Volume 31
Number 3
February 5, 1992

Inorganic Chemistry

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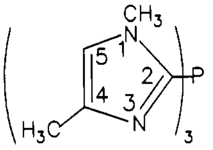
Communications

A Linear Triiron Core Structure Consisting of Fused (μ-Hydroxo)bis(μ-carboxylato)diiron(III) "Kernels"

The search for novel polynuclear Fe(II) and Fe(III) complexes with O,N donor ligands has been spurred by, among other things, their occurrence in proteins, their interesting magnetic behavior, and their potential use as catalysts for alkane oxidations.[1-3] A recent report from this laboratory showed that use of the tridentate nitrogen donor ligand tris(1-methylimidazol-2-yl)phosphine leads to formation of $[Fe_2O(OAc)_2(TMIP)_2]^{2+}$.[4,5] This complex contains the now familiar (μ-oxo)bis(μ-carboxylato)diiron(III) core, which can be capped by any of several different tridentate ligands.[1] In order to explore the effects on core structure of steric and electronic variations in the tridentate ligand, we introduced a methyl group ortho to the coordinating nitrogens (N3) of the constituent *N*-methylimidazolyl rings of TMIP, yielding tris(1,4-dimethylimidazol-2-yl)phosphine (T1,4DMIP).[6] This seemingly minor change leads to assembly of an unprecedented linear triiron core. $[Fe_3(\mu\text{-}OH)_2(\mu\text{-}OAc)_4(T1,4DMIP)_2](PF_6)_3\cdot THF$ (**1**) was prepared by dropwise addition of a solution of T1,4DMIP (1.0 g, 3.16 mmol) in 15 mL of water to a stirred solution of $Fe(ClO_4)_3\cdot 6H_2O$ (2.20 g, 4.76 mmol) and sodium acetate trihydrate (0.860 g, 6.32 mmol) in 40 mL of water. The reaction mixture was stirred for 3 h at room temperature, and the resulting orange precipitate was collected by filtration and dissolved in 20 mL of CH_3CN. KPF_6 (0.900 g, 4.89 mmol) was added, and the solution was stirred for 10 min, filtered through



T1,4DMIP

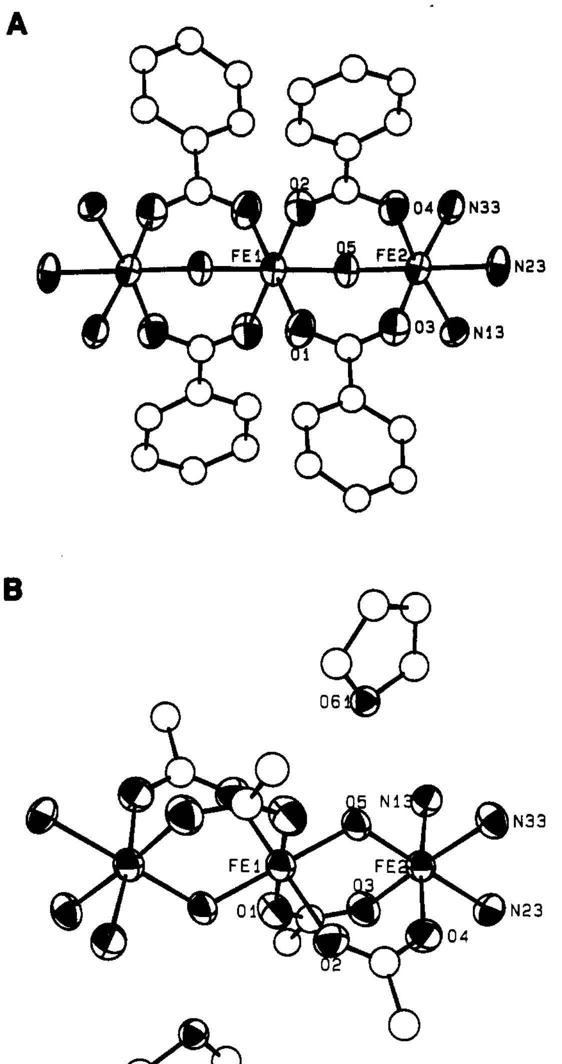


Figure 1. Structure of the triiron complex in **2**·4THF. View A shows all core non-hydrogen atoms. View B omits all phenyl carbons but those α to carboxylate carbons and includes H-bonded THF molecules. Both views omit all but ligand nitrogen atoms of T1,4DMIP for clarity. Structural and thermal parameters for the T1,4DMIP ligand are included in the supplementary material.

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(5) Abbreviations used: TMIP, tris(1-methylimidazol-2-yl)phosphine; T1,4DMIP, tris(1,4-dimethylimidazol-2-yl)phosphine; THF, tetrahydrofuran; OAc, acetate; OBz, benzoate; biphme, bis(1-methylimidazol-2-yl)phenylmethoxymethane; HB(pz)$_3$, tris(1-pyrazolyl)hydroborate(1−); *N*-MeIm, *N*-methylimidazole.

(6) 1,4-Dimethylimidazole was prepared by a previously described procedure[7] and purified by fractional distillation. T1,4DMIP was prepared by reaction of 1,4-dimethylimidazole and PCl_3 using the same procedure as used to prepare other tris(imidazolyl)phosphines.[8] The crude material was recrystallized from toluene. ^1H NMR (δ, ppm; $CDCl_3$): 2.15 (s, 3 H, 4-CH_3), 3.55 (s, 3 H, *N*-CH_3), 6.75 (s, 1 H, 5-H). ^{31}P NMR (δ, ppm, relative to H_3PO_4; $CDCl_3$): −26.81.

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glass wool, and reduced to a volume of 10 mL under vacuum. Orange crystals of **1** (1.4 g, 59 %) were obtained by vapor diffusion of THF.[9] X-ray diffraction data on these crystals[10] were sufficient to establish that the cation is essentially isostructural with that shown in Figure 1 (with acetato replacing benzoato ligands) but were of insufficient quality to obtain accurate bond distances and angles. A benzoate-bridged analogue, $[Fe_3(\mu\text{-}OH)_2(\mu\text{-}OBz)_4(T1,4DMIP)_2](PF_6)_3\cdot{}^9/_2THF$ (**2**$\cdot{}^9/_2$THF) was, therefore, prepared by addition of 0.500 g (5.09 mmol) of benzoic acid to a solution of **1** (0.300 g, 0.199 mmol) in 10 mL of CH_3CN. After 10 min of stirring at room temperature and filtration through glass wool, if necessary, orange crystals (0.26 g, 63%) were obtained by vapor diffusion of THF.[11] These crystals proved suitable for X-ray diffraction.[12]

The core structure of the cation in **2**$\cdot$4THF is shown in Figure 1 and consists of two (μ-hydroxo)bis(μ-carboxylato)diiron(III) "kernels" which are fused at the central iron. This central iron, Fe1, lies on a crystallographically imposed center of symmetry. The presence of hydroxo rather than oxo bridges in the cation is confirmed by the presence of three PF_6^- anions per cation in the crystal[17] and by a well-resolved THF molecule (Figure 1B) whose oxygen is well within hydrogen-bonding distance of O5 (O61–O5 = 2.663 (8) Å). A notable feature of this hydrogen bond is the nearly planar Fe1–O5- -(O61)–Fe2 unit.[18] Fe1 has an O_6 coordination sphere in contrast to the N_3O_3 coordination sphere of the outer iron atoms, Fe2, and also has significantly longer Fe–O bond distances than does Fe2. This statement applies to both the hydroxo bridge with Fe1–O5 = 1.964 (2) Å vs Fe2–O5 = 1.933 (3) Å and the carboxylato bridges with Fe1–O1,2(av) = 2.046 Å vs Fe2–O3,4(av) = 1.942 Å. This asymmetry can be attributed to the relative trans effects of the negatively charged O vs neutral N ligands on Fe1 and Fe2, respectively. The Fe2–O(carboxylato) bond distances in **2** appear to be unusually short, when compared with those of similar (μ-carboxylato)diiron(III) complexes.[19] For example, while the average Fe2–N bond distance in **2** is only ~0.03 Å shorter than the Fe–N bond distances in $[Fe_2O(OAc)_2(TMIP)_2]^{2+}$,[4] the average Fe2–O(carboxylato) bond distances in **2** are nearly 0.1 Å shorter than the corresponding distances in $[Fe_2O(OAc)_2(TMIP)_2]^{2+}$. A small trans effect of the hydroxo bridge in **2** on the Fe2–N bond distances is also evident, with Fe2–N23 = 2.144 (4) Å vs Fe2–N13,33(av) = 2.116 Å.

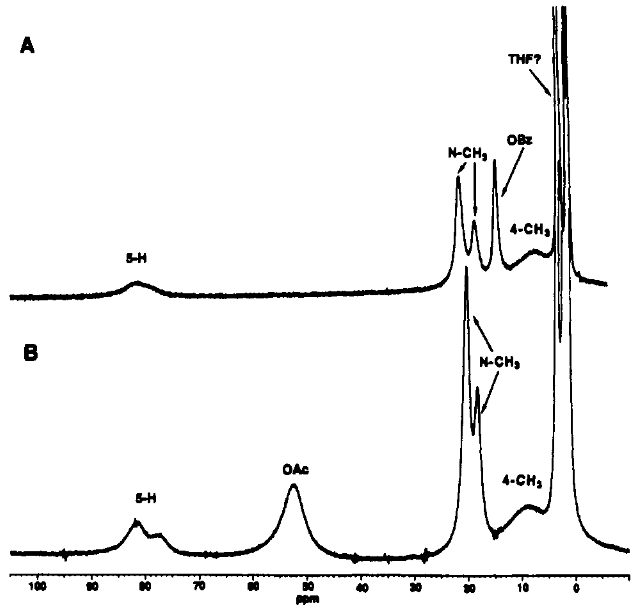

Figure 2. ^1H NMR spectra in CD_3CN at ~23 °C of (A) $[Fe_3(\mu\text{-}OH)_2(\mu\text{-}OBz)_4(T1,4DMIP)_2](PF_6)_3\cdot{}^9/_2THF$ and (B) $[Fe_3(\mu\text{-}OH)_2(\mu\text{-}OAc)_4(T1,4DMIP)_2](PF_6)_3\cdot THF$. Spectra were obtained on a Bruker AC-250 spectrometer. Assignments are listed above the paramagnetically shifted resonances.

The only other structurally characterized complex known to contain a (μ-hydroxo)bis(μ-carboxylato)diiron(III) core is $[Fe_2(OH)(OAc)_2(HB(pz)_3)_2]^+$, which shows an N_3O_3 coordination sphere around both iron atoms.[20] The average of the Fe–N bond distances for Fe2 in **2**, 2.130 Å, is only slightly longer than that in $[Fe_2(OH)(OAc)_2(HB(pz)_3)_2]^+$, 2.102 Å, and the Fe1–O5–Fe2 angle, 123.9 (2)°, and Fe1–Fe2 distance, 3.4400 (7) Å, in **2** are both nearly identical to the corresponding parameters in $[Fe_2(OH)(OAc)_2(HB(pz)_3)_2]^+$ (123.1 (2)°, 3.439 (1) Å). However, the latter complex does not exhibit the asymmetry in iron coordination spheres and Fe–O bridge bond distances noted above for **2**.

The ^1H NMR spectra (Figure 2) and magnetic moments of **1** and **2** nicely confirm the persistence of the triiron core in solution. The assignments given in Figure 2 are based on peak area ratios, deuteriation of the acetate methyl, and comparisons to spectra of an extensive set of Fe(III)–imidazole complexes studied previously in our laboratory.[21] The two sets of doublets with ~2:1 area ratios are assigned to the 5-H and N-CH_3 of the imidazolyl rings in the T1,4DMIP ligand. These doublets reflect the structural trans effect referred to above; the imidazolyl ligands cis to the hydroxo bridge have the shorter Fe–N distances and, therefore, show the larger shifts.[4,21] The crystal structure of **2** shows that the cis and trans 4-CH_3 groups are both significantly

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(9) Analytical and spectroscopic data for **1** are as follows. Anal. Calcd for $C_{42}H_{64}F_{18}Fe_3N_{12}O_{11}P_5$: C, 31.95; H, 4.06; N, 10.65. Found: C, 31.55; H, 4.26; N, 10.32. ^1H NMR at ~23 °C (δ, ppm; CD_3CN): 81.8, 77.9, 52.4, 20.5, 18.4, 9. Absorption spectral data (CH_3CN; λ_{max} nm, (ϵ, M^{-1} cm^{-1})): 230 (31 000), 265 (43 000), 310 sh (9900), 440 sh (500), 450 sh (440), 480 sh (280).

(10) Crystal data for **1**: monoclinic, space group $C2/c$, a = 36.41 (1) Å, b = 11.207 (4) Å, c = 24.251 (7) Å, β = 113.64 (2)°, R_w = 11.5%.

(11) Analytical and spectroscopic data for **2** are as follows. Anal. Calcd for $C_{76}H_{100}F_{18}Fe_3N_{12}O_{14.5}P_5$: C, 43.91; H, 4.81; N, 8.09; Fe, 8.09. Found: C, 43.96; H, 4.91; N, 8.19; Fe, 8.79. ^1H NMR at ~23 °C (δ, ppm; CD_3CN): 82.3, 80.0, 22.3, 19.4, 15.4, 9. Absorption spectral data (CH_3CN; λ_{max} nm (ϵ, M^{-1} cm^{-1})): 235 (86 000), 265 (64 000), 310 sh (20 000), 380 sh (6800), 440 sh (780), 480 sh (390).

(12) X-ray data for **2·4THF** were collected on an orange, platelike crystal of approximate dimensions 0.10 × 0.20 × 0.30 mm that had been sealed in a glass capillary tube. Data were collected at 23 ± 2 °C on an Enraf-Nonius CAD4 diffractometer equipped with a graphite crystal monochromator using Cu Kα radiation (λ = 1.541 84 Å). Cell dimensions were determined by least-squares refinement of the angular positions of 25 independent reflections in the 15–25° θ range during the normal alignment procedure. A total of 10 052 (9644 unique) reflections were collected over a θ range of 2–75° using the ω–2θ technique with variable scan width and scan range. After a Lorentz–polarization correction, averaging of redundant data, and elimination of systematic absences, a total of 4863 reflections ($F_o > 3\sigma$) were considered observed and unique and were used in the structural analysis. A semiempirical absorption correction was applied to the data.[13] The structural analysis was performed on a VAX 6210 computer using the MolEN structure analysis program system.[14] The structure was initially solved by direct methods using SIR88.[15] Additional atoms were located in several difference Fourier maps and then refined by full-matrix least-squares techniques, first isotropically and then anisotropically, to produce the final structural result. The final cycles of least-squares refinement employed non-Poisson weights modified by the Dunitz–Seiler technique.[16] Crystal data for **2**·4THF: $Fe_3P_5F_{18}O_{14}N_{12}C_{74}H_{94}$, fw = 2040.03, triclinic, space group $P\bar{1}$ (No. 2), a = 13.296 (3) Å, b = 13.839 (4) Å, c = 15.471 (4) Å, α = 97.48 (2)°, β = 114.28 (2)°, γ = 105.77 (2)°, V = 2400 (4) $Å^3$, Z = 1, D_{calcd} = 1.411 g cm^{-3}, D_{obsd} = 1.52 g cm^{-3} (by flotation in $CHCl_3/CCl_4$), R = 9.5%, R_w = 6.2%.

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(17) Neither PF_6^- anion in **2**·4THF occupies a crystallographic inversion center, which generates apparently four PF_6^- units per cell rather than the three expected. However, difference maps and subsequent refinement indicated only half-occupancy of the PF_6^- unit surrounding P3. Many peaks in the final difference map were near the P3 site, indicating a disordered unit. Occupancy of the P3 site may be shared with a solvent THF molecule.

(18) Pertinent angles (deg) around O5: Fe1–O5–Fe2, 123.9 (2); Fe1–O5–O61, 120.2 (3); Fe2–O5–O61, 115.4 (3). Their sum is 359.5° vs. 360° expected for coplanarity.

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closer to Fe2 than are the 5-H or the *N*-CH_3, and the expected dipolar broadening leads to assignment of the relatively broad feature at $\sim$9 ppm to the unresolved cis and trans 4-CH_3 resonances. We[21] and others[22] have previously shown that the bridging acetate chemical shifts in di- and trinuclear Fe(III) complexes vary monotonically with solution magnetic moments per iron atom and with the pairwise antiferromagnetic coupling constants, $-J$, in the $\hat{H}_{ex} = -2J\hat{S}_1 \cdot \hat{S}_2$ formalism. Solution magnetic moments measured at $\sim$296 K in CD_3CN by the Evans method[21] gave effective magnetic moments of 4.00 μ_B/Fe for **1** and 4.01 μ_B/Fe for **2**. These magnetic moments together with the bridging acetate chemical shift of **1** (52.4 ppm) at the same temperature indicate that the pairwise antiferromagnetic coupling between adjacent iron atoms in the cores of **1** and **2** is significantly stronger than that in the isostructural core of $[Fe_2(OH)(OAc)_2(HB(pz)_3)_2]^+$ (4.42 μ_B/Fe, 68.7 ppm, $-J = 17$ cm^{-1} [20]).[23] On the other hand, comparisons of the same parameters indicate that the antiferromagnetic coupling between adjacent iron atoms in the cores of **1** and **2** is significantly *weaker* than that between the iron atom pairs in the "basic iron acetate" cluster $[Fe_3(\mu_3\text{-}O)(\mu\text{-}OAc)_6(N\text{-}MeIm)_3]^+$ (3.34 μ_B/Fe,[21] 30.7 ppm,[21] $-J = 30$ cm^{-1} [24]). Thus, these comparisons indicate that the pairwise antiferromagnetic coupling strength between adjacent iron atoms in the cores of **1** and **2** is within the range 17 cm^{-1} $< -J <$ 30 cm^{-1}.

The ^{57}Fe Mössbauer spectrum of solid **1** (not shown) at 250 K shows a broadened but unresolved doublet with isomer shift (quadrupole splitting) of 0.41 (0.74) mm/s; these values indicate high-spin ferric iron and are close to those of two (μ-hydroxo)bis(μ-acetato)diiron(III) complexes.[1,4] At 1.8 K in a weak applied field (2.2 kG), the Mössbauer spectrum of **1** shows at least eight resolved components. Such a complex magnetic spectrum is indicative of a paramagnetic ground state. An X-band EPR spectrum at 15 K of a frozen solution of **1** in acetonitrile showed a strong first-derivative feature with zero-crossing at $g = 4.29$ and a much weaker feature at $g = 9.46$. This EPR spectrum is consistent with a $S_{tot} = {}^5/_2$ ground state for **1**, as expected for a complex consisting of three paramagnetic centers with $S_1 = S_2 = S_3 = {}^5/_2$ and antiferromagnetic coupling only between adjacent pairs of centers; i.e., $J_{12} = J_{23}$, and $J_{13} = 0$.[25]

The new structure reported here adds to the small but growing list of triiron-carboxylate core types[26] and further illustrates the recently recognized structural flexibility inherent in polynuclear ferric-carboxylate chemistry.[1,2] The trans configuration of the hydroxo bridges around the central iron atoms of **1** and **2** is unusual if not unique in discrete polynulear ferric complexes. The synthetic procedure for **1** is completely analogous to that for $[Fe_2O(OAc)_2(TMIP)_2]^{2+}$, but we have detected no diiron(III) complexes using T1,4DMIP. Examination of space-filling structures of $[Fe_2O(OAc)_2(TMIP)_2]^{2+}$ shows that steric overlap of methyl groups ortho to those coordinating nitrogens which are cis to the oxo bridge on adjacent iron atoms is likely to destabilize the analogous diiron complex with T1,4DMIP. Reactivities of **1** and **2** and synthetic routes to similar trimetal complexes are currently being explored. Preliminary results show that the mixed oxo/hydoxo-bridged complex $[Fe_3(\mu\text{-}O)(\mu\text{-}OH)(\mu\text{-}O_2CR)_4(T1,4DMIP)_2]^{2+}$, whose triiron core is isostructural with that in **1** and **2**, is readily accessible.[28]

Acknowledgment. This research was supported with funds made available by the University of Georgia as a result of an NIH Research Career Development Award to D.M.K. during 1988–93 (HL 02207). We thank Peter G. Debrunner for obtaining the Mössbauer spectra and Sonha C. Payne for assistance in synthesizing T1,4DMIP.

Supplementary Material Available: Listings of X-ray experimental details (Table S1) and atomic coordinates and anisotropic thermal parameters (Table SII) and distances (Table SIII) and angles (Table SIV) for non-hydrogen atoms and figures showing atom numbering and unit cell and packing diagrams (13 pages); a listing of observed and calculated structure factors (56 pages). Ordering information is given on any current masthead page.

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(23) This difference is difficult to attribute to differences in bond distances and angles between **2** and $[Fe_2(OH)(OAc)_2(HB(pz)_3)_2]^+$. The bridging hydroxide is believed to provide the main pathway for magnetic superexchange,[1] and in addition to the nearly identical Fe–(μ-OH)–Fe angles in the two complexes noted above, the average Fe–μ-OH bond distance in **2**, 1.948 Å, may not be significantly different from that in $[Fe_2(OH)(OAc)_2(HB(pz)_3)_2]^+$, 1.956 (4) Å.[20] Similarly, the average Fe–O(carboxylato) distance in **2**, 1.994 Å, is probably not significantly different from that in $[Fe_2(OH)(OAc)_2(HB(pz)_3)_2]^+$, 1.999 Å.[20]

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Received August 23, 1991

Synthesis and Crystal Structure of a Vanadium(V) Complex with a 2-Hydroxy Acid Ligand, $(NH_4)_2[V(OC(CH_2CH_3)_2COO)(O)_2]_2$: A Structural Model of both Vanadium(V) Transferrin and Ribonuclease Complexes with Inhibitors

Monomeric and polymeric vanadates are potent inhibitors for a variety of enzymes including ATPases, phosphatases, and nucleases.[1-5] V(V) can bind tightly into the active sites of these enzymes in a trigonal-bipyramidal geometry. This interaction is thought to mimic the hydrolytic transition states of their enzymic reactions.[3-5] Such a geometry has been established by X-ray crystallography[6] in the complex formed when ribonuclease A is inhibited by vanadate and uridine. More recently, the first X-ray structure of a V(V) synthetic model that mimics this coordination geometry has been published.[3] However, it contains a trigonal bipyramid of one chloride and four oxygen donors about the V center,[3] unlike the vanadate/uridine/ribonuclease complex.[6] In addition, it is unstable at room temperature, both in the solid state and in solution.[3] We report here the first example of a trigonal-bipyramidal V(V) complex with five oxygen donors which is a good structural model for the vanadate/uridine/ribonuclease complex. It is remarkably stable both in the solid state and in aqueous solutions at room temperature. The complex is also the best structural model that has been reported for the proposed active

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