

Preparation and structures of tetrameric and dimeric manganese carbonyl complexes incorporating thiosalicylato ligands

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Abstract

Orthomanganated *N,N*-dimethylbenzamide reacts with SO_2 to give a tetra-manganese complex $\text{Mn}_4(\text{thsa})_2(\text{CO})_{16}$ (thsa = thiosalicylate = 2-thiobenzoate di-anion) which an X-ray structure determination shows to contain four $\text{Mn}(\text{CO})_4$ units linked by two triply bridging (S,O,O) thsa ligands. Another product identified after aerobic work-up was the disulphide $[2-(^-\text{OOC})\text{C}_6\text{H}_4\text{S}^-]_2$. Reaction of thiosalicylic acid with $\text{BrMn}(\text{CO})_5$ in the presence of Et_3N gave good yields of $[\text{Et}_3\text{NH}]_2[\text{Mn}_2(\text{thsa})_2(\text{CO})_6]$, the anion of which contains two $[\text{Mn}(\eta^2\text{-thsa})(\text{CO})_3]^-$ units doubly-linked via the S atoms.

Keywords: Manganese; Carbonyl; Cluster; Thiosalicylato ligand; Crystal structure

1. Introduction

We have recently shown that reaction of orthomanganated aryl ketones such as **1** with SO_2 usually leads to insertion into the Mn–C bond, thus providing a specific method for forming C–S bonds ortho to a ketone substituent [1]. In some instances the resulting aryl–sulphinato complexes with a six-membered metalocyclic ring could be isolated and used for subsequent elaboration, whereas other examples readily evolved CO to give di-manganese complexes bridged by the aryl–sulphinato ligand [1].

In this present paper we describe the corresponding reaction of orthomanganated *N,N*-dimethylbenzamide **2** with SO_2 , which gave a tetra-manganese complex **3** containing a thiosalicylate ligand, formed in situ. We also describe the di-manganese product **4** from the reaction of thiosalicylic acid with $\text{BrMn}(\text{CO})_5$.

2. Experimental details

Infrared spectra were recorded on a Digilab FTS-45 FTIR instrument, while electrospray mass spectra

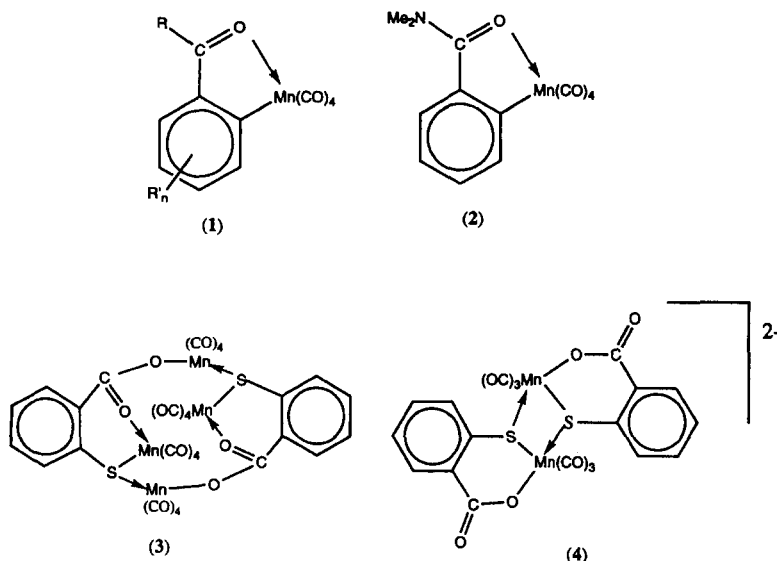
(ESMS) were recorded on a Fisons Platform II instrument, with $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ (1:1) as mobile phase. The cyclomanganated dimethylbenzamide **2** [2] and $\text{BrMn}(\text{CO})_5$ [3] were prepared by the published routes, while SO_2 and thiosalicylic acid were commercial samples.

2.1. Reactions of orthomanganated *N,N*-dimethylbenzamide with SO_2

A sample of η^2 -[2-(*N,N*-dimethylamido)phenyl]tetracarbonylmanganese (**2**) (0.179 g, 0.57 mmol) was placed in a glass ampoule which was attached to a conventional vacuum line and evacuated. SO_2 (ca. 10 ml) was distilled into the ampoule which was then sealed and placed in a Carius tube at 55 °C for 16 h. The ampoule was cooled, opened, and excess SO_2 was allowed to evaporate. This left a residue which was a mixture of two main products, both insoluble in CH_2Cl_2 ; one was an orange-brown crystalline species and the other was an off-white powder. Samples of each were hand-separated after removing other minor components by washing with CH_2Cl_2 .

The orange-brown crystals were essentially insoluble in all common organic solvents, so were characterised by microanalysis and an X-ray crystal structure determination which showed it to be the tetra-manganese complex $\text{Mn}_4(\text{thsa})_2(\text{CO})_{16}$ (**3**) (thsa = thiosalicylate = 2-thiobenzoate di-anion). Anal. Found: C, 37.22; H, 0.51;

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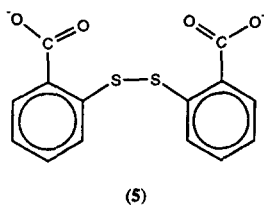


S, 6.88. $C_{30}H_8Mn_4O_{20}S_2$. Calc.: C, 37.06; H, 0.83; S, 6.59%. $\nu(\text{CO})$ (KBr disk, cm^{-1}) 2101s, 2092s, 2023vs, 2009vs, 2001vs, 1971vs, 1956vs.

The other product was shown to be mainly the 2,2'-dithio-dibenzoate di-anion **5**, probably as the Mn(II) salt, by GCMS and ESMS. GCMS: a sample was dissolved in methanol and treated with an excess of CH_2N_2 in Et_2O . Only one peak was observed in the subsequent GC trace, with an m/e of 334 corresponding to the dimethyl ester of **5**. ESMS: (–ve ion) m/e 152 (**5**); (+ve ion) m/e 360 (**5** + Mn^{2+} + H^+), 329 (**5** + 2H^+ + Na^+).

The reaction was repeated several times, with periods of heating up to 48 h without appreciable differences in the absolute or relative amounts of **3** and **5**.

To determine whether traces of water were important, the reaction was carried out as described above except that one ampoule included two drops of water, while for the other the SO_2 was purified by trap-to-trap distillation through a trap held at -46°C . The 'wet' reaction gave as a residue mainly the disulphide **5** (ca. 45% yield) with small amounts of the tetramanganese complex **3**, while the 'dry' reaction favoured the formation of **3** (ca. 27% after removal of **5** by dissolution in hot methanol).



2.2. Reaction of salicylic acid with $\text{BrMn}(\text{CO})_5$

A mixture of $\text{BrMn}(\text{CO})_5$ (0.15 g, 0.55 mmol), thio-salicylic acid (0.092 g, 0.59 mmol) and Et_3N (0.5 ml) in CH_2Cl_2 (14 ml) was stirred for 2 h at room temperature under a nitrogen atmosphere. The solution was filtered and evaporated to dryness under vacuum. The residue was recrystallised from CH_2Cl_2 to give orange crystals of $[\text{Et}_3\text{NH}]_2[\text{Mn}_2(\text{thsa})_2(\text{CO})_6]$, (0.114 g, 54%). $\nu(\text{CO})$ (CH_2Cl_2) 2000(s), 1905(vs, br); ESMS (–ve ion) m/e : 291(M) $^{2-}$, 583 ($\text{M} + \text{H}$) $^-$. The compound was further characterised by an X-ray structure determination (see below).

No other product was observed in repeat reactions with a thio-salicylic acid: $\text{BrMn}(\text{CO})_5$ ratio of 1:2, even after heating at reflux for up to 8 h.

2.3. X-ray crystal structure determination of $\text{Mn}_4(\text{thsa})_2(\text{CO})_{16}$ (**3**)

Well-formed orange-brown crystals were obtained directly from the reaction mixture. Preliminary precession photography indicated triclinic symmetry. Intensity data and cell parameters were obtained on a Nicolet P3 four-circle diffractometer at -141°C with monochromated Mo $\text{K}\alpha$ radiation.

Crystal data: $C_{30}H_8Mn_4O_{20}S_2$, $M_r = 972.26$, triclinic, space group $P\bar{1}$, $a = 9.819(3)$, $b = 10.298(3)$, $c = 10.858(3)$ Å, $\alpha = 111.95(1)$, $\beta = 116.66(4)$, $\gamma = 96.45(2)^\circ$, $U = 856.5(4)$ Å 3 , $D_{\text{calc}} = 1.88$ g cm^{-3} , $Z = 1$, $F(000) = 480$, $\mu(\text{Mo K}\alpha) = 1.65$ mm $^{-1}$. Crystal size $0.42 \times 0.40 \times 0.22$ mm 3 . A total of 2154 reflections in the range $4 < 2\theta < 45^\circ$ were collected, corresponding to 2006 unique reflections. These were corrected for Lorentz and polarisation effects and for linear absorp-

Table 1
Atomic coordinates and equivalent isotropic displacement parameters for $\text{Mn}_4(\text{thsa})_2(\text{CO})_{16}$ (**3**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Mn(1)	0.0736(1)	0.7787(1)	0.7987(1)	0.011(1)
Mn(2)	0.2366(1)	0.7758(1)	0.4994(1)	0.012(1)
S(1)	0.2872(1)	0.8264(1)	0.7500(1)	0.012(1)
C(1)	0.3796(5)	0.6930(4)	0.7792(4)	0.010(1)
C(2)	0.5128(5)	0.7390(4)	0.9269(4)	0.015(1)
C(3)	0.5870(5)	0.6405(4)	0.9602(4)	0.016(1)
C(4)	0.5287(5)	0.4944(4)	0.8474(4)	0.015(1)
C(5)	0.3936(5)	0.4465(4)	0.7007(4)	0.012(1)
C(6)	0.3181(5)	0.5442(4)	0.6634(4)	0.011(1)
C(31)	0.1744(5)	0.4833(5)	0.5014(4)	0.011(1)
O(7)	0.1380(3)	0.5600(3)	0.4323(3)	0.014(1)
C(11)	-0.0802(6)	0.7505(5)	0.8451(5)	0.019(1)
O(11)	-0.1729(4)	0.7363(4)	0.8781(4)	0.036(1)
C(21)	0.2243(5)	0.8991(5)	1.0032(5)	0.016(1)
O(21)	0.3178(4)	0.9736(3)	1.1342(3)	0.028(1)
O(31)	-0.0917(3)	0.6531(3)	0.5655(3)	0.012(1)
C(41)	0.1222(5)	0.6174(5)	0.8305(4)	0.012(1)
O(41)	0.1562(3)	0.5300(3)	0.8659(3)	0.019(1)
C(51)	0.0206(5)	0.9396(5)	0.7733(4)	0.018(1)
O(51)	-0.0150(4)	1.0368(4)	0.7619(4)	0.034(1)
C(61)	0.1955(5)	0.7263(4)	0.3036(5)	0.018(1)
O(61)	0.1718(4)	0.6993(3)	0.1824(4)	0.032(1)
C(71)	0.0339(6)	0.8013(4)	0.4379(4)	0.014(1)
O(71)	-0.0846(4)	0.8250(3)	0.3981(3)	0.023(1)
C(81)	0.3298(5)	0.9687(5)	0.5672(5)	0.019(1)
O(81)	0.3942(4)	1.0911(4)	0.6108(4)	0.031(1)
O(91)	0.5611(4)	0.7385(3)	0.5848(3)	0.024(1)
C(91)	0.4397(6)	0.7519(4)	0.5566(4)	0.016(1)

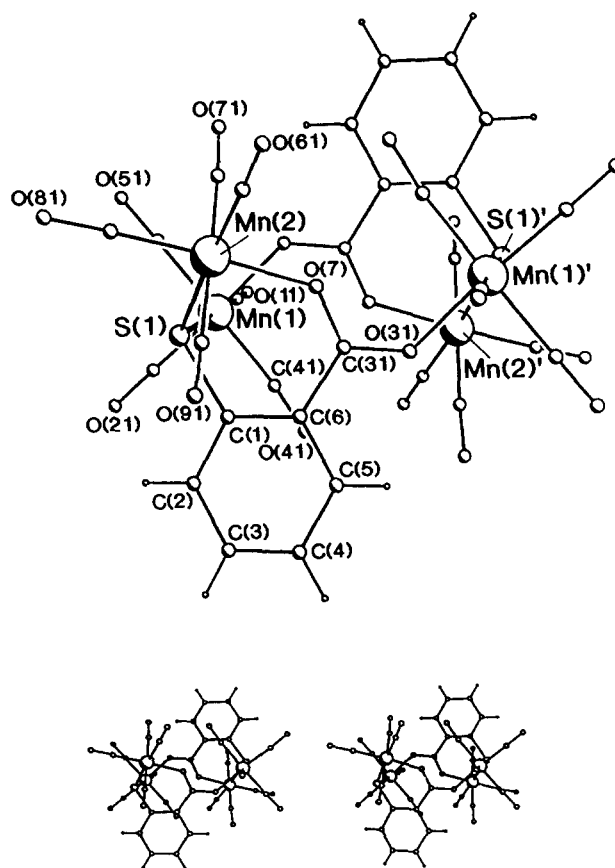


Fig. 1. A labelled and a stereo view of $\text{Mn}_4(\text{thsa})_2(\text{CO})_{16}$ (**3**). The molecule lies on a crystallographic inversion centre.

tion by an empirical method ($T_{\text{max, min}} = 0.884, 0.761$). The structure was solved using direct methods and developed routinely. In the final cycle of full-matrix least squares refinement based on F^2 all non-hydrogen atoms were assigned anisotropic temperature factors and hydrogen atoms were included in their calculated positions. The refinement converged with $R_1 = 0.0279$ (for 1687 data with $I > 2\sigma(I)$), $R_1 = 0.0385$, $wR_2 = 0.0655$, $\text{GoF} = 1.021$ (all data), with no parameter shifting more than 0.001σ . The final difference map showed no peak or trough of electron density greater than $0.30 \text{ e } \text{\AA}^{-3}$. Table 1 gives final positional parameters and the overall structure of **3** is illustrated in Fig. 1, with details of the core geometry in Fig. 2. A complete list of bond lengths and angles and tables of thermal parameters and H-atom coordinates have been deposited at the Cambridge Crystallographic Data Centre.

2.4. X-ray crystal structure determination of $[\text{Et}_3\text{NH}]_2[\text{Mn}_2(\text{thsa})_2(\text{CO})_6]$, ($[\text{Et}_3\text{NH}]_2[\mathbf{4}]$)

Orange crystals were from CH_2Cl_2 - Et_2O . Preliminary precession photography indicated triclinic symmetry. Intensity data and cell parameters were obtained on a Nicolet P3 four-circle diffractometer at -110°C with monochromated $\text{Mo K}\alpha$ radiation.

Crystal data: $\text{C}_{32}\text{H}_{40}\text{Mn}_2\text{N}_2\text{O}_{10}\text{S}_2$, $M_r = 786.68$, triclinic, space group $P1$ $a = 8.784(2)$, $b = 10.467(4)$, $c = 11.700(4)$ \AA , $\alpha = 102.54(3)$, $\beta = 105.68(3)$, $\gamma = 107.73(4)^\circ$, $U = 932.4(5)$ \AA^3 , $D_{\text{calc}} = 1.401 \text{ g cm}^{-3}$, $Z = 1$, $F(000) = 408$, $\mu(\text{Mo K}\alpha) = 0.843 \text{ mm}^{-1}$. Crystal size $0.90 \times 0.75 \times 0.50 \text{ mm}^3$. A total of 3278 reflections in the range $4 < 2\theta < 50^\circ$ were collected, corre-

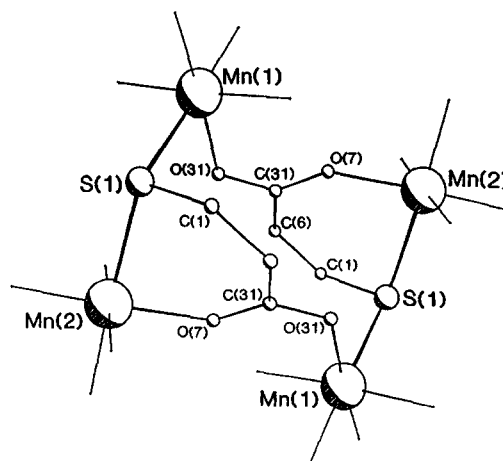


Fig. 2. The core geometry of $\text{Mn}_4(\text{thsa})_2(\text{CO})_{16}$ (**3**), showing the aggregation interactions.

Table 2
Atomic coordinates and equivalent isotropic displacement parameters for $[\text{Et}_3\text{NH}]_2[\text{Mn}_2(\text{thsa})_2(\text{CO})_6]$, $([\text{Et}_3\text{NH}]_2 \text{ (4)})$

Atom	x	y	z	U_{eq}
Mn(1)	0.0053(1)	0.3281(1)	0.9726(1)	0.021(1)
S(1)	0.2000(1)	0.5630(1)	1.0297(1)	0.022(1)
C(1)	0.1356(3)	0.4458(3)	1.2615(2)	0.021(1)
C(2)	-0.0167(4)	0.3020(3)	0.8125(3)	0.025(1)
O(2)	-0.0299(3)	0.2810(2)	0.7088(2)	0.039(1)
C(3)	-0.1616(4)	0.1525(3)	0.9213(3)	0.028(1)
O(3)	-0.2675(3)	0.0415(2)	0.8813(2)	0.053(1)
C(4)	0.1732(4)	0.2596(3)	0.9940(3)	0.027(1)
O(4)	0.2765(3)	0.2126(2)	1.0027(2)	0.041(1)
C(11)	0.3076(3)	0.5494(3)	1.2766(2)	0.021(1)
O(11)	0.0222(2)	0.3673(2)	1.1544(2)	0.024(1)
O(12)	0.1091(2)	0.4364(2)	1.3595(2)	0.027(1)
C(12)	0.3467(3)	0.6038(3)	1.1839(3)	0.022(1)
C(13)	0.5132(4)	0.6984(3)	1.2108(3)	0.029(1)
C(14)	0.6407(4)	0.7374(3)	1.3262(3)	0.034(1)
C(16)	0.4368(4)	0.5924(3)	1.3925(3)	0.027(1)
N(1)	0.1980(3)	0.7762(2)	0.7068(2)	0.024(1)
C(21)	0.1889(4)	0.9118(3)	0.7733(3)	0.031(1)
C(22)	0.0302(5)	0.9316(4)	0.7064(3)	0.046(1)
C(23)	0.2097(4)	0.7695(3)	0.5800(3)	0.032(1)
C(24)	0.3732(5)	0.8764(4)	0.5834(3)	0.045(1)
C(25)	0.3344(4)	0.7466(3)	0.7923(3)	0.031(1)
C(26)	0.3365(5)	0.6036(4)	0.7349(3)	0.044(1)

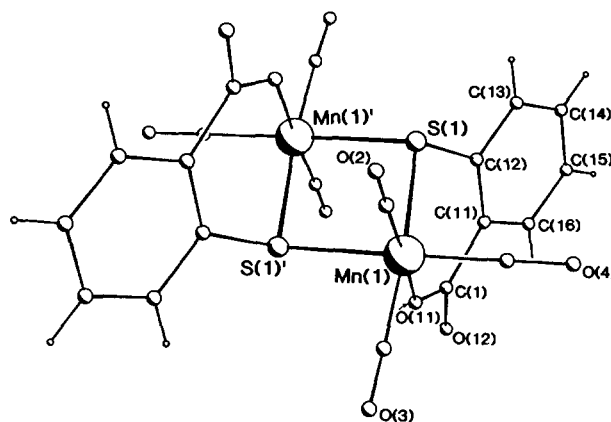


Fig. 3. The structure of the anion $[\text{Mn}_2(\text{thsa})_2(\text{CO})_6]^{2-}$, [4].

2681 data with $I > 2\sigma(I)$, $R_1 = 0.0464$, $wR_2 = 0.1172$, $\text{GoF} = 1.117$ (all data), with no parameter shifting more than 0.001σ . The final difference map showed no feature greater than $0.8 \text{ e } \text{\AA}^{-3}$. Table 2 gives final positional parameters, and a view of the anion (4) is presented in Fig. 3. The programs used for crystallography were SHELXS-86, SHELXA and SHELXL-93 [4]. A complete list of bond lengths and angles and tables of thermal parameters and H-atom coordinates have been deposited at the Cambridge Crystallographic Data Centre.

sponding to 3176 unique reflections. These were corrected for Lorentz and polarisation effects and for linear absorption by a Φ -scan method ($T_{\text{max, min}} = 0.586, 0.496$). The structure was solved using direct methods and developed routinely. In the final cycle of full-matrix least squares refinement based on F^2 all non-hydrogen atoms were assigned anisotropic temperature factors and hydrogen atoms were included in their calculated positions. The refinement converged with $R_1 = 0.0385$ (for

3. Results and discussion

3.1. Reaction of 2 with SO_2

For most of the orthomanganated ketones we have studied previously, reaction with SO_2 led to products

Table 3
Selected bond parameters for $\text{Mn}_2(\text{thsa})_2(\text{CO})_{16}$ (3)

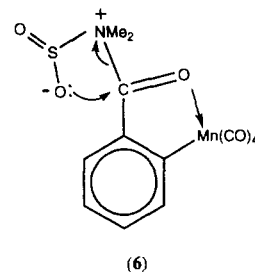
Bond lengths (\AA)			
Mn(1)–C(21)	1.800(5)	Mn(1)–C(11)	1.820(5)
Mn(1)–C(51)	1.871(5)	Mn(1)–C(41)	1.888(5)
Mn(1)–O(31)	2.028(3)	Mn(1)–S(1)	2.423(1)
Mn(2)–C(81)	1.794(5)	Mn(2)–C(61)	1.821(5)
Mn(2)–C(71)	1.880(5)	Mn(2)–C(1)	1.881(5)
Mn(2)–O(7)	2.020(3)	Mn(2)–S(1)	2.364(1)
S(1)–C(1)	1.777(4)	C(6)–C(31)	1.492(5)
C(31)–O(7)	1.257(5)	C(6)–C(31)	1.492(5)
O(31)–C(31)	1.270(5)		
Bond angles (deg)			
C(51)–Mn(1)–C(41)	177.0(2)	C(21)–Mn(1)–O(31)	176.4(2)
C(11)–Mn(1)–S(1)	177.2(1)	C(51)–Mn(1)–S(1)	89.7(1)
C(41)–Mn(1)–S(1)	93.0(1)	O(31)–Mn(1)–S(1)	91.2(1)
C(71)–Mn(2)–C(91)	178.3(2)	C(81)–Mn(2)–O(7)	177.6(2)
C(61)–Mn(2)–S(1)	176.9(1)	C(71)–Mn(2)–S(1)	91.6(1)
C(91)–Mn(2)–S(1)	89.9(1)	O(7)–Mn(2)–S(1)	86.4(1)
C(1)–S(1)–Mn(2)	100.6(1)	C(1)–S(1)–Mn(1)	102.4(1)
Mn(2)–S(1)–Mn(1)	123.1(6)	C(1)–C(6)–C(31)	123.8(3)
O(7)–C(31)–O(31)	121.2(3)	C(31)–O(7)–Mn(2)	132.5(3)
C(31)–O(31)–Mn(1)	124.7(2)		

which arose from straightforward insertion into the Mn–C bond, to give S–sulphinato complexes [1]. In contrast, the reaction of the orthomanganated benzamide **2** with SO₂ followed a different course. At the end of the reaction period a mixture of two products, both insoluble in CH₂Cl₂, had formed. The first of these was deposited as well-formed brown crystals which were essentially insoluble in all common organic solvents. Identification by X-ray crystallography showed a centrosymmetric molecule (Fig. 1) which contains four Mn(CO)₄ units linked by two thiosalicylate (thsa) anions. The thsa ligand links three manganese atoms by chelation through S and O to Mn(2), with the S atom bridging to Mn(1) and the remaining C=O group of the carboxylate bridging to Mn(1)'. All four manganese atoms are formally Mn(I) so that the overall complex is neutral. The core of the molecule (Fig. 2) contains a 12-membered ring consisting of four Mn, two S, four O and two C atoms (selected bond parameters are in Table 3). The Mn–O distances (2.024(3) Å average) are slightly shorter than those in orthomanganated ketones [5] and, surprisingly, shorter than typical Mn(II)–O distances in carboxylate complexes [6]. The Mn–S values of 2.365(1) and 2.424(1) Å are also at the lower end of the range found for Mn–S bonds with the manganese in various oxidation states [7]. Despite the complexity of the molecule, both chemically distinct Mn atoms have essentially octahedral geometry with all angles within 4° of the ideal values.

This appears to be a new mode of coordination for a thiosalicylate ligand, which has only been studied previously with higher-oxidation state transition-metal ions, such as Mn(III) [8,9], Fe(III) [8], Ni(II) [10] and Mo(IV) [11]. Crystal structure determinations of these examples show them to have a simple O,S-chelating mode to the metal ion [8–10]. Some organometallic examples involving main group metals are also known [12], and these also show either monodentate or O,S chelating thiosalicylate. Closer parallels to the bonding found in **3** come from complexes of the much more-commonly studied salicylate ligand, from 2-hydroxybenzoic acid [13]. In particular, the aggregated Mn(III) complexes from Christou and coworkers provide the related example [Mn(EtOH)₄][Mn₂(sal)(py)₂], in which triply-bridging ligands link the Mn(II) and Mn(III) centres, though in an infinite chain rather than into discrete units [14].

The second product from the reaction residue was shown to contain the di-anion bis(2-carboxyphenyl)disulphide (**5**), probably as the Mn²⁺ salt. This was identified directly by electrospray mass spectrometry, and by GC-MS after conversion to the dimethyl ester. Whether **5** is formed directly in the reaction, or whether it is formed via the ready aerobic oxidation of the thiosalicylate di-anion [9] during work-up is not clear.

Although the main products from the reaction of orthomanganated dimethylbenzamide with SO₂ have



been identified, the course of reaction is not at all clear. The formation of a C–S bond in the position on the ring originally attached to the Mn atom suggests that there has been insertion of SO₂ into the Mn–C bond, as observed with other substrates. Any initially-formed sulphinate must then be reduced to a sulphide, although the reducing agent has not been identified. Possible processes include conversion of some of the original Mn(I) to Mn(II), or disproportionation of S(IV) to S(VI) and S(II), similar to known processes for sulphinic acids which can give sulphonic acids and disulphides [15]. However, no similar reduction was observed in the SO₂ reactions with other orthomanganated substrates, so the reasons for the singular behaviour of **2** are not known.

The other change to the organic ligand during the reaction is the conversion of the dimethylamide group to a carboxylate group. Hydrolysis of amides is common under acidic or basic conditions, but is probably not involved here since the course of the reaction was not greatly affected by the amount of water in the mixture. Presumably the removal of the Me₂N group is by direct attack of SO₂ which, as a Lewis acid, could accept the lone pair of electrons from the N atom and then provide a nucleophilic oxygen able to cyclise and break the amide bond, as indicated in **6**. Alternatively, the SO₂ could act as nucleophile, attacking at the carbon atom of the amide group, similar to processes identified [16] in the conversion of orthomanganated ketones to imines with PhNSO, an analogue of SO₂. Whatever the process, coordination of the amide group to manganese is necessary since free *N,N*-dimethylbenzamide was quantitatively recovered after treating with SO₂ under the same conditions as those used for the reactions described above.

3.2. Reaction of thiosalicylic acid with BrMn(CO)₅

The recognition that the tetra-manganese complex contained a thiosalicylate ligand suggested that there may be a more rational synthesis based on the readily available thiosalicylic acid, thsaH₂. Simple thiols such as PhSH are known to react with manganese carbonyl species to give aggregated complexes [PhSMn(CO)₃]_n (*n* = 2, 4) [17].

Table 4
Selected bond parameters for the $[\text{Mn}_2(\text{thsa})_2(\text{CO})_6]$ anion (**4**)

Bond lengths (Å)			
Mn(1)–C(2)	1.781(3)	Mn(1)–C(4)	1.810(3)
Mn(1)–C(3)	1.814(3)	Mn(1)–O(11)	2.031(2)
Mn(1)–S(1)	2.351(1)	Mn(1)–S(1)'	2.406(1)
S(1)–C(12)	1.780(3)	C(1)–O(12)	1.248(3)
C(1)–O(11)	1.272(3)	C(1)–C(11)	1.505(4)
Bond angles (deg)			
C(2)–Mn(1)–C(4)	89.9(1)	C(2)–Mn(1)–C(3)	87.8(1)
C(4)–Mn(1)–C(4)	92.5(1)	C(2)–Mn(1)–O(11)	176.1(1)
C(4)–Mn(1)–O(11)	93.9(1)	C(3)–Mn(1)–O(11)	93.4(1)
C(2)–Mn(1)–S(1)	90.3(1)	C(4)–Mn(1)–S(1)	92.9(1)
C(3)–Mn(1)–S(1)	174.2(1)	O(11)–Mn(1)–S(1)	88.2(7)
C(2)–Mn(1)–S(1)'	96.0(1)	C(4)–Mn(1)–S(1)'	173.1(1)
C(3)–Mn(1)–S(1)'	91.3(1)	O(11)–Mn(1)–S(1)'	80.21(6)
S(1)–Mn(1)–S(1)'	83.44(4)	C(12)–S(1)–Mn(1)	106.4(1)
C(12)–S(1)–Mn(1)'	112.7(1)	Mn(1)–S(1)–Mn(1)'	96.56(4)
O(12)–C(1)–O(11)	120.5(2)	O(12)–C(1)–C(11)	117.1(2)
O(11)–C(1)–C(11)	122.3(2)	C(1)–O(11)–Mn(1)	136.5(2)
C(11)–C(12)–S(1)	125.5(2)		

When thsaH_2 was reacted with $\text{BrMn}(\text{CO})_5$ in the presence of Et_3N only one product was formed. This was identified by ESMS and by an X-ray structure analysis as the salt $[\text{Et}_3\text{NH}]_2[\text{Mn}_2(\text{thsa})_2(\text{CO})_6]$, the centrosymmetric anion **4** of which is illustrated in Fig. 3; selected bond parameters are given in Table 4. The anion contains two *fac*- $\text{Mn}(\text{CO})_3$ units which are chelated in an O,S fashion by the thiosalicylate di-anion. The sixth coordination site on each Mn is completed by acceptance of a lone pair of electrons from the S atom of the thiosalicylate in the other half of the unit. The Mn–S distances in **4** are significantly shorter than the corresponding ones in the tetra-manganese complex **3**, probably because the former contains an $\text{Mn}(\text{CO})_3$ unit while the latter involves $\text{Mn}(\text{CO})_4$ groups, but the Mn–O distance does not differ significantly. The coordinated oxygen of the carboxylate group has a longer C–O bond (1.272(3) Å) than the formally non-coordinated one (1.248(3) Å) which is, however, involved in hydrogen-bonding to the Et_3NH cations (N(1)–H(1) 0.98 Å, O(12)···H(1) 1.73 Å from the penultimate difference map).

The structure of the anion **4** is closely analogous to the neutral P,S-bonded species formed from *ortho*- $\text{C}_6\text{H}_4(\text{PPhH})(\text{SH})$ and $\text{BrMn}(\text{CO})_5$, described recently by Liu et al. [18]; corresponding bond parameters are very similar.

Formation of **4** presumably involves initial replacement of the Br and one CO ligand of $\text{BrMn}(\text{CO})_5$ by a chelating thsa ligand to give an $[\text{Mn}(\text{thsa})(\text{CO})_4]^-$ species. Combination of two of these by mutual displacement of CO ligands by the S atoms of the ligand would give the Mn–S–Mn–S core of **4**. All of this takes place under mild conditions, in CH_2Cl_2 at room temperature, and no other products were detected when

conditions were varied by heating to reflux in the presence of excess $\text{BrMn}(\text{CO})_5$. However, it may be that other products, such as **3**, would be accessible with different sources of the manganese carbonyl fragment or with different solvents.

A systematic examination of the use of the thiosalicylate ligand with a wide range of organometallic, low-oxidation state transition-metal substrates is undoubtedly justified, based on the initial observations made in this paper. The thsa ligand is an essentially unexplored example of a hybrid hard/soft (O,S) chelating ligand related to the (O,P) ligands that are currently attracting great interest [19], and it also has the potential for diverse aggregation processes, so that much novel chemistry can be anticipated.

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