Temperature Dependence of the Electron Transfer in a $Mn^{II}Mn^{III}(\mu\text{-}OH)$ Mixed-Valence Manganese Complex

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The (μ-oxo/hydroxo)-bis(μ-carboxylato)dimanganese moiety is a component of the active center of a number of metalloproteins such as the catalases[1] and the ribonucleotide reductase from *Brevibacterium ammoniagenis*.[2] A number of oxo-bridged dimanganese complexes in different oxidation states have been described in a recent publication.[3] As part of the application of synchrotron resonance scattering in site-specific, valence-selective diffraction analysis,[4] we have investigated a number of mixed-valence complexes containing both Mn^{III} and Mn^{IV} and found shifts of ≈3eV between the K-edges of the two valence states, in agreement with a theoretical calculation of the shift in binding energies.[5,6] However, surprisingly, we discovered a zero, or very small, valence shift in the study of the $Mn^{II}Mn^{III}$ complex $[ttacnMn^{II}(\mu\text{-}OH)(\mu\text{-}pivalonato)_2Mn^{III}ttacn](ClO_4)_2$ (**I**) (Figure 1, ttacn = 1,4,7-trimethyl-1,4,7-triazacyclononane),[7] even though a diffraction study showed the room-temperature $Mn^{II}O$ and $Mn^{III}O$ bond lengths to differ by as much as 0.14 Å. As the resonance-scattering method is site-specific, this indicates that there is only a small difference between the *average* valencies of the two sites.

Subsequent synchrotron radiation diffraction studies at 298, 62, and 20 K revealed a gradual increase in the asymmetry of the structure of the complex as the temperature was lowered,[8] while one of the perchlorate anions, which was disordered at room temperature, became fully ordered at 20 K. The Mn−O bond length variations are shown in Table 1. Similar, but somewhat smaller, variations are observed in the Mn−N distances.

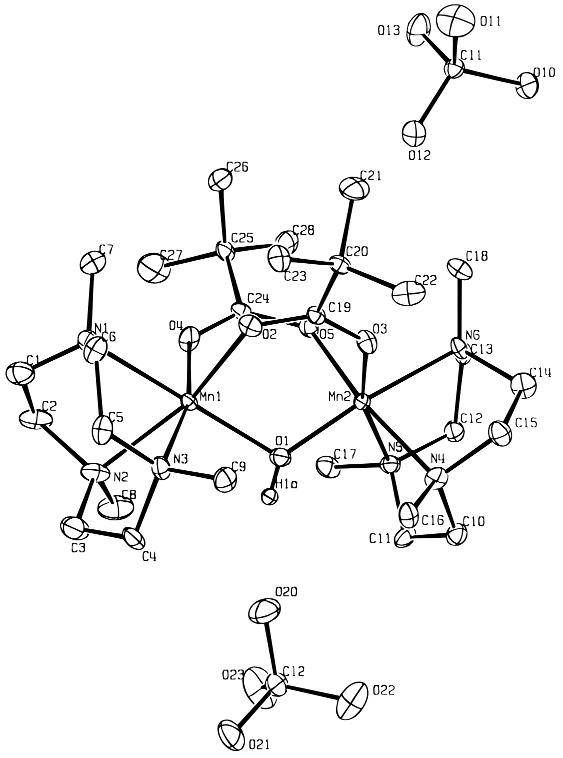

Figure 1. ORTEP drawing of the structure of **I** at 20 K. Ellipsoids are 50% probability surfaces.

As the asymmetry increases, the two Mn atoms become increasingly distinct. Assuming the temperature dependence to be due to a superposition of two states, and the experimental bond lengths to be the average over the two states, the relative populations p_1 and p_2 may be calculated from the expressions[9]

$$p_1(T) - p_2(T) = \Delta l(T)/(l_1 - l_2) \qquad (1)$$

$$p_1 + p_2 = 1 \qquad (2)$$

where $\Delta l(T)$ is the observed bond length difference within a pair and l_1 and l_2 are the bond lengths at 20 K, at which the separation is assumed to be complete. Use of the Mn−O(bridging) distances, which have the strongest asymmetry, leads to 74/26 and 97/3 population ratios at room temperature

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(8) Diffraction studies were performed at the SUNY X3 Beamline (station A1) at the National Synchrotron Light Source, using FUJI imaging plates, a BAS2000 scanner, and a DISPLEX cryostat. Integration of the diffraction maxima was performed with the program HIPPO (Bolotovsky, R.; White, M. A.; Darovsky, A.; Coppens, P. *J. Appl. Crystallogr.* **1995**, *28*, 86−95). 5000, 4732, and 5094 unique reflections with $I > 3\sigma(I)$ were obtained at 20, 62, and 298 K, respectively. Space group: $P2_1/n$. Cell dimensions: 20 K, $a = 11.811(1)$ Å, $b = 15.795(4)$ Å, $c = 21.106(5)$ Å, $\beta = 98.03(2)°$; 62 K, $a = 11.808(3)$ Å, $b = 15.813(8)$ Å, $c = 21.227(10)$ Å, $\beta = 98.25(1)°$; 298 K, $a = 11.862(1)$ Å, $b = 16.162(1)$ Å, $c = 21.640(1)$ Å, $\beta = 98.33(1)°$.

(9) As follows directly from the two equations $l_1(\text{obs}) = p_1l_1 + p_2l_2$ and $l_2(\text{obs}) = p_2l_1 + p_1l_2$.

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Table 1. Mn−O Bond Length Variations as a Function of Temperature

	298 K	62 K	20 K
Mn1−O1	2.058(4)	2.110(4)	2.113(3)
Mn2−O1	1.943(4)	1.887(4)	1.876(4)
Mn1−O4	2.108(4)	2.124(4)	2.143(5)
Mn2−O5	2.011(4)	1.965(4)	1.967(4)
Mn1−O2	2.062(4)	2.091(4)	2.105(3)
Mn2−O3	2.104(3)	2.110(4)	2.107(2)

and 62 K, respectively. With the statistical expression

$$p_2/p_1 = \exp(-\Delta E/kT) \qquad (3)$$

where k is the Boltzmann constant, this corresponds to an energy difference ΔE of $\approx$130 cm^{-1} or $\approx$1.5 kJ/mol. The energy difference is attributed to the packing forces in the crystal favoring one of the two arrangements of the symmetrically substituted Mn(OH)Mn core.

The observed bond length variation can be due either to the superposition of two molecules AB and BA in different orientations or to increased electron detrapping as the temperature is raised, the former corresponding to a very slow and the latter to a rapid electron transfer. The first choice is supported by the absence of an intervalence band in the visible spectrum of **I**,[3] characteristic for valence-detrapped type III and intermediate type II complexes,[10,11] and furthermore by an analysis of the observed mean-square displacement parameters at different temperatures. The absence of any pronounced intervalence band is observed both in solution and in the solid state, for which spectra, measured by transmission and reflection, respectively, are identical. While the Hirshfeld rigid-bond criterion, according to which thermal mean-square displacements of covalently bonded atoms should be the same in the bond direction,[12] is reasonably well obeyed at 20 K, we find large deviations in the analysis of the room-temperature structure, an indication of the presence of two superimposed species.

The temperature dependence of the experimental geometry of mixed-valence transition metal complexes was previously observed in trinuclear complexes containing the Fe_3O core.[13] 163 and 298 K diffraction studies of $[Fe_3O(O_2CCH_3)_6(4\text{-Et-py})_3(4\text{-Et-py})$ (Et = ethyl, py = pyridine) show that Fe−O bond lengths differ by up to 0.036 Å between the two temperatures.[14] At room temperature, these complexes show rapid electron transfer on the Mössbauer time scale. The rate of electron transfer is believed to be affected by the orientational disorder of the solvate molecule, which increases with increasing temperature. A comparable effect of the crystalline environment is observed in the series $[Fe_3O(CH_2XCO_2)_6(H_2O)_3]\cdot nH_2O$ (X = H, Cl, Br), in which the valence delocalization between the iron atoms is affected by the absence or presence of hydrogen bonding.[15] In the current study, the increasing disorder of one of the two independent perchlorate anions may play a similar role: while the anion is completely ordered at 20 K, 20/80 and 50/50 occupancy ratios of two 180°-rotation-related positions are observed at 62 and 298 K, respectively. In this study, however, the available evidence indicates that electron transfer is slow even at room temperature. In this case, the changing environment due to the decrease in disorder of the perchlorate groups affects the equilibrium between the two structures rather than the kinetic aspects of the electron transfer.

The present study implies that sub-liquid-nitrogen temperatures are often essential for a full characterization of mixed-valence species and suggests that the temperature dependence of the observed geometry of such complexes is more general than follows from the limited number of examples reported so far.

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