Preparation, Structure, and Properties of $[NEt_4][Mn(edt)_2(Him)]$ (H_2edt = ethane-1,2-dithiol; Him = imidazole), a Mononuclear Manganese(III) Thiolate possessing a Rare Manganese(III)–Imidazole Bond

Jeffrey L. Seela, John C. Huffman, and George Christou*

Department of Chemistry and the Molecular Structure Center, Indiana University, Bloomington, Indiana 47405, U.S.A.

$[Mn(edt)_2(Him)]^-$ (**1**), prepared from the reaction of $[Mn_2(edt)_4]^{2-}$ (**2**) with excess of imidazole (Him) or from the aerial oxidation of $MnCl_2$–Na_2edt–Him mixtures (H_2edt = ethane-1,2-dithiol), contains a distorted square-pyramidal $Mn(S)_4N$ co-ordination unit and represents the first example of a non-porphyrin manganese(III)–imidazole complex of relevance to the metal-binding modes of manganese(III)-containing biomolecules.

The number of metallobiomolecules known to contain tightly bound manganese atoms continues to grow.[1—6] In their as-isolated form, several of these systems, such as the superoxide dismutases,[2—4] acid phosphatases,[5] and catalases,[6] contain the metal in its +3 oxidation state. In no system has the exact nature of the metal-binding ligands been established and in no example to date has a manganese porphyrin been identified. Ligation must, therefore, be primarily by amino acid side-chain functions, *i.e.*, one or more of the following: thiolate, phenoxide, carboxylate, imidazole, and thioether. As preliminary to our ultimate aim of synthesising satisfactory inorganic models of the various Mn^{III} biomole-

cules, we are having first to develop the co-ordination chemistry of the +3 oxidation state with the above group of ligands; this is a poorly investigated area. In a recent publication,[7] we reported the preparation of $[Mn_2(edt)_4]^{2-}$ (**2**) (H_2edt = ethane-1,2-dithiol), the first manganese(III) thiolate. We now describe the preparation and structural characterization of the first example of a non-porphyrin complex containing a manganese(III)–imidazole (Him) bond, $[Mn(edt)_2(Him)]^-$ (**1**).

$$[Mn_2(edt)_4]^{2-} + \text{excess of Him} \xrightarrow{\text{DMF}} 2\,[Mn(edt)_2(Him)]^- \quad (1)$$
(**2**) (**1**)

Addition of excess of imidazole (10 equiv.) to a dark green solution of the $[NEt_4]_2$ salt of (**2**) in DMF (*N*,*N*-dimethylformamide) led to a colour change to bright green [reaction (1)]. Addition of an equal volume of acetone and cooling overnight gave crystals of the NEt_4 salt of (**1**) in 69% yield. Black prisms suitable for *X*-ray studies were obtained on recrystallisation from warm MeCN. The NEt_4 salt of (**1**) can also be conveniently obtained by controlled aerial oxidation in EtOH of the white slurry obtained on mixing $MnCl_2{\cdot}4H_2O$, Na_2edt, Him, and NEt_4Br in a 1 : 2 : 4 : 3 ratio. The white solid dissolves and the microcrystalline NEt_4 salt of (**1**) precipitates and may be obtained in >90% overall yield on recrystallisation from MeCN–tetrahydrofuran. Satisfactory analytical data have been obtained.

Crystal data: $C_{15}H_{32}N_3MnS_4$, M_r = 437.62, monoclinic, space group $P2_1/n$, Z = 4, a = 13.974(5), b = 14.317(5), c = 10.564(3) Å, β = 90.13(2)°, U = 2113(6) Å^3, t = −72 °C, crystal dimensions 0.18 × 0.23 × 0.23 mm; data were collected in the range 6° ≤ 2θ ≤ 45°. The structure was solved by a combination of direct methods and Fourier techniques, and refined by full-matrix least-squares. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located in a difference Fourier and included in the final refinement cycles with isotropic thermal parameters; 2152 unique reflections with $F > 3\sigma(F)$ were refined to conventional values of R = 5.86% and R_w = 5.80%.†

The structure of (**1**) is depicted in Figure 1. The manganese atom is five-co-ordinate and is in a slightly distorted square-pyramidal environment. Imidazole nitrogen, N(10), occupies the apex and two terminally bound dithiolates provide four basal sulphur atoms. The Mn atom is 0.385 Å above the S_4 least-squares plane and the imidazole ring is planar as expected, but tilted slightly such that it makes an angle of 13.52° with the Mn–N(10) vector. The N(10)–Mn–S(2,5,6,9) angles are in the narrow range 97.02(18)—102.88(18)° and the four basal S–Mn–S angles in the even narrower range 88.16(12)—89.13(13)°. The $MnNS_4$ core thus closely approximates C_{4v} symmetry. An alternative description of the geometry as distorted trigonal bipyramidal, as found for the Mn atoms in (**2**),[7,8] is unsatisfactory. If S(5)–Mn–S(9) [=164.28(9)°] is considered the axis, the equatorial angles are N(10)–Mn–S(6) = 99.52(19)°, N(10)–Mn–S(2) = 102.88(18)°, and S(2)–Mn–S(6) = 157.60(9)°, significantly different from the ideal value of 120°. The Mn–S(2,5,6,9) bond lengths [2.319(3)—2.334(3) Å] are, however, essentially identical to the terminal Mn–S lengths of (**2**) [2.319(2)—2.327(2) Å]. Isolated, well characterized examples (either structurally or otherwise) of manganese(III)–imidazole complexes are extremely rare in inorganic chemistry; indeed, (**1**) is only the second example of which we are aware, the other being bis(1-methylimidazole)(*meso*-tetraphenylporphinato)manganese(III).[9] The Mn–imidazole bond length [2.308(3) Å] of the latter compares favorably with that in (**1**) [2.224(7) Å], allowing for the different co-ordination number and nature of additional ligands.

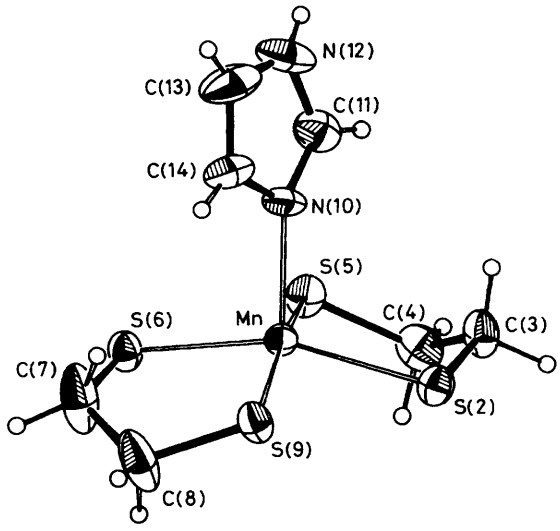

Figure 1. Structure of the $[Mn(edt)_2(Him)]^-$ anion (**1**), showing the atom labelling scheme. Non-hydrogen atoms are depicted as 50% probability ellipsoids; hydrogen atoms are depicted as spheres of arbitrary size.

While (**1**) can be recrystallised satisfactorily from MeCN or MeCN–acetone, attempts to recrystallise it from DMF–acetone (*in the absence of excess of imidazole*) yielded (**2**) (confirmed by i.r. and u.v.–visible spectroscopic comparison with an authentic sample), demonstrating the lability of the co-ordinated imidazole to good donor solvents [solv.; reaction (2)]. The equilibrium between the solvated monomer and (**2**) has been established previously.[8] Recrystallisation from DMF–acetone in the presence of excess of imidazole yields (**1**), as in the preparative procedure. A slight concentration-dependence of the u.v.–visible spectrum of (**1**) in MeCN suggests that some solvated monomer is also present in this solvent. The value of n is uncertain, n = 1 and 2 both being possibilities; solid material that precipitated directly from a solution containing a tenfold excess of imidazole was identified as (**1**) (by elemental analysis) rather than the six-co-ordinate $[Mn(edt)_2(Him)_2]^-$. Presumably the latter complex must be a more soluble species, if it is present at all.

$$[Mn(edt)_2(Him)]^- \underset{+\text{Him},\ -\text{solv.}}{\overset{+\text{solv.},\ -\text{Him}}{\rightleftharpoons}} [Mn(edt)_2(\text{solv.})_n]^- \underset{+\text{solv.}}{\overset{-\text{solv.}}{\rightleftharpoons}} [Mn_2(edt)_4]^{2-} \quad (2)$$
(**1**) (n = 1 or 2) (**2**)

The electrochemical behaviour of (**1**) in MeCN at a glassy carbon electrode is qualitatively very similar to that of (**2**)[7,8] displaying a reduction wave ($E_{p,c}$ ~ −1.45 V) and a subsequent oxidation wave ($E_{p,a}$ ~ −0.30 V *vs.* standard calomel electrode) on the reverse scan. The exact peak positions are very dependent on scan speed and cell configuration. However, under conditions sufficiently similar to justify comparisons between (**1**) and (**2**), the effect of the bound

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

imidazole appears to be to shift the reduction potential by 100—150 mV to a more negative potential. Assuming, for convenience, that (**1**) is the only species originally present in MeCN solution, we tentatively suggest that reaction (3) describes the electrochemical behaviour. A similar scheme has been described for (**2**).[8]

$$(\mathbf{1}) \xrightarrow[\text{ii, } -\text{Him}]{\text{i, } +e^-} [Mn(edt)_2]^{2-} \xrightarrow[\text{ii, + Him or MeCN}]{\text{i, } -e^-} (\mathbf{1}) \text{ and/or } [Mn(edt)_2(MeCN)_n]^- \quad (3)$$

Finally, we note with interest that preliminary *X*-ray structural analyses of the iron(III)–superoxide dismutases (SOD) from *Escherichia coli*[10] and *Pseudomonas ovalis*[11] both indicate a five-co-ordinate Fe^{III} atom with at least one imidazole ligand (histidine-26). Given the high homology between the Fe^{III}- and Mn^{III}-SODs,[2] it is very likely that similar features are present in the latter. Complex (**1**) is not, of course, a model for this or any other currently known Mn^{III} biomolecule; as the first non-porphyrin Mn^{III}-imidazole species, it does, however, represent a significant preliminary step towards the synthesis of such compounds.

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