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LETTER

Synthesis and Properties of Dinuclear Iron–Oxo Complexes with Tetradentate Tripodal Ligands

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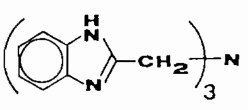
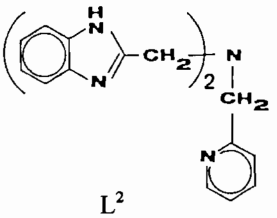
The study of synthetic models containing a [Fe_2-(μ-O)(μ-acetato)$_2$]$^{2+}$ core, established in the oxygen carrier protein hemerythrin [1], has received additional impetus and importance with the realization that such a unit may also be present in other binuclear iron biomolecules. These include the purple acid phosphatases [2] and ribonucleotide reductases [3]. By using a variety of tridentate N-based ligands (L), synthetic materials of formulation [$Fe_2O(O_2CR)_2L_2$] have been prepared [4], although the preparative methods of the authors are different from each other.

In previous papers [5], the present authors reported that binuclear Fe(III) and Mn(III) complexes with a (μ-oxo)bis(μ-acetato) core are obtained with some tridentate ligands by the use of [$M_3O(CH_3COO)_6(H_2O)_3$]$^+$ (M = Fe(III) and Mn(III)) as a starting material. The establishment of a general method to prepare the oxo-bridged binuclear iron(III) complexes seems to be very important, in order to model the binuclear sites of the iron biomolecules described above and also to elucidate the correlation between the function and the structure of these metalloenzymes. In this article we report that binuclear iron(III) complexes with a (μ-oxo)(μ-acetato) core can be obtained from the reaction of [$Fe_3O(CH_3COO)_6(H_2O)_3$]$^+$ and several tetradentate tripodal ligands.

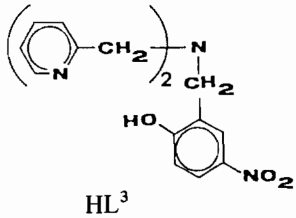
The ligands used in this study (shown below) were obtained according to the published methods. The iron(III) complexes were obtained from the reaction mixture (methanol–water) containing the ligand, [$Fe_3O(CH_3COO)_6(H_2O)_3$]$^+$ and $NaClO_4$. The analytical data given in Table 1 are consistent with the formula of binuclear complexes with a (μ-oxo)(μ-acetato) core. The infrared spectral data are also consistent with the assumed structure. In Fig. 1, the temperature dependence of the magnetic susceptibility (liquid nitrogen to room temperature) of the compound with L^1 is shown. The magnetic moments are 1.82 and 0.65 μ_B at 291.3 and 81.3 K, respectively, indicating that a strong antiferromagnetic interaction is operating between two iron atoms. The J values were calculated based on the theoretical expression obtained from the isotropic Heisenberg exchange Hamiltonian $\mathcal{H} = -2JS_1S_2$. The $-J$ values are 104.3, 107.4 and 100.5 cm^{-1} for the compounds with L^1, L^2 and HL^3, respectively, suggesting that these



L^1



L^2



HL^3

TABLE 1. Analytical data of new compounds

Compound	C (%)		H (%)		N (%)		Fe (%)	
	Found	(Calc.)	Found	(Calc.)	Found	(Calc.)	Found	(Calc.)
[$Fe_2O(CH_3COO)(L^1)_2$]$(ClO_4)_3\cdot 4H_2O$	43.55	(43.77)	3.74	(3.89)	14.22	(14.29)	8.3	(8.14)
[$Fe_2O(CH_3COO)(L^2)_2$]$(ClO_4)_3\cdot H_2O$	44.54	(44.56)	3.90	(3.66)	13.51	(13.55)	9.1	(9.01)
[$Fe_2O(CH_3COO)(L^3)_2$]$ClO_4\cdot 2H_2O$	46.97	(47.06)	3.81	(4.05	10.89	(10.98)	10.7	(10.94)

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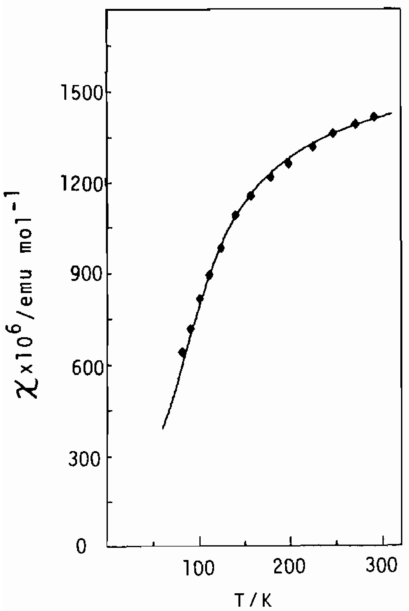

Fig. 1. Variation with temperature of molar susceptibility (per Fe) of $[Fe_2O(CH_3COO)(L^1)_2](ClO_4)_3$: (◆◆◆) experimental value; (——) calculated value based on isotropic Heisenberg equation for values of $g = 2.00$, $-J = 104.3$ cm^{-1} and $N\alpha = 0$ with 0.3% of high-spin Fe(III) impurity.

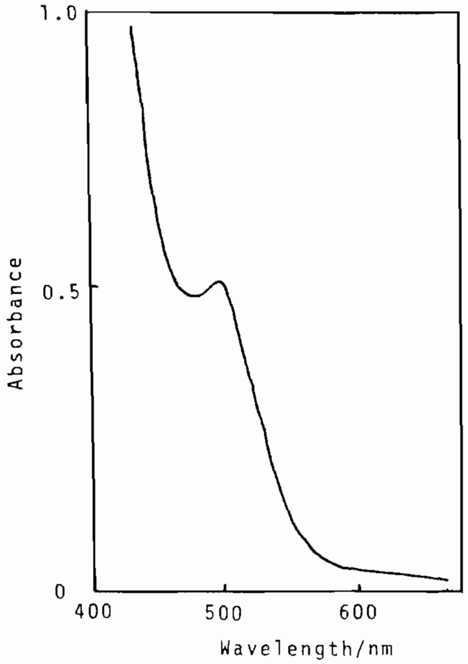

Fig. 2. Absorption spectrum of $[Fe_2O(CH_3COO)(L^3)_2]ClO_4$ (in acetonitrile, 1×10^{-4} mol dm^{-3} at 293 K).

complexes are of a binuclear structure with a μ-oxo bridge, as exemplified by one example [6]. The coordination of the phenol group in the compound with HL^3 is supported by the strong absorption band around 494 nm (ϵ/Fe = 5000), which should be associated with a phenol-Fe(III) charge-transfer transition [7], as illustrated in Fig. 2.

In Fig. 3, the cyclic voltammograms (CV) of the compounds are shown. Measurements over the range −0.9 to +1.5 V versus SCE revealed an irreversible wave at −0.18 V (reduction) and +0.4 V (oxidation) in the compound with L^1. The reduction wave may correspond to $Fe_2(III,III) \rightarrow Fe_2(II,III)$ [8]. The CV feature of the compound with L^2 is very similar to that of L^1. On the other hand, a quasi-reversible wave was observed at −0.68 V (reduction −0.72 V; oxidation −0.64 V) for the compound with HL^3. It has been postulated that the active site of the purple acid phosphatases consists of a binuclear iron complex with two accessible oxidation states: a catalytically inactive, purple Fe(III)–Fe(III) form; and an enzymatically active, pink Fe(III)–Fe(II) form [9]. The visible chromophore in these enzymes is associated with tyrosine coordination, however, the significance of the tyrosine coordination has not been elucidated until now. The results of the present study imply that the presence of tyrosine coordination plays an important role in the stabilization of the Fe(II)–Fe(III) mixed-valence state, and thus in the enzymatic function.

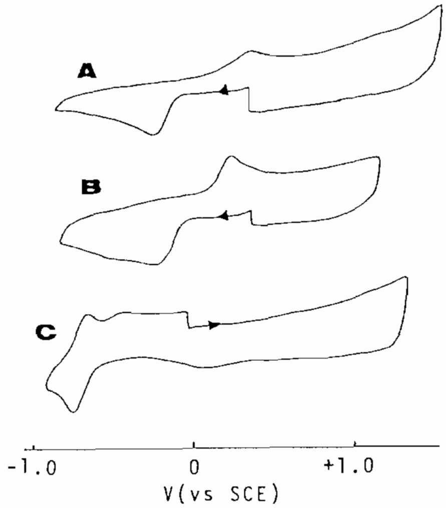

Fig. 3. Cyclic voltammograms (in acetonitrile containing 0.1 M tetra-n-butylammonium tetrafluoroborate; scan speed 500 mV/s, 293.6 K; voltage readings are referenced to a saturated Calomel electrode and a glassy carbon electrode): (A) $[Fe_2O(CH_3COO)(L^1)_2]^{3+}$; (B) $[Fe_2O(CH_3COO)(L^2)_2]^{3+}$; (C) $[Fe_2O(CH_3COO)(L^3)_2]^{+}$.

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