Preparation, Properties, and Reactions with Sulphur Dioxide of Triphenylphosphine Oxide Complexes of Manganese(II) Thiocyanate. Crystal Structures of $[\{Mn(OPPh_3)_2(NCS)(\mu\text{-}NCS)\}_2]$, $[Mn(OPPh_3)_4(NCS)_2]$, and $(PPh_3O)(PPh_3OH)(HSO_4)$, a Derivative of Sulphuric Acid formed under Ambient Air Oxidation of Sulphur Dioxide†

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Manganese(II) thiocyanate reacts with triphenylphosphine oxide to yield the complexes $[Mn(OPPh_3)_n(NCS)_2]$ (n = 1,2,3, or 4) which have been characterised by elemental analyses, i.r. and e.s.r. spectroscopy, and magnetic susceptibility measurements. These complexes are non-electrolytes in nitromethane solution. The crystal structures of the bis, $[\{Mn(OPPh_3)_2(NCS)(\mu\text{-}NCS)\}_2]$, and tetrakis, $[Mn(OPPh_3)_4(NCS)_2]$, complexes are reported. The former is centrosymmetric comprising two $Mn(OPPh_3)_2(NCS)_2$ units bridged by two NCS ligands, the geometry around each manganese atom being square pyramidal with an $OPPh_3$ ligand in the axial position; the latter is a *trans*-pseudo-octahedral monomer with inversion symmetry about the central manganese atom. The reactions of the complexes with sulphur dioxide in both the solid state and in toluene suspensions have been investigated. The tris and tetrakis complexes react reversibly to give 1 : 1 adducts, $[Mn(OPPh_3)_n(NCS)_2(SO_2)]$, whereas the mono and bis complexes are inactive towards sulphur dioxide. Dilute solutions of $[Mn(OPPh_3)_4(NCS)_2(SO_2)]$ in the presence of air result in the oxidation of sulphur dioxide to sulphuric acid, as evidenced by the isolation and *X*-ray crystallographic characterisation of $(PPh_3O)(PPh_3OH)(HSO_4)$. This derivative of sulphuric acid is characterised by extremely strong hydrogen bonds, 2.351 and 2.492 Å.

The current interest in manganese(II) complexes with phosphine oxides stems from earlier work on manganese(II) complexes of tertiary phosphines.[1] During the investigation of the reaction of small molecules with $[Mn(PR_3)X_2]$ (R = alkyl or aryl; X = Cl, Br, I, or NCS) correlations between the nature of the complex and its ability to bind small molecules were observed. It was noted that $[Mn(PPh_3)X_2]$ (X = Br or I) react with sulphur dioxide but are inactive towards dioxygen,[2] which suggested to us that, whilst the reaction with molecular oxygen is quite specific to certain phosphine manganese(II) complexes, the reaction with sulphur dioxide may be more general. This, and the increased interest in the co-ordination of sulphur dioxide by transition metals, has led to the investigation of other manganese(II) systems and their reaction with sulphur dioxide. In particular, triphenylphosphine oxide complexes of MnX_2 (X = Cl, Br, I, NCS, NO_3, or ClO_4) have been studied, although some phosphine sulphide[3,4] and arsine oxide[5–7] complexes have also been investigated. The manganese(II) thiocyanate complexes have provided the most interesting system and it is the reaction of these complexes that is described here.

Results and Discussion

The reaction of anhydrous manganese(II) thiocyanate with triphenylphosphine oxide in toluene in the appropriate molar ratio resulted in the formation of the pale green $[Mn(OPPh_3)_n(NCS)_2]$ complexes (n = 1, 2, 3, or 4). Physical properties and elemental analyses are given in Table 1. The preparation of $[Mn(OPPh_3)_5(NCS)_2]$ has been attempted without success. It appears that a maximum of four triphenylphosphine oxide molecules can be co-ordinated to the Mn^{2+} ion, probably due mainly to the bulkiness of the ligand. Infrared data for the complexes are given in Table 2 from which it can be seen that ν(PO) decreases upon co-ordination, as expected. The position of ν(CN) for the NCS ligand is sensitive to the bonding mode adopted[8] and can be used as a guide to prediction of structure. Table 2 shows that for the bis and tris complexes the ν(CN) region is similar, with absorptions at *ca.* 2 100 and 2 060 cm^{-1}. The bis complex $[\{Mn(OPPh_3)_2(NCS)_2\}_2]$ has been shown by *X*-ray crystallography to be dimeric in the solid state (Figure 1), similar to $[\{Mn(OPPh_3)_2(NCS)(\mu\text{-}Cl)\}_2]$,[9] and the ν(CN) stretches have been assigned to terminal (2 050 cm^{-1}) and bridging NCS (2 095 cm^{-1}). The similarity between the i.r. spectra of this bis and tris, complexes $[Mn(OPPh_3)_n(NCS)_2]$, suggests that $[Mn(OPPh_3)_3(NCS)_2]$ may also be a dimer, with the second axial position occupied by a triphenylphosphine oxide ligand.

The mono complex, $[Mn(OPPh_3)(NCS)_2]$, also shows ν(CN) in the bridging region at 2 130 and 2 100 cm^{-1}. This compares with the observed positions of ν(CN) at 2 124 and 2 106 cm^{-1} for the complex $[Ni(bipy)(NCS)_2]$(bipy = 2,2′-bipyridine),[10] which has been shown to be a polymer in which all the NCS groups are bridging. It would therefore seem likely that the mono complex is polymeric in the solid state.

The tetrakis complex, $[Mn(OPPh_3)_4(NCS)_2]$, exhibits a single ν(CN) at 2 065 cm^{-1}, assigned to terminal *N*-bonded NCS, suggesting a monomeric, pseudo-octahedral structure. This has been confirmed by *X*-ray crystallography (Figure 2).

Reaction of $[Mn(OPPh_3)_2(NCS)_2]$ with 2 mol of triphenyl-

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† Di-μ-thiocyanato-bis[isothiocyanatobis(triphenylphosphine oxide)-manganese(II)], bis(isothiocyanato)tetrakis(triphenylphosphine oxide)-manganese(II), and bis(triphenylphosphine oxide)hydrogen(1+) hydrogensulphate(1−).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Analytical data and physical properties for the $[Mn(OPPh_3)_n(NCS)_2]$ series

Complex	M.p. (°C)	Analysis[a] (%) C	H	N	P	$\mu_{eff.}$	θ^b	Λ^c_m/ ohm^{-1} cm^2 mol^{-1}
$[Mn(OPPh_3)(NCS)_2]$	232—238	53.5	3.3	6.1	6.8	5.47	−40.75	20
		(53.5)	(3.3)	(6.2)	(6.9)			
$[Mn(OPPh_3)_2(NCS)_2]$	209—210	62.5	4.1	3.9	8.4	5.82	−10.17	9
		(62.7)	(4.1)	(3.9)	(8.5)			
$[Mn(OPPh_3)_3(NCS)_2]$	150—153	67.9	4.4	2.5	9.6	5.80	−3.17	8
		(66.9)	(4.5)	(2.8)	(9.3)			
$[Mn(OPPh_3)_4(NCS)_2]$	164—168	69.1	4.7	2.3	9.7	5.93	−3.00	6
		(69.2)	(4.7)	(2.2)	(9.7)			

[a] Calculated values are given in parentheses. [b] Weiss constant (θ) calculated from $\chi = C/(T - \theta)$. [c] In nitromethane.

Table 2. I.r. data (cm^{-1}) for the $[Mn(OPPh_3)_n(NCS)_2]$ complexes in Nujol mulls

Complex	ν(CN)	ν(PO)	ν(CS)	δ(NCS)
PPh_3O		1 190		
$Mn(NCS)_2$	2 140		775, 720	452, 440
$[Mn(OPPh_3)(NCS)_2]$	2 130m, 2 100s, 2 060m	1 180s, 1 160s, 1 145 (sh)	850, 795	465
$[Mn(OPPh_3)_2(NCS)_2]$	2 095s, 2 055s	1 180s, 1 157s	820	480, 470
$[Mn(OPPh_3)_3(NCS)_2]$	2 100m, 2 060s	1 177s	820, 875	435, 445, 475
$[Mn(OPPh_3)_4(NCS)_2]$	2 065s	1 175s	785	473, 435

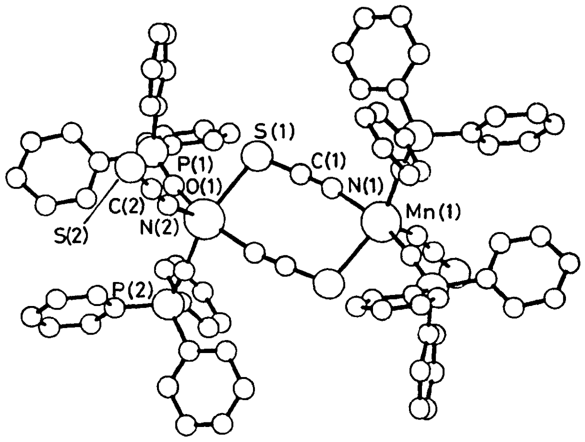

Figure 1. The molecular structure and atomic numbering scheme for $[\{Mn(OPPh_3)_2(NCS)(\mu\text{-}NCS)\}_2]$

phosphine oxide in toluene resulted in the formation of $[Mn(OPPh_3)_3(NCS)_2]$, and reaction of this complex with a further 2 mol of ligand again resulted in the isolation of $[Mn(OPPh_3)_3(NCS)_2]$. Failure to prepare the tetrakis complex by this method lends further support to a dimeric structure for $[Mn(OPPh_3)_3(NCS)_2]$ which would be co-ordinatively saturated, preventing further reaction with triphenylphosphine oxide. However, in oxygen donor solvents such as acetone, ethanol, and *m*-nitrobenzyl alcohol, thin-layer chromatography and mass spectrometry indicate* that the complexes dissociate into $Mn(NCS)_2$ and PPh_3O. Slow evaporation of solutions of the complexes in these solvents resulted in the isolation of the $[Mn(OPPh_3)_4(NCS)_2]$ complex only. Therefore it would seem likely that this is the thermodynamically most stable complex.

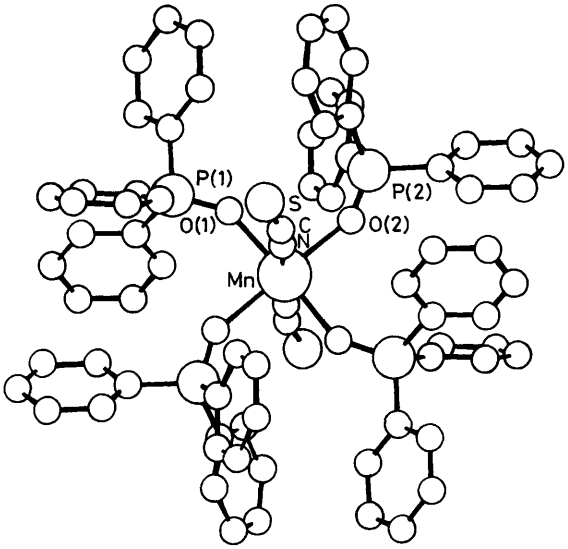

Figure 2. The molecular structure and atomic numbering scheme for $[Mn(OPPh_3)_4(NCS)_2]$

Magnetic moment data (Table 1) also support the proposals of a polymeric structure for $[Mn(OPPh_3)(NCS)_2]$ and a dimeric structure for $[Mn(OPPh_3)_3(NCS)_2]$. The mono complex has a magnetic moment of 5.47 μ_B at room temperature, considerably lower than the spin-only value of 5.92 μ_B expected for high-spin manganese(II). The value of 5.80 μ_B observed for the tris complex is similar to that found for the dimeric bis complex (5.82 μ_B). The monomeric tetrakis complex however, was found to have a magnetic moment of 5.93 μ_B. Thus the lower values found for $[Mn(OPPh_3)_n(NCS)_2]$ (n = 1, 2, or 3) may be attributed to antiferromagnetic coupling through NCS bridges.

The magnetic behaviour of the complexes has been studied in the temperature range 295—77 K. Least-squares computer fits of χ'^{-1}_M *vs.* T show all the complexes to obey the Curie–Weiss law. The magnitude of the Weiss constant θ (Table 1) indicates

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* Thin-layer chromatograms of solutions of all four complexes in these solvents showed two spots corresponding to PPh_3O and $Mn(NCS)_2$. Fast atom bombardment (f.a.b.) mass spectra of the complexes were similar to the mass spectrum of a mixture of free PPh_3O and $Mn(NCS)_2$.

Table 3. Atomic co-ordinates for $[\{Mn(OPPh_3)_2(NCS)(\mu\text{-}NCS)\}_2]$

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Mn(1)	6 003(1)	849(1)	3 881(1)	C(18)	10 873(13)	77(7)	3 339(16)
N(1)	4 812(8)	610(3)	4 949(9)	C(19)	10 390(13)	−39(6)	2 156(15)
C(1)	4 191(10)	396(4)	5 431(11)	C(20)	9 384(12)	183(5)	1 568(12)
S(1)	3 318(3)	103(1)	6 141(3)	O(2)	4 838(6)	1 368(3)	3 058(7)
N(2)	7 266(8)	1 180(4)	5 163(9)	P(2)	4 040(3)	1 729(1)	2 341(3)
C(2)	8 104(11)	1 263(4)	5 865(11)	C(21)	3 430(10)	1 526(4)	784(11)
S(2)	9 248(3)	1 385(1)	6 849(4)	C(22)	4 183(12)	1 430(5)	−22(16)
O(1)	6 771(5)	878(3)	2 351(6)	C(23)	3 733(17)	1 245(5)	−1 181(15)
P(1)	7 632(3)	842(1)	1 542(3)	C(24)	2 616(18)	1 133(5)	−1 506(15)
C(3)	7 069(9)	543(4)	106(11)	C(25)	1 914(15)	1 209(6)	−709(18)
C(4)	7 118(10)	722(4)	−1 048(12)	C(26)	2 307(11)	1 399(5)	455(14)
C(5)	6 681(13)	461(5)	−2 075(13)	C(27)	2 858(9)	1 851(4)	3 064(11)
C(6)	6 261(12)	21(6)	−2 027(14)	C(28)	2 269(11)	2 289(5)	2 845(13)
C(7)	6 159(13)	−175(5)	−905(17)	C(29)	1 340(15)	2 367(7)	3 388(18)
C(8)	6 584(11)	93(5)	171(12)	C(30)	1 059(15)	2 031(7)	4 159(18)
C(9)	8 094(9)	1 443(4)	1 210(11)	C(31)	1 614(13)	1 604(7)	4 431(16)
C(10)	7 589(10)	1 844(4)	1 630(11)	C(32)	2 525(11)	1 518(5)	3 859(12)
C(11)	7 954(12)	2 288(4)	1 372(14)	C(33)	4 737(9)	2 296(4)	2 218(11)
C(12)	8 802(12)	2 358(5)	746(16)	C(34)	4 416(10)	2 610(5)	1 225(11)
C(13)	8 985(11)	1 503(5)	575(12)	C(35)	4 938(11)	3 053(5)	1 206(13)
C(14)	9 304(13)	1 956(6)	315(16)	C(36)	5 754(11)	3 198(5)	2 163(14)
C(15)	8 864(10)	525(4)	2 224(13)	C(37)	6 094(10)	2 884(5)	3 144(13)
C(16)	9 383(11)	627(5)	3 433(13)	C(38)	5 574(9)	2 441(5)	3 195(11)
C(17)	10 356(13)	399(5)	3 986(13)				

Table 4. Selected bond lengths (Å) and angles (°) for $[\{Mn(OPPh_3)_2(NCS)(\mu\text{-}NCS)\}_2]$

Mn(1)–N(1)	2.114(10)	Mn(1)–O(2)	2.081(7)
Mn(1)–N(2)	2.069(9)	Mn(1)–S(1)	2.751(4)
Mn(1)–O(1)	2.062(7)		
N(1)–Mn(1)–N(2)	104.1(4)	O(1)–Mn(1)–O(2)	89.2(3)
N(1)–Mn(1)–O(1)	156.1(3)	N(1)–Mn(1)–S(2)	86.5(2)
N(2)–Mn(1)–O(1)	98.8(4)	N(2)–Mn(1)–S(1)	104.5(2)
N(1)–Mn(1)–O(2)	89.3(3)	O(1)–Mn(1)–S(1)	81.5(2)
N(2)–Mn(1)–O(2)	109.3(3)	O(2)–Mn(1)–S(1)	145.9(2)

most antiferromagnetic exchange for $[Mn(OPPh_3)(NCS)_2]$, as gauged by a more negative θ value.

The antiferromagnetic exchange energy, J, has been determined to the first order by using the Van Vleck dipolar coupling model.[11] Although this is usually applied to simple dimers it has also been used to represent polymers.[12] The equation for the susceptibility (per metal atom), using the model for a spin $S = \frac{5}{2}$, is shown by equation (1) where $x = -J/kT$. For these particular complexes there should be virtually no mixing in of excited states by spin–orbit coupling or magnetic fields. Thus, g is expected to be close to 2.0, which is consistent with the e.s.r. results, and $N\alpha$ (the temperature-independent paramagnetism) to be zero. Substituting these values into equation (1) gives J values of −4, −1.5, −1, and −0.5 cm^{-1} for $[Mn(OPPh_3)(NCS)_2]$, $[Mn(OPPh_3)_2(NCS)_2]$, $[Mn(OPPh_3)_3(NCS)_2]$, and $[Mn(OPPh_3)_4(NCS)_2]$ respectively. For an antiferromagnetic exchange J is negative and increases with increasing θ, as is observed here.

Solid-state X-band e.s.r. spectra of all the complexes showed only a single absorption centred at $g = 2$ which provides no unambiguous structural information. Any e.s.r.-active compound with regular cubic symmetry, such as MnL_6, gives a single line at $g = 2$, but some of the manganese complexes previously studied[13,14] also gave a single resonance at $g = 2$, even though it was clear that the structure could not be regular. Many of these complexes were polymeric and it is likely that the proximity of the neighbouring manganese ions resulted in magnetic interactions causing a single line to be observed at $g = 2$. Thus the e.s.r. spectra of the $[Mn(OPPh_3)_n(NCS)_2]$ complexes do not distinguish between a regular and a polymeric structure.

The conductivity of the complexes in nitromethane solution has been investigated. Previous work[15,16] has shown that the triphenylphosphine oxide complexes $[Mn(OPPh_3)_2X_2]$ (X = Cl, Br, or I) are non-conductors in both nitromethane and nitrobenzene. Similar results were found for the $[Mn(OPPh_3)_n(NCS)_2]$ series with the molar conductivities of all the complexes in nitromethane less than 30 ohm^{-1} cm^{-2} mol^{-1} (Table 1). Since values for 1 : 1 electrolytes in nitromethane lie in the range 60—115 ohm^{-1} cm^2 mol^{-1} [17] these complexes can be characterised as non-ionic in this solvent.

Crystallographic Studies.—The molecular structure of $[\{Mn(OPPh_3)_2(NCS)_2\}_2]$, together with the atom numbering scheme, is shown in Figure 1. Atomic co-ordinates and selected bond lengths and angles are given in Tables 3 and 4 respectively. The molecule is centrosymmetric and is comprised of two $Mn(OPPh_3)_2(NCS)_2$ units bridged by two NCS ligands. The geometry around each manganese atom is square pyramidal with an $OPPh_3$ ligand in the axial position. The structure appears to be similar to that of $[Mn_2(OPPh_3)_4(NCS)_2(\mu\text{-}Cl)_2]$ previously reported,[9] although a complete comparison cannot be made since no geometric details of the latter were given. The Mn–O bond lengths, however, are similar to those found for $[Mn(OPPh_3)_2Cl_2]$.[18]

The molecular structure and atom numbering scheme for

$$\chi'_M = \frac{3N\beta^2g^2}{3kT}\left[\frac{55 + 30\ \exp(10x) + 14\ \exp(18x) + 5\ \exp(24x) + \exp(28x)}{11 + 9\ \exp(10x) + 7\ \exp(18x) + 5\ \exp(24x) + 3\ \exp(28x) + \exp(30x)}\right] + N\alpha \qquad (1)$$

Table 5. Atomic co-ordinates (× 10^4) for $[Mn(OPPh_3)_4(NCS)_2]$

Atom	*X/a*	*Y/b*	*Z/c*
Mn	0	0	0
N(1)	1 282(8)	1 327(8)	−1 326(8)
C(1)	1 924(13)	2 030(12)	−1 987(11)
S(1A)	3 470(12)	2 198(18)	−2 933(14)
S(1B)	2 410(17)	3 384(14)	−2 837(16)
S(1C)	2 377(20)	3 039(16)	−2 664(18)
S(1D)	3 095(15)	3 181(17)	−3 315(16)
O(1)	1 480(5)	−1 457(5)	−577(5)
O(2)	−573(5)	491(5)	−1 432(5)
P(1)	2 504(2)	−2 490(2)	−361(2)
P(2)	−326(2)	283(2)	−2 473(2)
C(1E)	3 730(5)	−2 006(6)	−499(6)
C(2F)	3 820(5)	−744(6)	−1 166(6)
C(3F)	4 753(5)	−329(6)	−1 306(6)
C(4E)	5 595(5)	−1 176(6)	−779(6)
C(5F)	5 505(5)	−2 439(6)	−112(6)
C(6F)	4 573(5)	−2 854(6)	28(6)
C(2L)	3 649(29)	−1 815(28)	280(28)
C(3L)	4 556(25)	−1 282(23)	22(23)
C(5L)	5 950(36)	−2 097(36)	−1 478(35)
C(6L)	4 950(33)	−2 250(32)	−1 589(32)
C(7E)	3 229(6)	−3 177(5)	−1 459(5)
C(8F)	4 518(6)	−3 393(5)	−2 124(5)
C(9F)	5 035(6)	−3 930(5)	−2 966(5)
C(10E)	4 263(6)	−4 252(5)	−3 143(5)
C(11F)	2 974(6)	−4 036(5)	−2 478(5)
C(12F)	2 458(6)	−3 499(5)	−1 636(5)
C(8L)	3 447(24)	−4 392(23)	−1 129(19)
C(9L)	4 123(25)	−4 952(23)	−2 060(26)
C(11L)	4 038(25)	−2 916(26)	−3 609(20)
C(12L)	3 448(21)	−2 432(23)	−2 698(22)
C(13E)	2 115(7)	−3 764(6)	1 126(6)
C(14F)	1 244(7)	−3 454(6)	2 139(6)
C(15F)	925(7)	−4 388(6)	3 338(6)
C(16E)	1 476(7)	−5 632(6)	3 524(6)
C(17F)	2 347(7)	−5 942(6)	2 511(6)
C(18F)	2 666(7)	−5 008(6)	1 312(6)
C(14L)	353(25)	−3 909(22)	2 020(28)
C(15L)	519(24)	−4 877(22)	3 194(22)
C(17L)	2 666(24)	−5 615(21)	2 800(21)
C(18L)	2 988(18)	−4 642(17)	1 571(18)
C(13X)	1 533(17)	−3 362(16)	1 184(17)
C(14X)	1 951(17)	−3 969(16)	2 121(17)
C(15X)	1 269(17)	−4 790(16)	3 289(17)
C(16X)	168(17)	−5 005(16)	3 519(17)
C(17X)	−250(17)	−4 398(16)	2 582(17)
C(18X)	432(17)	−3 577(16)	1 414(17)
C(19E)	−486(7)	−1 303(6)	−1 971(8)
C(20F)	−1 060(7)	−2 012(6)	−704(8)
C(21F)	−1 202(7)	−3 220(6)	−291(8)
C(22E)	−771(7)	−3 719(6)	−1 144(8)
C(23F)	−198(7)	−3 010(6)	−2 411(8)
C(24F)	−56(7)	−1 801(6)	−2 824(8)
C(20L)	466(29)	−2 163(28)	−2 010(27)
C(21L)	107(31)	−3 388(30)	−1 341(29)
C(23L)	−1 256(38)	−2 881(38)	−2 097(37)
C(24L)	−1 205(41)	−1 155(41)	−2 704(40)
C(19X)	−1 085(15)	−780(15)	−2 281(15)
C(20X)	−1 565(15)	−777(15)	−2 969(15)
C(21X)	−1 826(15)	−1 878(15)	−2 696(15)
C(22X)	−1 605(15)	−2 983(15)	−1 737(15)
C(23X)	−1 125(15)	−2 985(15)	−1 049(15)
C(24X)	−865(15)	−1 884(15)	−1 322(15)
C(25E)	1 147(7)	541(7)	−3 724(8)
C(26F)	1 935(7)	1 075(7)	−3 782(8)
C(27F)	3 115(7)	1 207(7)	−4 756(8)
C(28E)	3 508(7)	806(7)	−5 671(8)
C(29F)	2 720(7)	272(7)	−5 612(8)
C(30F)	1 540(7)	140(7)	−4 639(8)
C(26L)	1 300(29)	1 162(27)	−5 176(26)
C(27L)	2 542(31)	1 259(25)	−6 165(29)
C(29L)	3 442(30)	53(35)	−4 795(32)
C(30L)	2 190(32)	−45(34)	−3 688(26)
C(25X)	1 313(13)	261(12)	−3 546(12)
C(26X)	2 252(13)	−630(12)	−3 977(12)
C(27X)	3 473(13)	−413(12)	−4 725(12)
C(28X)	3 755(13)	696(12)	−5 041(12)
C(29X)	2 817(13)	1 587(12)	−4 610(12)
C(30X)	1 596(13)	1 370(12)	−3 863(12)
C(31E)	−1 373(6)	1 365(6)	−3 180(6)
C(32F)	−2 626(6)	1 673(6)	−2 451(6)
C(33F)	−3 428(6)	2 570(6)	−3 012(6)
C(34E)	−2 977(6)	3 161(6)	−4 302(6)
C(35F)	−1 723(6)	2 853(6)	−5 031(6)
C(36F)	−921(6)	1 955(6)	−4 470(6)
C(32L)	−2 111(18)	892(19)	−3 185(18)
C(33L)	−3 077(21)	1 909(28)	−3 713(22)
C(35L)	−2 383(21)	3 488(19)	−4 097(20)
C(36L)	−1 495(17)	2 617(18)	−3 590(17)

Table 6. Selected bond lengths (Å) and angles (°) for $[Mn(OPPh_3)_4(NCS)_2]$

Mn–N(1)	2.183(9)	N(1)–C(1)	1.13(2)
Mn–O(1)	2.191(5)	O(1)–P(1)	1.469(6)
Mn–O(2)	2.196(8)	O(2)–P(2)	1.460(9)
O(1)–Mn–N(1)	89.6(3)	Mn–O(1)–P(1)	147.5(6)
O(2)–Mn–N(1)	90.2(4)	Mn–O(2)–P(2)	147.6(3)
O(2)–Mn–O(1)	89.2(3)	Mn–N(1)–C(1)	178.0(1)

Table 7. Uptake of sulphur dioxide by $[Mn(OPPh_3)_n(NCS)_2]$ in the solid state

Complex	Mass of complex*/g	Mass of SO_2 absorbed*/g	Mn/SO_2
$[Mn(OPPh_3)(NCS)_2]$	0.2178(4.85)	0.0013(0.20)	—
$[Mn(OPPh_3)_2(NCS)_2]$	0.4162(5.72)	0.0016(0.25)	—
$[Mn(OPPh_3)_3(NCS)_2]$	0.3893(3.87)	0.0258(4.03)	0.96
$[Mn(OPPh_3)_4(NCS)_2]$	0.5401(4.21)	0.0269(4.20)	1.00

* Number of moles (× 10^{-4}) in parentheses.

$[Mn(OPPh_3)_4(NCS)_2]$ is shown in Figure 2. Atomic co-ordinates and selected bond lengths and angles are given in Tables 5 and 6 respectively. The molecule is a pseudo-octahedral monomer with inversion symmetry about the central manganese atom. Both thiocyanate anions are co-ordinated to the manganese through their nitrogen atoms. These are disordered with each sulphur atom being distributed over four sites. There is also disorder in the triphenylphosphine oxide ligands and this is reflected in the high values of *R* and *R′*.

Reaction of $[Mn(OPPh_3)_n(NCS)_2]$ *with Sulphur Dioxide.—Solid state.* The reaction of the $[Mn(OPPh_3)_n(NCS)_2]$ complexes (n = 1, 2, 3, or 4) with sulphur dioxide has been studied in the solid state by monitoring the changes in the mass of the complexes when exposed to an atmosphere of sulphur dioxide. The results of these uptakes are shown in Table 7 from which it can be seen that there was no reaction between the mono and bis complexes and sulphur dioxide whereas the tris and tetrakis complexes reacted to give 1 : 1 adducts. Exposure of the tris and

Table 8. I.r. data (cm^{-1}) for sulphur dioxide adducts

Complex	ν(CN)	ν(SO)	ν(PO)	ν(CS)	δ(NCS)
$[Mn(OPPh_3)_3(NCS)_2(SO_2)]$	2 100, 2 055	1 285	1 178, 1 160	820, 780	480, 470, 460, 444, 420
$[Mn(OPPh_3)_4(NCS)_2(SO_2)]$	2 095, 2 060	1 288	1 180	785	480, 440
$[Mn(OPPh_3)_4(NCS)_2(SO_2)]$*	2 095, 2 060	1 288	1 180, 1 160	785	480, 465, 440

* $[Mn(OPPh_3)_2(NCS)_2] + 2PPh_3O + SO_2$.

Table 9. Sulphur dioxide loss from $[Mn(OPPh_3)_n(NCS)_2]$

Complex	Mass of sample /mg	Temperature of SO_2 loss (°C)	Mass loss /mg	Theoretical mass loss (%)
$[Mn(OPPh_3)_3(NCS)_2(SO_2)]$	8.4	25—100	0.5	99
$[Mn(OPPh_3)_4(NCS)_2(SO_2)]$	9.4	60—150	0.5	110

tetrakis complexes to sulphur dioxide caused an almost immediate colour change to yellow.

The i.r. spectra of the tris and tetrakis complexes showed changes after exposure to sulphur dioxide, with new bands assigned to ν(SO) appearing at *ca.* 1 285 cm^{-1} (Table 8). For the tetrakis complex a change in the ν(CN) region of the spectrum was also observed with the disappearance of the band at 2 065 cm^{-1} and two bands appearing at 2 060 and 2 095 cm^{-1}. These spectral changes could be reversed by removing the sulphur dioxide atmosphere and this change could be accelerated either by application of a vacuum or heating the adduct to 90 °C. Further exposure to sulphur dioxide regenerated the 1:1 adduct. The loss of sulphur dioxide from the adduct was monitored by thermogravimetric analysis which showed almost quantitative loss of sulphur dioxide (Table 9). These reactions can be summarised by equation (2) (n = 3 or 4).

$$[Mn(OPPh_3)_n(NCS)_2] + SO_2 \underset{90\,^{\circ}C}{\rightleftharpoons} [Mn(OPPh_3)_n(NCS)_2(SO_2)] \quad (2)$$

Toluene slurries. The reactions of the complexes with sulphur dioxide have also been studied in toluene slurries. As with the solid-state reactions the mono and bis complexes were recovered unchanged from the reaction mixtures and $[Mn(OPPh_3)_n(NCS)_2(SO_2)]$ (n = 3 or 4) were obtained from the reactions of the tris and tetrakis complexes. The physical properties and i.r. spectra of these adducts are identical to those obtained from the solid-state reactions. Elemental analyses are shown in Table 10. However, if 2 mol of PPh_3O were added after the reaction of $[Mn(OPPh_3)_2(NCS)_2]$ with sulphur dioxide the adduct $[Mn(OPPh_3)_4(NCS)_2(SO_2)]$ was formed and not $[Mn(OPPh_3)_3(NCS)_2(SO_2)]$ which might have been expected, as discussed above.

The structure of the sulphur dioxide adducts are, as yet, unconfirmed. Sulphur dioxide insertion into the Mn–N bond {in a manner analogous to that in $[Mn(OPPh_3)_4(O_2SI)_2]$[19]} is feasible, but the appearance of the second ν(CN) band in the case of the tetrakis complex suggests that the sulphur dioxide may be bound to the terminal sulphur of the isothiocyanate ligand to give $-NCS-(SO_2)$. Ligand-bound sulphur dioxide is well known[20–25] and is generally characterised by reversibility and unreactivity of the bound sulphur dioxide to dioxygen. However, whilst we observe reversibility, we also observe reactivity of SO_2 to oxidation (see below).

Only 1 mol of sulphur dioxide is absorbed per mol of complex even though there appear to be two potential binding sites (two NCS per manganese). This may be due to the steric requirements of the complex. In the solid state the complex $[Mn(OPPh_3)_4(NCS)_2]$ has a layered structure with a pseudo hexagonal-close-packed arrangement of $Mn(OPPh_3)_4(NCS)_2$ units. It is possible that addition of 1 mol of sulphur dioxide causes a disruption in the layer spacing, preventing a second molecule of sulphur dioxide from binding.

The reason for the inactivity of the mono and bis complexes is unclear. Moreover, since the bis complex contains terminal NCS ligands and also a vacant co-ordination site on the manganese, reactivity may be related to an electronic factor dictated by the number of triphenylphosphine oxide ligands bound to the manganese.

In the presence of sulphur dioxide all the $[Mn(OPPh_3)_n(NCS)_2]$ (n = 1, 2, or 3) complexes in toluene slurries yield small amounts of $[Mn(OPPh_3)_4(NCS)_2(SO_2)]$. Thus, after exposure of the $[Mn(OPPh_3)_n(NCS)]$ complexes to SO_2 and filtering off, a small amount of yellow solid forms in the filtrate. The i.r. spectrum of this solid is identical to that of $[Mn(OPPh_3)_4(NCS)_2(SO_2)]$. In all cases reduction of the filtrate to almost dryness yields $[Mn(OPPh_3)_4(NCS)_2]$. Exposure of this solid to sulphur dioxide again produces $[Mn(OPPh_3)_4(NCS)_2(SO_2)]$. Oxidation of sulphur dioxide to sulphuric acid occurs in the filtrates of all the reactions studied in toluene slurries. Exposing these sulphur dioxide-saturated filtrates to the atmosphere resulted in the formation of pale yellow crystals which have been shown by single-crystal *X*-ray analysis to be $(PPh_3O)(PPh_3OH)(HSO_4)$, the molecular structure of which is shown in Figure 3. Atomic co-ordinates and selected bond lengths and angles are given in Tables 11 and 12. Although it is clear that the two triphenylphosphine oxide moieties are linked to the sulphate anion by hydrogen bonds, the low scattering power of the hydrogen atoms makes them difficult to locate precisely. However, low peaks in the final difference map near to O(1P) and the increase in the P–O bond length from 1.46(1) Å in free PPh_3O[26] to 1.497(5) Å in the adduct indicate that one of the PPh_3O groups is protonated. The second proton could not be located conclusively but the longer S(1)–O(3S) bond compared to S(1)–O(4S) points to the protonation of O(3S). A consideration of the pK_a values of H_2SO_4 lends support for the transfer of one proton only. von Haupt *et al.*[27] have shown that the proton of HCl is transferred to PPh_3O in the crystalline state and Jonsson and Olovsson[28] have shown that a proton is transferred from H_2SO_4 to $MeCO_2H$ to give $MeC(O)OH\cdot HSO_4$. This strongly suggests that the first proton of H_2SO_4 will be transferred to PPh_3O. However, the second proton is not likely to be transferred since p$K_a(HSO_4^-)$ = 1.92[29] and Cl_3CO_2H(pK_a = 0.89) and $(CO_2H)_2$ (pK_a = 1.19) do not protonate PPh_3O in the crystalline state.[30,31] Shaking the adduct in a hexane–water mixture results in sulphuric acid being extracted into the aqueous layer (shown by its acidic nature and the presence of sulphate) and the triphenylphosphine oxide moieties go into hexane solution.

It is interesting that this reaction is not exclusive to the manganese(II) thiocyanate–triphenylphosphine oxide complexes; it

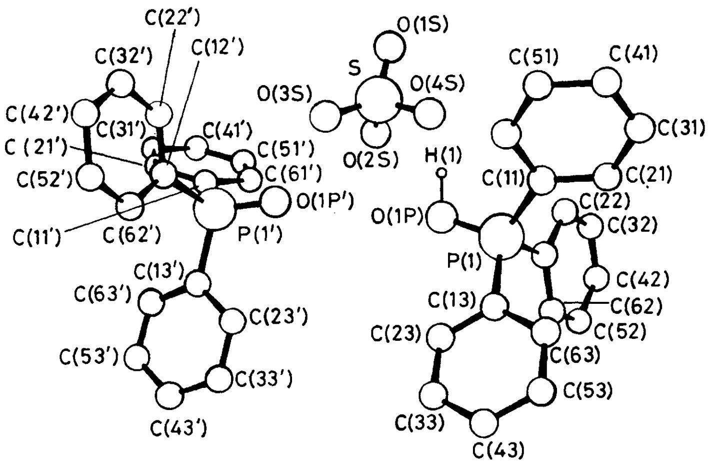

Figure 3. The molecular structure and atomic numbering scheme for $(PPh_3O)(PPh_3OH)(HSO_4)$

Table 10. Elemental analyses and physical properties of sulphur dioxide adducts

Reaction	Product	Colour	M.p. (°C)	Analysis (%)[a]			
				C	H	S	N
$[Mn(OPPh_3)(NCS)_2] + SO_2$	$[Mn(OPPh_3)(NCS)_2]$	White	226—230	52.4(53.5)	3.1(3.3)	13.1(14.3)	6.0(6.2)
$[Mn(OPPh_3)_2(NCS)_2] + SO_2$	$[Mn(OPPh_3)_2(NCS)_2]$	White	208—211	61.1(62.7)	3.9(4.1)	9.2(8.8)	3.7(3.9)
$[Mn(OPPh_3)_3(NCS)_2] + SO_2$	$[Mn(OPPh_3)_3(NCS)_2(SO_2)]$	Yellow	90[b]	62.7(62.9)	4.2(4.2)	7.5(9.0)	2.9(2.6)
$[Mn(OPPh_3)_4(NCS)_2] + SO_2$	$[Mn(OPPh_3)_4(NCS)_2(SO_2)]$	Yellow	90[b]	64.9(65.9)	4.3(4.5)	6.7(7.1)	2.0(2.1)
$[Mn(OPPh_3)_2(NCS)_2] + 2PPh_3O + SO_2$	$[Mn(OPPh_3)_4(NCS)_2(SO_2)]$	Yellow	90[b]	64.2(65.9)	4.3(4.5)	7.2(7.1)	2.3(2.1)

[a] Calculated values in parentheses. [b] Decomposes.

Table 11. Atomic co-ordinates for $(PPh_3O)(PPh_3OH)(HSO_4)$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
S	0	0	7 500
O(1S)	0	0	8 878(12)
O(2S)	−371(5)	348(11)	7 212(27)
O(3S)	−19(6)	−610(5)	6 636(16)
O(4S)	341(6)	391(13)	7 136(17)
P(1)	763(1)	1 215(1)	4 415(3)
C(1P)	444(1)	706(2)	4 760(6)
C(11)	1 209(2)	1 130(3)	5 447(7)
C(21)	1 479(2)	1 651(3)	5 696(8)
C(31)	1 819(2)	1 551(4)	6 488(8)
C(41)	1 899(2)	944(4)	7 014(8)
C(51)	1 635(2)	419(4)	6 782(8)
C(61)	1 288(2)	502(3)	6 002(7)
C(12)	572(2)	2 046(3)	4 606(7)
C(22)	515(2)	2 303(4)	5 881(8)
C(32)	330(2)	2 920(4)	6 018(10)
C(42)	211(2)	3 282(4)	4 951(11)
C(52)	271(3)	3 024(4)	3 693(10)
C(62)	449(2)	2 418(3)	3 513(8)
C(13)	913(2)	1 124(3)	2 690(7)
C(23)	665(2)	754(3)	1 869(9)
C(33)	765(4)	688(5)	537(11)
C(43)	1 101(4)	1 025(7)	45(13)
C(53)	1 345(3)	1 395(6)	858(11)
C(63)	1 252(3)	1 438(4)	2 183(9)

has also been observed with complexes of manganese(II) bromide and iodide and where the ligand is triphenylarsine oxide.[32] Indeed a mixed PPh_3O–$AsPh_3O$ sulphuric acid adduct has been crystallographically characterised.[33] It shows the same type of structure as that described above for $(PPh_3O)(PPh_3OH)(HSO_4)$. Manganese(II) is known to catalyse the oxidation of sulphur dioxide in the atmosphere,[34] therefore it seems likely that the triphenylphosphine oxide–sulphuric acid crystals are also formed by the oxidation of sulphur dioxide to sulphate, catalysed by the $[Mn(OPPh_3)_4(NCS)_2]$ species in solution, in the presence of air and moisture. The mechanism of this reaction is still under investigation.

Experimental

Preparation of $[Mn(OPPh_3)_n(NCS)_2]$ *Complexes.*—Although these complexes are air-stable the use of anhydrous reactants and solvents in an inert atmosphere appears to be beneficial to clean reaction products.

The apparatus employed was a round-bottomed flask (250 cm^3) equipped with a side arm containing a ground-glass tap. A weighed quantity of $Mn(NCS)_2$ was added to the pre-dried, argon-filled flask against a stream of argon. The flask was then evacuated and flame dried to ensure that no moisture contamination had occurred during handling and transfer of the $Mn(NCS)_2$ to the flask. After cooling to room temperature the calculated amount of PPh_3O was added against a stream of argon. A vacuum was again applied and removed with argon to ensure no dioxygen contamination. Freshly distilled toluene (50 cm^3) was then added to the flask, also against a stream of argon. As before a vacuum was applied and removed with argon. The resulting slurry was stirred under argon at room temperature for *ca.* 7 d. The solid was then isolated by standard Schlenk techniques and dried *in vacuo*.

Reaction with Sulphur Dioxide.—(*i*) *Solid state.* Approximately 0.4 g of sample was placed in a pre-weighed argon filled Rotaflow tube. The tube was then evacuated, filled with argon, and re-weighed to determine the mass of the sample. The vacuum was again applied and removed with 1 atm ($\approx$ 101 325

Table 12. Selected bond lengths (Å) and angles (°) for $(PPh_3O)(PPh_3OH)(HSO_4)$

S–O(1S)	1.381(12)	O(1P)–H(1)	1.06(27)
S–O(2S)	1.431(15)	O(4S)–H(1)	1.44(27)
S–O(3S)	1.500(12)	O(1P′)···O(3S)	2.351
S–O(4S)	1.403(12)	O(1P)···O(4S)	2.492
O(1P)–P(1)	1.497(5)		
O(1P)–H(1)–O(4S)	169.3	S–O(3S)–O(1P′)	123.5
P(1)–O(1P)···O(4S)	119.2	P(1′)–O(1P′)–O(3S)	130.6
S–O(4S)···O(1P)	119.2		

Pa) of sulphur dioxide. This was weighed immediately to give the starting mass for the uptake. More sulphur dioxide was added on a daily basis until constant mass was obtained. The total mass of sulphur dioxide added was converted into moles and the ratio $Mn:SO_2$ calculated.

(*ii*) *Toluene slurries.* In a procedure analogous to that used for the preparation of the complexes, complex (*ca.* 0.5 g) was placed in a side-arm flask against a stream of argon. Dry toluene (*ca.* 50 cm^3) was added to the flask which was then flushed several times with dry argon to guard against dioxygen contamination. The flask was then evacuated and the vacuum removed with sulphur dioxide. The contents of the flask were saturated with sulphur dioxide, the flask sealed, and the mixture left to stir for *ca.* 7 d. The product was isolated by standard Schlenk techniques.

Elemental analyses were performed by the U.M.I.S.T. microanalytical service. I.r. spectra were recorded as Nujol mulls between KBr plates in the range 4 000—400 cm^{-1} on a Perkin-Elmer 598 spectrophotometer, e.s.r. spectra on a Varian E9 spectrometer, and f.a.b. mass spectra on a VG Analytical MS9 spectrometer using Xe atoms at 8 keV (eV $\approx 1.6 \times 10^{-19}$J). Magnetic susceptibility measurements were determined using the Faraday method. The apparatus was calibrated with $HgCo(NCS)_4$ and diamagnetic corrections were calculated from Pascal's constants.[35] Thermogravimetric analyses were carried out on a Stanton Redcroft TG 750 thermobalance.

X-*Ray Structure Determinations.*—All crystallographic measurements were made at ambient temperature on an Enraf-Nonius CAD4 diffractometer, operating in the ω–2θ scan mode with graphite-monochromatised Mo-K_α radiation ($\lambda = 0.710\,69$ Å). Structure calculations were performed using the SHELX 76 program.[36]

Crystal data for $[\{Mn(OPPh_3)_2(NCS)(\mu\text{-}NCS)\}_2]$. $C_{76}H_{60}Mn_2N_4O_4P_4S_4$, $M = 1\,454$, monoclinic, space group $P2_1/c$, $a = 11.963(6)$, $b = 27.603(8)$, $c = 10.956(5)$ Å, $\beta = 101.02(4)°$, $U = 3\,551(3)$ Å^3, $Z = 2$, $D_c = 1.361$ Mg m^{-3}, μ(Mo-K_α) = 0.56 mm^{-1}, $F(000) = 1\,492$.

5 150 Reflections ($0 < \theta < 25°$) were measured of which 1 927 were independent [$F_o > 3\sigma(F_o)$]. Direct methods were employed to solve the structure followed by blocked-matrix least-squares refinement. All non-hydrogen atoms were treated anisotropically and the hydrogen atoms were constrained to chemically reasonable positions with a common isotropic vibrational parameter [0.11(1) Å^2]. A final R of 0.072 was attained and $R' = 0.061$; $w = 1.4807/[\sigma^2(F_o) + 0.000\,548F_o^2]$.

Crystal data for $[Mn(OPPh_3)_4(NCS)_2]$. $C_{74}H_{60}MnN_2O_4P_4S_2$, $M = 1\,283$, triclinic, space group $P\bar{1}$, $a = 12.940(3)$, $b = 12.852(3)$, $c = 13.977(2)$ Å, $\alpha = 57.87(2)$, $\beta = 57.47(2)$, $\gamma = 65.57(2)°$, $U = 1\,633(1)$ Å^3, $Z = 1$, $D_c = 1.31$ Mg m^{-3}, μ(Mo-K_α) = 0.37 mm^{-1}, $F(000) = 665$.

5 829 Reflections ($0 < \theta < 25°$) were measured of which 2 792 were independent [$F_o > 4\sigma(F_o)$]. The structure was solved by normal heavy-atom techniques followed by blocked-matrix least-squares refinement. All the phenyl rings displayed torsional disorder about the P–C bonds. Three phenyls showed additional disorder related to variation in the C–P–C angles. The thiocyanate ligand was also disordered with the sulphur being distributed over four sites. A final R of 0.097 was attained and $R' = 0.104$; $w = 3.349/[\sigma^2(F_o) + 0.0007F_o^2]$.

Crystal data for $(PPh_3O)(PPh_3OH)(HSO_4)$. $C_{36}H_{32}O_6P_2S$, $M = 654.7$, orthorhombic, space group $Fdd2$, $a = 32.606(5)$, $b = 20.079(3)$, $c = 10.019(3)$ Å, $U = 6\,559.4$ Å^3, $Z = 8$, $D_c = 1.261$ g cm^{-3}.

3 203 Reflections were measured giving 1 008 independent reflections with $F_o^2 > 3\sigma(F_o^2)$. The structure was solved by the heavy-atom method, and full-matrix least-squares refinement with all non-hydrogen atoms anisotropic gave a final $R = 0.045$ ($R' = 0.042$) $w = 1.1293/[\sigma^2(F_o) + 0.001\,308F_o^2]$.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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