrystallization of **2** from acetonitrile is consistent with a complex formulated as [(tpa)FeO(CH_3CONH)Fe(tpa)](ClO_4)$_3$ (**5**). The UV–vis and resonance Raman data for **5** (discussed below; data listed in Table 6) suggest that the Fe–O–Fe angle in **5** is similar to that observed in the prevously reported (μ-oxo)(μ-acetato)-bridged complex, [(tpa)FeO(CH_3CO_2)Fe(tpa)](ClO_4)$_3$.[13a] This evidence implies an isostructural arrangement of the diiron core, i.e. that the μ-acetamidato ligand is coordinated in an *O,N*-bridging mode imposing a Fe–O–Fe angle close to 130°.

Apparently the solvent, acetonitrile, has been hydrolyzed under the mild conditions prevailing during the recrystallization ($t < 70$ °C). A reaction scheme is suggested in Scheme 1. In the first step the labile terminal water is replaced by acetonitrile. The carbon atom of the coordinated acetonitrile is then conveniently positioned to undergo nucleophilic attack by the hydroxide group bound to the adjacent iron(III). This crucial step is probably facilitated by the anchimer effect and the polarization of the coordinated acetonitrile by Fe(III). In the last step a very stable (μ-acetamidato-*N,O*)-bridged complex is formed. Reaction mechanisms closely similar to that in Scheme 1 have been proposed previously for the nitrile hydrolysis reactions catalyzed at the dinuclear sites of dipalladium[20] and dicobalt[21] complexes. A related mechanism involving the nucleophilic attack by a hydroxide ligand on an adjacent nitrile ligand coordinated in a *cis* position to the same metal ion in a mononuclear complex, resulting in the formation of a chelated amide, has also been postulated.[22]

Table 4. Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) for [tpa(Cl)FeOFe(Cl)tpa](ClO_4)$_2$ (**3**)

	x	*y*	*z*	*U*(eq)[a]
Fe	0.1177(1)	0.1615(1)	0.2894(1)	0.037(1)
Cl(1)	0.1459(2)	0.1365(2)	0.4334(1)	0.058(2)
O(1)	0.0000	0.1663(5)	0.2500	0.040(4)
N(1)	0.1264(4)	0.1959(4)	0.1633(4)	0.041(4)
N(2)	0.2628(4)	0.1547(4)	0.3158(4)	0.047(4)
N(3)	0.1172(4)	0.0513(4)	0.2292(4)	0.043(5)
N(4)	0.1305(4)	0.2866(4)	0.2940(4)	0.042(4)
C(1)	0.2181(7)	0.2117(9)	0.1716(7)	0.057(8)
C(2)	0.2877(6)	0.1806(5)	0.2524(6)	0.049(6)
C(3)	0.3756(7)	0.1796(7)	0.2614(8)	0.069(8)
C(4)	0.4372(8)	0.1501(9)	0.3345(9)	0.096(10)
C(5)	0.4124(7)	0.1224(9)	0.3988(8)	0.087(9)
C(6)	0.3232(7)	0.1245(7)	0.3873(7)	0.068(7)
C(7)	0.0871(9)	0.1319(7)	0.1039(7)	0.058(8)
C(8)	0.1058(5)	0.0523(6)	0.1444(5)	0.047(6)
C(9)	0.1073(7)	−0.0134(7)	0.0998(6)	0.061(7)
C(10)	0.1169(8)	−0.0844(7)	0.1417(9)	0.082(9)
C(11)	0.1258(9)	−0.0854(8)	0.2265(9)	0.082(10)
C(12)	0.1269(6)	−0.0172(7)	0.2688(7)	0.059(7)
C(13)	0.0741(7)	0.2676(6)	0.1397(6)	0.048(6)
C(14)	0.1023(5)	0.3223(5)	0.2162(5)	0.046(6)
C(15)	0.1008(8)	0.4014(7)	0.2088(8)	0.072(8)
C(16)	0.1284(9)	0.4455(8)	0.2832(8)	0.085(10)
C(17)	0.1574(8)	0.4095(7)	0.3631(8)	0.079(9)
C(18)	0.1585(6)	0.3306(7)	0.3663(6)	0.057(7)
Cl(2)	0.1899(2)	0.3954(2)	−0.0011(2)	0.066(2)
O(2)	0.2526(13)	0.3796(11)	0.0731(11)	0.309(19)
O(3)	0.1350(11)	0.4471(7)	0.0140(12)	0.218(16)
O(4)	0.1535(7)	0.3215(6)	−0.0248(7)	0.144(10)
O(5)	0.2234(13)	0.4205(7)	−0.0531(12)	0.266(20)
H(1A)	0.233(6)	0.192(5)	0.125(6)	0.06(3)
H(1B)	0.227(5)	0.025(5)	0.169(5)	0.04(3)
H(3)	0.390(7)	0.204(6)	0.217(6)	0.09(4)
H(4)	0.503(9)	0.146(7)	0.343(7)	0.12(4)
H(5)	0.444(5)	0.097(5)	0.0440(5)	0.04(3)
H(6)	0.301(6)	0.117(5)	0.428(6)	0.07(3)
H(7A)	0.024(8)	0.138(6)	0.086(7)	0.11(5)
H(7B)	0.102(5)	0.130(4)	0.076(5)	0.01(3)
H(9)	0.097(6)	−0.009(6)	0.035(6)	0.08(3)
H(10)	0.124(6)	−0.131(5)	0.110(5)	0.06(3)
H(11)	0.139(5)	−0.126(5)	0.0254(5)	0.04(3)
H(12)	0.135(4)	−0.019(3)	0.323(4)	0.01(2)
H(13A)	0.020(5)	0.257(4)	0.129(4)	0.03(2)
H(13B)	0.077(4)	0.293(4)	0.091(4)	0.01(2)
H(15)	0.075(5)	0.425(5)	0.155(5)	0.05(2)
H(16)	0.126(8)	0.497(8)	0.276(8)	0.11(5)
H(17)	0.185(7)	0.432(6)	0.417(7)	0.09(4)
H(18)	0.178(5)	0.302(5)	0.421(6)	0.06(3)

[a] $U(eq) = {}^1/_3\sum_i\sum_j U_{ij} a^*_i a^*_j \mathbf{a}_i \mathbf{a}_j$.

Table 5. Selected Bond Distances (Å) and Angles (deg) for [tpa(Cl)FeOFe(Cl)tpa](ClO_4)$_2$ (**3**)

Fe–N(2)	2.245(6)	Fe–Fe′	3.565(2)
Fe–N(3)	2.138(7)	Fe–Cl(1)	2.298(2)
Fe–N(4)	2.158(7)	Fe–O(1)	1.785(1)
Fe–O(1)–Fe′	174.7(5)	Fe–N(1)	2.227(6)
Cl(1)–Fe–O(1)	99.3(1)	O(1)–Fe–N(4)	92.5(3)
Cl(1)–Fe–N(1)	165.2(2)	N(1)–Fe–N(2)	76.5(2)
Cl(1)–Fe–N(2)	89.9(2)	N(1)–Fe–N(3)	77.8(3)
Cl(1)–Fe–N(3)	106.5(2)	N(1)–Fe–N(4)	74.3(3)
Cl(1)–Fe–N(4)	99.7(2)	N(2)–Fe–N(3)	82.3(3)
O(1)–Fe–N(1)	94.6(2)	N(2)–Fe–N(4)	87.9(3)
O(1)–Fe–N(2)	170.6(2)	N(3)–Fe–N(4)	151.9(3)
O(1)–Fe–N(3)	93.0(3)		

The intramolecular attack by a hydroxide ion coordinated to one iron center on the carbon atom of the acetonitrile coordinated to the adjacent iron atom is closely similar to a reaction scheme suggested for phosphate-ester hydrolysis catalyzed by the purple acid phosphatases.[23] These metalloenzymes are known to have

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[20] (a) Louey, M.; McKenzie, C. J.; Robson, R. *Inorg. Chim. Acta* **1986**, *111*, 107. (b) McKenzie, C. J.; Robson, R. *J. Chem. Soc., Chem. Commun.* **1988**, 112.

[21] Curtis, N. J.; Hagen, K. S.; Sargeson, A. M. *J. Chem. Soc., Chem. Commun.* **1984**, 1571.

[22] Kim, J. H.; Britten, J.; Chin, J. *J. Am. Chem. Soc.* **1993**, *115*, 3618.

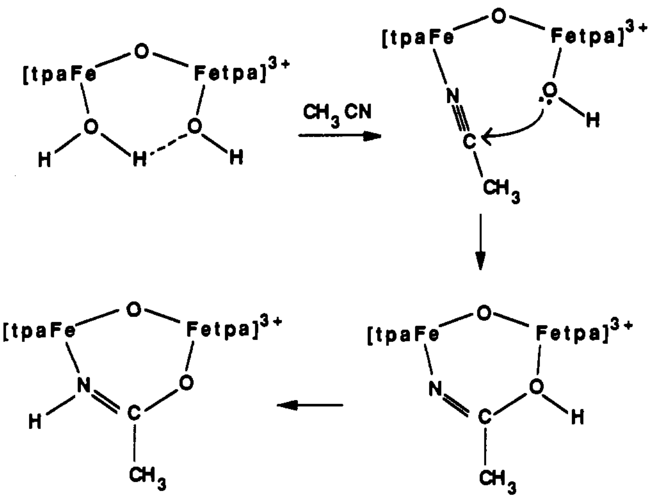
[23] (a) Hendry, P. H.; Sargeson, A. M. *Prog. Inorg. Chem.* **1990**, *38*, 201. (b) Aquino, M. A. S.; Lim, J.-S.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1992**, 2135.

Table 6. Spectroscopic and Magnetic Properties of $[(tpa)_2Fe_2OX](ClO_4)_n$ Complexes

	compound no. (X)					
	1 ($(H_2O)_2$)	**2** ($HOH\cdots OH^-$)	**3** ($(Cl)_2^{2-}$)	**4** (SO_4^{2-})	**5** (CH_3CONH^-)	($CH_3CO_2^-$)[e]
			Electronic Spectra[a]			
λ_{max}, nm	319 (13 280)	330 (11 089)	320 (12 704), sh	313 (11 000)	321 (12 912)	332(10 000)
(ϵ, M^{-1} cm^{-1})	358 (8056), sh	359 (8252), sh	380 (11116)	365 (6707)	370 (6234), sh	366 sh
		420 (1289), sh		424 (1368), sh		425 sh
	452 (457), sh	448 (735), sh		447 (939), sh	464(1425)	458 (1200)
	498 (283), sh	490 (516)	490 (645), sh	490 (751)	503 (1336)	492 (1000)
				521 (268), sh	542 (347), sh	530 sh
	572 (125)	608 (165)	573 (280), sh	660 (161)	708 (169)	700 (140)
			ν_{FeOFe} Data[b]			
ν_{as}, cm^{-1}	806	768	816	770	770	770
ν_s, cm^{-1}	353	435	363	478	495	499
			Magnetic Properties			
$-J$, cm^{-1}	105	97	116	117	118	114
TIP, cgs/mol	0.000 12	0.000 40	0.000 260	0.000 340	0.000 180	0.000 03
p, mol %	0.0016	0.021	0.0015	0.0024	0.0080	0.058
g	1.98	1.90	2.03	1.98	1.95	2.04
			Structural Data[c]			
$r_{Fe(1)-(\mu\text{-}O)}$, Å		1.780(6)	1.785(1)[d]			1.790(5)
$r_{Fe(2)-(\mu\text{-}O)}$, Å		1.839(6)				1.800(4)
∠Fe–O–Fe, deg		138.9(4)	174.7(5)			129.2(3)
Fe···Fe, Å		3.389(2)	3.565(2)			3.243(1)

[a] CH_3CN solution; the spectrum of **2** was recorded on a freshly prepared solution (**2** reacts with the solvent to give **5**). [b] ν_{as} from IR spectrum; ν_s from resonance Raman spectrum. [c] Fe(1)–(μ-O) refers to the bond trans to the $Fe–N_{amine}$ bond; Fe(2)–(μ-O) refers to bond trans to the $Fe–N_{py}$ bond. [d] The Fe–(μ-O) bonds in each half of $[tpa(Cl)FeOFe(Cl)tpa](ClO_4)_2$ are equivalent. [e] Data from refs 13d and 33.

Scheme 1



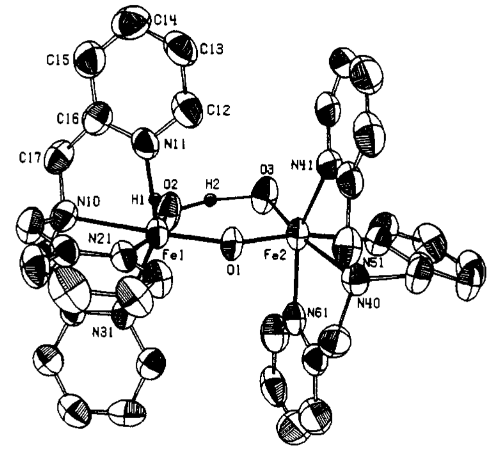


Figure 1. ORTEP drawing of $[tpa(OH)FeOFe(H_2O)tpa]^{3+}$ showing the partial numbering scheme. All hydrogen atoms, except those bound to the water ligand, O(2), are omitted for clarity.

a diiron active site. The reactivity of **2** with acetonitrile prompted us to try triphenyl phosphate as a substrate. Preliminary studies show that hydrolysis of $OP(OPh)_3$ to $O_2P(OPh)_2$ can indeed be facilitated by **2**.[24]

X-ray Crystal Structure of $[(tpa)(OH)FeOFe(H_2O)(tpa)](ClO_4)_3$ (2). The cation in **2**, $[(tpa)(OH)FeOFe(H_2O)(tpa)]^{3+}$, is depicted in Figure 1. The iron atoms are each coordinated to the four nitrogen atoms of (tpa) and the bridging oxygen atom. The sixth coordination site is taken by a water ligand on one iron atom and an hydroxo ligand on the adjacent iron atom. The iron centers are arranged in an approximate octahedral geometry. Selected bond lengths and angles are listed in Table 3.

The two tpa ligands of the cation in **2** have different orientations, as depicted by the asymmetrical structure **VI** in Chart 1. The tpa ligand associated with Fe(1) has the tertiary amine located *trans* to the oxo-bridge while that associated with Fe(2) has a pyridine located *trans* to the oxo bridge. This unsymmetric configuration is often found for dibridged diiron(III) complexes of tpa.[13] An exception is the (μ-phthalato)-bridged system, in which both tpa ligands are coordinated with the tertiary amine nitrogen atoms located *cis* to the oxo bridge (structure **V** in Chart 1).[13a] The unsymmetric tpa configuration is apparently favored for Fe–O–Fe angles lower than the 143° observed for the (μ-phthalato)-bridged complex.[13a] The switch in configuration probably stems from potentially unfavorable steric contacts between the α-hydrogen atoms of the pyridyl groups in adjacent tpa ligands in structure **IV** if the M–O–M angle is more acute than 143°.

The water and hydroxyl oxygen atoms are located *cis* to each other and are linked by a strong intramolecular hydrogen bond, O(2)···O(3) = 2.419(10) Å, which probably stabilizes the *cis* configuration. The water and hydroxyl oxygens are identified as O(2) and O(3), respectively, by the distances O(2)–H(2) = 1.15(6) Å and O(3)–H(2) = 1.36(6) Å and because Fe(1)–O(2) (2.040(9) Å) is significantly longer than Fe(2)–O(3) (1.913(7) Å). The H-bonded system is not entirely planar with a Fe(1)–O(2)–O(3)–Fe(2) torsion angle of 24.0(5)°. The coordinated water molecule is hydrogen bonded also to a perchlorate ion, O(2)···O(4) = 2.791(12) Å.

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[24] The UV–visible spectrum of a solution of **2** heated with an excess of $OP(OPh)_3$ is identical to the spectrum of the authentic diphenyl phosphato bridged complex $[(tpa)FeO(O_2P(OC_6H_5)_2)Fe(tpa)](ClO_4)_3$.[13b] Studies on the hydrolysis reactions catalyzed by (μ-oxo)diiron complexes are continuing in this laboratory.

The geometries of (μ_2-oxo)-bridged diiron compounds can be placed into two categories. For the monobridged compounds the Fe–O–Fe angle varies from 140 to 180° and Fe···Fe from 3.4 to 3.6 Å; for multiply-bridged compounds, ∠Fe–O–Fe varies from 110 to 143° and Fe···Fe from 3.0 to 3.4 Å.[25] The Fe(1)–O(1)–Fe(2) angle for **2** is 138.9(4)°, and Fe(1)···Fe(2) is 3.389(2) Å. These values are in the border region between those found so far for singly- and multiply-bridged diiron(III) complexes since the "bite" distance for the μ-$H_3O_2^-$ bridge is a little greater than for the usual supporting oxo acido bridging groups in multiply-bridged (μ-oxo)diiron(III) complexes.

The (μ-$H_3O_2^-$) structural motif was suggested by Springborg and Toftlund for dinuclear hydroxo–aqua–chromium(III) complexes.[26] The (μ-$H_3O_2^-$) bridge found in Δ,Λ-$[(en)_2(H_2O)Ir(OH)Ir(OH)(en)_2]^{4+}$ showed a symmetric hydrogen bond of O(2)···O(3) = 2.429(9) Å.[27a] The structure of **2** can be contrasted to this diiridium complex and other structurally characterized dinuclear complexes known to incorporate an $H_3O_2^-$ bridging unit, where a distinction between *cis* H-bonded hydroxo and aquo ligands is usually impossible because they merge into a symmetrical $H_3O_2^-$ moiety.[27] The characterization of the hydrogen-bonded aquo–hydroxo ligands in the solid state lends support to the existance of such a species in solution. As mentioned above aquo–hydroxo–(μ-oxo)diiron(III) complexes have been postulated previously as reactive intermediates.[19]

The two Fe–(μ-O) distances 1.780(6) and 1.839(6) Å are significantly different, the one *cis* to the hydroxy group being the shortest. Such a large difference in the lengths of the two bonds in the Fe–O–Fe unit has not been observed before in a structurally characterized (μ-oxo)diiron complex. The two Fe–(μ-O) distances in the active centers of methemerythrin and azidomethemerythrin, calculated from the X-ray crystal structural determinations, appear to be extremely different, due probably to the asymmetry of the surrounding protein.[28] This result has been regarded with some suspicion, due to difficulties in locating the bridging oxygen atom and because of the comparison to model compounds which consistently show two very similar Fe–(μ-O) distances. Complex **2** shows not only an asymmetrical arrangement of the tpa ligands but also a formal chemical difference between the iron atoms, due to their slightly different ligand fields. The significant difference in the two Fe–(μ-O) distances may be one of the consequences. The structure of **2** implies that the two very different Fe–(μ-O) distances in the structures of methemerythrin and azidomethemerythrin may be real and a consequence of the two very different coordination environments around the two iron atoms.

X-ray Crystal Structure of [tpa(Cl)FeOFe(Cl)tpa](ClO_4)$_2$ (3). The cation in **3**, $[tpa(Cl)FeOFe(Cl)tpa]^{2+}$, is depicted in Figure 2. The cation lies on a crystallographic 2-fold axis and, accordingly, has exact 2-fold symmetry. The iron atoms are each coordinated to one terminal chlorine atom, the bridging oxygen atom, and the four nitrogen atoms of the tpa in a distorted octahedral geometry. Selected bond lengths and angles are listed in Table 5. The bridging oxygen atom lies on the 2-fold axis, and the distance to the two symmetry-related iron atoms is Fe–(μ-O) = 1.785(1) Å. The Fe–O–Fe angle is 174.7(5)°, and Fe···Fe = 3.565(2) Å. These values are typical for unsupported (μ-oxo)-diiron(III) core structures.[1]

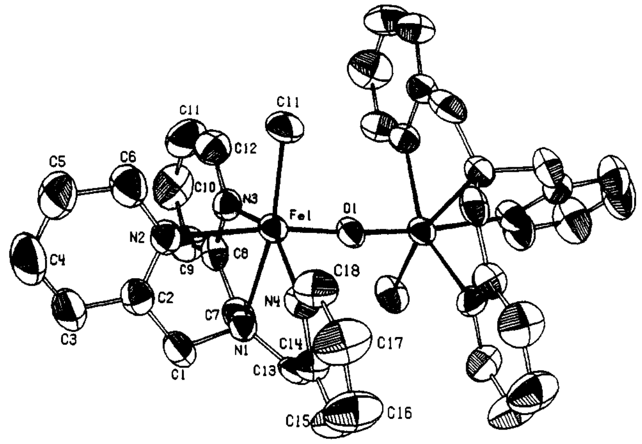

Figure 2. ORTEP drawing of $[tpa(Cl)FeOFe(Cl)tpa]^{2+}$ viewed along the effective 2-fold axis. The numbering scheme is shown. Hydrogen atoms are omitted for clarity.

Complex **3** exhibits the symmetric structure **IV** in Chart 1 in which the tertiary amines of both tpa ligands are located *cis* to the μ-oxo bridge. In contrast to comparable complexes of ligands containing both amine and pyridyl donors, where there are less steric constraints the tertiary nitrogen atoms tend to be in a *trans* position, as expected from the electronic preference for a weaker ligand *trans* to the oxo bridge. There are apparently steric grounds for the observed conformation of tpa in **3**.[11,13] An examination of the present structure suggests that the ring-stacking interactions between the tpa pyridine rings facing the oxo bridge become sufficiently favorable at high Fe–O–Fe angles to overcome the preference of the tertiary nitrogen atoms to be *trans* to the bridge. This geometrical arrangement (**IV** in Chart 1) was also found for corresponding tpa complexes containing the linear V–O–V[11] and Cr–O–Cr[10] cores. That the ligand *trans* to the bridge is the weakest can be concluded from the *trans* influence of the μ-oxo group observed in the structure of **3**. The Fe–N(2) distance of 2.245(6) Å is longer than the distance to the tertiary nitrogen atom, Fe–N(1) = 2.227(6) Å and much longer than the average distances to the two pyridine nitrogen atoms located *cis* to the (μ-oxo)-bridge, 2.148(12) Å. The chlorine atom, *trans* to the tertiary nitrogen atom, is located at an unusually short distance from the iron center, Fe–Cl = 2.298(2) Å.

Magnetic Properties. Typically the effective magnetic moment for complexes **1**–**5** declines from approximately 2.5 μ_B at room temperature to approximately 0.4 μ_B below 50 K. The variation of susceptibility with temperature for complexes **1**–**5** is well described by the equation derived from the Heisenberg, Dirac, Van Vleck model for isotropic dinuclear magnetic exchange interactions ($H = -2JS_1 \cdot S_2$).[29] The molar susceptibility was fitted by a least squares method to

$$\chi_M = (1-p)\left(\frac{Ng^2{\mu_B}^2}{kT}\right) \times \left(\frac{2e^{2x} + 10e^{6x} + 28e^{12x} + 60e^{20x} + 110e^{30x}}{1 + 3e^{2x} + 5e^{6x} + 7e^{12x} + 9e^{20x} + 11e^{30x}}\right) + \frac{p35}{8T} + \text{TIP}$$

where $x = J/kT$, p = mole fraction of paramagnetic impurities with ($S = {}^5/_2$) spin-only behavior, and TIP = temperature-independent paramagnetism (or diamagnetism). The values for the four independent parameters determined by the fitting procedure are listed in Table 6, corresponding to strong antiferromagnetic coupling in all cases.

Que *et al.* have reported (μ-oxo)diiron(III) tpa complexes with the following supporting bridges: acetate, benzoate, carbonate, phenyl phosphate, diphenyl phosphate, diphenylphosphinate, hydrogen maleate, and phthalate.[13] With the five new complexes described in the present work, the tpa family of (μ-oxo)diiron(III)

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(25) Values from the Cambridge Structural Database: Allen, F. H.; Kennard, O.; Taylor, R. *Acc. Chem. Res.* **1983**, *16*, 146.

(26) Springborg, J.; Toftlund, H. *Acta Chem. Scand., Ser. A* **1976**, *30*, 171.

(27) (a) Galsbøl, F.; Larsen, S.; Rasmussen, B.; Springborg, J. *Inorg. Chem.* **1986**, *25*, 290. (b) Ardon, M.; Bino, A.; Michelsen, K. *J. Am. Chem. Soc.* **1987**, *109*, 1986. (c) Ardon, M.; Bino, A. *Inorg. Chem.* **1985**, *24*, 1343.

(28) (a) Stenkamp, R. E.; Sieker, L. C.; Jensen, L. H. *J. Am. Chem. Soc.* **1984**, *106*, 618. (b) Sheriff, S.; Hendrickson, W. A.; Smith, J. L. *J. Mol. Biol.* **1987**, *197*, 273.

(29) O'Connor, C. J. *Prog. Inorg. Chem.* **1982**, *29*, 203.

complexes form one of the most extensive series of complexes of a constant ligand, to date, allowing an assessment of the spectral and magnetic properties of the (μ-oxo)diiron(III) core unit in a homologous series of complexes. It has been suggested that the two most crucial geometrical parameters are the Fe–O–Fe[1d] angle and the Fe–(μ-O) distance.[30] The Fe–O–Fe angles for the series of diiron complexes of tpa vary over the rather wide range 125.4(3)–174.7(5)°. However, the $-J$ values fall in the narrow range 97–129 cm^{-1}. In accordance with other workers no correlation between $-J$ and the Fe–O–Fe angle is apparent from the present data and that reported by Que *et al.*[13] for (μ-oxo)diiron(III) complexes of tpa. Hotzelmann *et al.* have suggested that multiple pathways for ferro- and antiferromagnetic exchange coupling are available for multielectron metal centers.[31] As coupling via these pathways may maximize at different angles, the resulting $-J$ seems to be rather insensitive to the Fe–O–Fe angle.

Gorun and Lippard[30] have advocated an exponential dependence of $-J$ with the shortest superexchange path, in this case the Fe–(μ-O) distance, for supported (μ-oxo)-bridged systems. Many (μ-oxo)diiron complexes of tpa are unsymmetric, and for some of these systems the two Fe–(μ-O) distances differ significantly. Using an average Fe–(μ-O) distance for the correlation can be misleading as the symmetric case, other things being equal, always shows the strongest coupling. On the basis of a search of systems having unequal Fe–(μ-O) distances, we have reached the conclusion that a better correlation between J and the Fe–(μ-O) distance might be obtained if the longest distance is chosen. Gomez-Romero *et al.*[32] have reported an unusually strong coupling in a highly unsymmetrical system; however, that particular complex has an unusally short Fe–(μ-O), whereas the other distance is in the normal range for this type of complexes.

The two Fe–(μ-O) distances for the aquo–hydroxo complex **2** are significantly different, the longest of them, 1.839(2) Å, being in the very high end of the range observed for (μ-oxo)diiron(III) complexes. It is, therefore, not surprising that this complex has a rather weak antiferromagnetic coupling, $-J = 97$ cm^{-1}. The fact that the corresponding diaquo complex **1** exhibits a higher $-J$ value of 105 cm^{-1} is consistent with the anticipated symmetric Fe–O–Fe geometry (i.e. the two Fe–(μ-O) distances being similar). The structurally characterized linear dichloro complex, **3**, shows a higher $-J$ value of 116 cm^{-1} consistent with the short and equivalent Fe–(μ-O) distances seen in the structure. The acetamidato- and sulfato-bridged systems have coupling constants, 117 and 118 cm^{-1}, respectively, rather close to their anticipated isostructural doubly-bridged counterpart [(tpa)FeO(CH_3CO_2)Fe(tpa)](ClO_4)$_3$.[13d]

Electronic Spectra. The electronic spectra of (μ-oxo)diiron(III) complexes in the UV–visible region have been discussed several times in the literature, but a reliable assignment of the bands has not been reached.[1a–c] Que *et al.* have pointed out that the electronic spectra seem to be more sensitive to structural variations in the Fe–O–Fe core than are the magnetic properties.[13a] A comparison of the electronic spectral features of the complexes in the present study is shown in Table 6. A band in the region 490–503 nm, of medium intensity, is present in the spectra of all the complexes. This band has been assigned to a $^6A_1 \rightarrow (^1E,^4A_1)$ ligand field transition, enhanced by nearby oxo LMCT bands.[13a] A band at about 530 cm^{-1} is seen only in the doubly-bridged systems, **4** and **5**, and is assigned to weak oxo LMCT transitions. The assignment is supported by the observation of a resonance enhanced symmetric Fe–O stretching vibration in the Raman spectra using excitation in this region; *vide infra.*

A band in the 550–700-nm region has been attributed to an oxo-to-Fe(III) CT transition, and this band has been observed to blue-shift as the Fe–O–Fe angle increases.[13a] This trend is clearly demonstrated by complexes **1–5**. The acetamidato-bridged complex is expected to have the most acute Fe–O–Fe angle, probably close to the value for [(tpa)FeO(CH_3CO_2)Fe(tpa)](ClO_4)$_3$. The λ_{max} for this band for **5** occurs at the highest wavelength at 708 nm. This λ_{max} shifts to 660 nm for the sulfato-bridged complex and to 608 nm for the aquo–hydroxo-bridged complex. For the almost linear dichloro complex and the anticipated almost linear diaquo complexes, **3** and **1**, the λ_{max} for this band is seen at 573 and 572 nm, respectively. The electronic spectral characteristics for the acetamidato-bridged complex, **5**, show striking similarities to the previously reported, structurally characterized, acetato-bridged complex, [(tpa)FeO(CH_3CO_2)Fe(tpa)](ClO_4)$_3$, for which the spectral and magnetic data[13d] are listed in Table 6 for comparison. An isostructural arrangement for the acetamidato bridge in **5**, i.e. bidentate, bridging coordination *via* the oxygen and nitrogen atoms of a deprotonated acetamide, where the Fe–O–Fe angle is very close to the 129.23)° reported for [(tpa)FeO(CH_3CO_2)Fe(tpa)](ClO_4)$_3$,[13d] accounts for the nearly identical spectral properties.

The differences between the acetonitrile-solution spectra of the diaquo complex **1**, and its conjugate base, the hydroxo–aquo complex **2**, indicate that the hydrogen-bonded structure of **2** found in the solid state is maintained in solution. The spectrum of **2** shows a far greater resemblance to the spectra of dibridged complexes. This is a consequence of a system containing a bent μ-oxo bridge. The spectra of the linear diaquo and dichloro complexes, **1** and **3**, in acetonitrile, are very similar showing that the Fe–O–Fe angle is a more important factor than the nature of the terminal groups or the arrangement of the tpa ligand in the determination of the spectral features.

The reaction of Fe(ClO_4)$_3$·10H_2O and tpa in methanol in the absence of coordinating anions has been previously reported to give a complex of the formula $Fe_2tpa_2O(ClO_4)_4$, the spectroscopic features of which are diagnostic of a bent (μ-oxo)diiron core.[33] It was thus proposed that the μ-oxo is supported by a μ-perchlorato bridge.[33] The coordination of water to iron(III) is generally favored over the coordination of a perchlorate ion if both species are available. Given that the preparation of this complex was not carried out using strictly anhydrous conditions, we believe that the possibility of water or hydroxide coordination in the sixth position on each iron atom cannot be ruled out. The spectral evidence for a bent μ-oxo bridge may imply that the H-bonded aquo–hydroxo-bridged complex, **2**, rather than a (μ-oxo)(μ-perchlorato)-bridged complex was isolated. In fact, the electronic spectrum presented for $Fe_2(tpa)_2O(ClO_4)_4$ in ref 32b is almost identical to the spectrum we recorded for **2** in acetonitrile (and indeed significantly different to the spectrum of the sulfato-bridged complex **4**, which can be regarded as an isostructural analogue to "[(tpa)FeO(ClO_4)Fe(tpa)](ClO_4)$_3$"). It is, however, important to note that the possibility of a structure containing terminal aquo/hydroxo ligands is assignable to the complex formulated previously as a "$Fe_2(tpa)_2O(ClO_4)_4$" does not alter the chemical significance[33] of this complex. A labile site on each of the iron atoms of the (μ-oxo)diiron core is still available.

Resonance Raman Spectra. Solid-state Raman spectra were recorded for complexes **1–5** using the three excitation wavelengths 457.9, 487.9, and 514.5 nm. Enhanced lines in the range 350–500 cm^{-1} are assigned to the symmetric Fe–O–Fe stretch vibration. These are listed in Table 6.

A linear relationship between the square of ν_s observed for (μ-oxo)-bridged dimers and the cosine of the M–O–M angle is

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[30] Gorun, S. M.; Lippard, S. J. *Inorg. Chem.* **1991**, *30*, 1625.

[31] Hotzelmann, R.; Wiegardt, K.; Flörke, U.; Haupt, H.-J.; Weatherburn, D. C.; Bonvoisin, J.; Blondin, G.; Blondin, G.; Girerd, J.-J. *J. Am. Chem. Soc.* **1992**, *114*, 1681.

[32] Gomez-Romero, P.; Witten, E. H.; Reiff, W. M.; Jameson, G. B. *Inorg. Chem.* **1990**, *29*, 5211.

[33] (a) Que, L., Jr. In *Bioinorganic Catalysis*; Reedijk, J., Ed.; Marcel Dekker: New York, 1993. (b) Leising, R. A.; Brennan, B. A.; Que, L., Jr.; Fox, B. G.; Münck, E. *J. Am. Chem. Soc.* **1991**, *113*, 3988.

predicted from theory.[34] Sanders-Loehr *et al.* have published a correlation between the Fe–O–Fe angle and the ν_s observed in the resonance Raman spectra for an extensive series of structurally characterized (μ-oxo)iron(III) complexes.[35] Good estimates of the Fe–O–Fe angle can be obtained from this correlation. The data for the structurally characterized (μ-oxo)-bridged Fe(III) complexes of tpa, **2**, **3**, and the previously reported dibridged acetato, benzoato, and diphenylphosphinato complexes[35] fit reasonably well into this correlation with exception of complex **2** for which the ν_s value is somewhat low, although in the appropriate region between these values recorded for mono- and di-bridged complexes.[35] It is significant that the two Fe–μ-O bond distances in this complex show the largest difference yet observed for a (μ-oxo)-bridged Fe(III) complex of tpa. The long Fe–(μ-O) bond of 1.839(6) Å in complex **2** is the longest reported for a Fe–O–Fe unit.[25] The asymmetry between the lengths of the two bonds in the Fe–O–Fe unit is greater also than in any of the structurally characterized complexes included in the correlation reported by Sanders-Loehr *et al.*[35] Thus, we conclude, that a correlation between Fe–O–Fe and ν_s is probably only valid if the force constants for the two Fe–(μ-O) bonds of the Fe–O–Fe unit are similar. The one rather long Fe–(μ-O) distance observed for **2** is expected to have an unusually low force constant, and this is most likely the source of the deviation of ν_s compared to other (μ-oxo)diiron(III) complexes. If complex **2** is omitted from the correlation of Fe–O–Fe angle against ν_s, the following Fe–O–Fe angles are predicted for the tpa complexes reported here which lack crystal structural analysis: **1**, 177°; **4**, 136°; **5**, 130°. These values are all in accordance with the expected doubly- and singly-bridged structures, respectively.

Conclusions

We have succeeded in preparing (μ-oxo)diiron complexes containing labile aquo/hydroxo ligands. Complexes **1** and **2** represent an advancement toward the ultimate goal of achieving functional model complexes for the non-heme proteins. We have shown that the water ligands of the diaquo complex **1** can be replaced by a series of incoming ligands to produce singly- or doubly-bridged complexes. These substitution reactions have the potential to model some of the important steps in the chemical transformations catalyzed by the non-heme enzymes. Perhaps of greater significance is the fact that the aquo–hydroxo complex, **2**, is capable of promoting hydrolysis reactions. Heating acetonitrile solutions of **2** results in the formation of the acetamidato-bridged complex **5**. A diphenyl phosphate-bridged product can be obtained from the reaction of **2** with excess triphenyl phosphate.[24] These unusual reactions are proposed to occur by an intramolecular hydrolysis mechanism and are pertinant to the assignment of possible mechanisms for phosphate-ester hydrolysis catalyzed by the purple acid phosphatases.

The X-ray crystal structure of complex **2** shows a hydrogen-bonded aquo–hydroxo bridging moiety. The characterization of the Fe(μ-O)(μ-H_3O_2)Fe core in the solid state is unprecedented for (μ-oxo)diiron complexes. The spectral characteristics of the aquo–hydroxo complex are very similar to those of the structurally characterized dibridged complexes, showing the system is strongly hydrogen bonded, even in solution. The (μ-O)(μ-H_3O_2) core may be an important structural motif under biological conditions. The Fe–O–Fe core of **2** is highly unsymmetrical, reminiscent of the crystal structures of metHr and azidometHr.

We have at our disposal a series of singly- and doubly-bridged (μ-oxo)diiron complexes of tpa with a range of Fe–O–Fe angles between 174.7(5) and 125.4(3)°.[13a] The magnetic data suggest that the Fe–O–Fe angle has little effect on the magnitude of the coupling between the iron centers. A pronounced angle dependence is evident in the visible and Raman spectra of these complexes.

Acknowledgment. A.H. is indebted to the Carlsberg Foundation and to the Danish Natural Science Research Council for the diffractometer. This work is supported by grants from the Danish Natural Science Research council (11-9227 to H.T. and C.J.M. and 11-7916 to K.B.J.). We wish to thank Hanne Christensen and P. Waage Jensen for assistance with the resonance Raman measurements and Solveig Kallesøe for collecting the susceptibility data.

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(34) Wing, R. M.; Callahan, K. P. *Inorg. Chem.* **1969**, *8*, 871.

(35) Sanders-Loehr, J.; Wheeler, W. D.; Shiemke, A. K.; Averill, B. A.; Loehr, T. M. *J. Am. Chem. Soc.* **1989**, *111*, 8084.