Isolation of a Novel Singly Oxo-bridged Low-spin Fe(II) Dimeric Complex: Synthesis, Crystal Structure, and Spectroscopic Study

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(Received July 16, 2003; CL-030642)

Redox reaction between [(phen)$_4$Fe$_2$(Cl)$_2$(μ-O)]Cl$_2$·4.5H$_2$O (phen = 1,10-phenanthroline) and Mn(OH)$_2$·xH$_2$O in water methanol solution at refluxing temperature under inert atmosphere gives a novel low-spin iron(II)–oxo complex [(phen)$_4$Fe$_2$(Cl)$_2$(μ-O)]·4H$_2$O (**1**) which has been characterised by IR, Mössbauer, electrochemical and magnetic studies. The crystal structure shows that complex **1** is a dinuclear single oxo-bridged Fe(II) species with distorted octahedral geometry.

The chemistry of binuclear oxo-bridged iron complexes has experienced a resurgence of interest with the discovery of bridged units of this general type in a number of nonheme proteins and enzymes.[1,2] The Fe–O–Fe bridge is a constituent of synthetic iron complexes and is also of biological significance. The reactivity of the metal site in terms of redox reactions has been relatively little explored.[3] In the literature, the paucity of data about stable iron(II) μ-oxo complexes has been noted and this promted us to take this opportunity for isolation of Fe(II) system.[2,4,5] In the present work, our interest is to investigate the possible conversion of μ-oxo diiron(III) complex to μ-oxo diiron(II) complex.

+II state is generally the most stable for manganese in neutral, or acidic aqueous solution and posses very pale pink color and quite resistant to oxidation ($E_{\mathrm{Mn^{3+}}/\mathrm{Mn^{2+}}} = 1.5\,\mathrm{V}$). However, in basic medium Mn(OH)$_2$ is formed and is more easily oxidized as shown by the potential $E_{\mathrm{Mn_2O_3\cdot xH_2O/Mn(OH)_2}} = 0.1\,\mathrm{V}$ and $E_{\mathrm{Mn_2O_3/MnO_2}} = 0.2\,\mathrm{V}$.[6] Here, we have used a basic solution of Mn(II) salt to carry out the reduction. The reduction potential of (phen)$_3$Fe^{3+} to (phen)$_3$Fe^{2+} is 1.12 V.[6] All the potential values are versus NHE.

The starting complex [(phen)$_4$Fe$_2$(Cl)$_2$(μ-O)]Cl$_2$·4.5H$_2$O was prepared by the reported procedure.[7,8] Complex [(phen)$_4$Fe$_2$(Cl)$_2$(μ-O)]·4H$_2$O (**1**) was prepared in a closed dinitrogen atmosphere in the presence of triethylamine and MnCl$_2$ at pH = 9.5.[9]

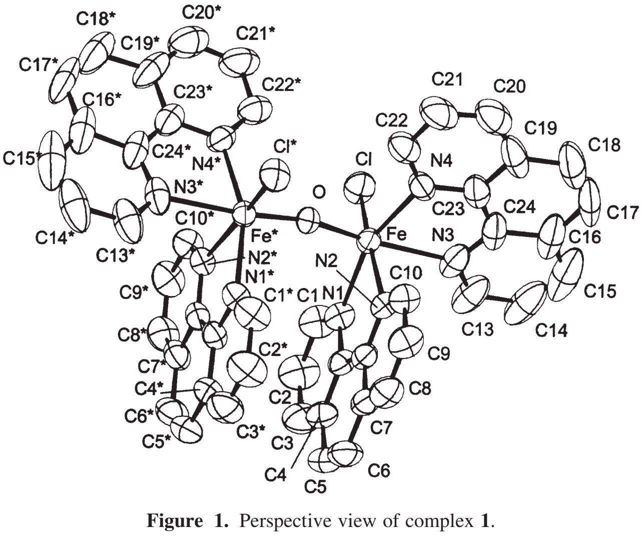


Figure 1. Perspective view of complex **1**.

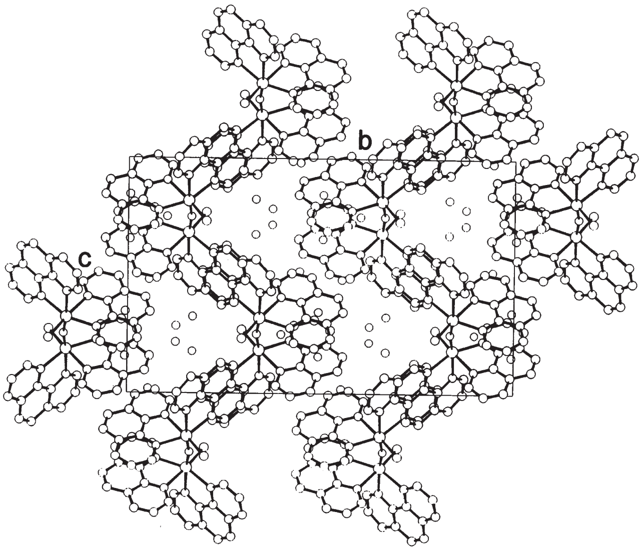


Figure 2. Polymeric view of complex **1**.

The perspective view of complex **1** is shown in Figure 1.

Dark red crystals of **1** were monoclinic polymorphs.[10] Crystallographic result shows the two ferrous irons (Fe and Fe*) are bridged by a single oxo (O^{2-}) ligand. The remaining coordination sites of each Fe are completed by the coordination of four nitrogens from two phen ligands and one chloride ligand which is cis to the bridging oxo in each case. The Fe–N distances lie between 2.134(4) to 2.249(4) Å which are nearly comparable to the similar compounds.[2,4,5,11] The Fe–Cl bond distance is 2.319(1) Å, typical Fe(II)–Cl distance for terminal chlorine.[12] The Fe–O–Fe* linkage

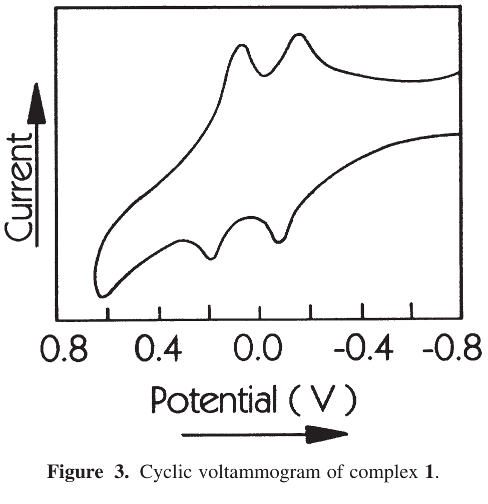
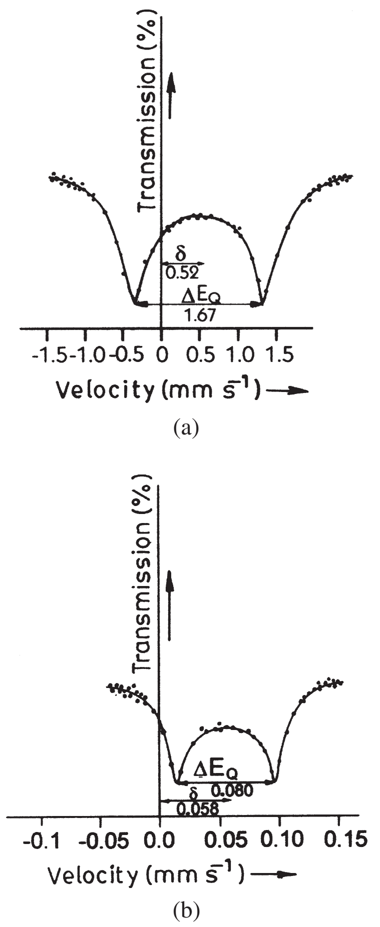


Figure 3. Cyclic voltammogram of complex **1**.



(a)

(b)

Figure 4. Mössbauer spectra of starting complex and complex **1**.

is distinctly nonlinear, exhibiting an angle of 168.6(1)°. The Fe–μ–O distance is 1.778(1) Å, which is more or less comparable to the corresponding diiron(II) complexes.[4,5]

The Fe–Fe distance 3.538 Å is typical for monobridged Fe–O–Fe cores.[1,4,13]

The polymeric view of complex **1** is shown in Figure 2.

Figure 2 shows the complex **1** forms an infinite helical chains through π–π stacking of the phenanthrene rings of the neighbouring molecules. The closest distances between rings centroids and carbon atoms are 3.493(13) and 3.511(12) Å. Here, the molecules are held together by strong intermolecular interactions.

The dimer has a strong absorption at 814 cm^{-1}, which significantly differs from the starting complex.[7,8,13] This is the characteristic of the asymmetric stretch of a Fe–O–Fe moiety. The symmetric Fe–O–Fe vibration found in the 390–415 cm^{-1} region, could not be unambiguously assigned.[14]

The electrochemical study was carried out in acetonitrile. Measurements versus SCE revealed two quasi-reversible redox processes at $E_{1/2} = -0.1$ V ($\Delta E_p = -0.08$ V) and $E_{1/2} = 0.14$ V ($\Delta E_p = 0.1$ V) vs standard SCE at a scan rate 0.05 V s^{-1}.[15,16] This supports the assignment of the observed redox processes as shown in Eq 1.[15–17]

$$\begin{aligned}&[\mathrm{Fe(II)Fe(II)(phen)_4(Cl)_2}(\mu\text{-O})]\\&\rightarrow [\mathrm{Fe(II)Fe(III)(phen)_4(Cl)_2}(\mu\text{-O})]^{+}\\&\rightarrow [\mathrm{Fe(III)Fe(III)(phen)_4(Cl)_2}(\mu\text{-O})]^{2+}\end{aligned} \qquad (1)$$

The 80 K Mössbauer spectrum of the starting complex (shown in Figure 4) showed a single quadrupole doublet with δ of 0.52 mms^{-1}, ΔE_Q of 1.67 mms^{-1} which is characteristics of high-spin d^5 systems, with the ΔE_Q value being at the high end of μ-oxo compounds having six-coordinate Fe(III).[1,13,18]

Zero field Mössbauer spectrum of **1** (shown in Figure 4) shows a single quadrupole doublet with δ value of 0.058 mms^{-1} and ΔE_Q value of 0.08 mms^{-1} supporting low spin Fe(II).[15,19]

Magnetic moment shows that **1** is diamagnetic whereas the starting complex is paramagnetic and exhibits a strong antiferromagnetic coupling.[20] The diamagnetic nature of **1** unambiguously proves that Fe(II) is in low-spin state.

Crystallographic, spectroscopic, electrochemical, and magnetic data confirm that **1** is diiron(II) species and the reaction described definitely proves that manganese(II) cation promotes reduction of μ-oxo diiron(III) complex to form one novel low-spin μ-oxo diiron(II) complex.

This work is supported by CSIR, UGC, and DST (New Delhi) India. We are also grateful to Dr. S. Bhattacharya, J. U., Kolkata and Dr. A. Ghosh, C. U., Kolkata for academic help.

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9 Preparation of **1** 1:2 water–methanol solution of $[\mathrm{(phen)_4Fe_2(Cl)_2}(\mu\text{-O})]\mathrm{Cl_2}\cdot4.5\mathrm{H_2O}$ (1 mmol) was treated with $\mathrm{MnCl_2}$ (1 mmol) and trimethylamine (1 mmol) in a closed nitrogen atmosphere at pH ca. 9.5. The mixture was refluxed for 2 h and then cooled to RT and precipitated $\mathrm{MnO_2}$ was removed. On standing, the filtrate yields dark red crystals of **1** which are also suitable for X-ray analysis. Yield: 46%. Calcd for $\mathrm{C_{48}H_{40}Cl_2Fe_2N_8O_5}$, C, 58.09; H, 4.03; N, 11.29; Fe, 11.26; Cl, 7.16%. Found: C, 58.00; H, 4.10; N, 11.34; Fe, 11.38; Cl, 7.11%.

10 Crystallographic data for **1**: $\mathrm{C_{48}H_{40}Cl_2Fe_2N_8O_5}$, $M_r = 990.70$, monoclinic phase, space group $C2/c$, $a = 13.1120(1)$ Å, $b = 24.932(2)$ Å and $c = 15.8010(1)$ Å, $\beta = 107.645(6)°$, $Z = 4$, $\mu = 0.750$, $F(000) = 2040$, crystal size $= 0.18 \times 0.70 \times 0.70$ mm, $V = 4922.5(6)$ Å^3, 5636 reflections collected, 4200 independent reflections used in the refinement. Final $R_1 = 0.0779$, $wR_2 = 0.2447$. CCDC reference number 185366 for crystallographic data in CIF or other electronic format.

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Published on the web (Advance View) November 17, 2003; DOI 10.1246/cl.2003.1136