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Preparation, properties and reactions with sulfur dioxide in the solid state of complexes of the type $[Mn(Ph_2E(O)–Y–E(O)Ph_2)_2(H_2O)_2](ClO_4)_2$ (E = As, P; Y = C_2H_4, *cis*-C_2H_2). The formation of bis-sulfur dioxide complexes which contain both weakly bound and strongly bound sulfur dioxide

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Abstract

Hexacoordinate manganese(II) perchlorate complexes containing diphosphine dioxide, diarsine dioxide or a mixed phosphine oxide/arsine oxide ligand, $[Mn(ligand)_2(H_2O)_2](ClO_4)_2$, react in the solid state with sulfur dioxide to form the $[Mn(ligand)_2(H_2O)_2(SO_2)_2](ClO_4)_2$ adducts, as shown by weight increases. One sulfur dioxide molecule is readily lost on exposure to air, but the second is much more strongly held and is only lost on heating to 65–108 °C. Absorption isotherms have been obtained for the uptake of two molecules of sulfur dioxide by $[Mn(dpaeO_2)_2(H_2O)_2](ClO_4)_2$ and of one molecule of SO_2 by $[Mn(dpaeO_2)_2(H_2O)_2(SO_2)](ClO_4)_2$ ($dpaeO_2 = Ph_2P(O)CH_2CH_2As(O)Ph_2$).

Introduction

We are currently investigating the binding of sulfur dioxide by a wide range of manganese(II) complexes containing tertiary phosphine oxides and arsine oxides [1–5]. Their reaction with SO_2 is both ligand and halide dependent, and triphenylphosphine oxide complexes of MnI_2 and $Mn(NCS)_2$ are proving to be of particular interest. For example, $Mn(OPPh_3)_4I_2$ reacts with two moles of SO_2 to form the unique Mn–I insertion complex $[Mn(OPPh_3)_4\{OS(O)I\}_2]$, which has been crystallographically characterised [6]. This complex loses one SO_2 molecule when heated to 129 °C, but, when exposed to SO_2 again forms the bis-SO_2 adduct. This unusual reactivity towards SO_2 is further illustrated by the reaction of SO_2 with $Mn(OAsPh_3)_4I_2$ which displaces one $OAsPh_3$ to form $Mn(OAsPh_3)_3I_2(SO_2)$; heating the latter under vacuum produces PhAs–I–I, indicating that the coordinated SO_2 can induce a facile reduction of $OAsPh_3$ [2]. Furthermore, we have shown that Mn(II)- [1] and Fe(III)-bound [7] SO_2 can undergoe facile oxidation to sulfuric acid under ambient conditions. We have recently added diphosphine dioxide ligands to our study [8, 9] and obtained some intriguing results. To extend the scope of this work it was decided to explore the reaction of perchlorate complexes with SO_2, in order to investigate the role of a poor coordinating anion on the activity of the complex towards SO_2.

We thus report a series of new manganese(II) perchlorate complexes, $[MnL_2(H_2O)_2](ClO_4)$ when L has the general formula $Ph_2E(O)–Y–E(O)Ph_2$ (E = P or As; Y = C_2H_4 or *cis*-C_2H_2). Abbreviations used are: $dpeO_2$ where E = P, Y = C_2H_4; $vppO_2$ where E = P, Y = *cis*-C_2H_2; $daeO_2$ where E = As, Y = C_2H_4; $dpaeO_2$ where E = P and As, Y = C_2H_4; and $vpaO_2$ where E = As, Y = *cis*-C_2H_2. The reaction of sulfur dioxide with these material is also reported.

Results and discussion

The reaction of hydrated manganese(II) perchlorate (1.0 mol) with a slight excess of the appropriate ligand (2.2 mol) in freshly distilled toluene results in the formation of air stable compounds of general formula $[MnL_2(H_2O)_2](ClO_4)_2$:

$$Mn(ClO_4)_2\cdot 6H_2O + 2L \xrightarrow[\text{10 days}]{\text{toluene}} [MnL_2(H_2O)_2](ClO_4)_2 + 4H_2O$$

The presence of two water molecules in the isolated complexes is confirmed by elemental analysis and the

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presence of a broad band due to (OH) at 3430–3370 cm^{-1} in their IR spectra. The presence of water molecules is not uncommon in other metal perchlorate complexes and has also been observed in $[Co(dpeO_2)_2(H_2O)_2](ClO_4)_2$, $[Ni(dpeO_2)_2(H_2O)_2](ClO_4)_2$ [10] and $[Mn(OPPh_3)_4(ClO_4)(H_2O)](ClO_4)$ [11]. However, anhydrous complexes, for example, $[Cu(dpeO_2)_2](ClO_4)_2$ [10] have also been obtained.

Physical properties and elemental analyses are given in Table 1, and IR data is given in Table 2. The coordination of the ligands to the manganese(II) centre is confirmed by the decrease in (EO) compared with the free ligands. In the IR spectra of perchlorate complexes, unsplit absorptions at 1100 and 624 cm^{-1} are consistent with the presence of free uncoordinated perchlorate ions [12, 13]. However, it is recognised that IR alone is not a reliable criterion since anion coordination has been established for a number of compounds which do not show splitting of the anion absorptions [14–16]. Additional information about these complexes was therefore obtained by studying their molar conductivities. All were found to be 2:1 electrolytes in nitrobenzene [17] (see Table 1) which supports the ionic structure $[MnL_2(H_2O)_2](ClO_4)_2$.

Magnetic susceptibility measurements gave magnetic moments ranging from 5.74 $\mu\beta$ for the $dpeO_2$ complex to 5.86 $\mu\beta$ for the $daeO_2$ complex. These values are slightly lower than the expected spin-only value of 5.92 $\mu\beta$.

Reaction of $[MnL_2(H_2O)_2](ClO_4)_2$ *with sulfur dioxide*

The reaction of the $[MnL_2(H_2O)_2](ClO_4)_2$ complexes with sulfur dioxide has been studied in the solid state by monitoring the changes in the mass of the complexes when exposed to an atmosphere of SO_2. The results of these uptakes (Table 3) suggest that each complex absorbs 2 mol of SO_2 per mole of manganese. One mole of SO_2 is very labile and is released immediately the SO_2 pressure is reduced. Indeed we could only identify an uptake of 2 mol from the mass change. Attempts to analyse the bis-SO_2 adduct, either by elemental or thermogravimetric analyses, gave results corresponding to the mono-SO_2 adduct only, Table 4. However, the mono-SO_2 adduct is relatively stable with respect to the bis-SO_2 adduct as the second mole of SO_2 is much more strongly held. It is only released when heated considerably above room temperature or when a vacuum is applied. The loss of SO_2 from the mono adduct was monitored by TG analysis which showed almost quantitative loss of SO_2, Table 5. (A finely ground sample was heated at a rate of *c.* 25° min^{-1}.) The temperature range at which SO_2 is lost gives a guide to the extent of the interaction between the complex and SO_2. If it is assumed that loss at low temperature is equivalent to weak interaction, then, by taking the temperature at which loss of SO_2 begins, we can say that the ease of loss of SO_2 for the $[MnL_2(H_2O)_2](ClO_4)_2$ follows the order of complexes: $daeO_2 > dpeO_2 > dpacO_2 > vppO_2 > vpaO_2$.

The observation that the complexes containing ligands with vinyl backbones between the donor atoms bind SO_2 strongest may suggest that this property reflects the much less stringent steric demands of the *cis*-CHCH–backbone *vis-à-vis* the $-CH_2CH_2-$backbone.

The IR spectra of the SO_2 adducts show new absorptions assignable to (SO) in the 1260–1285 cm^{-1} region. These absorptions merely indicate the presence of SO_2 and do not necessarily indicate the mode of binding. However, since the rest of the spectrum is virtually unchanged it is probable that the SO_2 is ligand-bound. Ligand-bound sulfur dioxide is well known [18–23] and is generally characterised by reversibility and unreactivity of the bound SO_2 to dioxygen. Both of these criteria are met here. It is possible that the SO_2 inserts between the manganese and coordinated water, similar to the insertion between manganese and iodide in $[Mn(OPPh_3)_4(O_2SI)_2]$ [5] but, because no oxidation of SO_2 to sulfate is observed, this is unlikely. IR bands at 3430–3370 cm^{-1}, attributable to H_2O molecules, occur in the original complexes and in the SO_2 adducts.

Sulfur dioxide absorption by mono-SO_2 adducts

Following our observations that 2 mol of SO_2 are absorbed per mole of perchlorate complex, and that one of these is very labile, we thought it appropriate

TABLE 1. Analytical data and physical properties for $[MnL_2(H_2O)_2](ClO_4)_2$ complexes

Complex	Melting point (°C)	μ_{eff}	Λ_m (Ω^{-1} cm^2 mol^{-1})	Anal: Found (calc.) (%)			
				C	H	Cl	Mn
$[Mn(dpeO_2)_2(H_2O)_2](ClO_4)_2$	308–312	5.74	53.0	56.3(54.3)	4.6(4.5)	6.0(6.2)	
$[Mn(vppO_2)_2(H_2O)_2](ClO_4)_2$	192–194	5.83	62.2	56.3(54.5)	4.3(4.2)	6.3(6.2)	
$[Mn(daeO_2)_2(H_2O)_2](ClO_4)_2$	200–206	5.86	61.0	46.6(47.0)	4.0(3.9)	5.7(5.4)	
$[Mn(dpaeO_2)_2(H_2O)_2](ClO_4)_2$	240–242	5.79	51.2	50.5(50.4)	4.3(4.2)		3.4(4.0)
$[Mn(vpaO_2)_2(H_2O)_2](ClO_4)_2$	158–161	5.84	56.4	47.2(47.2)	3.3(3.6)		4.3(4.2)

TABLE 2. IR data for the $[MnL_2(H_2O)_2](ClO_4)_2$ complexes (all values in cm^{-1})

Complex	ν(AsO)	ν(PO)	$\nu_3(ClO_4^-)$	$\nu_4(ClO_4^-)$	Free ligand	
					ν(AsO)	ν(PO)
$[Mn(dpeO_2)_2(H_2O)_2](ClO_4)_2$		1175	1085–1080	618(sh)		1185
$[Mn(vppO_2)_2(H_2O)_2](ClO_4)_2$		1160(s)	1115–1095	620(sh)		1185
$[Mn(daeO_2)_2(H_2O)_2](ClO_4)_2$	875(s)		1105–1068	618(sh)	878	
$[Mn(dpaeO_2)_2(H_2O)_2](ClO_4)_2$	870(sh)	1161(s)	1098–1083	620(sh)	880	1180
$[Mn(vpaO_2)_2(H_2O)_2](ClO_4)_2$	870(sh), 860(w)		1110–1055	620–614	895	

TABLE 3. Uptake of sulfur dioxide by $[MnL_2(H_2O)_2](ClO_4)_2$ in the solid state

Complex	Mass of complex[a] (g)	Mass of SO_2 absorbed[a] (g)	SO_2/Mn
$[Mn(dpeO_2)_2(H_2O)_2](ClO_4)_2(SO_2)$	1.0 (8.69)	0.1052 (16.4)	1.89
$[Mn(vppO_2)_2(H_2O)_2](ClO_4)_2(SO_2)$	1.0 (8.73)	0.1145 (17.89)	2.05
$[Mn(daeO_2)_2(H_2O)_2](ClO_4)_2(SO_2)$	1.0 (7.54)	0.0970 (15.16)	2.01
$[Mn(dpaeO_2)_2(H_2O)_2](ClO_4)_2(SO_2)$	1.0 (8.08)	0.1029 (16.07)	1.99
$[Mn(vpaO_2)_2(H_2O)_2](ClO_4)_2(SO_2)$	1.0 (7.56)	0.0968 (15.13)	2.00

[a]Number of moles ($\times 10^{-4}$) in parentheses.

TABLE 4. Analytical data and physical properties for $[MnL_2(H_2O)_2(SO_2)](ClO_4)_2$ adducts

Complex	Melting point (°C)	μ_{eff}	Anal.: found (calc.) (%)				ν(SO)
			C	H	S	P	
$[Mn(dpeO_2)_2(H_2O)_2(SO_2)](ClO_4)_2$	d.298	5.78	52.7(51.4)	4.3(4.3)	3.0(2.6)		1260
$[Mn(vppO_2)_2(H_2O)_2(SO_2)](ClO_4)_2$	d.170	5.84	52.0(51.6)	4.1(4.0)	1.8(2.6)		1275
$[Mn(daeO_2)_2(H_2O)_2(SO_2)](ClO_4)_2$	d.196	5.86	45.3(44.9)	3.6(3.7)	2.0(2.3)		1285
$[Mn(dpaeO_2)_2(H_2O)_2(SO_2)](ClO_4)_2$	234–236	5.78	46.8(47.9)	3.9(4.0)		5.0(4.8)	1280
$[Mn(vpaO_2)_2(H_2O)_2(SO_2)](ClO_4)_2$	145–149	5.86	44.6(45.0)	3.9(3.8)	1.2(2.3)		1260

TABLE 5. Sulfur dioxide loss from $[MnL_2(H_2O)_2(SO_2)](ClO_4)_2$

Complex	SO_2 lost per Mn	Temperature of SO_2 loss (°C)
$[Mn(dpeO_2)_2(H_2O)_2(SO_2)](ClO_4)_2$	1.00	68–108
$[Mn(vppO_2)_2(H_2O)_2(SO_2)](ClO_4)_2$	1.02	80–105
$[Mn(daeO_2)_2(H_2O)_2(SO_2)](ClO_4)_2$	0.99	65–90
$[Mn(dpaeO_2)_2(H_2O)_2(SO_2)](ClO_4)_2$	1.00	72–95
$[Mn(vpaO_2)_2(H_2O)_2(SO_2)](ClO_4)_2$	1.04	85–108

to follow the SO_2 uptake over a range of partial pressures of SO_2. Thus the absorption of SO_2 by the complex $[Mn(dpaeO_2)_2(H_2O)_2](ClO_4)_2$ and its mono-SO_2 adduct, $[Mn(dpaeO_2)_2(H_2O)_2(SO_2)](ClO_4)_2$, were investigated using a gas burette technique [24].

SO_2 uptake by $[Mn(dpaeO_2)_2(H_2O)_2](ClO_4)_2$

The absorption isotherm is shown in Fig. 1(a). The isotherm is sigmoidal in shape and shows that SO_2 uptake commences when $P_{SO_2}=0.11$ atm and increased until $P_{SO_2}=0.91$ atm, when approximately 2 mol of SO_2 have been absorbed per mole of complex. The isotherm shows a slight 'saddle' when the SO_2/Mn ratio is 1.0 – this is significant in that it reflects the formation of the mono-SO_2 adduct.

SO_2 uptake by $[Mn(dpaeO_2)_2(H_2O)_2(SO_2)](ClO_4)_2$

The absorption isotherm is shown in Fig. 1(b). It, too, is sigmoidal and shows that SO_2 absorption begins at $P_{SO_2}=0.23$ atm and increases until $P_{SO_2}=0.82$ atm when approximately 0.8 mol of SO_2 has been absorbed per mole of mono-SO_2 adduct, giving a total of 1.8 mol of SO_2.

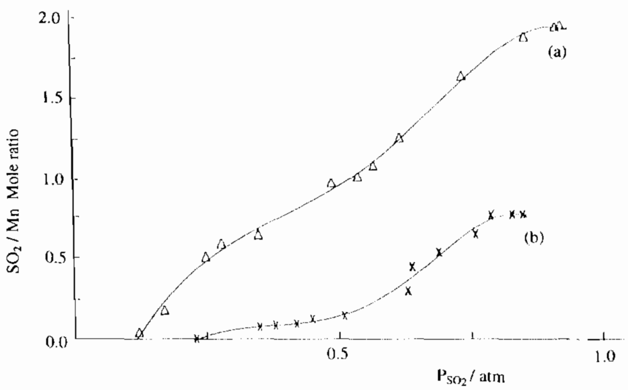

Fig. 1. SO_2 absorption isotherms for $[Mn(dpaeO_2)_2(H_2O)_2](ClO_4)_2$ (a) and $[Mn(dpaeO_2)_2(H_2O)_2(SO_2)](ClO_4)_2$ (b).

A comparison of these two isotherms shows that the original complex requires a relatively small P_{SO_2} to start the reaction whilst twice the P_{SO_2} is required before any absorption is seen with the mono-SO_2 adduct. This is not unexpected since the original complex presumably has two binding sites whereas the mono-SO_2 adduct only has one.

Experimental

Preparation of $[MnL_2(H_2O)_2](ClO_4)_2$ complexes

The preparation of $[Mn(vpaO_2)_2(H_2O)_2](ClO_4)_2$ outlined below is typical. 5.08 g (9.8 mmol) of $vpaO_2$ ligand were placed in a 250 cm^3 round-bottomed flask, equipped with a side-arm containing a ground-glass tap. Manganese(II) perchlorate hexahydrate (1.63 g; 4.5 mmol) was added to the flask, followed by approximately 100 cm^3 of freshly distilled toluene. The head-space was evacuated and flushed with dry argon several times to ensure an inert atmosphere. The mixture was stirred under argon for 10–14 days and the resulting product isolated by standard Schlenk techniques.

Reaction with SO_2 in the solid state

A known mass of sample (0.2–0.8 g) was placed in a pre-weighed argon filled Rotaflo tube. The tube was then evacuated and flushed with argon several times. The vacuum was again applied and removed with 1 atm of SO_2. This was weighed to give the starting mass for the uptake. More SO_2 was added on a daily basis until constant mass was obtained. The total mass of SO_2 added was converted into moles and the ratio Mn:SO_2 calculated.

Isotherm measurements using a gas burette

The apparatus employed consisted of a gas burette connected to a reaction vessel (containing a powdered sample of the complex under investigation) via a 2l reservoir. The whole apparatus was evacuated, the reaction vessel was isolated and the reservoir was then filled with an SO_2–argon mixture of known composition. This was allowed to equilibrate, and the reaction vessel was then opened to the gas reservoir. The volume of SO_2 absorbed was measured with the gas burette.

Elemental analyses were performed by the UMIST microanalytical service. IR spectra were recorded as Nujol mulls between KBr plates in the range 4000–400 cm^{-1} on a Perkin-Elmer 598 spectrophotometer. Magnetic susceptibility measurements were determined using the Faraday method and thermogravimetric analyses were carried out on a Stanton Redcroft TG 750 thermobalance.

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