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Journal of Organometallic Chemistry 517 (1996) 155–159

Journal
of Organometallic
Chemistry

Some pyridine-2-thiolato and 6-methylpyridine-2-thiolato complexes of manganese: crystal structure of $[\text{Mn}_2(\mu\text{-pyS})_2(\text{CO})_6]$ (pyS = pyridine-2-thiolato ligand)

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Received 6 November 1995

Abstract

The complexes $[\text{Mn}_2(\mu\text{-pyS})_2(\text{CO})_6]$ (**1**) and $[\text{Mn}_2(\mu\text{-MepyS})_2(\text{CO})_6]$ (**2**), where pySH = pyridine-2-thiol and MepySH = 6-methylpyridine-2-thiol, have been made by reaction of $\text{Mn}_2(\text{CO})_{10}$ with the appropriate pyridinethiol in refluxing hexane. In these complexes pyS and MepyS act as both six electron donor chelating and bridging groups which form four-membered N,S chelate rings at one metal centre and bridge to the other metal atom through sulphur. Complex **2** reacts with PPh_3 and $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dppm) in refluxing cyclohexane to give $[\text{Mn}(\text{MepyS})(\text{PPh}_3)(\text{CO})_3]$ (**3**) and $[\text{Mn}(\text{MepyS})(\eta^1\text{-dppm})_2(\text{CO})_2]$ (**4**) respectively. The crystal structure of **1** was determined.

Keywords: Manganese; Carbonyl; Pyridinethiolato; Crystal structure

1. Introduction

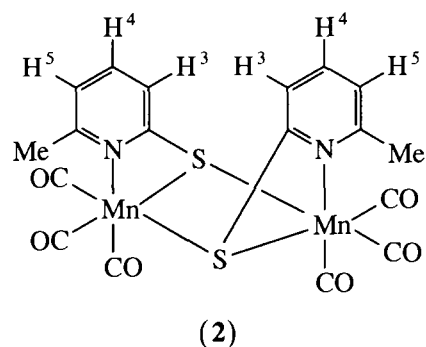
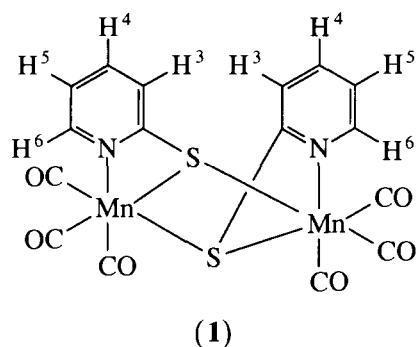
The pyridine-2-thiolato ligand (pyS) displays unusual versatility and has been found to coordinate to metals in several ways: (i) as a monodentate S-coordinated ligand, e.g. in $[\text{Rh}(\text{pyS})_3(\text{pySH})]$ [1,2] and $[\text{Ru}(\text{pyS})_2(\text{CO})_2(\text{PPh}_3)]$ [3], both of which contain an S-bonded pyS ligand; (ii) as a bidentate N,S chelating ligand, e.g. in $[\text{Ru}(\text{pyS})_2(\text{PPh}_3)_2]$ [4,5] and $[\text{Rh}(\text{pyS})_3]$ [2]; (iii) as a doubly bridging ligand linked through both the N and S atoms, e.g. in $[\text{Rh}_2(\mu\text{-pyS})_2(\text{CO})_4]$ [6], or just through the S atom, e.g. in $[\text{Rh}_2(\mu\text{-pyS})_2(\text{tfbb})_2]$ [6] (tfbb = tetrafluorobenz[5.6]bicyclo[2.2.2]octa-2,5,7-triene), in which one of the pyS ligands bridges through the sulphur atom only; (iv) as a triply bridging ligand, e.g. in $[\text{Os}_3\text{H}(\mu_3\text{-pyS})(\text{CO})_9]$ [7] and $[\text{Rh}_3(\mu_3\text{-pyS})_2(\text{CO})_6]^+$ [8], in both of which the pyS ligand is

linked to one metal atom through N and to two others through S; and (v) as a quadruply bridging ligand, e.g. in $[\text{Ru}_3(\mu\text{-H})(\mu_4\text{-pyS})(\text{CO})_7]_3$ [9], where the pyS ligand bridges three Ru atoms through S and one through N. Deeming et al. [10] reported a new type of doubly bridging pyS complex, $[\text{Re}_2(\mu\text{-pyS})_2(\text{CO})_6]$ and $[\text{Re}_2(\mu\text{-MepyS})_2(\text{CO})_6]$, in which the pyS or MepyS ligand forms bridges to two metal centres through the S atom and the N atom is also coordinated to one of these metal centres; the $\mu_2\text{-pyS}$ or $\mu_2\text{-MepyS}$ ligand in this case serves as a six electron donor. We now report that both pySH and MepySH react with $\text{Mn}_2(\text{CO})_{10}$ to give this last type of doubly bridging complex.

2. Results and discussion

The reaction of $\text{Mn}_2(\text{CO})_{10}$ with pySH or MepySH in 1 : 2 molar ratio in refluxing hexane for 62 h gave the corresponding pyridinethiolato complexes $[\text{Mn}_2(\mu\text{-pyS})_2(\text{CO})_6]$ (**1**) and $[\text{Mn}_2(\mu\text{-MepyS})_2(\text{CO})_6]$ (**2**):

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The infrared spectra of the complexes in cyclohexane showed five ν CO absorption bands [1: 2040(s), 2022(vs), 1958(m), 1944(vs) and 1930(vs) cm^{-1} ; 2: 2038(s), 2019(vs), 1950(m), 1938(s) and 1927(s) cm^{-1}], which support their non-centrosymmetric dimeric structure [10]. The ν CO values also rule out the presence of any bridging carbonyl groups [11]. The ^1H NMR spectra [CDCl_3 , 1: δ 6.49 (d, $^2J = 8$ Hz, H^3), 6.97 (t, $^2J = 8$ Hz, H^5), 7.28 (t, $^2J = 8$ Hz, H^4), 7.99 (d, $^2J = 8$ Hz, H^6); 2: δ 2.40 (s, Me), 6.43 (d, $^2J = 8$ Hz, H^3), 6.74

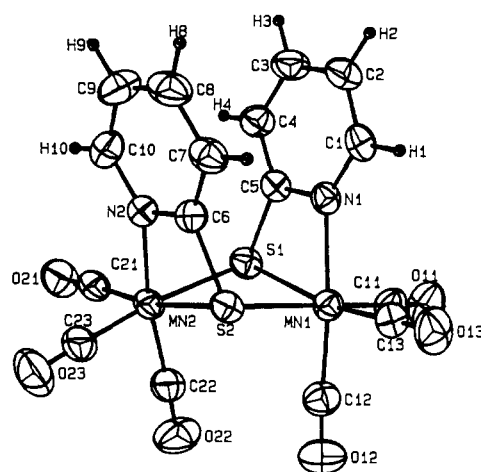


Fig. 1. An ORTEP drawing of $[\text{Mn}_2(\text{pyS})_2(\text{CO})_6]$ (1).

(d, $^2J = 8$ Hz, H^5), 7.17 (t, $^2J = 8$ Hz, H^4) indicate the presence of only one type of pyS or MepyS ligand. The dimeric nature of the complexes was confirmed by their mass spectra which showed the parent molecular ions at m/z 498 and 526 for 1 and 2, respectively. Mass peaks for successive loss of six CO groups were also observed. This ruled out the possibility of a cubane-type structure such as $[\text{Mn}_4(\text{pyS})_4(\text{CO})_{12}]$ with non-coordinated nitrogen atoms as in $[\text{Re}_4(\text{SMe})_4(\text{CO})_{12}]$ [12]. The pyridine-thiolato ligands serve as six electron donor chelating and bridging groups and the resulting complexes (1 and 2) comply with the 18-electron formalism. The structure of 1 was determined by an X-ray diffraction study and is illustrated in Fig. 1. Selected bond lengths and angles are shown in Table 1. The molecule

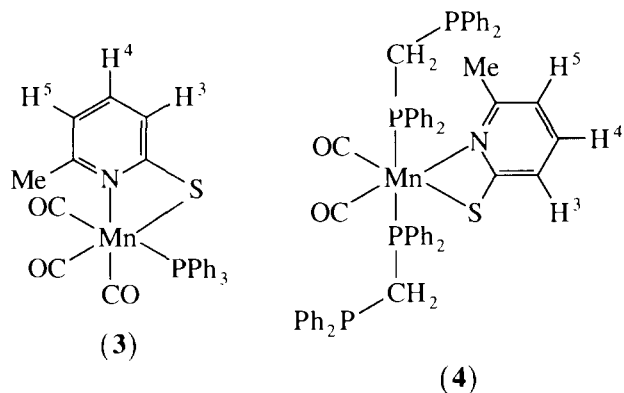
Table 1
Selected bond lengths (\AA) and angles (deg) for 1 with estimated standard deviations in parentheses

Bond lengths			
Mn(1)–S(1)	2.434(1)	N(1)–C(1)	1.342(4)
Mn(1)–S(2)	2.430(1)	N(1)–C(5)	1.343(4)
Mn(1)–N(1)	2.026(3)	C(1)–C(2)	1.374(5)
Mn(2)–S(1)	2.443(1)	C(2)–C(3)	1.366(5)
Mn(2)–S(2)	2.417(1)	C(3)–C(4)	1.382(5)
Mn(2)–N(2)	2.012(3)	C(4)–C(5)	1.370(5)
S(1)–C(5)	1.768(3)	N(2)–C(6)	1.339(4)
S(2)–C(6)	1.762(3)	C(6)–C(7)	1.376(5)
Mn–C(CO)	1.796(4) ^a	C(7)–C(8)	1.386(6)
C–O(CO)	1.145(5) ^a	C(8)–C(9)	1.366(6)
N(2)–C(10)	1.351(5)	C(9)–C(10)	1.375(6)
Bond angles			
S(1)–Mn(1)–S(2)	83.11(3)	N(2)–Mn(2)–C(22)	169.6(1)
S(1)–Mn(1)–N(1)	69.22(8)	Mn(1)–S(1)–Mn(2)	93.12(4)
S(2)–Mn(1)–C(12)	90.6(1)	Mn(1)–S(1)–C(5)	77.5(1)
N(1)–Mn(1)–C(12)	170.9(1)	Mn(2)–S(1)–C(5)	109.7(1)
S(1)–Mn(2)–N(2)	88.64(8)	Mn(1)–S(2)–Mn(2)	93.87(4)
S(1)–Mn(2)–S(2)	83.17(3)	Mn(2)–N(2)–C(6)	103.6(2)
S(2)–Mn(2)–N(2)	69.32(8)	Mn(1)–N(1)–C(5)	103.5(2)
S(2)–Mn(2)–C(22)	100.8(1)	S(1)–C(5)–N(1)	109.7(2)
		S(2)–C(6)–N(2)	109.3(2)

^a Average values.

has a chiral structure with C_2 symmetry. The overall structure is remarkably similar to that of the rhenium analogue $[\text{Re}_2(\text{MepyS})_2(\text{CO})_6]$ [10]. Each pyS ligand bridges two manganese centres through the sulphur atom and the nitrogen atom coordinates to one manganese centre to form a four-membered chelate ring. Overall, **1** is a dinuclear manganese complex with three fused four-membered rings and ancillary ligands. The coordination geometry around Mn is octahedral, with distortions resulting from the small ligand bite; the N–Mn–S angles with the chelate rings are $69.22(8)$ and $69.32(8)^\circ$. The Mn–N and Mn–S bond lengths are in the ranges reported for related compounds [1,10]. The most notable differences between **1** and the analogous rhenium compound $[\text{Re}_2(\text{MepyS})_2(\text{CO})_6]$ are the N–metal–S angles [$69.22(8)$ and $69.32(8)^\circ$ for **1** and $65.8(3)$ and $65.6(3)^\circ$ for the rhenium analogue] within the chelate rings and the S–metal–S angles [$83.17(3)$ and $83.11(3)^\circ$ for **1** and $80.7(2)$ and $81.2(2)^\circ$ for the rhenium compound] within the M_2S_2 ring [10]. The Mn_2S_2 ring is non-planar with a dihedral angle of 151.1° between Mn(2)Mn(1)S(2) and Mn(2)Mn(1)S(1) planes, which may be compared with the corresponding dihedral angle of $150.5(1)$ between the Re(2)Re(1)S(1) and Re(2)Re(1)S(2) planes in $[\text{Re}_2(\text{MepyS})_2(\text{CO})_6]$ [10].

Treatment of complex **2** with 2 equivalents of PPh_3 in boiling cyclohexane gives the monomeric complex *fac*- $[\text{Mn}(\text{MepyS})(\text{PPh}_3)(\text{CO})_3]$ (**3**). The infrared spectrum [cyclohexane, νCO 2023(vs), 1944(s) and 1909(s) cm^{-1}] showed three strong νCO absorption bands which support the *fac* configuration of the complex [13,14a].



The ^1H NMR spectrum of **3** [CDCl_3 , δ 2.17 (s, Me), 5.97 (d, $^2J = 8$ Hz, H^3), 6.34 (d, $^2J = 8$ Hz, H^5), 6.82 (t, $^2J = 8$ Hz, H^4), 7.27–7.46(m) (Ph)] showed signals for only one set of MepyS ligand and the intensity of the peaks was in good agreement with the presence of one MepyS and one PPh_3 ligand in the complex. The mass spectrum showed the molecular ion peak at m/z 525 and peaks for successive losses of three CO groups at m/z 497 $[\text{M}-\text{CO}]^+$, 469 $[\text{M}-2\text{CO}]^+$ and 441 $[\text{M}-3\text{CO}]^+$ (100%) which confirm the monomeric structure of the complex.

Thus, the outcome of the reaction of **2** with PPh_3 contrasts with that of the reaction of $[\text{Re}_2(\text{pyS})_2(\text{CO})_6]$ with PMe_2Ph , which afforded a mixture of the chelating pyS compound *fac*- $[\text{Re}(\text{pyS})(\text{CO})_3(\text{PMe}_2\text{Ph})]$, the monodentate pyS compound *fac*- $[\text{Re}(\text{pyS})(\text{CO})_3(\text{PMe}_2\text{Ph})_2]$, and bridging pyS compounds $[\text{Re}_2(\text{pyS})_2(\text{CO})_5(\text{PMe}_2\text{Ph})]$ and $[\text{Re}_2(\text{pyS})_2(\text{CO})_4(\text{PMe}_2\text{Ph})_2]$.

Treatment of complex **2** with 4 equivalents of $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dppm) in refluxing cyclohexane for 8 h afforded $[\text{Mn}(\text{MepyS})(\eta^1\text{-dppm})_2(\text{CO})_2]$ (**4**) as the main product. The infrared spectrum of complex **4** showed two strong νCO bands at 1917 and 1842 cm^{-1} , consistent with the proposed structure. The ^1H NMR spectrum [CDCl_3 , δ 1.52 (s, 3H, Me), 5.62 (d, $^2J = 8$ Hz, 1H, H^3), 5.90 (d, $^2J = 8$ Hz, 1H, H^5), 7.00 (t, $^2J = 8$ Hz, 1H, H^4), 7.06–7.60 (m, 40H, Ph), 3.30 (m, $^2J_{\text{HH}} = 15$ Hz, $^2J_{\text{PH}} = 8$ Hz, 1.5 Hz, 2H, CH), 3.60 (m, $^2J_{\text{HH}} = 15$ Hz, $^2J_{\text{PH}} = 8$ Hz, 1.5 Hz, 2H, CH)] showed the intensity ratio of Me, CH_2 and Ph protons corresponding to the presence of one MepyS and two dppm ligands in the molecule. The methylene protons appeared in the spec-

Table 2
Crystal data collection and refinement parameters for **1**

Formula	$\text{C}_{16}\text{H}_8\text{Mn}_2\text{N}_2\text{O}_6\text{S}_2$
Formula weight	498.26
Crystal dimensions (mm^3)	$0.20 \times 0.35 \times 0.51$
Radiation, wavelength (\AA)	Mo, 0.71073
Temperature ($^\circ\text{C}$)	25 ± 1
Crystal system	orthorhombic
Space group	<i>Pbca</i>
<i>a</i> (\AA)	12.925(3)
<i>b</i> (\AA)	17.106(5)
<i>c</i> (\AA)	17.119(4)
<i>V</i> (\AA^3)	3785(3)
<i>Z</i>	8
Density (g cm^{-3})	1.75
Absorption coefficient μ (cm^{-1})	15.3
Relative transmission coefficient	0.863–1.000
Scan type	$\omega-2\theta$
Scan rate (deg min^{-1})	8.23
Scan width (deg)	$0.8 + 0.350 \tan(\theta)$
<i>hkl</i> ranges	<i>h</i> : -15 to 15 <i>k</i> : 0 to 21 <i>l</i> : 0 to 21
2θ range (deg)	4.0 – 52.0
Structure solution	Patterson method
No. of unique data	4162
No. of data used in least-squares refinement with $F_o > 3.0\sigma(F_o)$	2882
Weighting scheme <i>w</i>	$4F_o^2 / [\sigma(F_o)^2]^2$
No. of parameters refined	253
R^a	0.0397
R_w^b	0.0438
E.s.d. of unit weights observed (GOF)	0.95
Largest shift/e.s.d.	0.02
Highest peak in final difference map (e \AA^{-3})	0.41(9)

$$^a R = \sum (| |F_o| | - |F_c| |) / \sum |F_o| \quad ^b R_w = [(\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)]^{1/2}$$

trum as two eight-line multiplets indicating that there are two different diastereotopic protons [14b,15]. The two $^2J_{\text{PH}}$ values (8 and 1.5 Hz) indicate that the two phosphorus atoms in dppm are also different, one is coordinated to metal and the other is not. The coupling constants are in good agreement with the values observed for other η^1 -dppm complexes, e.g. in $[\text{Fe}(\text{CO})_4(\eta^1\text{-dppm})]$ [16] [$^2J_{\text{PH}} = 9.3$ Hz (coordinated P), 1.5 Hz (non-coordinated P)]. Thus, its ^1H NMR spectrum unambiguously established the η^1 mode of coordination of dppm in complex **4**. (The pendant mode of the dppm ligand in the analogous compound $[\text{Mn}(\text{pyS})(\text{dppm})_2(\text{CO})_2]$ was established by a ^{31}P NMR study [17]). The mass spectrum of **4** showed the parent molecular ion at m/z 1003 to be consistent with the assigned formulation of **4**.

All four complexes are quite stable at room temperature in an inert atmosphere, and show no sign of decomposition after six months.

3. Experimental

Reactions were carried out under dry nitrogen. Dry and distilled solvents were used. IR spectra were

recorded on a PE 983 spectrophotometer, ^1H NMR spectra on a Varian XL-200 spectrometer, and mass spectra on a VG ZAB F-1 instrument.

3.1. Synthesis of $[\text{Mn}_2(\mu\text{-pyS})_2(\text{CO})_6]$ (**1**)

Pyridine-2-thiol (0.570 g, 5.128 mmol) was added to a solution of $\text{Mn}_2(\text{CO})_{10}$ (1.00 g, 2.564 mmol) in hexane (50 cm³). The mixture was refluxed for 62 h during which time the colour of the solution changed from pale yellow to orange–yellow. The solvent was removed under reduced pressure and the residue chromatographed on a column of silica gel [60–120 mesh; eluant: light petroleum (b.p. 40–60°C)/ CH_2Cl_2 mixture (3:2, v/v)] to give $[\text{Mn}_2(\mu\text{-pyS})_2(\text{CO})_6]$ (**1**) as yellow crystals (0.74 g, 58%), m.p. 150–151°C, from CH_2Cl_2 /hexane mixture.

Anal. Found: C, 38.50; H, 1.60; N, 5.45. $\text{C}_{16}\text{H}_8\text{N}_2\text{Mn}_2\text{O}_6\text{S}_2$ Calc.: C, 38.55; H, 1.61; N, 5.62%.

3.2. Synthesis of $[\text{Mn}_2(\mu\text{-MepyS})_2(\text{CO})_6]$ (**2**)

This was prepared by the method used for complex **1**. It was obtained as honey-yellow needles (m.p. 169°C)

Table 3
Fractional atomic coordinates for **1**

Atom	x	y	z	B (Å ²)
MN1	0.21718(4)	0.01762(3)	0.18560(3)	2.76(1)
MN2	0.13024(4)	0.16114(3)	0.31943(3)	2.92(1)
S1	0.05323(7)	0.05377(5)	0.24544(5)	3.07(2)
S2	0.26631(7)	0.14943(5)	0.22327(5)	2.81(2)
O11	0.1400(2)	−0.1405(2)	0.1546(2)	5.20(7)
O12	0.3298(2)	−0.0530(2)	0.3175(2)	5.45(7)
O13	0.4035(2)	0.0032(2)	0.0878(2)	4.66(6)
O21	−0.0525(2)	0.1946(2)	0.4168(2)	4.99(7)
O22	0.1958(2)	0.0451(2)	0.4359(2)	6.26(8)
O23	0.2478(3)	0.2787(2)	0.4071(2)	5.93(8)
N1	0.1191(2)	0.0627(2)	0.1050(2)	2.66(6)
N2	0.1029(2)	0.2319(2)	0.2278(2)	3.00(6)
C1	0.1201(3)	0.0758(2)	0.0277(2)	3.23(7)
C2	0.0368(3)	0.1094(2)	−0.0091(2)	3.50(8)
C3	−0.0472(3)	0.1310(3)	0.0342(2)	3.86(8)
C4	−0.0491(3)	0.1173(2)	0.1137(2)	3.47(8)
C5	0.0355(3)	0.0825(2)	0.1472(2)	2.75(7)
C6	0.1802(3)	0.2154(2)	0.1784(2)	2.76(7)
C7	0.1868(3)	0.2487(2)	0.1054(2)	3.44(8)
C8	0.1109(3)	0.3019(2)	0.0844(2)	4.34(9)
C9	0.0322(3)	0.3194(2)	0.1348(3)	4.8(1)
C10	0.0291(3)	0.2837(2)	0.2067(2)	4.19(9)
C11	0.1721(3)	−0.0783(2)	0.1656(2)	3.46(8)
C12	0.2870(3)	−0.0220(2)	0.2677(2)	3.69(8)
C13	0.3308(3)	0.0082(2)	0.1250(2)	3.19(7)
C21	0.0154(3)	0.1811(2)	0.3767(2)	3.44(8)
C22	0.1702(3)	0.0892(3)	0.3892(2)	3.81(8)
C23	0.2010(3)	0.2342(2)	0.3720(2)	3.87(8)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3) \cdot [a^2 \cdot B(1, 1) + b^2 \cdot B(2, 2) + c^2 \cdot B(3, 3) + ab(\cos \gamma) \cdot B(1, 2) + ac(\cos \beta) \cdot B(1, 3) + bc(\cos \alpha) \cdot B(2, 3)]$.

in 54% yield. Anal. Found: C, 41.30; H, 2.25; N, 5.45. $C_{18}H_{12}N_2Mn_2O_6S_2$ Calc.: C, 41.06; H, 2.28; N, 5.32%.

3.3. Reaction between $[Mn_2(\mu\text{-MepyS})_2(CO)_6]$ (2) and PPh_3 : synthesis of $[Mn(MepyS)(PPh_3)(CO)_3]$ (3)

PPh_3 (0.398 g, 1.51 mmol) was added to a solution of $[Mn_2(\mu\text{-MepyS})_2(CO)_6]$ (0.40 g, 0.76 mmol) in cyclohexane (40 cm³) and the mixture was heated under reflux for 8 h. The solvent was then removed under reduced pressure and the residue subjected to TLC on silica gel [60 HF₂₅₄; eluant: light petroleum (b.p. 40–60°C)/CH₂Cl₂ (3:1, v/v)] to give $[Mn(MepyS)(PPh_3)(CO)_3]$ (3) as pale yellow crystals (0.28 g, 70%), m.p. 104–105°C, from CH₂Cl₂/methanol mixture. Anal. Found: C, 61.65; H, 3.95; N, 2.60. $C_{27}H_{21}NMnO_3PS$ Calc.: C, 61.71; H, 4.00; N, 2.66%.

A similar reaction between complex 2 and dppm (1:4 molar ratio) afforded complex $[Mn(MepyS)(\eta^1\text{-dppm})_2(CO)_2]$ (4) as orange–yellow needles, m.p. 172–173°C, in 62% yield. Anal. Found: C, 69.25; H, 4.85; N, 1.30. $C_{58}H_{50}NMnO_2P_4S$ Calc.: C, 69.39; H, 4.98; N, 21.39%.

3.4. Crystal structure determination

Crystals of compound 1 for X-ray studies were obtained from a saturated solution of hexane/dichloromethane at 0°C. Suitable crystals were mounted on glass fibres, placed in a goniometer head on an Enraf-Nonius CAD4 diffractometer, and centred optically. Unit cell parameters and an orientation matrix for data collection were obtained using the centring programme in the CAD4 system. Details of data collection and structure refinement parameters are listed in Table 2. As a check on instrument and crystal stability, two representative reflections were measured every 60 min. Lorentz, polarization, and decay corrections were applied as an empirical absorption correction based on a series of ψ scans.

The structure was solved by the Patterson method using SHELXS-86 [18], which revealed the positions of the metal atoms. All other non-hydrogen atoms were found by successive difference Fourier syntheses. Hydrogen atoms were positioned using the programme HYDRO [19] and included in the structure factor calculations as riding atoms with fixed U_{ij} s in the final least-squares cycles. Scattering factors were taken from Cromer and Waber [20]; anomalous dispersion corrections were those of Cromer [21]. All calculations were carried out on a MicroVAX II computer using the Molen/VAX system of programmes [19]. Atom coordinates are shown in Table 3.

Tables of hydrogen atom coordinates and anisotropic thermal parameters and a complete list of bond lengths

and angles have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgements

We thank Mr. Moshfiqur Rahman of the Department of Chemistry, University of Central Lancashire for the IR and ¹H NMR spectra, Dr. J. David Smith of the School of Chemistry and Molecular Sciences, University of Sussex, and Ms. Laila Arjumannessa of the Department of Chemistry, University of Manchester, for the mass spectra.

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