

Preparation and Structural Characterisation of $[\text{NEt}_4]_2[\text{Mn}_2(\text{SCH}_2\text{CH}_2\text{S})_4]$, a Stable Manganese(III)–Thiolate Dimer

George Christou*^a and John C. Huffman^b

^a *Department of Chemistry, Imperial College of Science and Technology, South Kensington, London, SW7 2AY, U.K.*

^b *Molecular Structure Centre, Indiana University, Bloomington, Indiana 47405, U.S.A.*

Controlled air oxidation of $[\text{Mn}(\text{edt})_2]^{2-}$ (edt = ethane-1,2-dithiolate) in ethanolic solution yields deep green $[\text{Mn}_2(\text{edt})_4]^{2-}$ which has been structurally characterised as its NEt_4^+ salt; the anion consists of a bis-thiolate-bridged manganese(III) dimer, establishes the existence of a stable manganese(III)–thiolate bond, and supports the possible occurrence of this linkage in manganese(III)-containing biological systems.

The presence of tightly bound manganese atoms in various metallo-biomolecules is now firmly established.¹ Of particular

interest is the apparent occurrence of high oxidation states of this metal (>II) in several systems such as the water-oxidation

site of photosystem II,² and the manganosuperoxide dismutases^{3,4} and acid phosphatases.^{5a,b} The identity of the ligands binding the metal atom(s) in these molecules is unknown, however, but recent studies on the acid phosphatase from the sweet potato have led the authors to propose the presence of an Mn^{III}-thiolate (cysteinate RS⁻) bond.^{5b} This linkage has, hitherto, been unknown in manganese chemistry, a fact rationalised as being due to a combination of the strong oxidising power of Mn^{III} and the susceptibility to oxidation of the thiolate function. However, its possible occurrence in Nature has prompted us to investigate the oxidation of various Mn^{II}-thiolate solutions using, as a first approach, molecular dioxygen, and we herein report the isolation and structure of [NEt₄]₂[Mn₂(edt)₄] (1), (edt = ethane-1,2-dithiolate) the first Mn^{III}-thiolate complex.

When an ethanolic solution of [NEt₄]₂[Mn(edt)₂] (prepared *in situ* from stoichiometric amounts of MnCl₂·4H₂O, Na₂edt, and NEt₄Br under nitrogen) is exposed to the atmosphere in a controlled fashion, an immediate deep green colour is generated, followed by the rapid appearance of small green-black crystals. Isolation of the product (under nitrogen) and recrystallisation from MeCN-tetrahydrofuran (THF), initially at *ca.* 60 °C, yields analytically pure, well formed black prisms in 50% overall yield which are suitable for X-ray studies.

Crystal data: C₂₄H₅₆N₂S₈Mn₂, *M_r* 739.08, monoclinic, space group P2₁/c, *Z* = 2, *a* = 12.139(2), *b* = 10.447(2), *c* = 15.182(3) Å, β = 115.05(1)°, *U* = 1744.29 Å³, *t* = -165 °C, crystal dimensions 0.32 × 0.35 × 0.35 mm; 1966 unique reflections with *F* > 2.33σ(*F*) were refined to conventional values of *R* = 4.48 and *R_w* = 4.88%.†

The structure of the anion of (1) is depicted in Figure 1. The molecule is centrosymmetric with *C_i* symmetry, the asymmetric unit containing half the molecule and one cation. The metal atoms [Mn(1)-Mn(1') = 3.543(2) Å] are in a distorted trigonal bipyramidal co-ordination environment with each Mn

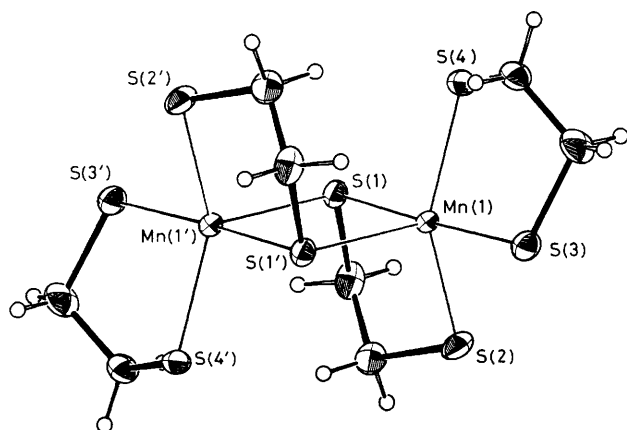
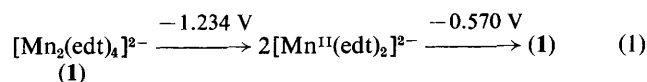


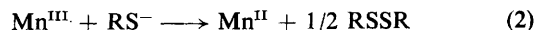
Figure 1. Structure of centrosymmetric [Mn₂(edt)₄]²⁻ showing the heavy atom labelling scheme; atoms are depicted as 50% probability ellipsoids.

terminally ligated by sulphur atoms S(3) and S(4) of one bidentate dithiolate, and one of the sulphur atoms, S(2), of a second dithiolate group. These Mn-S contacts are in the range 2.319–2.327 Å [mean 2.322(3) Å]. The other sulphur atom, S(1), of the second dithiolate group bridges the Mn atoms in an asymmetric fashion, the Mn-S lengths being Mn(1)-S(1) = 2.341(2) Å and Mn(1)-S(1') = 2.606(2) Å. The similarity between the Mn(1)-S(1) and Mn(1)-S(2,3,4) distances suggests that the molecule could be considered as two monomeric [Mn(edt)₂]⁻ units dimerising *via* two weaker Mn-S interactions, Mn(1)-S(1') and Mn(1')-S(1). The Mn(1)-Mn(1') distance [3.543(2) Å] precludes direct metal-metal bonding. The same bonding pattern is observed in the structurally analogous iron(III) complex, [NBu₄]₂[Fe₂(edt)₄],^{6,7} which has an Fe(1)-Fe(1') distance of 3.410(3) Å and Fe-S contacts in the range 2.220–2.247 Å [mean 2.234(11) Å] for the terminal ligands and 2.265(3) and 2.503(3) Å for the bridging ligands. The Mn₂S₂ bridging unit of (1) is planar and almost a square, with S(1)-Mn(1)-S(1') = 88.7(1)° and Mn(1)-S(1)-Mn(1') = 91.3(1)°, essentially identical to the corresponding angles [88.8(1)° and 91.2(1)°, respectively] of the iron complex.⁸

Cyclic voltammetric studies on (1) at a glassy carbon electrode in dimethylformamide solution containing NBu₄ClO₄ as supporting electrolyte display a well formed but slightly broad reduction peak at *E_{p,c}* = *ca.* -1.234 V (vs. S.C.E.) with negligible reverse current and the appearance on the reverse scan of an oxidation peak at *E_{p,a}* = *ca.* -0.570 V with no reduction partner. Consecutive multiple scans between -0.1 V and -1.4 V repeatedly show the same two-peak pattern, with approximately constant peak ratios, and the absence of other peaks which might indicate chemical decomposition. In addition, the -0.570 V peak is absent in scans between -0.1 V and -0.8 V. The possible break-up and reformation of the dimeric unit *via* redox sequence (1) is, therefore, suggested.



Structurally-identified homoleptic Mn-thiolates have hitherto been limited to tetrahedral [Mn^{II}(SPh)₄]²⁻ which⁸ has Mn-S lengths in the range 2.421–2.454 Å [mean 2.442(13) Å], significantly longer than the terminal Mn-S distances of (1) in accord with the lower oxidation state of the former. Some Mn^{III} complexes with sulphur ligands are known, *e.g.*, the octahedral monomers Mn(dtc)₃ (dte = *N,N*-diethyldithiocarbamate)⁹ and Mn(mtb)₃ (mtb = *N*-methylthiobenzohydroxamate),¹⁰ but such ligands cannot be considered electronic analogues of the thiolate (RS⁻) function as found in the cysteine amino acid. Complex (1), therefore, represents the first example of a true Mn^{III}-thiolate. Its stability to the usual redox reaction (2) is remarkable, especially since a recrystallisation temperature of *ca.* 60 °C was employed. That this stability is in part a function of the bidentate nature of the ethane-1,2-dithiolate ligand, and its formation of a five-



membered chelate ring on complexation, is supported by parallel aerial oxidation experiments employing monodentate thiolates which have yielded only intractable light brown solids, presumably Mn^{II}-oxide species. Nevertheless, the isolation of (1) firmly establishes the existence of the Mn^{III}-thiolate bond and suggests that the possibility of its occurrence in Mn^{III}-containing biomolecules such as acid phosphatase should continue to be actively entertained.

† 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.

The authors thank the Bloomington Academic Computing Service for a gift of computer time, and the S.E.R.C. for an Advanced Fellowship (G. C.).

Received, 2nd March 1983; Com. 283

References

- 1 G. D. Lawrence and D. T. Sawyer, *Coord. Chem. Rev.*, 1978, **27**, 173.
 - 2 G. C. Dismukes and Y. Siderer, *Proc. Natl. Acad. Sci. USA*, 1981, **78**, 274.
 - 3 V. M. Fernandez, F. Sevilla, J. Lopez-Gorge, and L. A. del Rio, *J. Inorg. Biochem.*, 1982, **16**, 79.
 - 4 J. A. Fee, E. R. Shapiro, and T. H. Moss, *J. Biol. Chem.*, 1976, **251**, 6157.
 - 5 (a) Y. Sugiura, H. Kawabe, and H. Tanaka, *J. Am. Chem. Soc.*, 1980, **102**, 6581; (b) Y. Sugiura, H. Kawabe, H. Tanaka, S. Fujimoto, and A. Ohara, *ibid.*, 1981, **103**, 963.
 - 6 M. R. Snow and J. A. Ibers, *Inorg. Chem.*, 1973, **12**, 249.
 - 7 T. Herskovitz, B. V. DePamphilis, W. O. Gillum, and R. H. Holm, *Inorg. Chem.*, 1975, **14**, 1426.
 - 8 D. Swenson, N. C. Baenziger, and D. Coucouvanis, *J. Am. Chem. Soc.*, 1978, **100**, 1932.
 - 9 P. C. Healy and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1972, 1883.
 - 10 D. P. Freyberg, K. Abu-Dari, and K. N. Raymond, *Inorg. Chem.*, 1979, **18**, 3037.
-