# A Dinuclear Iron(II,III) Mixed Valence Complex with the Dinucleating Ligand, 2,6-Bis[bis(2-benzimidazolylmethyl)aminomethyl]-4-methylphenol: a Model for Pink Uteroferrin and Semi-methemerythrin

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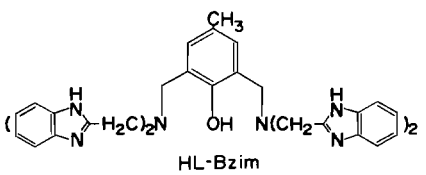
Pink uteroferrin and semi-methemerythrin have been shown to be dinuclear iron(II,III) mixed valence complexes [1–4]. ESR, NMR and magnetic studies of the above proteins reveal that iron(II) and iron(III) ions are in high-spin electronic configuration and antiferromagnetically coupled to yield an $S = ½$ spin ground state ($J \approx -7 - -10$ cm$^{-1}$ for pink uteroferrin) [2, 3]. Possible ligands for irons in hemerythrin are imidazoles of histidine, carboxylates of glutamic and aspartic acids [5]. The coordination of imidazole and phenolate of tyrosine is suggested for uteroferrin [3, 6]. Details of structures, and spectroscopic and magnetic properties of the dinuclear mixed valence iron(II,III) centers of the proteins still remain equivocal. Therefore, synthetic dinuclear iron(II,III) mixed valence complexes with the above coordinating groups are useful for elucidating those properties of the dinuclear iron(II,III) mixed valence centers.

In this communication, we report the synthesis and some physicochemical properties of a novel dinuclear iron(II,III) mixed valence complex with the dinucleating ligand (L-Bzim) [7] which contains phenolate and benzimidazole groups, $[Fe_2^{II,III}(L\text{-}Bzim)(PhCOO)_2](BF_4)_2 \cdot 3H_2O$, where HL-Bzim is 2,6-bis[bis(2-benzimidazolylmethyl)aminomethyl]-4-methylphenol (Scheme 1) and PhCOOH, benzoic acid.




HL-Bzim

Scheme 1.

The complex was prepared as follows. To a solution of HL-Bzim (1 mmol), PhCOOH (2 mmol), and triethylamine (2 mmol) in ethanol (40 cm$^3$) was added $Fe(BF_4)_2 \cdot 6H_2O$ (2 mmol) under nitrogen atmosphere. The resulting pale yellow solution was exposed to air to cause a simultaneous color change to brown. The brown solution was allowed to stand for a few hours in the air at room temperature to give greenish-brown crystals, $[Fe_2^{II,III}(L\text{-}Bzim)(PhCOO)_2](BF_4)_2 \cdot 3H_2O$. The complex was recrystallized from acetonitrile-diethylether. *Anal.* Calc. for $C_{45}H_{47}N_{10}O_5B_2F_8Fe_2 \cdot 3H_2O$; C, 52.12; H, 4.21; N, 11.05; $Fe^{II}$, 4.41; $Fe^{III}$, 4.41. Found: C, 51.87; H, 4.12; N, 11.12; $Fe^{II}$, 4.2; $Fe^{III}$, 4.4%.

The contents of iron(II) and iron(III) ions were determined colorimetrically as follows. To a solution of phenanthroline (200 mg) in DMF (20 cm$^3$) was added a known amount of the complex (*ca.* 40 mg) under nitrogen atmosphere. The solution was stirred for 1 min, and then an aqueous suspension (20 cm$^3$) of $H_4$edta was added to the resulting reddish-orange solution for preventing the reduction and masking of iron(III) ion present. The mixture was diluted to *ca.* 250 cm$^3$ with water and the pH of the solution was adjusted to *ca.* 4 with acetic acid. The volume of the resulting solution was adjusted to 500 cm$^3$. After filtration, iron(II) content was determined spectrophotometrically at 510 nm ($\epsilon = 11\,300$ mol$^{-1}$ dm$^3$ cm$^{-1}$). Total iron content was also determined colorimetrically according to an usual method [8]. The analyses of iron(II) and iron(III) ions revealed that the complex contains both iron(II) and iron(III) ions in 1:1 ratio. The molar conductivity of the complex in acetonitrile was 227 $\Omega^{-1}$ cm$^2$ mol$^{-1}$, indicative of the presence of a 2:1 electrolyte. From the dinucleating nature of L-Bzim [7, 10] and the elemental analysis as well as the molar conductivity, it is concluded that the complex can be formulated as $[Fe_2^{II,III}(L\text{-}Bzim)(PhCOO)_2](BF_4)_2 \cdot 3H_2O$ and two irons are bridged by phenolate. The complex in acetonitrile was gradually oxidized for a day by molecular oxygen at room temperature but not in the solid state.

The magnetic moment of the complex is 7.7 BM/2Fe at room temperature. This indicates that both iron(II) and iron(III) ions are in high-spin electronic configuration. The magnetic susceptibilities were also measured over the temperature range of 80–300 K. The results were analyzed with the spin–spin interaction Hamiltonian $\mathcal{H} = -2JS_1 \cdot S_2$. The molar susceptibility ($\chi_A$) of an $S_1 = 2 \sim S_2 = 5/2$ exchange coupling dimer is given by the following equation,

$$\chi_A = \frac{N\beta^2 g^2}{4kT} \frac{X^{24} + 10X^{21} + 35X^{16} + 84X^9 + 165}{X^{24} + 2X^{21} + 3X^{16} + 4X^9 + 5}$$

where $X = \exp(-J/kT)$ and the symbols have their usual meanings. The solid line in Fig. 1 is the calculated curve by using the parameters, $J = -5$ cm$^{-1}$

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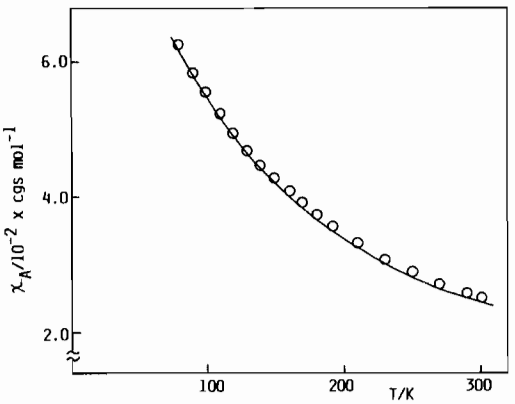


Fig. 1. Temperature dependence of magnetic susceptibilities of $[Fe_2^{II,III}(L\text{-}Bzim)(PhCOO)_2](BF_4)_2 \cdot 3H_2O$.

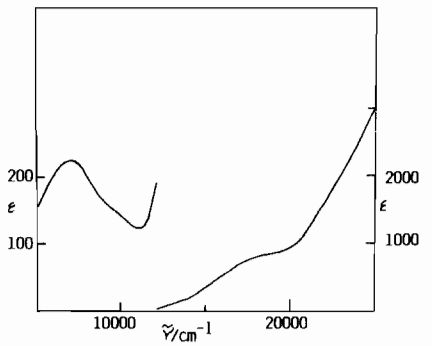


Fig. 2. Absorption spectrum of $[Fe_2^{II,III}(L\text{-}Bzim)(PhCOO)_2](BF_4)_2 \cdot 3H_2O$ in acetonitrile under $N_2$.

and $g = 2.10$. This indicates that high spin iron(II) and iron(III) ions are weakly antiferromagnetically coupled. Thus the antiferromagnetic exchange interaction in the present complex is comparable to that of pink uteroferrin ($J = -7 - -10$ cm$^{-1}$) [2, 3]. The presence of hydroxo bridge(s) has been suggested in pink uteroferrin. It has been shown that, in a series of dinuclear iron(III,III) complexes with $\mu$-hydroxo, $\mu$-alkoxo, or $\mu$-phenoxo bridging group ($Fe_2O_2$ bridging unit), variation in the above bridging groups has no significant influence on the antiferromagnetic exchange interactions in the complexes ($J = -7 - -17$ cm$^{-1}$) [10]. Since the antiferromagnetic interaction of the present complex is comparable to that of pink uteroferrin, the present result also supports the presence of $\mu$-hydroxo bridge(s) in pink uteroferrin.

The electronic spectrum of the complex in acetonitrile displays a broad band in the visible region (Fig. 2). The band is assigned to the L → M CT transition from the $P_\pi$ orbital of the bridging phenolate oxygen to the half-filled $d_{\pi^*}$ orbital of iron(III) on the basis of its intensity ($\epsilon \approx 900$ mol$^{-1}$ dm$^3$ cm$^{-1}$/Fe$^{III}$ at 550 nm) [11]. The complex also exhibits an intense band at 7100 cm$^{-1}$ ($\epsilon = 220$ mol$^{-1}$ dm$^3$ cm$^{-1}$/Fe$^{II}$·Fe$^{III}$). Since it is well known that iron(II) and iron(III) complexes have no such intense band in this region [12], we tentatively assigned the band to an intervalence charge transfer transition (IT) from the iron(II) to the iron(III) moiety. The ligand field bands of the iron(II) and iron(III) moieties which occur in the visible and near-infrared regions may be obscured by the CT bands. The presence of the IT band indicates that the complex belongs to the class II mixed valence system [13]. It should be noted that no such IT band is detected in semi-methemerythrin in the visible and near-infrared regions [12]. In semi-methemerythrin, therefore, it is possible that the IT band is hidden under intense CT bands in the near-ultraviolet region; if not, semi-methemerythrin belongs to the class I mixed valence system. Further studies of this type of dinuclear mixed valence complexes are in progress.

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