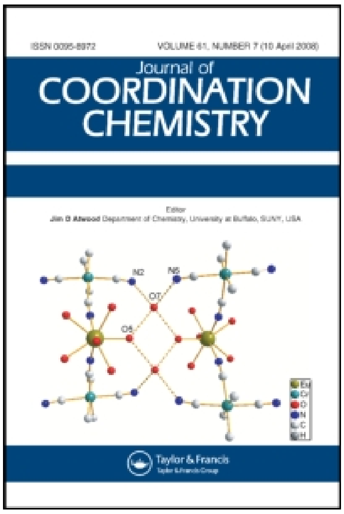

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SYNTHESIS, STRUCTURE, AND PROPERTIES OF TETRAETHYLAMMONIUM BIS[BIS(2-OXYPHENYL)-DISULFIDE-O,O′,S] MANGANESE(III)

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The title compound $(Et_4N)[Mn(MP\text{–}MP)_2]$ (**1**) was obtained by air oxidation of an acetonitrile solution of $MnCl_2{\cdot}4H_2O$ and Na_2MP. The structure of **1** was determined by single crystal X-ray diffraction methods. Crystal data: $C_{32}H_{36}MnNO_4S_4$, monoclinic, $P2_1/c$, $a = 9.598(3)$, $b = 16.845(3)$, $c = 10.702(3)$ Å, $\beta = 111.20(1)°$, $V = 1613.1$ Å^3, $Z = 2$; $Mr = 681.84$; $d_x = 1.40\,g\,cm^{-3}$; $F(000) = 712$; $\mu = 6.8\,cm^{-1}$, crystal dimensions $0.40 \times 0.20 \times 0.20\,mm^3$. The Mn atom is octahedrally and symmetrically coordinated by two $MP\text{-}MP^{2-}$ ligands, each providing two phenolate–oxygen and one disulfide–sulfur atoms to form a terdentate. The presence of an S–S bond is revealed by the distance of 2.093 Å, which constitutes the first disulphide chelated to the Mn(III) ion. The paramagnetic nature of the high spin Mn(d^4) ion is reflected in a value of μ_{eff} of 4.83 μ_B and broad ^1H NMR absorptions at 23 ~ 25 ppm and −12 ~ −17 ppm.

Keywords: Manganese, *o*-mercaptophenol, crystal structure, paramagnetism, disulfide

INTRODUCTION

Manganese complexes have attracted increasing attention because of their relevance to the active sites of many biological systems.[1,2,3,4] In a recent study of the reactions of transition metals with *o*-mercaptophenolate (MP^{2-}), a series of metal complexes of different coordination modes has been synthesized.[5-9] Herein we report a study of a complex obtained by the oxidative coordination of *o*-mercaptophenolate to Mn where Mn(III)-disulfide ligation is found for the first time; Mn(II) ligated to a disulfide Schiff base has previously been reported.[10]

EXPERIMENTAL

Preparation of $(Et_4N)[Mn(MP\text{–}MP)_2]$ (1)

When 60 cm^3 of dry air was passed into a reaction vessel in which an acetonitrile solution (40 cm^3) of 0.16 g (0.8 mmol) of $MnCl_2{\cdot}4H_2O$ and 0.34 g (2 mmol) of Na_2MP had reacted for 30 min, the original red solution turned deep brown with stirring for 14 h at room temperature. To the solution was then added 0.13 g (0.8 mmol) of Et_4NCl, and the mixture was stirred, filtered, and reduced to 25 cm^3.

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Dark brown, rhombic crystals of 1 were obtained after addition of 25 cm^3 of THF and keeping the mixture at 4°C for several days. The product (40%) was collected at the pump, washed with THF and dried *in vacuo*. *Anal.*; Calcd. for $C_{32}H_{36}MnNO_4S_4$: H, 5.53; Mn, 9.11; S, 18.41%. Found: H, 5.32; Mn, 8.06; S, 18.81%. IR (KBr): 315(m), 330(m), 420(m), 440(s), 460(s), 550(m), 605(s), 625(s) cm^{-1}.

Instruments

IR: Perkin-Elmer 577. NMR: Varian FT-80A or Varian XL-200. ^1H NMR spectra were recorded in solution at ambient temperature and are referenced to Me_4Si. Magnetic susceptibility was measured on a Gouy-Faraday magnetic balance by the Faraday method. Cyclic voltammetry was studied on a DHE-1 multipurpose instrument and performed with a working Pt electrode, an SCE reference electrode and a Pt auxiliary electrode with 0.1 M $(Bu_4N)BF_4$ as supporting electrolyte.

Crystallographic data collection and refinement of structure

Crystallographic data for 1 are summarized in Table I. Diffraction data were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromatized MoKα radiation ($\lambda = 0.71073$ Å). An empirical absorption correction (ψ scan) was applied (0.899 to 1.033). After data reduction (including correction for Lorentz and polarization effects), the remaining 1753 unique reflections with $I \geqslant 3\sigma(I)$ were used for subsequent structure solution and refinement. Calculations were performed on a VAX 11/785 computer with the SDP program package.

TABLE I
Crystal Structure Parameters for 1.

Formula	$C_{32}H_{36}MnNO_4S_4$
Molecular weight (g mol^{-1})	681.84
Colour	deep brown
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	9.598(3)
b (Å)	16.845(3)
c (Å)	10.702(3)
β (deg)	111.20(1)
V (Å^3)	1613.1
Z	2
d_x (g/cm^3)	1.40
$F(000)$	712
μ (cm^{-1})	6.8
Crystal dimensions (mm^3)	0.40 × 0.20 × 0.20
Radiation (Å)	Mo K_α (0.71073)
2θ range (deg)	2.0 to 50.0
No. reflections measured	3105
No. reflections used ($I > 3\sigma(I)$)	1753
Transmission coefficients	0.899 to 1.033
R[a]	0.057
R_w[b]	0.074

[a] $R = \Sigma(|Fo|-|Fc|)/\Sigma|Fo|$. [b] $R_w = [\Sigma w(|Fo|-|Fc|)^2/\Sigma w|Fo|^2]^{1/2}$, where $w = 4|Fo|^2/\sigma^2(|Fo|)^2$.

The positions of Mn and S atoms were obtained by direct methods and the remaining non-hydrogen atoms were located by successive cycles of difference Fourier maps. Full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms led to convergence.

RESULTS AND DISCUSSION

The synthesis of **1** depends more on the amount of air involved than on the Mn^{2+}/MP^{2-} ratio or the reaction medium. As long as the volume of air added was sufficient ($75 \sim 120\,cm^3$/mmol Mn^{2+}), **1** was obtained irrespective whether the solvent was acetonitrile or ethanol, or the ratio Mn^{2+}/MP^{2-} was 2/3, 1/2 or 1/3. Complex **1** was therefore the final product of the oxidative coordination reaction of *o*-mercaptophenolate to manganese where MP^{2-} has been oxidized to $MP\text{–}MP^{2-}$ ($o\text{–}OC_6H_4S\text{–}SC_6H_4O\text{–}o^{2-}$). As the oxidation of *o*-mercaptophenol by air is possible but slow, the formation of disulfide in **1** must have been catalyzed by the metal ion. Such was also found for the Mn complexes[10,11] [Mn(SALPS)(CH_3OH)] and $[Mn_2(SCH_2CH(S)CH_2SSCH_2CH(S)CH_2S)_2]^{2-}$, and more recently in an Mo(V)–MP complex.[12]

TABLE II
Fractional Positional Parameters for **1**.

Atom	*x/a*	*y/b*	*z/c*	$B(\text{Å}^2)$
Mn	0.0000(0)	0.0000(0)	0.0000(0)	3.15(3)
S(1)	0.1902(2)	−0.01175(9)	−0.1325(2)	4.37(4)
S(2)	0.0625(2)	0.0385(1)	−0.3175(2)	4.88(4)
O(1)	0.1225(4)	0.0901(2)	0.0680(4)	3.77(9)
O(2)	−0.1300(4)	0.0588(2)	−0.1452(4)	3.9(1)
C(11)	0.2950(6)	0.0692(4)	−0.0450(6)	3.9(1)
C(12)	0.4251(7)	0.0932(4)	−0.0630(7)	5.6(2)
C(13)	0.5057(7)	0.1576(5)	0.0059(9)	6.3(2)
C(14)	0.4561(7)	0.1585(4)	0.0931(8)	5.4(2)
C(15)	0.3283(6)	0.1758(4)	0.1135(7)	4.4(2)
C(16)	0.2466(6)	0.1100(3)	0.0449(6)	3.4(1)
C(21)	−0.0090(6)	0.1262(4)	−0.2742(6)	3.5(1)
C(22)	0.0228(7)	0.1969(4)	−0.3250(7)	4.8(2)
C(23)	−0.0338(7)	0.2674(4)	−0.3024(7)	5.6(2)
C(24)	−0.1218(7)	0.2686(4)	−0.2249(8)	5.4(2)
C(25)	−0.1500(7)	0.1992(4)	−0.1695(7)	4.7(2)
C(26)	−0.0949(6)	0.1267(3)	−0.1935(6)	3.5(1)
N	0.5000(0)	0.5000(0)	0.0000(0)	4.5(2)
C(31)*	0.385(1)	0.5732(8)	−0.059(1)	5.9(4)
C(32)*	0.465(2)	0.5229(9)	0.124(1)	5.6(4)
C(33)*	0.358(1)	0.4654(9)	−0.114(1)	6.2(4)
C(34)*	0.432(2)	0.437(1)	0.061(1)	7.0(4)
C(35)	0.2872(9)	0.3956(5)	−0.060(1)	7.9(3)
C(36)	0.3492(8)	0.6033(5)	0.0736(9)	9.5(3)

* Disordered atom with an occupancy of 0.5.

The cell of 1 contains well-separated cations and anions with no unusually close contacts. The cation structure is unexceptional, but the free rotation of ethyl groups causes large thermal parameters for the atoms involved. Disorder of the methylene groups, C(31), C(32), C(33), and C(34), is also present. The Mn atom in the anion is octahedrally coordinated by two $(MP\text{–}MP)^{2-}$ groups, each providing two phenolate-oxygen atoms and one disulfide sulfur atom to form a terdentate ligand. Positional parameters are given in Table II and selected atomic distances and bond angles in Table III.

TABLE III
Selected atomic distances (Å) and bond angles (deg) for 1.*

(a) distances			
Mn–S(1)	2.693(2)	Mn–O(1)	1.897(3)
Mn–O(2)	1.884(3)	S(1)–S(2)	2.093(2)
S(1)–C(11)	1.751(6)	S(2)–C(21)	1.759(6)
O(1)–C(16)	1.344(6)	O(2)–C(26)	1.348(6)
(b) angles			
S(1)–Mn–S(1′)	180.01(7)	S(1)–Mn–O(1)	79.4(1)
S(1)–Mn–O(1′)	100.6(1)	S(1)–Mn–O(2)	88.7(1)
S(1)–Mn–O(2′)	91.3(1)	O(1)–Mn–O(1′)	180.01(7)
O(1)–Mn–O(2)	91.8(1)	O(1)–Mn–O(2′)	88.3(1)
O(2)–Mn–O(2′)	180.01(8)	Mn–S(1)–C(11)	91.7(3)
Mn–O(1)–C(16)	126.6(3)	Mn–O(2)–C(26)	125.4(4)
Mn–S(1)–S(2)	101.06(7)	S(2)–S(1)–C(11)	102.6(2)
S(1)–S(2)–C(21)	104.0(2)		

* Numbers in parentheses are estimated standard deviations.

The structure of the anion in 1 as depicted in Figure 1 shows that the centre of symmetry at the Mn atom makes the MnO_4 unit perfectly planar and the two sulfur atoms are *trans* to each other. The Mn–O distances (1.884–1.897 Å) are significantly shorter than Mn(III)–O bonds of common six-coordinate Mn complexes such as $Mn(acac)_3$[13] (1.95–2.00 Å), and slightly shorter than those in *trans*-$[Mn(acac)_2(N_3)]_n$ (1.912 Å)[14] and *trans*-$[Mn(acac)_2(NCS)]_n$ (1.912 Å).[15] They are only comparable to those in $[Mn(salen)(AcO)]_n$ (salen = *N*,*N*′-ethylenebis(salicylideneamide), 1.888 Å).[16] This could be ascribed to the Jahn–Teller effect of the high spin Mn(III) ion. Another characteristic feature of 1 is that an S–S bond (2.093 Å) is present and which coordinates unsymmetrically to the Mn atom with only one sulfur atom (S(1)); the other sulfur atom (S(2)) is 3.71 Å away from the Mn atom. The Mn(III)–S(1) distance of 2.693 Å is much longer than in Mn(III)-thiolates (2.35 Å[11,17,18]) and is shorter than the Mn(III)–S(disulfide) distances[10] in $[Mn(SALPS)(CH_3OH)]$ and $[Mn(SALPS)]_2$. Comparison of the five-membered chelate rings in the M–MP series (M = V,[5] Fe,[6,7] Co,[8] Ni[9]) indicates that the small bite angle (S–Mn–O) of 79.4° and the long bite distances S–O (2.997 Å) in 1 are due to the high coordination number of Mn atom and the presence of the disulfide bond.

The ^1H NMR spectrum of 1 in CD_3CN (or DMSO-d_6) shows a sharp peak at 7.2 ppm and two broad bands of nearly equal area in the regions $23 \sim 25$ ppm and $-12 \sim -17$ ppm, respectively. The measured magnetic moment at 295 K is 4.83 BM, which is very close to the d^4 spin-only value.

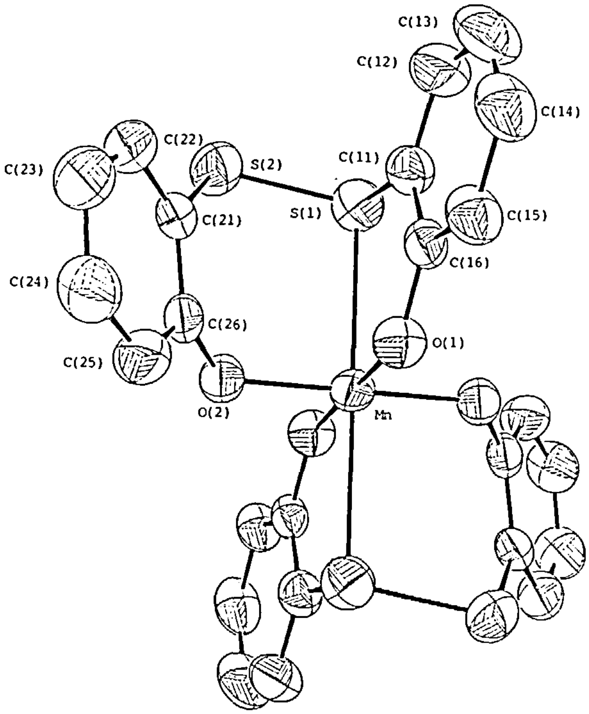

FIGURE 1 Structure of the anion $[Mn(OC_6H_4S_2C_6H_4O)_2]^-$.

The cyclic voltammograms obtained for the complex are slightly different in MeCN and DMF due to the differing coordination abilities of the solvents. In addition to irreversible reduction wave at ~ −1.1 V and oxidation wave at ~0.87 V in both solvents, there is another irreversible peak at 1.1 V in DMF, possibly due to oxidation of a fractionally dissociated (the weak Mn–S bond) and/or solvated anion of **1**.

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SUPPLEMENTARY MATERIAL

Complete lists of thermal parameters, bond distances, bond angles and observed and calculated structure factor tables for **1** (12 pages) have been deposited with the Editor and are available upon request.

REFERENCES

1. G.D. Lawrence and D.T. Sawyer, *Coordination Chemistry Reviews*, **27**, 173 (1978).
2. W.C. Stallings, K.A. Pattridge, R.K. Strong and M.L. Ludwig, *J. Biol. Chem.*, **259**, 10695 (1984).

3. W.F. Beyer, Jr. and I. Fridovich, *Biochemistry*, **24**, 6460 (1985).
4. G.C. Dismukes and Y. Siderer, *Proc. Natl. Acad. Sci. U.S.A.*, **78**, 274 (1981).
5. L.H. Weng, unpublished results.
6. B.S. Kang, L.H. Weng, D.X. Wu, F. Wang, Z. Guo, L.R. Huang, Z.Y. Huang and H.Q. Liu, *Inorg. Chem.*, **27**, 1128 (1988).
7. B.S. Kang, L.H. Weng, D.X. Wu, L.R. Huang, F. Wang, Z. Guo and H.Q. Liu, *Inorg. Chim. Acta*, **148**, 147 (1988).
8. L.H. Weng, L.R. Huang and B.S. Kang, *Jiegou Huaxue*, **8**, 136 (1989).
9. C.Z. Lu, J.H. Cai, Z.Y. Huang, L.H. Weng and B.S. Kang, *Jiegou Huaxue*, **7**, 241 (1988).
10. SALPS = *N*,*N*′-[1,1′-dithiobis(phenylene)]bis(salicylideneaminato); D.P. Kessissoglou, N.M. Butler and V.L. Pecoraro, *Inorg. Chem.*, **26**, 495 (1987).
11. J.L. Seela, K. Folting, R.J. Wang, J.C. Huffman, G. Christou, H.R. Chang and D.N. Hendrickson, *Inorg. Chem.*, **24**, 4454 (1985).
12. S.A. Roberts, G.P. Darsey, W.E. Cleland, Jr. and J.H. Enemark, *Inorg. Chem. Acta*, **154**, 95 (1988).
13. J.P. Fackler, Jr. and A. Avdeef, *Inorg. Chem.*, **13**, 1864 (1974).
14. B.R. Stults, R.S. Marianelli and V.W. Day, *Inorg. Chem.*, **14**, 722 (1975).
15. B.R. Stults, R.O. Day, R.S. Marianelli and V.W. Day, *Inorg. Chem.*, **18**, 1847 (1979).
16. J.E. Davis, B.M. Gatehouse and K.S. Murry, *J. Chem. Soc., Dalton Trans.*, 2523 (1973).
17. T. Costa, J.R. Dorfman, K.S. Hagen and R.H. Holm, *Inorg. Chem.*, **22**, 4091 (1983).
18. X.T. Chen, L.R. Huang, L.H. Weng, M.C. Hong and B.S. Kang, *Jiegou Huaxue*, **8**, 128 (1989).