

anisotropic thermal parameters, and hydrogen coordinates, a computer-generated thermal ellipsoid plot of  $\text{Co}[\text{N}(\text{SiMe}_3)_2]_3$ , **2**, and synthetic details (10 pages); listing of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

### Synthesis and Properties of a Novel Oxo-Bridged Dinuclear Iron(III) Complex Containing Only Oxygen Donating Ligands

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The iron-containing enzymes, methane monooxygenase (MMO),<sup>1</sup> ribonucleotide reductase (RR),<sup>2,3</sup> and purple acid phosphatase (PAP),<sup>4,5</sup> are believed to contain oxo- or hydroxo- and carboxylato-bridged dinuclear iron centers similar to that in hemerythrin.<sup>6</sup> Despite this similarity, the functions of these proteins are intriguingly diverse, comprising monooxygenase, reductase, and oxygen transport activities.<sup>7</sup> This diversity may be caused by different coordination environments in the proteins afforded, inter alia, by different terminal ligands that anchor the bridged dinuclear iron cores to the polypeptide chains. For example, EXAFS data for MMO and RR indicate more oxygen coordination to iron in these enzymes than in hemerythrin.<sup>1c,2</sup> Many  $\mu$ -oxobis( $\mu$ -carboxylato)diiron(III) complexes have been prepared by using either exclusively nitrogen or mixed oxygen/nitrogen donor terminal ligands to model physical properties of these proteins.<sup>8</sup> We report here the synthesis and characterization of the first such complex with exclusive oxygen coordination,  $[\text{Fe}_2\text{O}(\text{O}_2\text{CCH}_3)_2][\text{OP}(\text{OEt})_2]_3\text{Co}(\text{C}_5\text{H}_5)_2$  (**1**). The unique magnetic and spectroscopic properties exhibited by this complex afford important new benchmarks for evaluating structural proposals concerning the diiron centers in MMO, RR, and PAP.

An acetonitrile solution of  $\text{Na}[\text{OP}(\text{OEt})_2]_3\text{Co}(\text{C}_5\text{H}_5)_2$ <sup>9</sup> (1.10 g, 1.97 mmol, 20 mL) was slowly added to a mixture of  $(\text{Et}_4\text{N})_2[\text{Fe}_2\text{O}(\text{OC}_6\text{H}_5)_4]$ <sup>10</sup> (0.600 g, 1.0 mmol) and excess  $\text{NaO}_2\text{C}\cdot\text{CH}_3\cdot 3\text{H}_2\text{O}$  (0.40 g, 2.9 mmol) in 20 mL of acetonitrile. After

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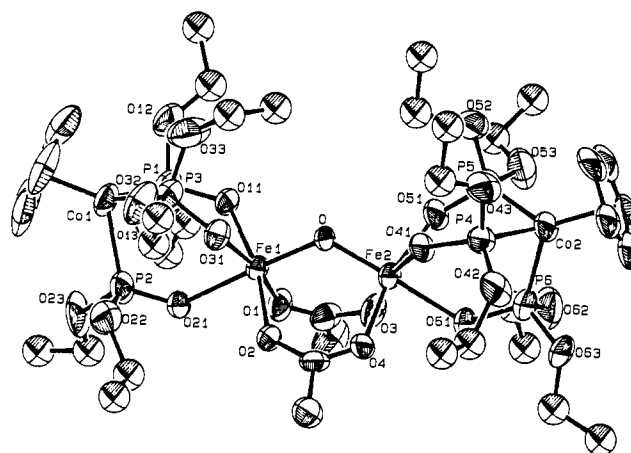
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**Figure 1.** ORTEP drawing of **1** showing the 40% probability thermal ellipsoids and atom labels for all the metal oxygen and phosphorus atoms. Carbon atoms on ethyl groups are represented as isotropic spheres with  $B = 6.0 \text{ \AA}^2$  for clarity; atom disorder is not shown. Selected interatomic distances ( $\text{\AA}$ ) and angles ( $\text{deg}$ ) are as follows:  $\text{Fe}(1)\text{-O}$ , 1.799 (6);  $\text{Fe}(2)\text{-O}$ , 1.791 (6);  $\text{Fe}(1)\text{-O}(11)$ , 2.066 (6);  $\text{Fe}(1)\text{-O}(21)$ , 2.137 (7);  $\text{Fe}(1)\text{-O}(31)$ , 2.048 (8);  $\text{Fe}(2)\text{-O}(41)$ , 2.057 (7);  $\text{Fe}(2)\text{-O}(51)$ , 2.079 (8);  $\text{Fe}(2)\text{-O}(61)$ , 2.125 (7);  $\text{Fe}(1)\text{-O}(1)$ , 2.012 (9);  $\text{Fe}(1)\text{-O}(2)$ , 2.023 (7);  $\text{Fe}(2)\text{-O}(3)$ , 2.039 (8);  $\text{Fe}(2)\text{-O}(4)$ , 2.036 (8);  $\text{Fe}(1)\text{-O-Fe}(2)$ , 124.4 (4).

**Table I.** Selected Structural, Magnetic, and Spectroscopic Properties of **1** and **2**

	1 <sup>a</sup>	2 <sup>b</sup>
Structural Properties		
$\angle\text{Fe-O-Fe}$ , deg	124.4 (4)	123.6 (1)
$\text{Fe-O}_{\text{oxo}}$ , $\text{\AA}$	1.799 (6), 1.791 (6)	1.788 (2), 1.780 (2)
$\text{Fe}\cdots\text{Fe}$ , $\text{\AA}$	3.174 (2)	3.146 (1)
av $\text{Fe-O}$ $\mu$ -carboxylate, $\text{\AA}$	2.028	2.043
av $\text{Fe-L}$ cis to $\mu$ -oxo, $\text{\AA}$	2.06	2.15
av $\text{Fe-L}$ trans to $\mu$ -oxo, $\text{\AA}$	2.13	2.19
Mössbauer <sup>c</sup> and Magnetic Data		
$\delta$ , $\text{mm s}^{-1}$	0.58 (3)	0.52 (3)
$\Delta E_Q$ , $\text{mm s}^{-1}$	1.84 (5)	1.60 (5)
$J$ , $\text{cm}^{-1}$	-108.5 (4)	-121.3 (1)
$\mu_{\text{eff}}/\text{Fe}$ , $\mu_B^d$	1.87	1.71
Electronic Spectral Data <sup>e</sup>		
	247 ( $2.91 \times 10^4$ )	262 (3375), 339 (4635)
	357 ( $6.63 \times 10^3$ )	358 (sh), 457 (505)
	471 (208)	492 (460)
	501 (94, sh)	528 (sh)
	569 (95)	695 (70)
		993 (3.5)
Resonance Raman Data		
$\nu_s$ $\text{Fe-O-Fe}$ , $\text{cm}^{-1/f}$	510 (496)	528 (511)
max enhancement, $\text{nm}^g$	356.4 ( $1.87 \times 10^3$ )	406.7 ( $1.78 \times 10^3$ ) <sup>h</sup>

<sup>a</sup>This work. <sup>b</sup>Reference 8a. <sup>c</sup>Mössbauer parameters are obtained at 4.2 K. <sup>d</sup>Values of  $\mu_{\text{eff}}$  are reported for  $\text{CDCl}_3$  solution at 298 K as measured by the Evans NMR method (Evans, D. F. *J. Chem. Soc.* **1958**, 2003). <sup>e</sup> $\lambda$  reported in nm in a  $\text{CH}_3\text{CN}$  solution of **1** and a  $\text{CH}_2\text{Cl}_2$  solution of **2**. Numbers in parentheses are molar extinction coefficients per iron atom. <sup>f</sup>Numbers in parentheses are the  $^{18}\text{O}$  shifted values. <sup>g</sup>Values in parentheses are molar Raman scattering intensities relative to the  $704 \text{ cm}^{-1}$  methylene chloride band.

stirring for an hour, the red reaction mixture was filtered and concentrated. Slow cooling to  $-10^\circ\text{C}$  afforded red prisms (0.800 g, 57%) which proved to be suitable for X-ray diffraction study.<sup>11</sup>

(11) Crystal data for  $1\cdot 2\text{CH}_3\text{CN}$  ( $\text{C}_{42}\text{H}_{82}\text{P}_6\text{O}_{23}\text{N}_2\text{Co}_2\text{Fe}_2$ ),  $M_r = 1398.52$  at 298 K: space group  $P1$ ,  $a = 12.062$  (2)  $\text{\AA}$ ,  $b = 15.733$  (4)  $\text{\AA}$ ,  $c = 18.667$  (6)  $\text{\AA}$ ,  $\alpha = 111.64$  (2) $^\circ$ ,  $\beta = 96.62$  (2) $^\circ$ ,  $\gamma = 98.83$  (2) $^\circ$ ,  $V = 3196 \text{ \AA}^3$ ,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.453 \text{ g cm}^{-3}$ ,  $\rho_{\text{meas}} = 1.44$  (1)  $\text{g cm}^{-3}$ . For 4719 unique, observed reflections and 610 parameters, the current discrepancy indices are  $R = 0.0704$ ,  $R_w = 0.0849$ . Recollection of the data at low temperature and further refinement to resolve solvent and partial disorder are planned, details of which will be reported at a later date.

Elemental analysis, IR,  $^1\text{H}$  NMR, Mössbauer and electronic spectroscopic studies as well as magnetic measurements were performed on these crystals.<sup>12</sup>

The molecular structure of **1** is shown in Figure 1. Features of the  $[\text{Fe}_2\text{O}(\text{O}_2\text{CCH}_3)_2]^{2+}$  core geometry in **1** compare favorably with those in the  $[\text{Fe}_2\text{O}(\text{O}_2\text{CCH}_3)_2(\text{HBpz}_3)_2]$  analogue (**2**), in which the terminal ligands are all nitrogen donors (Table I).<sup>8a</sup> Both compounds have distorted octahedral geometry around each iron atom and lengthened Fe-ligand bonds trans to the short Fe-O<sub>oxo</sub> bridge. The Fe-O<sub>oxo</sub> bond lengths fall within the known range for  $[\text{Fe}_2\text{O}(\text{O}_2\text{CCH}_3)_2]^{2+}$  complexes. The terminal Fe-O bond lengths in **1** are significantly shorter than the analogous Fe-N distances in **2**. This result supports the geometric criterion previously used to assign oxygen donor terminal ligands in dinuclear iron-oxo proteins.<sup>2</sup> Slightly but significantly weaker antiferromagnetic coupling occurs between the two iron(III) centers in **1** compared to that in **2** (Table I). This difference is reflected in the ambient temperature solution magnetic moments for the two complexes. The observed reduction in the exchange coupling constant ( $J$ ) for **1** versus **2** is in accord with expectations based upon an empirical correlation of  $J$  with molecular geometry parameters;<sup>13</sup> the slightly longer Fe-O bridge bonds lead to weaker magnetic coupling. The electronic spectrum of **1** differs from that of **2** mainly in the visible region, the respective low-energy bands occurring at 569 and 695 nm. This shift is attributed to the weaker ligand field strength of the triphosphite ( $\text{O}_3$ ), compared to the tris(pyrazolyl)borate ( $\text{N}_3$ ), tripod anions coordinated to the high spin iron(III) centers.

Resonance Raman studies of iron-oxo proteins and their model complexes have shown that excitation at or near the UV-vis absorption bands can afford large enhancements of the Fe-O-Fe symmetric stretch.<sup>14</sup> One exception is purple acid phosphatase in which the existence of a binuclear iron-oxo center implied by magnetic and Mössbauer measurements could not be confirmed by a resonance enhanced  $\nu_s(\text{Fe-O-Fe})$  band in the resonance Raman spectrum.<sup>5</sup> This failure was attributed to the lack of histidine-type unsaturated nitrogen donor ligands in positions trans to the oxo bridge.<sup>5,15</sup> The solution Raman spectrum of **1** reveals, however, that scattering due to the Fe-O-Fe symmetric stretch at  $510\text{ cm}^{-1}$  is enhanced to approximately the same extent as in solutions of **2** at their respective enhancement maxima (Table I).<sup>16</sup>

Cyclic voltammograms of **1** in methylene chloride display a quasireversible reduction wave with  $E_{p,c} = -0.55\text{ V}$  and  $E_{p,a} = -0.25\text{ V}$  vs Ag/AgCl. The cathodic current of this wave is greatly increased by addition of protons, which presumably stabilize the reduced species. A second irreversible reduction wave appears at  $E_c = -0.8\text{ V}$ . The electrochemical behavior of **1** is thus significantly different from that of **2**, which decomposes to mono-

nuclear  $[\text{Fe}(\text{HBpz}_3)_2]^+$ , under electrochemical conditions.<sup>8a</sup> No evidence was obtained for  $[\text{Fe}(\text{CpCo}[\text{OP}(\text{OEt})_2]_3)_2]^+$ ,<sup>16</sup> which has a reversible  $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$  couple at  $-0.8\text{ V}$  vs Ag/AgCl. Attempts to isolate and characterize the species obtained upon reduction of **1** are currently in progress.

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**Supplementary Material Available:** Tables of atomic positional (including a model defining the disordered acetonitrile molecules listed in the table) and thermal parameters for 1-2CH<sub>3</sub>CN (5 pages). Ordering information is given on any current masthead page.

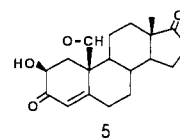
### A Model Study on Aromatase Cytochrome P-450 Reaction: Transformation of Androstene-3,17,19-trione to 10 $\beta$ -Hydroxyestr-4-ene-3,17-dione

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The metabolic transformation of androgens (**1**) to estrogens (**2**) by placental aromatase cytochrome P-450 (P-450<sub>arom</sub>) is known to consist of three consecutive oxidations, each of which requires 1 mol of O<sub>2</sub> and 1 mol of NADPH<sup>1</sup> (Scheme 1). The conversion of a formyl cyclohexenone moiety of the 19-aldehyde intermediates (**4**) to the phenol derivatives, the last step in aromatization, is unique in many reactions catalyzed by cytochrome P-450.<sup>2</sup> Among mechanisms proposed for the aromatization reaction, an involvement of 2 $\beta$ -hydroxylation of **4** has received attention as an attractive mechanism.<sup>2c</sup> Fishman and his co-workers showed that nonenzymatic aromatization of 2 $\beta$ -hydroxy-4-androstene-3,17,19-trione (**5**) proceeded with stereo-



5

specific 1 $\beta$  hydrogen elimination identical with that in estrogen biosynthesis.<sup>3</sup> However, Caspi et al. showed no incorporation of the oxygen atom of the 2 $\beta$ -hydroxyl of **5** into formic acid in the aromatization reaction.<sup>4</sup> The intermediacy of **5** appears also less favor in view of the following considerations.

(12) Anal. ( $\text{C}_{38}\text{H}_{76}\text{P}_6\text{O}_{23}\text{Co}_2\text{Fe}_2$ ) C, H, P, Fe; IR (KBr,  $\text{cm}^{-1}$ ) 2978, 2929, 2905, 2860, 1578, 1425, 1389, 1162, 1123, 1096, 1076, 1036, 933, 832, 761, 729, 592;  $^1\text{H}$  NMR (250 MHz, 297 K,  $\text{CDCl}_3$ )  $\delta$  10.0 (CH<sub>3</sub>, acetate), 5.10 (C<sub>5</sub>H<sub>5</sub>), 4.08 (CH<sub>2</sub>), 1.26 (CH<sub>3</sub>) ppm.

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(16) The Raman spectra of a 0.043 M  $\text{CH}_2\text{Cl}_2$  solution of **1** exhibited a  $510\text{-cm}^{-1}$  band (overtone,  $1020\text{ cm}^{-1}$ ) assigned as  $\nu_s(\text{Fe-O-Fe})$  that shifted to  $496\text{ cm}^{-1}$  upon  $^{18}\text{O}$  substitution into the oxo bridge. A methylene chloride solution of **2** at the same concentration was studied for comparison. Laser lines with wavelengths of 350.7, 356.4, 406.7, 413.1, 457.9, 488.0, and 514.5 nm were employed. Relative Raman scattering intensities were calculated as the ratio of the molar scattering intensities (peak height/concentration) of the  $\nu_s(\text{Fe-O-Fe})$  at  $510\text{ cm}^{-1}$  to the molar scattering intensities of the methylene chloride peak at  $704\text{ cm}^{-1}$ . The maximum enhancement was observed at 356.4 nm for **1** and at 406.7 nm for **2**, with the maximum relative Raman scattering intensity for **1** being 1.05 that of **2**.

(17) The mononuclear complex  $[\text{Fe}[\text{OP}(\text{OEt})_2]_3\text{Co}(\text{C}_5\text{H}_5)_2]\text{BF}_4$  was synthesized by a procedure analogous to that previously reported for  $[\text{Fe}[\text{OP}(\text{OEt})_2]_3\text{Co}(\text{C}_5\text{H}_5)_2]\text{PF}_6$ : Kläui, W.; Eberspach, W.; Schwarz, R. J. *Organomet. Chem.* **1983**, 252, 347.

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