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Two Modifications of Bridged Oxygen Atom in Binuclear Iron(III) Complexes with N-Alkyl-N,N-bis(benzimidazol-2-ylmethyl)amine

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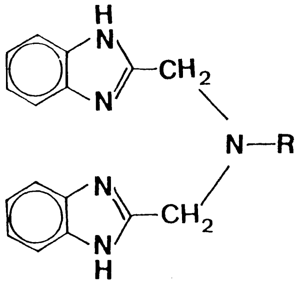
From the reaction mixture of $[Fe_3O(CH_3COO)_6(H_2O)_3]Cl$ and N-alkyl(R)-N,N-bis(benzimidazol-2-ylmethyl)amine, (μ-oxo)bis(μ-acetato)diiron(III) complexes were prepared for R=ethyl, n-propyl, n-butyl, and benzyl. On the other hand, (μ-hydroxo)bis(μ-acetato) structure was inferred for the complexes with R=$-CH_2CH_2OH$ based on the magnetic and spectroscopic results.

Recently the synthesis and properties of binuclear iron(III) complexes that serve as structural, spectroscopic, and chemical models for (μ-oxo)bis(μ-carboxylato)diiron(III) core of the met forms of marine invertebrate respiratory proteins hemerythrin(Hr) were described.[1,2] Oxo-bridged binuclear iron centers are also believed to occur in ribonucleotide reductase from Esherichia coli[3] and in some purple acid phosphatases.[4] Very recently we have reported[5,6] the preparations of (μ-oxo)bis(μ-acetato)dimanganese(III) complexes with N-alkyl-N,N-bis(benzimidazol-2-ylmethyl)amine, as illustrated below. In this article we wish to report that the magnetic and spectroscopic properties of analogous diiron(III) complexes with R=$-CH_2CH_2OH$(see below) are greatly different from those of other compounds with R=ethyl or n-propyl, etc. The origin of the above fact will be developed.



R	abbreviation
$=C_2H_5$	(Et-L)
$=n\text{-}C_3H_7$	(Pr-L)
$=n\text{-}C_4H_9$	(Bu-L)
$=CH_2C_6H_5$	(Bz-L)
$=CH_2CH_2OH$	(OH-L)

The ligands used in this study were prepared according to the published methods.7) The iron(III) complexes were obtained from the reaction mixture(methanol-water) containing ligand, $[Fe_3O(CH_3COO)_6(H_2O)_3]^+$, and $NaClO_4$(or NH_4PF_6). The analytical data8) of all the compounds are consistent with the formula, $[Fe_2O(CH_3COO)_2(R\text{-}L)_2]X_2$($X=ClO_4$ or PF_6). The complexes with (Et-L), (Pr-L), (Bu-L) and (Bz-L) are green, whereas the compounds with (OH-L), yellow.

In Fig. 1, temperature dependence of magnetic susceptibility(liquid nitrogen-room temperature) of the compound with (Et-L) is shown. The magnetic moments are 1.67 and 0.40 μ_B at 291.3 and 78.1, respectively, suggesting that 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, $\mathcal{H}=-2JS_1\cdot S_2$, and are summarized in Table 1. The -J values of the green compounds are in the range 109.1-116.7 cm^{-1}, indicating that these complexes are of a binuclear structure with μ-oxo and di-μ-acetato bridges, as exemplified by several examples.9,10) Contrary to this, -J values of the yellow compounds with (OH-L) are in the range 19-20 cm^{-1}, which are much smaller than those of the green complexes(cf. Table 1).

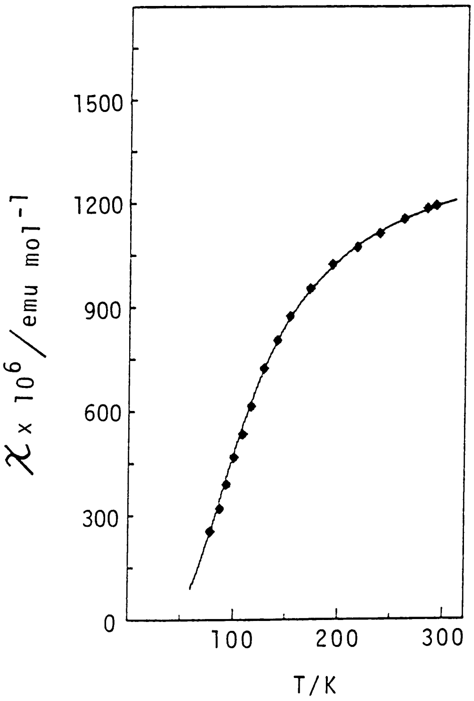


Fig. 1. Variation with temperature of molar susceptibility(per Fe) of $[Fe_2O(CH_3COO)_2(Et\text{-}L)_2](ClO_4)_2$: ◆◆◆ experimental value; ——— calculated value based on isotropic Heisenberg equation for values of g=2.00, J=-116.7 cm^{-1}, and $N\alpha=0$.

The infrared spectra of the green complexes(ν_{as}(OCO), 1560-1580 cm^{-1}; ν_{as}(Fe-O-Fe), 740-750 cm^{-1}; ν_s(Fe-O-Fe), 530-540 cm^{-1}) are consistent with the assumed structure. The IR spectra of the yellow compounds with (OH-L) are similar to those of the green complexes in the range of ν_{as}(OCO), whereas no band was observed in the range 500-550 cm^{-1}. In addition to this, a sharp band

Table 1. Color and Magnetic Data of New Compounds

Complex	Color	$-J/cm^{-1}$
$[Fe_2O(CH_3COO)_2(Et\text{-}L)_2](ClO_4)_2$	green	116.7
$[Fe_2O(CH_3COO)_2(Pr\text{-}L)_2](ClO_4)_2$	green	110.9
$[Fe_2O(CH_3COO)_2(Bu\text{-}L)_2](ClO_4)_2$	green	109.1
$[Fe_2O(CH_3COO)_2(Bz\text{-}L)_2](ClO_4)_2$	green	109.1
$[Fe_2O(CH_3COO)_2(OH\text{-}L)_2](ClO_4)_2$	yellow	20.2
$[Fe_2O(CH_3COO)_2(OH\text{-}L)_2](PF_6)_2$	yellow	18.9
$[Fe_2O(C_6H_5COO)_2(OH\text{-}L)_2](ClO_4)_2$	yellow	19.1

is observed around 3580 cm^{-1} for the yellow compounds. In the absorption spectra, no band was observed in the range 400-500 nm for the yellow (OH-L)-compounds, whereas some shoulders are found in the range for the green complexes, as illustrated in Fig. 2. These shoulders are known to be characteristic of the (μ-oxo)bis(μ-acetato)diiron(III) compounds.10)

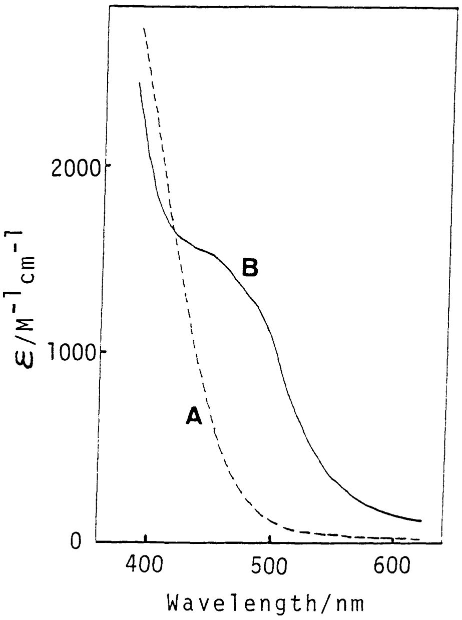
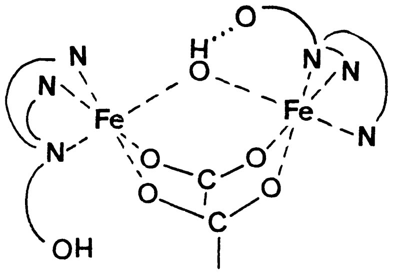


Fig. 2. Absorption spectra of
A: $[Fe_2O(CH_3COO)_2(OH\text{-}L)_2](ClO_4)_2$ (in acetonitrile),
B: $[Fe_2O(CH_3COO)_2(Et\text{-}L)_2](ClO_4)_2$ (in dmf).

Lippard et al.11) reported that -J value of (μ-hydroxo)bis(μ-acetato)diiron(III) complex is 17 cm^{-1}; this value is very similar to those observed for the yellow compounds with (OH-L) ligand. Based on the above facts, it is very likely that the yellow compounds with (OH-L) are of a binuclear structure of μ-hydroxo-di-μ-acetato bridges, as shown below; this implies that tha bridging oxo atom has a tendency to form hydrogen bonding as suggested for the oxyhemerythrin.12) This discovery raises the possibility that analogous hydroxo-bridged diiron(III) center may exist in biological reaction,11) and may give a reasonable explanation for the presence of the deprotonated tyrosine residue in the ribonucleotide reductase.13)



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