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(μ-Alkoxo)diiron(II,II) Complexes of *N,N,N',N'*-Tetrakis(2-(6-methylpyridyl)methyl)-1,3-diaminopropane-2-olate and the Reversible Formation of the O_2-Adducts

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(μ-Alkoxo)(μ-carboxylato)diiron(II,II) complexes with hindered dinucleating ligand were synthesized and the structure of μ-benzoato derivative was determined by X-ray analysis. The complexes showed reversible oxygenation in acetonitrile and dichloromethane. Resonance Raman spectra of these species demonstrated a possibility of unsymmetrical μ-η^1-$\eta^{1'}$ binding of the oxygen toward the diiron centers.

Dioxygen binding of diiron(II,II) compounds has been of interest because of the biological importance of oxygen activation and oxygen transport.[1] While there are a number of examples of oxygen binding dinuclear cobalt complexes,[2] a few iron(II) complexes which form (μ-peroxo)diiron(III,III) species are known.[3] In particular for reversible oxygenation, only one known example is $[Fe\{HB(3,5\text{-}iPr_2Pz)_3\}(C_6H_5CO_2)]$.[3c] Recently Que et al. reported that the diiron(II,II) complex with dinucleating ligand $[Fe_2(N\text{-Et-HPTB})(C_6H_5CO_2)]^{2+}$ forms a (μ-peroxo)diiron(III,III) species at -60 °C, but the oxygenation is irreversible.[3d] We have currently studied the factors which affect the oxygen affinity and reversibility of (μ-peroxo)dicobalt(III,III) complexes using a series of dinucleating ligands.[4] Our interest in the (μ-peroxo)diiron(III,III) chemistry is also focused on controlling the oxygen affinity and reversibility of those complexes using various types of dinucleating ligands.

In this study, the two types of (μ-alkoxo)diiron(II,II) complexes $[Fe_2(6\text{-Me-tpdp})(RCO_2)(H_2O)](BF_4)_2$ (R = CF_3: **1**, C_6H_5: **2**) were synthesized with the dinucleating ligand with hindered base, 6-Me-tpdp (*N,N,N',N'*-tetrakis(2-(6-methylpyridyl)methyl)-1,3-diamino-

propane-2-olate), and showed the reversible oxygenation of diiron complexes.

$Fe(BF_4)_2 \cdot 6H_2O$ (1 mmol) in methanol (10 cm^3) was treated with 6-Me-tpdp (0.5 mmol) and RCO_2Na (0.5 mmol, **1**: CF_3CO_2Na; **2**: $C_6H_5CO_2Na$) under an argon atmosphere, followed by addition of sodium hydroxide (0.5 mmol), to give diiron(II,II) complex (**1**: 30% yield; **2**: 50% yield).[5] Complex **2** was recrystallized from methanol/water, producing yellow needle crystals suitable for X-ray analysis.

X-Ray structure analysis[6] of complex **2** revealed that two iron atoms are linked with the dinucleating ligand, 6-Me-tpdp, through μ-alkoxo and benzoate bridges (Fig. 1). Interestingly, in spite of using symmetrical ligands, the iron centers have different coordination geometries: one is trigonal bipyramidal and the other is octahedral geometry with coordination of a water molecule located in the *trans* position to μ-alkoxo oxygen. The bond lengths in the octahedral moiety are longer than those in the trigonal bipyramidal one (Table 1). Such elongation of the bond lengths in the octahedral moiety may be attributable to steric crowding due to methyl groups on pyridyl rings. On the other hand, it seems to be enough room in the trigonal bipyramidal Fe(2) moiety to avoid steric crowding due to the methyl groups, resulting in normal bond lengths.

The complexes **1** and **2** are stable toward molecular oxygen in solid state, however, they react with molecular oxygen to give deep blue color in dichloromethane and acetonitrile even at ambient temperature, then the color fades away within several minutes.

The reversible formation of dioxygen complexes of **1** and **2** was observed below -20 °C in acetonitrile or dichloromethane.[7] When oxygen was passed through the solution, the

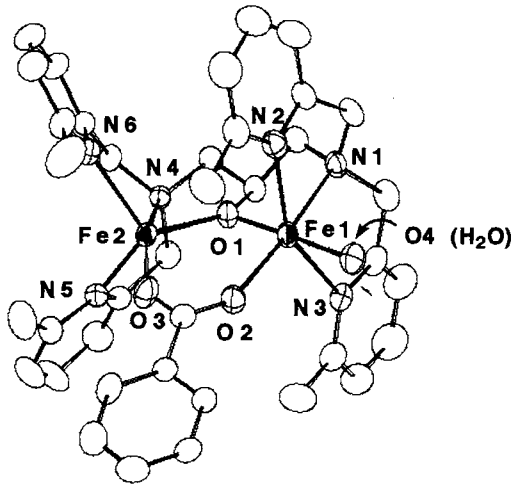

Fig. 1. Molecular structure of **2**.

Table 1. Selected Bond Lengths (Å) and Angles (deg) of **2**

Type	Value	Type	Value
Bond lengths /Å			
Fe(1)—O(1)	2.060(2)	Fe(2)—O(1)	1.984(2)
Fe(1)—O(2)	2.066(2)	Fe(2)—O(3)	1.995(2)
Fe(1)—O(4)	2.142(3)	Fe(2)—N(4)	2.195(2)
Fe(1)—N(1)	2.200(3)	Fe(2)—N(5)	2.202(3)
Fe(1)—N(2)	2.287(3)	Fe(2)—N(6)	2.175(3)
Fe(1)—N(3)	2.337(3)	Fe(1)—Fe(2)	3.684(1)
Bond angeles /deg			
Fe(1)-O(1)-Fe(2)	131.2(1)	O(1)-Fe(2)-O(3)	95.7(1)
O(1)-Fe(1)-O(2)	89.8(1)	O(1)-Fe(1)-O(4)	175.9(1)
O(2)-Fe(1)-O(4)	91.9(1)		

color of the solution changed from pale yellow to deep blue and a new feature of electronic spectrum appears at 618 nm. Bubbling argon gas through the resulting deep blue solution caused the complete disappearance of the band at 618 nm and retrieved an original spectrum. These spectral changes are observed repeatedly.

An analogous dinuclear complex $[Fe_2(tpdp)(C_6H_5CO_2)]^{2+}$ where tpdp has no methyl groups in the 6-positions on pyridyl rings showed a spontaneous irreversible oxidation of the iron(II) ions by molecular oxygen and no oxygenated species was observed even at -40 °C. These observations indicate that the introduction of methyl groups in the 6-positions on pyridyl rings in tpdp weakens the donation of pyridyl nitrogen toward the iron ions to stabilize (μ-peroxo)diiron(III,III) species effectively and brings about reversible oxygenation.

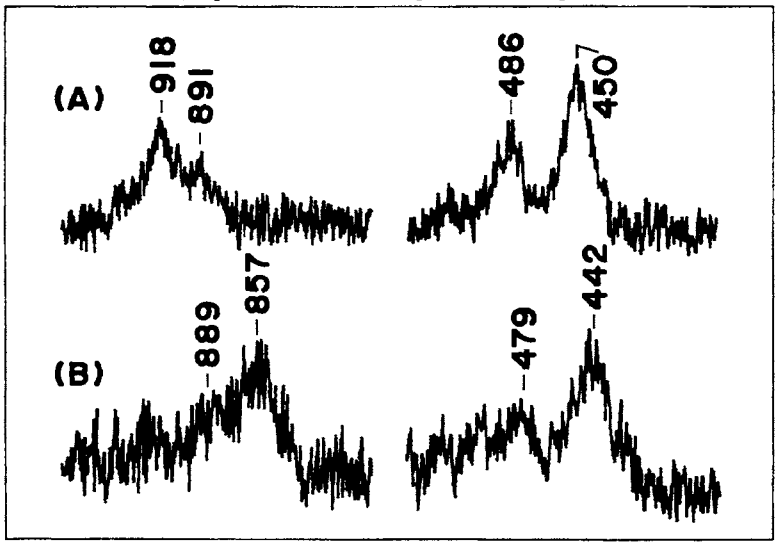

Fig. 2. Resonance Raman spectra of **2**. (A): $^{16}O_2$ derivative, and (B): $^{18}O_2$ derivative in dichloromethane at -80 °C.

Resonance Raman spectra of the $^{16}O_2$ derivative of complex **1** observed in resonance with the 618 nm band[8] showed two pairs of bands at 918 and 891, and 486 and 450 cm^{-1} (Fig. 2(A)). These Raman bands are apparently shifted to 889 and 857, and 479 and 442 cm^{-1} for the $^{18}O_2$ derivative, respectively (Fig. 2(B)). Therefore, the 918 and 891 cm^{-1} bands are assigned to the O—O stretching mode (ν_{O-O}), and the 486 and 450 cm^{-1} bands are to the Fe—O stretching mode (ν_{Fe-O}). The ν_{O-O} frequency indicates the presence of peroxo species. Temperature dependence and solvent effects were not recognized in these pairs of signals. Therefore, it is unlikely to assume the presence of two species.[9] The pair of ν_{O-O} bands can be interpreted as Fermi resonance between ν_{O-O} and $2\nu_{Fe-O}$.[10] The presence of two ν_{Fe-O} bands is compatible with unsymmetrical coordination of peroxo group to two iron(III) ions

(μ-η^1-$\eta^{1'}$ type). Such unsymmetly of coordination environments of two iron sites was also suggested for complex **2**. Further discussion of these results will be reported elsewhere.

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5) Anal. **1**, Found: C, 41.10; H, 4.48; N, 8.96%. Calcd for $[Fe_2(6\text{-Me-tpdp})(CF_3CO_2)](BF_4)_2 \bullet 2H_2O$: C, 41.20; H, 4.51; N, 8.74%. **2**, Found: C, 48.95; H, 4.79; N, 9.02%. Calcd for $[Fe_2(6\text{-Me-tpdp})(PhCO_2)](BF_4)_2 \bullet (H_2O)$: C, 48.86; H, 4.75; N, 9.00%

6) Crystal data for **2**: space group, $P2_1/n$; a = 12.558 (2) Å, b = 17.166 (3) Å, c = 19.257 (2) Å, V = 4124 (1) Å^3; Z = 4; μ = 8.12 cm^{-1}. Total 3707 independent reflections with $|Fo| > 3.0\sigma|Fo|$ ($2° < 2\theta < 60°$) were used for calculation. The structure was solved by SHLEX76 and refined by full-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms. R/R_W = 0.046/0.058 were obtained.

7) 1:1 stoichiometry ($[Fe_2:O_2]$) of oxygenation was confirmed by electronic spectral changes under various oxygen partial pressures.[4c] $P_{1/2}$ values of **1** and **2** are 43 and 6 Torr, respectively at -35 °C in dichloromethane.

8) Resonance Raman spectra were measured at -80 °C with spinning cell excited by He-Ne laser (632.8 nm, 15 mW).

9) The presence of a single oxygenated species is strongly suggested by ^{1}H NMR and oxygen affinity measurement[7] which will be reported elsewhere.

10) The stronger band is assigned to ν_{O-O}. Details will be explained elsewhere.

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