Manganese(II) Complexes Containing Polystyryl Diphenylphosphine Oxide as Ligand and their Reactivity with Sulfur Dioxide†

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The ligand polystyryl diphenylphosphine oxide (L) and several manganese(II) complexes with empirical formulae $MnL_mX_2 \cdot nH_2O$ and $MnL_mSO_4 \cdot 3H_2O$ ($m = 2, 3; n = 1-4; X = Cl, Br, I, NCS, NO_3$) have been synthesised and characterised. The absorption of sulfur dioxide by these complexes has been examined in the solid state, at room temperature and in the 230–30 °C temperature range, and also in SO_2-saturated toluene suspensions. After the interaction between sulfur dioxide and metallic complexes some air-stable SO_2 adducts of accurate formulae could be isolated. Nitrate complexes appear to exhibit distinct behaviour due to an additional reaction with SO_2; viz. nitrate ions appear to be replaced by sulfate ions in the SO_2 adducts. Sulfur dioxide desorption was studied for SO_2 adducts by heating at 160 °C under reduced pressure for 1 h or at 300 °C for about 15 min at atmospheric pressure.

There is considerable interest in the binding of sulfur dioxide to transition metal complexes, not only because of its academic interest[1–3] due to its versatility as a ligand, but also because of its role in environmental pollution as a prime cause of insidious acid rain.

The aim of this study has been to develop an effective method for the removal of SO_2 from industrial gas streams, preferably by employing reusable metallic adducts. A fundamental requirement of these adducts must be their operation at elevated temperatures (typically 100–300 °C), to give gases sufficient velocity to rise beyond the chimney stack and disperse effectively. Once the adduct is saturated under these operating temperatures, the SO_2 adduct obtained would be isolated from the gas flow and the SO_2 released. The adduct would then be re-used, whilst the sulfur dioxide collected could be transferred to a process which requires SO_2. Furthermore, the adduct needs to be highly active, rapidly absorbing/desorbing SO_2. Clearly a complex supported on an inert material would be required to give a large surface area through which gas can flow. As well as increasing the efficiency of the complex, such a support

would also make the overall material easy to handle whilst not playing any part in the absorption process.

We are currently investigating the binding of SO_2 by a wide range of phosphine oxide manganese(II) complexes.[4–8] As a continuation of our studies we have further extended our investigations to examine manganese(II) complexes containing a polymeric phosphine oxide ligand.

In this paper we report the synthesis and characterisation of bis and tris complexes of polystyryl diphenylphosphine oxide, L (Scheme 1) with manganese(II) halides, isothiocyanates, nitrates and sulfates, and the study of their sulfur dioxide absorption in the solid state at room temperature and from 230 to 30 °C, and as a toluene slurry. High-temperature sulfur dioxide desorption of these complexes has also been studied.

Experimental

Preparation of the polystyryl diphenylphosphine oxide. The polyphosphine oxide ligand (L) was prepared by standard Grignard techniques according to Scheme 1. A THF solution (1 L) of 4-bromostyrene (I) (100 g, 0.55 mol) was slowly dropped on a THF slurry (1 L) of magnesium powder (14.7 g, 0.60 mol) under an inert

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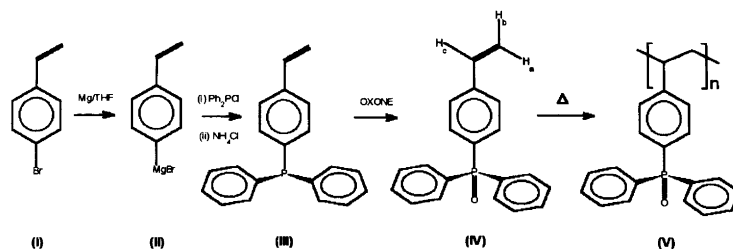
Scheme 1. Synthetic route used to prepare the polystyryl diphenylphosphine oxide.

atmosphere. A THF solution (1 L) of Ph_2PCl (121.3 g, 0.55 mol) was added to the Grignard reagent, p-CH_2= CHC_6H_4MgBr (**II**), at low temperature dropwise. After hydrolysis with NH_4Cl (29.4 g, 0.55 mol), at room temperature, the top organic layer was separated and the solvent removed *in vacuo*. The resultant brown oily product was then dissolved in warm ethanol and placed in a freezer for ca. 24 h. The white crystalline solid (**III**) was then isolated, washed and dried. Yield 103 g (65%), m.p. = 80 °C. The phosphine (25 g, 0.087 mol) dissolved in dichloroethane (500 cm^3), was then oxidized with a saturated aqueous solution of oxone ($2KHSO_5$ · $KHSO_4$·K_2SO_4: 106.7 g, 0.17 mol) and a small quantity of methanol. The mixture was left to stir for ca. 24 h; then a large excess of water was added and two layers separated. The lower organic layer was retained and the solvent removed *in vacuo*; the sticky solid remaining was stirred with cyclohexane and then filtered and washed, to yield a white air-stable solid powder (**IV**). Yield 18.5 g (70%). $C_{20}H_{17}PO$: [Found (Calc.): C 78.6(78.9); H 5.6(5.6); P 10.0(10.2)%]. IR [v(P–O): 1188 cm^{-1}]. ^1H NMR in $CDCl_3$ [H_{arom} 7.43–7.70 ppm; H_c 6.75 ppm(m); H_b 5.85 ppm(d); H_a 5.37 ppm(d)]. Mass spectrum (FAB) [305 (100%); 609 (50%); 913 (5%)].

The polystyryl diphenylphosphine oxide (**V**) was then obtained by heating a chloroformic solution of the monomeric phosphine oxide at ca. 100 °C, to yield an air- and thermally stable glassy solid of the polymeric material. m.p. > 400 °C. $(C_{20}H_{17}POH_2O)_n$; Elementary anal. [Found (Calc.): C 74.8(74.5); H 5.5(5.9); P 9.2(9.6)%]. IR [v(P–O): 1173 cm^{-1}]. ^1H NMR in $CDCl_3$ [H_{arom} 7.48–7.75 ppm; H_c 6.74 ppm(m); H_b 5.85 ppm(d); H_a 5.37 ppm(d)]. Mass spectrum (FAB) [305 (100%), 609 (10%)].

Preparation of complexes. The syntheses were performed using the metallic salts: $MnCl_2$, $MnBr_2$, MnI_2, $Mn(NCS)_2$, $MnSO_4$·H_2O and $Mn(NO_3)_2$·$6H_2O$ and chloroform, as solvent, without further purification. The final products are air and thermally stable. The syntheses of MnL_2SO_4·$3H_2O$ and MnL_3SO_4·$3H_2O$ could be considered as typical.

MnL_2SO_4·$3H_2O$. A chloroform slurry (100 cm^3) of the polymeric ligand $(C_{20}H_{17}PO$·$H_2O)_n$ (0.7060 g, 2.19 mmol) and manganese sulfate monohydrate (0.1962 g, 1.16 mmol) was left to stir in a round-bottomed flask

for ca. 7 d. After this it was filtered to yield a gelatinous solid, washed with ethanol (3 × 10 cm^3) and petroleum ether 40–60 °C (3 × 10 cm^3) and dried. The solid appeared as a plastic material and was ground.

MnL_3SO_4·$3H_2O$. A chloroform slurry (100 cm^3) of the polymeric ligand $(C_{20}H_{17}PO$·$H_2O)_n$ (1.3800 g, 4.29 mmol) and manganese sulfate monohydrate (0.1918 g, 1.14 mmol) was stirred for ca. 7 d. After filtration the residue was washed with chloroform, ethanol and petroleum ether 40–60 °C (3 × 3 × 10 cm^3). In all cases the reaction of manganese salts with L in a 1:4 molecular ratio yielded metallic precursors of the type MnL_2X_2·nH_2O (X = Cl, Br, I, NCS, NO_3; n = 1–4).

Reactions with sulfur dioxide.

(i) Solid state at room temperature. Exposure to sulfur dioxide was carried out by observing the increase in mass of a sample (0.05–0.30 g) of metallic precursor contained in a small Rotaflo tube. The vessel was initially charged with the complex and filled with an argon atmosphere. This was then replaced with sulfur dioxide to a pressure of 1 atm. Further sulfur dioxide was added over several days until a constant mass was achieved. Full details of this procedure have been previously published.[9]

(ii) Solid state in 230–30 °C temperature range. Thermogravimetrical analyses were performed using a CAHN Instruments TG131 apparatus, the gas flow being maintained at 50 cm^3 min^{-1} and the relative proportions of SO_2 and nitrogen being controlled with Rosemount mass/flow meters. The uptake of SO_2, in the range 230–30 °C, was monitored for samples (0.04–0.08 g) using a series of temperature/partial pressure programmes.

(iii) Toluene slurries. Slurries were prepared using dry distilled toluene (Na, benzophenone) performed in a pre-dried round-bottomed flask fitted with a side-arm and ground-glass tap. Manganese precursors (0.05–0.30 g) were added to the flask against a flow of argon. The flask was then evacuated, flame-dried and refilled with argon and freshly distilled toluene (100 cm^3). The flask was then evacuated and the vacuum let down with sulfur dioxide. Further sulfur dioxide was added until the solvent was saturated and the pressure within the flask reached 1 atm. The flask was then sealed and the contents stirred for ca. 7 d, after which the products

were isolated by Schlenk techniques and dried in a stream of argon.

(iv)   High-temperature SO₂ desorption. Sulfur dioxide desorption studies were performed by heating the SO_2 adducts in a small rotaflo tube at 160 °C and reduced pressure for about 1 h, or at 300 °C at atmospheric pressure for about 15 min. Then the resultant complexes were studied by elemental analyses and infrared spectroscopy.

Elemental analyses were performed by the USC and UMIST Microanalytical Services. Infrared spectra were obtained on KBr pellets or as Nujol mulls and on KBr plates or polyethylene, respectively, using a Nicolet PC5 FT-IR spectrophotometer in the ranges 2100–400 and 500–100 cm^{-1}, respectively. Magnetic moments were measured at room temperature using an Oxford Instruments Faraday balance with a 5 in. (0.1016 m) Newport N100 electromagnet, and corrected for diamagnetism using Pascal's constants. NMR spectra were recorded as $CDCl_3$ solution for the monomeric phosphine oxide using a Bruker WP80 spectrometer. Mass spectra were recorded in a MNBA matrix using a Kratos MS-50 spectrometer controlled by a DS90 data system.

Results and discussion

The neutral ligand polystyryl diphenylphosphine oxide (L)[10] can be considered as a polymer of $OPPh_3$ supported on a polyvinyl matrix. Whereas its monomer is rather soluble in most organic solvents, the polymer is best solvated by chlorinated solvents to form gelatinous slurries. The v(P–O) band of the ligand (1173 cm^{-1}) is slightly lower than in its monomer (1188 cm^{-1}), or in $OPPh_3$ (1195 cm^{-1}).[11]

Manganese(II) complexes. The complexes were synthesised by slurrying the manganese(II) salts with stoichiometric ratios (1:2 and 1:4) of ligand in chloroform.

The manganese(II) salts are virtually insoluble in that solvent but their complexes form gelatinous jelly slurries, and as a result can be isolated by filtration. Possible excesses of salts and ligand are eliminated by washing with ethanol and chloroform, respectively. The complexes obtained are of the type $MnL_2X_2 \cdot nH_2O$ and $MnL_mSO_4 \cdot 3H_2O$ [X=Cl, Br, I, SCN, NO₃; m=2, 3; n=1–4]. The fact that formation of the tetrakis complexes of this polymeric ligand does not occur, when with same salts and similar non-polymeric ligands such complexes are formed,[12] is probably due to the high steric hindrance of the polymeric structure of the ligand. The complexes are air stable and show a high thermal stability, with melting points above 300 °C; their formulation is confirmed by the elemental analysis, magnetic susceptibility measurents and infrared spectroscopy, shown in Table 1.

The low solubility of these complexes and the formation of gelatinous slurries, a predictable result due to the nature of the ligand, prevent their study in solution and subsequent structure determination by single-crystal X-ray diffraction studies. Instead, physical characterisation and analogies with other structurally well characterised triphenyl phosphine oxide complexes,[9,13–15] have been drawn to postulate possible structures for the complexes reported here.

Studies on the magnetic properties of the complexes do not give much structural information. Some representative magnetic moments are shown in Table 1. It is clear that only their combination with infrared spectroscopy would provide a reliable structural diagnosis. Room-temperature magnetic moments are close to those expected for d^5 high-spin manganese(II). Some complexes, such as the two nitrates and the tris(ligand) bromide, exhibit a slightly lower than the expected spin-only value of 5.9 MB. These reduced values seem not be caused by antiferromagnetic superexchange through bridges, because infrared spectroscopy is consistent with the absence of bromide or nitrate bridges.

Table 1. Elemental analyses and some significative physical properties of the metallic precursors.

Metallic precursor	Analysis (%)^a				Colour	μ^b	v(PO)^c
	C	H	N	S/X			
MnL₂Cl₂·3H₂O	61.4(61.1)	4.6(5.1)		9.8(9.0)	White	6.0	1155
MnL₃Cl₂·3H₂O	66.4(66.1)	4.8(4.2)		7.2(6.5)	White	5.9	1155
MnL₂Br₂·2H₂O	56.4(55.9)	4.1(4.4)		18.7(18.6)	Pale yellow	5.9	1155
MnL₃Br₂·4H₂O	60.4(60.1)	4.6(4.9)		12.9(13.3)	White	5.6	1160*
MnL₂I₂·H₂O	51.1(51.3)	3.9(3.9)		26.7(27.2)	Brown	5.8	1160*
MnL₃I₂·H₂O	59.1(58.1)	4.1(4.3)		20.2(20.5)	Brown	5.9	1162*
MnL₂(NCS)₂·2H₂O	61.7(61.8)	4.8(4.7)	3.3(3.3)	7.7(7.9)	White	6.0	1155
MnL₃(NCS)₂·3H₂O	65.6(65.4)	5.1(5.0)	2.3(2.5)	5.5(5.6)	White	6.2	1157
MnL₂(NO₃)₂·H₂O	60.3(59.6)	4.1(4.5)	2.5(3.5)		Pale grey	5.7	1162*
MnL₃(NO₃)₂·2H₂O	64.2(63.9)	4.6(4.9)	2.7(2.5)		White	5.8	1163*
MnL₂SO₄·3H₂O	58.1(57.8)	5.3(4.8)		4.2(3.9)	White	6.2	1161
MnL₃SO₄·3H₂O	64.2(64.5)	5.7(5.1)		2.6(2.9)	White	6.0	1161

^{a} Calculated values in parentheses; ^{b} In BM; ^{c} v(PO) in free ligand: 1173 cm^{-1}. All the spectra has been performed in Nujol, excluding those with asterisk, which have been made in KBr pellets. The range 500–100 cm^{-1} has been performed in Nujol with polyethylene windows.

The infrared spectra of all the complexes show a negative shift $(10-20 \text{ cm}^{-1})$ in the $\nu(\text{P}-\text{O})$ stretching frequency (Table 1). These shifts reflect a decrease in P–O bond order. Coordination through the phosphoryl oxygen of the ligand causes a net decrease in the back donation from oxygen $(p\pi-d\pi)$ and causes a net decrease in the P–O bond order. Broad IR bands at 3500–3300 cm^{-1}, attributable to H_2O molecules, can be observed in all the complexes. The *isothiocyanate* complexes exhibit strong bands in the region 2050–2060 cm^{-1}, which, according to Norbury,[12] suggests that these complexes contain only terminal *N*-bonded NCS and Mn–NCS linkage, according with a pseudotetrahedral environment for the metal in $\text{MnL}_2(\text{NCS})_2 \cdot 2\text{H}_2\text{O}$ and five-coordination in $\text{MnL}_3(\text{NCS})_2 \cdot 3\text{H}_2\text{O}$, as occurs in $\text{Mn}(\text{OPPh}_3)_3(\text{NCS})_2$.[9] The bis (ligand) complexes of *halides* are probably pseudotetrahedral species, similar to those of the corresponding $\text{Mn}(\text{OPPh}_3)_2\text{X}_2$ (X = Cl, Br or I) complexes.[14,15] The tris(ligand) complexes could be five-coordinated, like other manganese pseudohalide complexes with triphenylphosphine oxide and a well known structure.[9] Terminal stretching Mn–Cl and Mn–Br bands usually appear at ca. 300 and 225 cm^{-1}, respectively, but unfortunately an Mn–O band and ligand band, both very intense, are present in all the adducts in the same region. Thus it was possible to observe a new band at 173 cm^{-1} assignable to the Mn–I vibration for the iodide derivatives. The infrared spectra of the *nitrate* complexes show bands at ca. 1304 and 829 cm^{-1} assignable to a coordinated monodentate nitrate group;[16,17] this suggests pseudotetrahedral geometry for the bis (ligand) complexes and five-coordination for the tris (ligand) complexes, similar to the halides and isothiocyanates. In the infrared spectra of the *sulfate* complexes the $\nu(\text{P}-\text{O})$ band at ca. 1160 cm^{-1} can be observed broadened and connected to a sulfate absorption band in that region (ca. 1170 cm^{-1}), so this and the other bands at ca. 660 and 610 cm^{-1} are typical of chelating behaviour.[18] This suggests pseudotetrahedral geometry for the bis(ligand) complexes and five-coordination for the tris(ligand) complexes.

Reactivity towards sulfur dioxide. This reactivity was studied by absorption of SO_2 by the metallic precursors and by desorption of the SO_2 adducts formed.

The sulfur dioxide absorption has been examined in the solid state, at room temperature and in the 230–30 °C temperature range by thermogravimetrical analyses. An absorption study was also performed in suspension, as SO_2-saturated toluene slurries of the initial complexes.

The sulfur dioxide desorption was studied for SO_2 adducts by heating at 160 °C under reduced pressure for 1 h or at 300 °C at atmospheric pressure for about 15 min.

Structural characterisation of these new SO_2 adducts was based on elemental analyses, comparisons with other well characterised complexes, and infrared and desorption studies. The infrared spectra of SO_2 adducts showed little or no shift in the phosphine oxide bands.

Nevertheless, significative modifications in the Mn–X bands were noticed when sulfur dioxide was inserted. No changes were observed in the isothiocyanate and sulfate bands.

Mingos[19] indicates that in general, if the M–SO_2 geometry is bent or in S-bridged SO_2 complexes, the S=O stretching frequencies occur near to 1200 and 1050 cm^{-1}, while if the M–SO_2 geometry is planar or in S,O-bridged SO_2 complexes[1] these frequencies occur near 1300 and 1100 cm^{-1}. Ligand-bound SO_2 coordination[1,20] is characterised generally by occurrence of $\nu(\text{SO})$ in the ranges 1325–1210 and 1145–1060 cm^{-1}. Unfortunately, in several cases bands attributable to bound SO_2 cannot be observed in these ranges. The overlap of the wide $\nu(\text{SO})$ and $\nu(\text{PO})$ ranges is presumably the cause of this. In the remaining cases IR studies suggest the presence of five-coordination modes, some of those in the same molecule:

Ligand bound. Sulfur dioxide could be bound by sulfur to oxygen of the O–P bond of the polymeric ligand, as illustrated in Fig. 1 for $\text{MnL}_2(\text{SO}_2)_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$. This bonding mode, described for $\text{Cu}(\text{PPh}_2\text{Me})_3(\text{SPh})(\text{SO}_2)$,[21] presents two characteristic vibration bands in the ranges 1325–1210 and 1145–1060 cm^{-1}. Another indicative feature of this bonding mode could be the decrease in the intensity of the $\nu(\text{P}-\text{O})$ band observed the IR spectra of the SO_2 adducts, probably due to the linkage of sulfur dioxide to the P–O bond. A subsequent increase in the intensity of this band is observed after SO_2 desorption.

Unfortunately, it was not possible to observe the band assignable to ligand bound SO_2 in the 1325–1210 cm^{-1} range. However, in most of the SO_2 adducts with this bonding mode a new band near to 1080 cm^{-1}, presumably due to ligand-bound sulfur dioxide, is present.
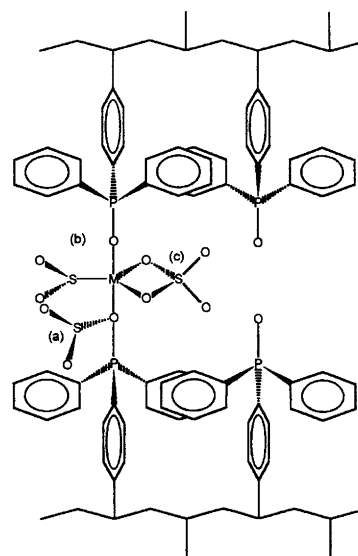

Fig. 1. A possible structure for $\text{MnL}_2(\text{SO}_2)_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ with: (a) ligand-bound, (b) η^1-S planar and (c) as sulfate bonding modes proposed.

Generally, characteristic behaviour of ligand-bound sulfur dioxide coordination is the readily reversible SO₂ ligation. Thus, desorption studies in combination with IR studies were used in this work to assign this binding mode, especially in the cases where it was not possible to observe bands associated with sulfur dioxide, $MnL_3(SO_2)Br_2$, $ML_2(SO_2)SO_4 \cdot H_2O$ and $ML_3(SO_2)SO_4 \cdot 2H_2O$. Table 2 shows the analytical data of adducts found after the SO₂ desorption study. According to these results, at least 1 mol of sulfur dioxide present in $MnL_3(SO_2)Br_2$, $MnL_2(SO_2)_2SO_4 \cdot 4H_2O$, $MnL_2(SO_2)SO_4 \cdot H_2O$, $MnL_3(SO_2)SO_4 \cdot 2H_2O$ and $MnL_2(SO_2)_2SO_4 \cdot 6H_2O$ could be bound to the polymeric ligand.

η^1-S planar. In these cases SO₂ is S-coordinated to the manganese centre, as Fig. 1 shows. Kubas[1,19] indicates that in general the η^1-S planar binding mode, as seen in $Co(NO)(SO_2)(PPh_3)_2$,[22] is characterised by irreversible sulfur dioxide ligation and the presence of $v(SO_2)$ in the 1300–1190 and 1140–1045 cm⁻¹ ranges. Obviously, these ranges are practically the same as those described for ligand-bound sulfur dioxide. Consequently, if SO₂ adducts present both binding modes these bands could be partially or totally obscured. Some SO₂ adducts, $MnL_2(SO_2)_2SO_4 \cdot 4H_2O$ and $MnL_3(SO_2)_2SO_4 \cdot 6H_2O$, exhibit new bands near 1055 cm⁻¹. In addition, after SO₂ desorption, the IR spectrum of $MnL_2(SO_2)SO_4 \cdot 2H_2O$ (Table 2) shows the same band at 1057 cm⁻¹ found before the desorption in $MnL_2(SO_2)_2SO_4 \cdot 4H_2O$. These reasons allow us to propose a η^1-S planar bonding mode for 1 mol of SO₂ in $MnL_2(SO_2)_2SO_4 \cdot 4H_2O$, $MnL_3(SO_2)_2SO_4 \cdot 6H_2O$, $MnL_2(SO_2)_2SO_4 \cdot 6H_2O$, $MnL(SO_2)SO_4 \cdot 2H_2O$ and $MnL_3(SO_2)SO_4 \cdot H_2O$.

As sulfate. Chelating sulfates exhibit some bands near to 1170, 880, 660 and 610 cm⁻¹. $MnL_2(SO_2)_2SO_4 \cdot 4H_2O$ could be a good example to illustrate this coordination mode. The bidentate sulfate form, as described[23] for $Ir(OMe)(CO)(PPh_3)_2(SO_4)$, can usually be characterised[18] by three IR bands at ca. 1296, 1172 and 880 cm⁻¹ and other bands near 856, 662, 610 and 549 cm⁻¹, but unfortunately some of these bands are obscured by polymeric ligand bands. Thus, only some of

these bands around 1170 [broadened by $v(PO)$], 880, 660 and 610 cm⁻¹ can be observed for the sulfate complexes.

S-bridge. This bonding mode is characterised by the presence of SO₂ bands in a similar region of the spectrum as those observed for adducts with an η^1-S planar coordination mode. This bonding mode could be present in $MnL_3(SO_2)_{1.5}Br_2 \cdot 3H_2O$ and $MnL_2(SO_2)_{0.5}SO_4 \cdot 3H_2O$. Recently Kubas[1] indicated that, generally, the S-bridge bonding mode, as described[24] for $[CpFe(CO)]_2$-$(CO)(SO_2)$, is characterised by the presence of stretching frequencies at 1240–1135 and 1085–975 cm⁻¹. The ligand absorptions in the 1160–1060 cm⁻¹ range consequently could be an obstacle to observing these bands. The SO₂ adducts in which an S-bridge is postulated present in addition coordinated sulfate or insertion of SO₂ in the M–X bond. Thus it was not possible to observe new bands near those regions.

Insertion. The first crystallographically characterised example of O-bonded sulfur dioxide in a transition-metal complex was $Mn(OPPh_3)_4(SO_2)_2I_2$.[25] Perhaps the most important facts accompaning this coordination mode could be the absence of Mn–X bands in the SO₂ adducts with 2 mol of SO₂ per mol of adduct, or the decreased intensity when the ratio is 1:1 (SO₂:adduct) and the presence of new bands at 1279 and 1260 cm⁻¹. SO₂ desorption studies could be a way of recognising this bonding mode because the new group M–OSO–X could probably allow the halide to be readily removed. In this way, analytical data listed in Table 2 seem to indicate the loss of one molecule of HX and another of SO₂ for $MnL_3(SO_2)_{1.5}Br_2 \cdot H_2O$, $MnL_2(SO_2)I_2 \cdot H_2O$ and $MnL_2(SO_2)_2I_2 \cdot H_2O$. Furthermore, the IR spectra of these adducts between 100–500 cm⁻¹ show a decrease in the intensity of the band corresponding to the Mn–X vibration or its disappearance (Fig. 2), which seems to confirm the insertion of the SO₂ into the metal–halide bond. This fact seems to indicate that sulfur dioxide insertion has ocurred in these adducts.

The desorption study of the complex $MnL_3(SO_2)_2$-$I_2 \cdot H_2O$ shows the loss of one molecule of sulfur

Table 2. Elemental analysis and some physical properties of the found complexes after SO₂ desorption studies.

| SO₂ adducts | Found complexes | Analysis(%)[a] | | | Colour | $v(PO)$[b] | $v(SO_2)$ |
		C	H	S			
$MnL_3(SO_2)Br_2$	MnL_3Br_2	63.6(63.7)	4.8(4.5)		White	1161	
$MnL_3(SO_2)_{1.5}Br_2 \cdot H_2O$	$MnL_3(SO_2)_{1.5}Br(OH)$	62.8(62.1)	4.7(4.5)	3.3(4.1)	Yellow	1170	
$MnL_2(SO_2)I_2 \cdot H_2O$	$MnL_2(SO_2)I(OH)$	55.7(55.0)	4.5(4.2)	3.8(3.7)	Yellow	1165	
$MnL_3(SO_2)_2I_2 \cdot H_2O$	$MnL_3(SO_2)I(OH)$	60.6(61.1)	4.4(4.7)	2.6(2.7)	Yellow	1164	
$MnL_2(SO_2)_2I_2 \cdot H_2O$	$MnL_2SO_4 \cdot H_2O$	61.6(61.8)	4.5(4.5)	4.2(4.1)	Yellow	1161	
$MnL_2(SO_2)_2SO_4 \cdot H_2O$	$MnL_2(SO_2)SO_4 \cdot 2H_2O$	55.0(55.7)	4.3(4.4)	7.3(7.4)	Yellow	1167	1057
$MnL_3(SO_2)_2SO_4 \cdot 6H_2O$	$MnL_3(SO_2)_2SO_4 \cdot 6H_2O$	55.7(55.4)	4.3(4.6)	6.7(7.4)	White	1163	1059
$MnL_3(SO_2)SO_4 \cdot H_2O$	$MnL_3(SO_2)SO_4 \cdot H_2O$	62.7(62.9)	4.9(4.6)	4.7(5.6)	Yellow	1168	

[a] Calculated values in parentheses. [b] $v(PO)$ in free ligand: 1173 cm⁻¹ in Nujol. All spectra performed in KBr pellets.
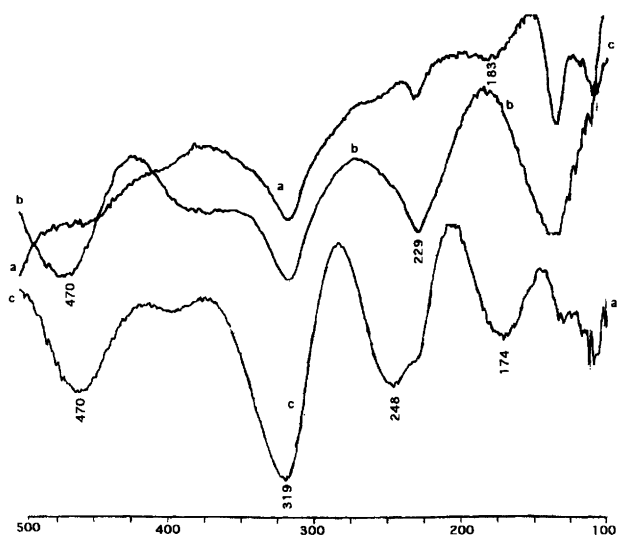
Fig. 2. Comparative IR spectra for (a) $MnL_3I_2 \cdot H_2O$, (b) $MnL_3(SO_2)_2I_2 \cdot H_2O$ and (c) $MnL_2(SO_2)I_2 \cdot H_2O$.

dioxide when the complex is heated to 160 °C at reduced pressure for 7 h.

Absorption study in the solid state at room temperature. The aim of this study was to gain a more extensive knowledge of the sulfur dioxide reactivity and if the adducts could be active at high temperature. Analytical data and some significant infrared bands of the resultant adducts formed after interaction of the metallic precursors with SO_2 are listed in Table 3.

No chloride or isothiocyanate SO_2 adducts were obtained after sulfur dioxide interaction with initial complexes in contrast with previous findings. Particularly interesting is the behaviour of iodide and nitrate complexes, which absorb 2 and 3 mol of sulfur dioxide per mol of metallic precursor, respectively.

Thus, iodide and nitrate complexes appear to represent good scrubbing systems for SO_2 emissions. The next step will be to check these complexes attentively at high temperature.

A comparative study of IR spectra of $MnL_2(SO_2)I_2 \cdot H_2O$ and $MnL_3(SO_2)_2I_2$ with $MnL_3I_2 \cdot H_2O$ (Fig. 2) shows a very important aspect of the SO_2 bonding mode in both adducts. It is clear that the absence of the $v(Mn-I)$ band in $MnL_3(SO_2)_2I_2$ must be associated with SO_2 insertion in the Mn–I bond to give Mn–OSO–I. In contrast, the decreased intensity of the $v(Mn-I)$ band at 173 cm^{-1} for $MnL_2(SO_2)I_2 \cdot H_2O$, if compared with the same band for the metallic precursor, seems to indicate the existence of one Mn–I bond in the new adduct.

On the other hand, the presence of some new bands ca. 1220, 1080 and 1060 cm^{-1} for $MnL_2(SO_2)_2SO_4 \cdot 4H_2O$ and $MnL_3(SO_2)_2SO_4 \cdot 6H_2O$, attributable to sulfur dioxide, suggests a ligand-bound and η^1-S planar coordination modes for the two compounds.

Reactivity study in the solid state in the 230–230 °C temperature range. The interaction of the free ligand and

the metallic precursors with sulfur dioxide were studied by TGA, monitored by short (4 h) and long (12 h) temperature–gas-flow programmes. Results are represented as curves of mass and temperature variation versus time. Analytical data of the adducts formed after TGA studies and some physical properties are shown in Table 4.

In the short programme, the compounds were first exposed at high temperature (250–200 °C) in a nitrogen stream for about 1 h until a constant mass was achieved. The compounds were exposed to a sulfur dioxide atmosphere for about 2.5 h, and a mass increase was observed in the 200–230 and 230–30 °C ranges. After this, the samples were exposed to a pure nitrogen stream at 30 °C for 30 min. A very small increase of mass can be observed in the free ligand exposed to the SO_2 atmosphere. No mass increase is observed at high temperatures (200–230 °C) for most of the complexes. However, the two nitrate complexes appear to take up significant amounts of SO_2.

The behaviour of the nitrate complexes towards sulfur dioxide is particularly interesting because, as has been shown in the absorption study in the solid state at room temperature (*vide supra*), sulfur dioxide is linked by the manganese complexes to form sulfate complexes.

Thus no evidence for the presence of nitrate ion appears in the infrared spectra of these SO_2 adducts. The bidentate sulfate form can usually be characterised[18] by three IR bands near 1296, 1172 and 880 cm^{-1} and other four bands near 856, 662, 610 and 549 cm^{-1}, but unfortunately some of these bands are obscured by ligand bands. The band at 1170 cm^{-1} can be observed broadened to $v(PO)$.

The variation of mass vs. time and temperature for $MnL_3(NO_3)_2 \cdot 2H_2O$ during interaction with sulfur dioxide has been studied using the short programme. In the 100–130 °C temperature range the studied metallic precursors take up significant amounts of SO_2, but these are rapidly lost as soon as the sample is exposed to a pure nitrogen stream, probably because the sulfur dioxide was only physically adsorbed. This behaviour can be observed in all cases, but it is illustrated by the thermogram of $MnL_3I_2 \cdot H_2O$, which loses all the SO_2. Elemental analysis of this past TGA sample indicates no SO_2 is present (Table 4).

The absorption of sulfur dioxide at high temperature by $MnL_2(NO_3)_2 \cdot H_2O$ has been studied using the long programme. After the absorption of SO_2 it was possible to isolate $MnL_2(SO_2)SO_4 \cdot H_2O$ from the nitrate complex. One observes a rapid increase in weight at 210 °C. Then the compound continues increasing its mass, but more slowly, until the temperature decreases to 30 °C. When the compound is exposed to a nitrogen stream at this temperature, a small quantity of SO_2 is lost. This sulfur dioxide is probably physically adsorbed.

The study of the reactivity by TGA is particularly interesting because it could be useful to know the possible operating range of the complexes to reduce sulfur dioxide

Table 3. Elemental analyses and some physical properties of the found adducts after interaction of the metallic precursors with SO$_2$ in solid state at room temperature.

Metallic precursor	Found adduct	Analysis(%)^a				Colour	v(PO)^b	v(SO$_2$)	Proposed SO$_2$ coord. mode
		C	H	N	S				
MnL$_2$Cl$_2$·3H$_2$O	MnL$_2$Cl$_2$·3H$_2$O	61.3(61.1)	4.6(5.1)			Pale yellow	1153		
MnL$_2$Cl$_2$·3H$_2$O	MnL$_3$Cl$_2$·3H$_2$O	65.8(66.1)	4.3(4.2)			Pale yellow	1153		
MnL$_2$Br$_2$·2H$_2$O	MnL$_2$Br$_2$·2H$_2$O	55.0(55.9)	4.1(4.1)			Yellow	1153		
MnL$_3$Br$_2$·4H$_2$O	MnL$_3$(SO$_2$)Br$_2$	61.2(60.5)	4.2(4.3)		2.4(2.7)	Yellow	1160*		Ligand-bound
MnL$_2$I$_2$·H$_2$O	MnL$_2$(SO$_2$)I$_2$·H$_2$O	47.8(48.1)	3.7(3.6)		3.0(3.2)	Ochre	1164*		Insertion
MnL$_3$I$_2$·H$_2$O	MnL$_3$(SO$_2$)$_2$I$_2$	54.0(53.4)	4.2(3.8)		4.8(4.8)	Ochre	1159*		Insertion
MnL$_2$(NCS)$_2$·2H$_2$O	MnL$_2$(NCS)$_2$·2H$_2$O	61.5(61.8)	4.3(4.7)	4.2(3.3)	8.2(7.9)	White	1151		
MnL$_3$(NCS)$_2$·3H$_2$O	MnL$_3$(NCS)$_2$	68.2(68.7)	4.7(4.7)	2.3(2.6)	6.6(6.9)	Yellow	1159		
MnL$_2$(NO$_3$)$_2$·H$_2$O	MnL$_2$(SO$_2$)$_2$SO$_4$·4H$_2$O	50.1(50.1)	4.9(4.4)		9.8(10.0)	Beige	1162*	1081,1057	Ligand bound + η^1-S planar + sulfate
MnL$_3$(NO$_3$)$_2$·2H$_2$O	MnL$_3$(SO$_2$)$_2$SO$_4$·6H$_2$O	54.9(55.4)	4.7(4.6)		8.1(7.4)	White	1163*	1059	η^1-S planar + sulfate
MnL$_2$SO$_4$·3H$_2$O	MnL$_2$(SO$_2$)$_{0.5}$SO$_4$·3H$_2$O	55.4(55.6)	4.4(5.3)		5.4(5.6)	White	1161		S-bridge
MnL$_3$SO$_4$·3H$_2$O	MnL$_3$SO$_4$	68.8(67.7)	5.7(5.8)		2.9(3.0)	white	1162		

^{a} Calculated values in parentheses. ^{b} v(PO) in free ligand: 1173 cm^{-1}. All the spectra has been performed in Nujol excluding those marked by an asterisk which has been done in KBr pellets. The range 500–100 cm^{-1} has been performed in Nujol with polyethylene windows.

Table 4. Elemental analyses and some physical properties of the found adducts after interaction of the metallic precursors with SO$_2$ in 230–30 °C temperature range.

Metallic precursor	Found adduct	Analysis(%)^a				Colour	v(PO)^b	Proposed SO$_2$ coord. mode
		C	H	N	S			
MnL$_2$Cl$_2$·3H$_2$O	MnL$_2$Cl$_2$	65.2(65.4)	4.8(4.6)			White	1153	
MnL$_3$Cl$_2$·3H$_2$O	MnL$_3$Cl$_2$·H$_2$O	68.3(68.3)	5.5(5.0)			White	1153	
MnL$_2$Br$_2$·2H$_2$O	MnL$_2$Br$_2$	58.5(58.3)	4.7(4.1)			Yellow	1150	
MnL$_3$Br$_2$·4H$_2$O	MnL$_3$Br$_2$	65.0(63.9)	5.1(4.5)			White	1153	
MnL$_2$I$_2$·H$_2$O	MnL$_3$I$_2$	60.4(59.0)	5.1(4.2)			Ochre	1155	
MnL$_2$(NCS)$_2$·2H$_2$O	MnL$_2$(NCS)$_2$	64.7(64.7)	4.8(4.4)	3.4(3.6)	8.2(8.2)	White	1153	
MnL$_3$(NCS)$_2$·3H$_2$O	MnL$_3$(NCS)$_2$	68.0(68.7)	4.5(4.7)	2.6(2.6)	6.6(6.9)	White	1155	
MnL$_2$(NO$_3$)$_2$·H$_2$O	MnL$_2$(SO$_2$)SO$_4$·H$_2$O	57.0(57.1)	4.8(4.3)		7.3(7.6)	Pale grey	1155	Ligand bound + sulfate
MnL$_3$(NO$_3$)$_2$·2H$_2$O	MnL$_3$(SO$_2$)SO$_4$·2H$_2$O	61.7(61.9)	4.8(4.7)		5.5(5.5)	White	1155	Ligand bound + sulfate
MnL$_2$SO$_4$·H$_2$O	MnL$_2$SO$_4$·H$_2$O	61.2(61.8)	5.3(4.5)		4.5(4.1)	White	1160	
MnL$_3$SO$_4$·3H$_2$O	MnL$_3$SO$_4$	68.2(67.7)	5.4(5.8)		2.9(3.0)	Pale yellow	1164	

^{a} Calculated values in parentheses. ^{b} In Nujol; v(PO) in free ligand, 1173 cm^{-1}.

in the emissions from industrial chimneys. Consequently, only $MnL_2(NO_3)_2 \cdot H_2O$ and $MnL_3(NO_3)_2 \cdot 2H_2O$ could be useful at elevated temperatures (200–230 °C). It is obvious that this process could evolve another harmful gas i.e. NO_2, but it would not be difficult to convert[26] this into NO, and then into N_2 and H_2O or O_2.

The most interesting bonding modes of SO_2, in terms of utilising the binding in a scrubber system, are sulfate- and ligand-bound, because both can occur at high temperature and moreover, the latter mode is reversible.

Reactivity study in toluene slurries. Studies in toluene slurries were performed to compare the effect of slurrying the complexes with the results obtained in solid state at room and high temperature. Analytical data and some significant infrared bands are listed in Table 5.

It is clear that SO_2 adducts obtained by this method are practically the same as those obtained from the metallic precursors in solid-state reactions. Thus, chloride and isothiocyanate complexes do not absorb sulfur dioxide, whilst iodides and nitrates still represent good potential scrubbing systems. Nitrate complexes show the same behaviour previously observed in the solid state at room and high temperature. Moreover, $MnL_3(NO_3)_2 \cdot 2H_2O$, after the interaction with sulfur dioxide, lost two molecules of polymeric ligand, as observed for other similar complexes with O donors.[27]

Magnetic susceptibility measurements for some representative SO_2 adducts obtained from toluene slurries gave magnetic moments in the range 5.5–6.0 BM. The value for $MnL_3(SO_2)_2I_2 \cdot H_2O$ is slightly lower than the expected spin only value of 5.9 BM.

Sulfur dioxide desorption study. This study is a very important aid, in combination with infrared spectroscopy and the analogy with other well characterised complexes, in postulating the possible bonding mode of sulfur dioxide in SO_2 adducts. Kubas[19] indicates that in general, if the bonding mode is ligand bound, SO_2 may be lost by heating in a reversible process, in contrast with η^1-S planar coordination. However, when iodide adducts insert one molecule of SO_2 into each Mn–I bond, one of them may be lost in a semireversible global process.

Another very important aspect is that if the process is reversible the adducts would be re-used to reduce the SO_2 in gas flow with the consequent economic interest. In this way we are interested in understanding the behaviour of $MnL_2(SO_2)SO_4 \cdot H_2O$ and $MnL_3(SO_2)$-$SO_4 \cdot 2H_2O$, as they are the compounds that can bind sulfur dioxide at high temperature. Table 2 shows analytical data and some significant infrared bands for the complexes found after the SO_2 desorption study, indicating that the SO_2 is labilely linked in $MnL_2(SO_2)SO_4 \cdot H_2O$.

Sulfur dioxide desorption studies were performed at 160 °C *in vacuo* for the SO_2 adducts obtained from toluene slurries, from solid state at room temperature and at 300 °C and atmospheric pressure for

Table 5. Elemental analyses and some physical properties of the found adducts after interaction of the metallic precursor with SO_2 in toluene slurries.

Metallic precursor	Found Adduct	Analysis(%)^a C	H	N	S	Colour	μ^b	ν(SO2)^c	Proposed SO2 coord. mode
$MnL_2Cl_2 \cdot 3H_2O$	$MnL_2Cl_2 \cdot 2H_2O$	62.9(62.5)	5.0(5.0)		<0.3(0.0)	White			
$MnL_3Cl_2 \cdot 3H_2O$	$MnL_3Cl_2 \cdot 2H_2O$	66.8(67.0)	4.9(5.1)		<0.3(0.0)	White			
$MnL_3Br_2 \cdot 2H_2O$	MnL_3Br_2	59.2(58.3)	4.8(4.1)		<0.3(0.0)	Yellow			
$MnL_3Br_2 \cdot 4H_2O$	$MnL_3(SO_2)_{1.5}Br_2 \cdot H_2O$	58.3(58.0)	4.5(4.3)		4.2(3.9)	Yellow	5.8		Insertion+S-bridge
$MnL_2I_2 \cdot H_2O$	$MnL_2(SO_2)I_2 \cdot H_2O$	47.8(48.1)	3.5(3.6)		3.6(3.2)	Ochre	5.8		Insertion
$MnL_3I_2 \cdot H_2O$	$MnL_3(SO_2)_2I_2 \cdot H_2O$	52.8(52.6)	4.5(3.9)		4.9(4.7)	Ochre	5.5		Insertion
$MnL_2(NCS)_2 \cdot 2H_2O$	$MnL_2(NCS)_2$	64.3(64.7)	4.9(4.4)	3.0(3.6)	7.9(8.2)	White			
$MnL_3(NCS)_2 \cdot 3H_2O$	$MnL_3(NCS)_2 \cdot 4H_2O$	64.4(64.4)	5.1(5.1)	1.7(2.4)	5.7(5.5)	Grey			
$MnL_2(NO_3)_2 \cdot H_2O$	$MnL_2(SO_2)_2SO_4 \cdot 6H_2O$	47.9(48.2)	4.6(4.8)	0.0(0.0)	9.6(9.6)	Pale grey	6.1	1081	Ligand bound + η^1-S planar+sulfate
$MnL_3(NO_3)_2 \cdot 2H_2O$	$MnL(SO_2)SO_4 \cdot 2H_2O$	43.8(43.2)	4.6(3.9)	0.0(0.0)	11.4(11.5)	Beige	5.9		η^1-S planar +sulfate
$MnL_2SO_4 \cdot 3H_2O$	MnL_2SO_4	61.8(61.8)	5.5(4.4)		4.6(4.1)	White			
$MnL_3SO_4 \cdot 3H_2O$	$MnL_3(SO_2)SO_4 \cdot H_2O$	62.2(62.9)	5.2(4.6)		5.6(5.6)	Yellow	6.0		η^1-S planar

^a Calculated values in parentheses. ^b In BM. ^c ν(PO) in free ligand: 1173 cm^−1. All the spectra has been performed in Nujol excluding those marked by an asterisk which has been done in KBr pellets. The range 500–100 cm^−1 has been performed in Nujol with polyethylene windows.

MnL$_2$(SO$_2$)SO$_4$·H$_2$O which were obtained at high temperature. It was observed that the desorption process is very fast and associated with little change of colour.

Desorption studies for MnL$_3$(SO$_2$)Br$_2$ allow us to conclude that the reaction is reversible, a ligand bound in this adduct.

$$MnL_3Br_2 \underset{160\,°C,\,vacuum}{\overset{RT,\,SO_2}{\rightleftharpoons}} MnL_3(SO_2)Br_2$$
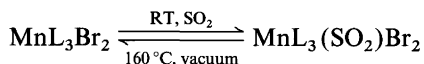
Moreover, MnL$_2$(SO$_2$)SO$_4$·H$_2$O and MnL$_2$(SO$_2$)$_2$-SO$_4$·4H$_2$O lose a molecule of sulfur dioxide in a reversible process when they are heated at 300 and 160 °C, respectively. This fact, and the presence of a band at 1081 cm^{-1} in the IR spectrum, for the latter complex, and its absence for the new adduct after desorption (Tables 2, 3 and 5) suggest a ligand-bound mode for one of the sulfur dioxide molecules present in these adducts. Finally, MnL$_2$(SO$_2$)$_2$SO$_4$·4H$_2$O and MnL$_3$(SO$_2$)-SO$_4$·H$_2$O could present a η^1-S planar binding mode for the sulfur dioxide because they do not lose at least one molecule of SO$_2$ when the desorption occurs.

The stoichiometry suggests for MnL$_3$(SO$_2$)$_{1.5}$Br$_2$·H$_2$O the presence of a S-bridge bonding mode. In addition, the behaviour of MnL$_3$(SO$_2$)$_{1.5}$Br$_2$·H$_2$O, MnL$_2$(SO$_2$)I$_2$·H$_2$O and MnL$_3$(SO$_2$)$_2$I$_2$·H$_2$O could be understood if an insertion bonding mode was assumed. This mode would explain the loss of an iodide, labilely bounded to the SO$_2$ adduct.

Conclusions

A comparative study of these results of absorption and desorption studies allows us to conclude the following:

The formation of SO$_2$ adducts occurs with slight changes in colour, but never with exchange from the solid to liquid state as we have observed in trialkylphosphine oxide complexes.[28]

The highest mass increases occur at room temperature, and consequently the M:SO$_2$ ratios are higher in the SO$_2$ adducts formed in studies at room temperature, via solid-state or toluene slurry reactions.

Previous work[29] allows us to conclude that the reactivity of the metallic complexes towards SO$_2$ is directly related to the metal, neutral and anionic ligands and experimental conditions. In this work we have studied the anionic ligand influence and suggest the following reactivity sequence:

$$NO_3^- > I^- > Br^- \approx SO_4^{2-} > Cl^- = SCN^-$$

The versatility of the sulfur dioxide ligand is demonstrated by the presence, in the same compound, of one, two or even three different bonding modes.

The most interesting bonding modes of SO$_2$, in view of its utility as a scrubber system for the adducts studied herein, are sulfate- and ligand-bound, because both can occur at high temperature, the latter being reversible.

Among the studied precursors, it seems that only nitrate complexes could be useful at high temperatures as scrubber systems of sulfur dioxide in industrial chimneys.

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