Reactivity of Trialkylphosphine Oxide Complexes of Divalent Cobalt, Nickel, Copper and Zinc with Sulfur Dioxide. Reversible Co-ordination of SO_2 in Ligand-bound Adducts†

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Bis(trialkylphosphine oxide) complexes, $[M(OPPr^n_3)_2Br_2]$ (M = Co, Ni, Cu or Zn) and $[M(OPEt_3)_2X_2]$ (M = Co, X = I; M = Zn, X = Br), have been synthesised. Magnetic susceptibility measurements have been made (M = Co, Cu or Ni), and electronic (M = Cu or Co), ^{31}P-{^1H} NMR (M = Zn), and infrared spectra (all complexes) have been recorded. Characterisation strongly supports the hypothesis that the complexes are pseudo-tetrahedral, with significant distortion in the case of copper. On exposure to SO_2 all the complexes display mass increases commensurate with the absorption of 2 equivalents of SO_2. During this process solid complexes become liquid, whilst oils appear visibly less viscous. The co-ordination of SO_2 is easily reversed in a flow of dinitrogen or at reduced pressures and the original complexes are recovered without apparent decomposition. These properties, along with the infrared absorptions observed for co-ordinated SO_2, are indicative of the formation of ligand-bound adducts, $[M\{O(SO_2)PR_3\}_2X_2]$. The equilibrium between free and co-ordinated SO_2 has been examined for the complex $[Zn(OPEt_3)_2Br_2]$ using thermogravimetric analysis; $K_{eqm} = 3.96$ atm^{-2} (295 K), $\Delta H = -26.1$ kJ mol^{-1} per binding site, whilst a Hill plot indicates no significant co-operativity between the co-ordination sites. Several complexes and their sulfur dioxide adducts were investigated by visible (M = Cu or Co), ESR (M = Cu) and ^{31}P-{^1H} NMR (M = Zn) spectroscopy. Visible spectroscopy indicates that little change occurs in the cobalt co-ordination sphere as a result of binding of SO_2, but $[Cu(OPPr^n_3)_3Br_2]$ appears to change ground state and possibly geometry on co-ordination. The ESR spectra indicate that changes do occur in the metal environment for $[Cu(OPPr^n_3)_2Br_2]$, but fail to provide detailed information. The ^{31}P-{^1H} NMR spectra for $[Zn(OPR_3)_2Br_2]$ (R = Et, Pr^n, Bu^n or C_8H_{17}) and their adducts, surprisingly, show small negative (upfield) shifts on co-ordination of SO_2. Since the effect is opposite to that observed when SO_2 binds to free OPR_3 ligands, it is suggested that the net deshielding caused by zinc(II) and SO_2 in the $[Zn\{O(SO_2)PR_3\}_2Br_2]$ complexes is comparable to that of zinc(II) alone in the $[Zn(OPR_3)_2Br_2]$ precursors, and thus that significant competition occurs between the two Lewis-acid species in the $[Zn\{O(SO_2)PR_3\}_2Br_2]$ complexes.

There is considerable interest in the binding of sulfur dioxide to transition-metal complexes. This stems both from the versatility of co-ordination of SO_2 and from its role as a significant atmospheric pollutant.[1] Our interest in this area began with the observation that SO_2 co-ordinates to manganese(II) phosphine complexes in an unusual $MnX_2(PR_3)(SO_2)_{2/3}$ stoichiometry.[2] On extending this work to phosphine oxide complexes of manganese(II) we discovered a novel form of reactivity involving insertion of SO_2 into the Mn–I bonds of $[Mn(OPPh_3)_4I_2]$ to give $[Mn(OPPh_3)_4\{OS(O)I\}_2]$[3] [equation (1), r.t. = room

$$[Mn(OPPh_3)_4\{OS(O)I\}_2] \underset{\text{r.t.}}{\overset{127\,^{\circ}\text{C}}{\rightleftharpoons}} [Mn(OPPh_3)_4\{OS(O)I\}I] + SO_2 \quad (1)$$

temperature]. Subsequent studies have shown that SO_2 is co-ordinated and activated by other manganese(II) complexes. For example, exposure of $[Mn(OPPh_3)_4(NCS)_2(SO_2)]$ to moist air induces the facile oxidation of SO_2 to sulfuric acid, isolated as the ligand adduct $(PPh_3O)(PPh_3OH)(HSO_4)$.[4] Activation also occurs with analogous complexes containing $OAsPh_3$ ligands and unusual products such as Ph_3AsI_2, Ph_3AsI_4 and $[\{AsPh_3O\}_2H]I_3$ have been characterised from the reaction of $[Mn(OAsPh_3)_4I_2]$ with SO_2, suggesting that a considerable amount of interesting redox chemistry is involved.[5-7] This work has also been extended to iron(III)[8] and cobalt(II)[9] complexes of $OPPh_3$ and $OAsPh_3$ which also co-ordinate and activate SO_2 in a manner dependent on the metal, ligand and anion present.

We have recently examined the behaviour of complexes containing other phosphine oxide ligands in order further to elucidate the structure–reactivity relationships already observed. Thus, manganese(II) complexes with trialkylphosphine oxide ligands also co-ordinate SO_2, but in a radically different binding mode compared to their $OPPh_3$ and $OAsPh_3$ analogues.[10] These trialkylphosphine oxide complexes display reversible co-ordination involving a Lewis acid–base interaction between sulfur dioxide and the complexed trialkylphosphine oxide ligands. Such binding is facilitated by the approximate sp^2 hybridisation of the OPR_3 oxygen, thus allowing simultaneous σ donation to both SO_2 and metal.

Ligand co-ordination of SO_2 is rare compared with direct metal binding, and those examples available bear[1] little resemblance to both the complexes studied here and those reported in our previous work.[10] In our characterisation of manganese(II) complexes of trialkylphosphine oxides and their interaction with SO_2 few physical techniques, other than

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† *Non-SI unit employed:* atm = 101 325 Pa.

Table 1 Elemental analyses and physical properties of the $\mathrm{M(OPR_3)_2X_2}$ complexes

Complex	M.p./ °C	Colour	ν(PO)[a]/ cm^{-1}	Analysis (%)[b] C	H
$[\mathrm{Co(OPEt_3)_2I_2}]$	98	Blue	1105s, 1130 (sh)	25.3 (24.8)	5.1 (5.2)
$[\mathrm{Co(OPPr^n{}_3)_2Br_2}]$	Oil	Blue	1108s	37.5 (37.8)	7.2 (7.4)
$[\mathrm{Ni(OPPr^n{}_3)_2Br_2}]$	Oil	Dark blue	1120s	38.1 (37.8)	7.7 (7.4)
$[\mathrm{Cu(OPPr^n{}_3)_2Br_2}]$	Oil	Brown	1105s	37.2 (37.5)	7.5 (7.3)
$[\mathrm{Zn(OPEt_3)_2Br_2}]$	111	White	1103, 1113s, 1135 (sh)	29.3 (29.2)	6.0 (6.1)
$[\mathrm{Zn(OPPr^n{}_3)_2Br_2}]$	Oil	Colourless	1115s	37.2 (37.4)	7.4 (7.3)

[a] ν(PO) for free ligands: $\mathrm{OPEt_3}$, 1155s; $\mathrm{OPPr^n{}_3}$, 1160s cm^{-1}. [b] Calculated values in parentheses.

Table 2 Electronic spectra and magnetic susceptibilities for cobalt, nickel and copper complexes of phosphine oxides

Complex	μ_{eff}	Visible spectrum λ/nm (ε/dm^3 mol^{-1} cm^{-1})	Ref.
$[\mathrm{Co(OPPr^n{}_3)_2Br_2}]$	4.7	620 (495), 647 (540), 684 (595)	This work
$[\mathrm{Co(OPPh_3)_2Br_2}]$	4.8	620 (350), 650 (520), 675 (690)	11, 13
$[\mathrm{Co(OPEt_3)_2I_2}]$	4.8	627 (680), 656 (700), 722 (685)	This work
$[\mathrm{Co(OPPh_3)_2I_2}]$	5.0	645 (sh), 680 (685), 715 (670)	11, 13
$[\mathrm{Ni(OPPr^n{}_3)_2Br_2}]$	4.0	673 (85), 743 (91)	This work
$[\mathrm{Ni(OPPh_3)_2Br_2}]$	4.0	487 (22), 645 (101), 750 (sh)	16
$[\mathrm{Cu(OPPr^n{}_3)_2Br_2}]$	1.9	414 (1414), 640 (225)	This work
$[\mathrm{Cu(OPPh_3)_2Br_2}]$	2.0	431 (1115), 643 (575)	17

infrared spectroscopy, proved informative. Moreover, since the adducts with $\mathrm{SO_2}$ invariably form as oils, crystallographic structure determinations are impossible. Hence, to ascertain whether the ligand co-ordination of $\mathrm{SO_2}$ is a general feature of trialkylphosphine oxide complexes, and further to elucidate the nature of the $\mathrm{SO_2}$–complex interaction, should it occur, we have studied and report here observations on the reactivity of a number of other divalent first-row transition-metal complexes containing $\mathrm{OPR_3}$ ligands.

Results and Discussion

Synthesis of Complexes.—Bis(trialkylphosphine oxide) complexes $[\mathrm{M(OPPr^n{}_3)_2Br_2}]$ (M = Co, Ni, Cu or Zn) and $[\mathrm{M(OPEt_3)_2X_2}]$ (M = Co, X = I; M = Zn, X = Br) were synthesised from 1 : 2 ratios of metal salt to ligand, a formulation confirmed by elemental analysis, Table 1. The air-stable products dissolve completely in dichloromethane without decomposition. The absence of insoluble material precludes the possibility that the apparent bis complexes are, in fact, compounds of higher ligand-to-metal stoichiometry contaminated with unreacted metal salts. Triethylphosphine oxide complexes are solids, whilst those of tri-*n*-propylphosphine oxide are oils. The nature of the latter complexes prevents comprehensive characterisation; moreover, unequivocal structural assignment in each metal environment would require the determination of numerous trivial crystal structures. Instead, physical characterisation and analogy with other structurally characterised phosphine oxide complexes has been used to postulate structures with some confidence for the compounds reported here.

Triphenylphosphine oxide complexes of cobalt(II) have been thoroughly characterised. Comprehensive studies of $[\mathrm{Co(OPPh_3)_2X_2}]$ (X = Cl, Br or I) clearly identified the compounds as pseudo-tetrahedral monomers.[11–13] Magnetic and spectroscopic properties were particularly diagnostic of the metal geometry and donor set, as confirmed by later crystallographic studies of $[\mathrm{Co(OPPh_3)_2Cl_2}]$ and $[\mathrm{Co(OPPh_3)_2Br_2}]$.[14,15] Since the magnetic and spectroscopic properties of $[\mathrm{Co(OPPr^n{}_3)_2Br_2}]$ and $[\mathrm{Co(OPEt_3)_2I_2}]$ are in excellent agreement with the published data for their $\mathrm{OPPh_3}$ analogues, Table 2, it is therefore reasonable to assign monomeric tetrahedral geometries to these compounds.

The characterisation of $[\mathrm{Ni(OPPr^n{}_3)_2Br_2}]$ initially appears more difficult since three metal geometries are feasible, and because the corresponding $\mathrm{OPPh_3}$ complexes have not been crystallographically characterised. However, magnetic and spectroscopic data are once again quite adequate to reach firm conclusions. Both $[\mathrm{Ni(OPPh_3)_2X_2}]$ (X = Cl, Br or I)[16] and $[\mathrm{Ni(OPMe_3)_2X_2}]$ (X = Cl or Br)[17] complexes have been previously reported, the former existing as blue-green products whilst the latter can be isolated in both blue-green and pale pink forms. The magnetic susceptibilities of the blue complexes, as well as that of $[\mathrm{Ni(OPPr^n{}_3)_2Br_2}]$, Table 2, rule out square-planar geometries. Moreover, the visible spectra are in accord with a tetrahedral geometry, and the spectrum of $[\mathrm{Ni(OPPr^n{}_3)_2Br_2}]$ is analogous to that reported for $[\mathrm{Ni(OPPh_3)_2Br_2}]$,[16] strongly suggesting this complex is also tetrahedral.

The structural assignment for $[\mathrm{Cu(OPPr^n{}_3)_2Br_2}]$ must be more tentative; magnetic susceptibilities are not diagnostic and visible spectra are poorly resolved. However, $[\mathrm{Cu(OPPr^n{}_3)_2Br_2}]$ and $[\mathrm{Cu(OPPh_2)_2Br_2}]$ both exhibit a charge-transfer band at *ca.* 400 nm suggesting the complexes have similar ground states and geometries.[18] Since the crystal structures of $[\mathrm{Cu(OPPh_3)_2Br_2}]$[19] and $[\mathrm{Cu(OPPh_3)_2Cl_2}]$[20] both indicate a flattened distorted-tetrahedral copper geometry, it can be concluded, with reasonable confidence, that $[\mathrm{Cu(OPPr^n{}_3)_2Br_2}]$ is isostructural.

The 2 : 1 stoichiometries of the $[\mathrm{Zn(OPR_3)_2Br_2}]$ (R = Et or $\mathrm{Pr^n}$) complexes point to a tetrahedral geometry. Whilst this cannot be confirmed without crystallographic characterisation, the crystal structures of $[\mathrm{Zn(OPPh_3)_2X_2}]$ (X = Cl or Br) have been reported and both exhibit regular tetrahedral geometries.[21,22] Additionally, infrared studies of the corresponding $\mathrm{OPMe_3}$ complexes, $[\mathrm{Zn(OPMe_3)_2X_2}]$ (X = Cl or Br), indicate that they are isostructural with their $\mathrm{OPPh_3}$ analogues.[23]

Reactivity towards Sulfur Dioxide.—Our published studies of the reactivity of $\mathrm{SO_2}$ with manganese(II) trialkylphosphine oxide complexes provide important comparisons with the work presented here.[10] Bis and tetrakis manganese(II) complexes, $[\mathrm{Mn(OPR_3)_2X_2}]$ (X = Cl, Br, I or NCS; R = Et, $\mathrm{Pr^n}$ or $\mathrm{Bu^n}$) and $[\mathrm{Mn(OPR_3)_4(NCS)_2}]$ (R = Et or $\mathrm{Bu^n}$), absorb 1 equivalent of gaseous $\mathrm{SO_2}$ per ligand. The infrared spectra of these adducts exhibit intense bands indicative of the symmetric stretching mode of $\mathrm{SO_2}$. The position of this band, close to that of unco-ordinated $\mathrm{SO_2}$, is consistent with ligand binding. This form of co-ordination is also suggested by the facile reversibility of co-ordination of $\mathrm{SO_2}$, and whilst such bonding at either anion or ligand moieties is conceivable, several factors make binding to the trialkylphosphine oxide ligands more likely. No changes were observed in the infrared bands of the thiocyanate anions on sulfur dioxide co-ordination, no anion dependence in reactivity could be detected, and similar reactivity does not occur for the $[\mathrm{Mn(OPPh_3)_2X_2}]$ (X = Cl, Br, I or NCS) complexes.[4,24] Exposure of the complexes $[\mathrm{M(OPPr^n{}_3)_2Br_2}]$ (M = Co, Ni, Cu or Zn) and $[\mathrm{M(OPEt_3)_2X_2}]$ (M = Co, X = I; M = Zn, X = Br) to gaseous sulfur dioxide results in a

Table 3 Mass changes on exposure of the $[M(OPR_3)_2X_2]$ complexes to gaseous SO_2

Complex	Amount g	Amount mol $\times 10^{-4}$	Increase in mass/g	Ar/SO_2 Corr./g	Amount observed g	Amount observed mol $\times 10^{-4}$	$M:SO_2$
$[Co(OPEt_3)_2I_2]$	0.4234	7.29	0.1385	0.0503	0.0882	13.80	1:1.89
$[Co(OPPr^n_3)_2Br_2]$	0.0832	1.46	0.0222	0.0030	0.0192	3.00	1:2.05
$[Ni(OPPr^n_3)_2Br_2]$	0.1840	3.22	0.0435	0.0030	0.0405	6.33	1:1.97
$[Cu(OPPr^n_3)_2Br_2]$	0.1724	2.99	0.0435	0.0030	0.0405	6.33	1:2.12
$[Zn(OPEt_3)_2Br_2]$	0.5260	10.69	0.1362	0.0030	0.1332	20.81	1:1.95
$[Zn(OPPr^n_3)_2Br_2]$	0.1016	1.76	0.0243	0.0030	0.0213	3.33	1:1.89

Table 4 Important infrared bands (cm^{-1}) for the $[M\{O(SO_2)PR_3\}_2X_2]$ complexes

	Colour	$\nu_{sym}(SO)$[a]	$\delta(OSO)$[a]	$\nu(PO)$[b]
$[Co\{O(SO_2)PEt_3\}_2I_2]$	Blue	1326s	525s	1100s, 1130s
$[Co\{O(SO_2)PPr^n_3\}_2Br_2]$	Blue	1322s	522s	1108s
$[Ni\{O(SO_2)PPr^n_3\}_2Br_2]$	Dark blue	1319s	522s	1120s
$[Cu\{O(SO_2)PPr^n_3\}_2Br_2]$	Green	1324s	522s	1104s
$[Zn\{O(SO_2)PEt_3\}_2Br_2]$	Colourless	1327s	525s	1103s, 1111s
$[Zn\{O(SO_2)PPr^n_3\}_2Br_2]$	Colourless	1322s	524s	1115s (br)

[a] $\nu(SO)$ 1340, 1150 and $\delta(OSO)$ 524s cm^{-1} for unbound SO_2. [b] $\nu(PO)$ 1155s (free $OPEt_3$), 1160s cm^{-1} (free $OPPr^n_3$).

rapid increase in mass to maxima commensurate with the co-ordination of two SO_2 moieties to each complex, Table 3. The solid complexes readily liquefy during this uptake while the oils become visibly less viscous. The co-ordination of SO_2 is reversible and it is lost at reduced pressure or in a flow of dinitrogen. Solid precursor complexes are observed to resolidify during this process. Repeated cycles of absorption and desorption of SO_2 occur with no apparent degradation of the complexes.

Unfortunately, the lability of the absorbed SO_2 prevents accurate or consistent elemental analyses. Infrared spectra, Table 4, confirm the presence of co-ordinated SO_2. Intense bands at *ca.* 1320 and *ca* 520 cm^{-1} can be assigned to the symmetric and bending modes of SO_2, respectively. The asymmetric bend is obscured by the broad phosphine oxide vibrations masking the 1150–1100 cm^{-1} region. Little or no changes could be detected in the phosphine oxide bands. Moreover, since phosphine oxide and asymmetric SO_2 stretches overlay each other it would be unwise to interpret changes in band profiles in this region purely as shifts in $\nu(PO)$.

These results clearly indicate co-ordination of SO_2 by trialkylphosphine oxide complexes of divalent cobalt, nickel, copper and zinc. Moreover, the properties of the complexes mirror those reported for manganese(II) complexes containing these ligands. Stoichiometries, physical properties (liquefaction on exposure to SO_2 and the lability of its binding) and infrared data are all consistent with the conclusions from our earlier work.[10] In this previous work the properties of the sulfur dioxide adducts, as well as the propensity of the unco-ordinated trialkylphosphine oxide ligands to bind SO_2, suggested a Lewis acid–base interaction between the oxygen centre of the OPR_3 ligands and SO_2. Since the trialkylphosphine oxide complexes of cobalt, nickel, copper and zinc exhibit reversibility and infrared spectra consistent with ligand co-ordination of SO_2, it is logical to conclude the formation of $M\{O(SO_2)PR_3\}_2X_2$ adducts, Fig. 1.

Our studies of manganese(II) complexes were limited by the high-spin d^5 electronic configuration of the metal, and we have therefore attempted further characterisation of the complexes reported here. However, all the $[M\{O(SO_2)PR_3\}_2X_2]$ complexes form as oils and therefore cannot be characterised by single-crystal X-ray diffraction.

Thermogravimetric Measurements of the Uptake of SO_2 *for a Zinc Complex.*—The thermodynamics of the interaction of $[ZnBr_2(OPEt_3)_2]$ and SO_2 was studied using isothermal thermogravimetric analysis. The complex was exposed to varying partial pressures of SO_2 in a nitrogen stream, and the consequent mass increases were assigned to formation of the complex $[ZnBr_2\{O(SO_2)PEt_3\}_2]$, Fig. 2. In all cases complete reversibility was observed and the original complex could be recovered in a stream of pure nitrogen.

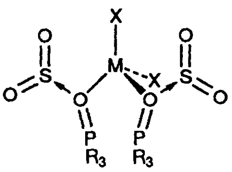

Fig. 1 Proposed co-ordination of sulfur dioxide to a lone pair of the metal-co-ordinated trialkylphosphine oxide ligand to yield $[M\{O(SO_2)PR_3\}_2X_2]$

Data were fitted by use of equilibrium (2) using the Hill

$$[ZnBr_2(OPEt_3)_2] + 2SO_2 \overset{K_{eqm}}{\rightleftharpoons} [ZnBr_2\{O(SO_2)PEt_3\}_2] \quad (2)$$

$$Y/(1 - Y) = K_{eqm}\,p(SO_2)^{2n} \quad (3)$$

$$\log[Y/(1 - Y)] = \log K_{eqm} + n \cdot \log p(SO_2)^2 \quad (4)$$

equation (3), where Y corresponds to the fraction of co-ordination sites occupied by SO_2. A plot of $\log[Y/(1 - Y)]$ *versus* $\log p(SO_2)^2$, Fig. 3, gives an adequate linear relationship from which equilibrium data can be extracted, Table 5. The variation of K_{eqm} with temperature also allows the calculation of the reaction enthalpy using the Van't Hoff equation (5), Fig. 4. The value of ΔH obtained from the co-ordination of SO_2 is -52.2 kJ mol^{-1} or -26.1 kJ mol^{-1} per binding site. This result, and the equilibrium data in Table 5, are comparable with those recorded for $[Cu_2(PR_3)_4I_2]$ complexes of 36–60 kJ mol^{-1} and 14 kJ mol^{-1} for the formation of the $[NCS{\cdot}SO_2]^-$ anion.[25,26] It is also comparable with the dissociation data recorded for the adducts of $[Mn(OPPh_3)_4(NCS)_2]$ and $[Mn(OPPh_3)_4I_2]$ with SO_2 of 17–32 kJ mol^{-1},[27]

$$\frac{d \ln K_{eqm}}{d(1/T)} = \frac{-\Delta H}{R} \quad (5)$$

Table 5 Thermodynamic data for co-ordination of SO_2 by $[ZnBr_2(OPEt_3)_2]$

T/°C	K_{eqm}/ atm^{-2}	Hill coefficient	$p_{\frac{1}{2}}$/atm
22	3.96	1.0	0.503
25	2.72	1.0	0.607
33	1.77	1.0	0.752

Table 6 Phosphorus-31 NMR data for the trialkylphosphine oxide ligands, their zinc complexes and sulfur dioxide adducts

	δ[a]	
Compound	SO_2-free solvent	SO_2-saturated solvent
$OPEt_3$[28]	48.3	53.0 (4.7)
$OPPr^n_3$	42.6	49.3 (6.7)
$OPBu^n_3$[29]	43.1	53.7 (10.6)
$OP(C_8H_{17})_3$[30]	42.0	52.7 (10.7)
$[Zn(OPEt_3)_2Br_2]$	72.5 (24.2)	69.3 (21.0)
$[Zn(OPPr^n_3)_2Br_2]$	67.1 (24.5)	63.9 (21.3)
$[Zn(OPBu^n_3)_2Br_2]$	64.3 (21.2)	62.4 (19.3)
$[Zn(OPBu^n_3)_2Br_2]$[b] + 10 $OPBu^n_3$	64.3[c] (21.2)	62.0[c] (18.9)
$[Zn\{OP(C_8H_{17})_3\}_2Br_2]$	64.0 (22.0)	62.5 (20.5)
$[Zn\{OP(C_8H_{17})_3\}_2Br_2]$[b] + 10 $OP(C_8H_{17})_3$	64.4[c] (22.4)	61.8[c] (19.8)

[a] Δ values in parentheses denote shifts from free-ligand values. [b] Value corresponds to co-ordinated ligand; free-ligand values omitted for clarity. [c] Broad.

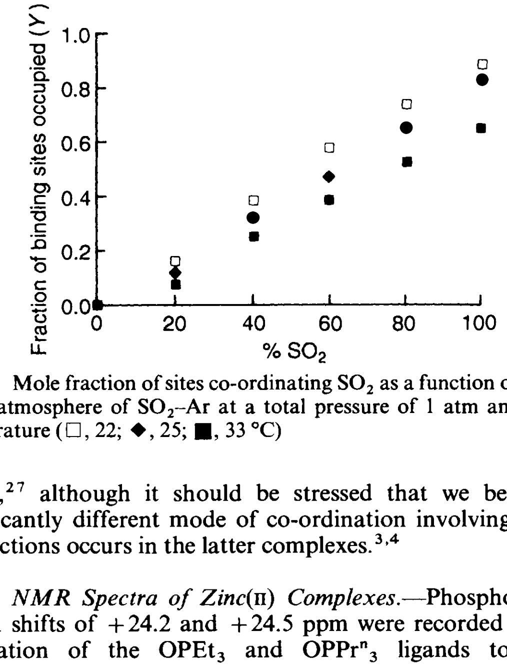

Fig. 2 Mole fraction of sites co-ordinating SO_2 as a function of %SO_2 in an atmosphere of SO_2–Ar at a total pressure of 1 atm and room temperature (□, 22; ◆, 25; ■, 33 °C)

mol^{-1},[27] although it should be stressed that we believe a significantly different mode of co-ordination involving anion interactions occurs in the latter complexes.[3,4]

^{31}P *NMR Spectra of Zinc*(II) *Complexes*.—Phosphorus-31 NMR shifts of +24.2 and +24.5 ppm were recorded on co-ordination of the $OPEt_3$ and $OPPr^n_3$ ligands to form $[Zn(OPEt_3)_2Br_2]$ and $[Zn(OPPr^n_3)_2Br_2]$, Table 6. Such studies of zinc–phosphine oxide complexes are scarce, but comparable shifts have been reported (+25.7 ppm) for the complex $[Zn(OPBu^n_3)_4(ClO_4)_2]$ by Grim and Satek.[31] Significant ligand exchange was observed for this complex, giving a singlet spectrum shifting from δ +68.7 to *ca.* 80 in the presence of an excess of ligand. This dependence on free-ligand concentration was attributed to rapid exchange in solution and time averaging of equilibrium (6). Since such an equilibrium

$$[Zn(OPBu^n_3)_4(ClO_4)_2] \rightleftharpoons [Zn(OPBu^n_3)_3(ClO_4)_2] + OPBu^n_3 \quad (6)$$

could be significantly affected by the co-ordination of SO_2 to both complexed and free ligands, and produce spurious results, we have examined the behaviour of $[Zn(OPR_3)_2Br_2]$ (R = Bu^n or *n*-octyl) complexes in the presence of an excess of ligand. Similar shifts to those for $OPEt_3$ and $OPBu^n_3$ were noted on co-ordination of these ligands to $ZnBr_2$, Table 6. However, whilst some line broadening was observed in the presence of an excess of ligand, suggestive of some dynamic behaviour in solution, no movement in peak positions was recorded. It is therefore reasonable to conclude that any changes which occur in the presence of SO_2 are a result of its co-ordination to the complexes rather than equilibrium shifts.

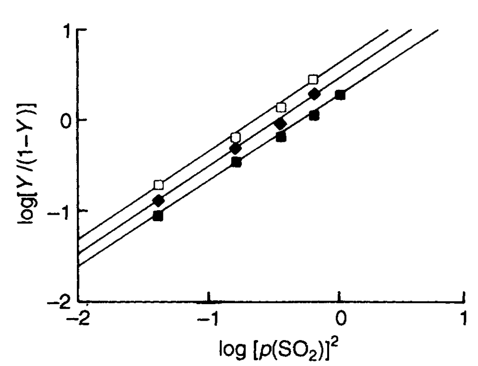

Fig. 3 Hill plot of SO_2 uptake as a function of log $[p(SO_2)]^2$; temperatures as in Fig. 2

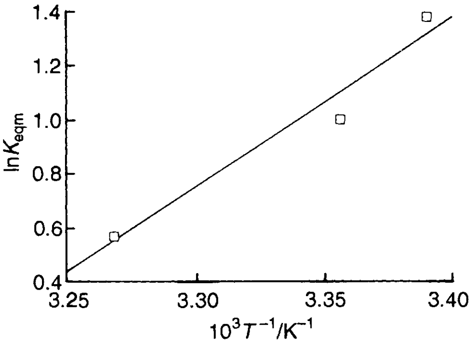

Fig. 4 Enthalpy of reaction for $[Zn(OPEt_3)_2Br_2] + SO_2$ obtained from a plot of ln K_{eqm} *versus* $1/T$

We have previously recorded the ^{31}P NMR spectra of the free OPR_3 ligands (R = Et, Pr^n or Bu^n) and their SO_2 adducts.[10] A similar shift of +10.7 ppm is recorded here for the formation of $SO_2{\cdot}OP(C_8H_{17})_3$, Table 6. Such results are consistent with Lewis acid–base interaction involving donation by the oxygen centre of the trialkylphosphine oxide ligands and consequent deshielding of the phosphorus atom.

More surprising results are obtained on saturation of $CDCl_3$ solutions of $[Zn(OPR_3)_2Br_2]$ (R = Et, Pr^n, Bu^n or C_8H_{17}) with SO_2. In each case small negative (upfield) changes in the singlet spectra, with respect to the $[Zn(OPR_3)_2Br_2]$ complexes, are observed. These vary in magnitude from 1.5 to 3.2 ppm. Since both co-ordination of OPR_3 to zinc(II) and Lewis-base donation to sulfur dioxide separately induce polarisation of the O=P bond in a $^-$O–P$^+$ manner, the cumulative effect of both forms of co-ordination might be expected to exceed any individual contribution. In fact, the results show that polarisation of the O=P bond and consequent deshielding of the phosphorus centre are comparable, if not marginally less for the $[Zn\{O(SO_2)PR_3\}_2Br_2]$ complexes rather than for their $[Zn(OPR_3)_2Br_2]$ analogues.

Precise determination of the bonding present is impossible in the absence of crystallographic data; however, such apparently contradictory NMR results may be rationalised by considering the O=P bonding system of OPR_3 ligands. Early work[32,33] suggested that the nominally O–P double bond was derived from a single σ bond, with significant d_π–p_π backbonding from the sp- or sp^2-hybridised oxygen providing the secondary interaction. A hybridisation scheme between sp and sp^2 would produce a lone pair making a 120–180° M–O–P bond on co-ordination. Most of the crystallographically characterised first-row transition-metal complexes, including structurally characterised [Zn(OPPh$_3$)$_2$X$_2$] (X = Cl or Br), give a M–O–P angle in the region of 150°,[14,15,19–22] suggesting an intermediate hybridisation scheme. However, larger M–O–P angles, and even linear co-ordination in Group 13 adducts, have been reported.[34] This tendency towards bond angles greater than 150° suggests significant sp character which could lead to the conclusion that the oxygen centre exhibits only one effective lone pair. However, this is refuted by the characterisation of η^2 double proton-bridged systems[35,36] with M–O–H angles of *ca.* 150°.

Therefore, the literature evidence suggests that η^2 co-ordination is feasible for phosphine oxide systems, but also that bond angles of at least 150° are favoured. Steric interaction and bonding competition between SO$_2$ and zinc(II) is unlikely to allow such bond angles and should force the overall geometry around the central oxygen towards 120°. As a result, the overall donation by the OPR$_3$ ligands to zinc(II) and SO$_2$ may be significantly less than for the individual co-ordination of either component, thus making the overall deshielding at the phosphorus centres of the [Zn{O(SO$_2$)PR$_3$}$_2$Br$_2$] complexes comparable to that in [Zn(OPR$_3$)$_2$Br$_2$].

Electronic Spectra of Cobalt and Copper Complexes.—These were recorded for [Co(OPPr$^n{}_3$)$_2$Br$_2$] and [Cu(OPPr$^n{}_3$)$_2$Br$_2$], and for their sulfur dioxide adducts. For cobalt little change is observed between the precursor complex and its adduct, save for a greater absorption in the ultraviolet region of the latter which is commonly observed in the presence of SO$_2$, Fig. 5. Both cobalt complexes give spectra comparable to that of [Co(OPPh$_3$)$_2$Br$_2$], and are typical of pseudo-tetrahedral compounds of C_{2v} symmetry. Whilst the limited spectral changes may appear at odds with co-ordination of SO$_2$, we have already noted only minor changes in the ^{31}P-{^{1}H} NMR spectra as a result of sulfur dioxide binding. Moreover, relatively small changes in band positions and intensity were noted between [Co(OPPh$_3$)$_2$Cl$_2$] and [Co(OPPh$_3$)$_2$Br$_2$],[13] suggesting the minor changes in the metal donor set result in only small shifts in UV/VIS spectra.

On exposure to SO$_2$ neat oils and solutions of [Cu(OPPr$^n{}_3$)$_2$Br$_2$] turn from brown to green. Electronic spectra for [Cu(OPPr$^n{}_3$)$_2$Br$_2$] and [Cu{O(SO$_2$)PPr$^n{}_3$}$_2$Br$_2$] are illustrated in Fig. 6. The d–d transitions for both complexes are poorly resolved in the 600–700 nm region, preventing any determination of the copper ground state. However, it is clear that the colour change results from the loss of an intense charge-transfer band at 414 nm (ε 1450 dm^3 mol^{-1} cm^{-1}) on co-ordination of sulfur dioxide. Such bands are a common feature of copper(II) complexes and are sensitive to the ground state of the metal and therefore its geometry.[37] They are observed in [Cu(OPPh$_3$)$_2$Br$_2$], but not in [Cu(OPPh$_3$)$_2$Cl$_2$], and can therefore be assigned to metal–anion interaction.[18]

The loss of this charge-transfer band in [Cu{O(SO$_2$)PPr$^n{}_3$}$_2$Br$_2$] may be the result of several processes. However, most, such as insertion of SO$_2$ into the copper–bromide bond, can be ruled out by the conclusive infrared characterisation of the interaction as being in the form of ligand binding. In fact, copper(II) is unique amongst the compounds characterised here, in exhibiting considerable distortion from classic tetrahedral co-ordination. Flattened tetrahedra are common for copper(II) and have been structurally characterised in [Cu(OPPh$_3$)$_2$X$_2$] (X = Cl or Br).[19,20] Therefore, binding of SO$_2$ may produce a steric interaction between the anions and bulky O(SO$_2$)PR$_3$ ligands forcing copper(II) to adopt a less-hindered pseudo-tetrahedral geometry. A change in the copper(II) ground state and resultant loss of the copper–bromide charge-transfer band could then occur. Such a hypothesis would agree with the different ESR spectra observed for [Cu(OPPr$^n{}_3$)$_2$Br$_2$] and [Cu{O(SO$_2$)PPr$^n{}_3$}$_2$Br$_2$] at low temperature, Fig. 7.

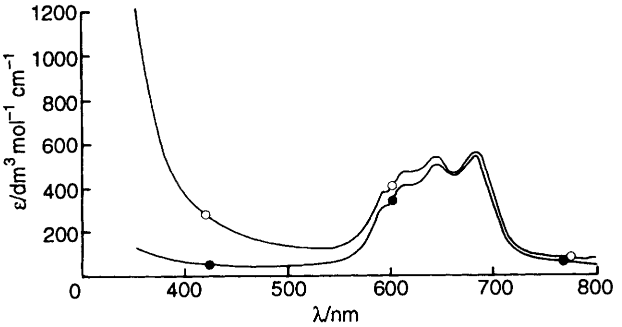

Fig. 5 Visible spectra of [Co(OPPr$_3{}^n$)$_2$Br$_2$] (●) and [Co{O(SO$_2$)PPr$^n{}_3$}$_2$Br$_2$] (○) in dichloromethane

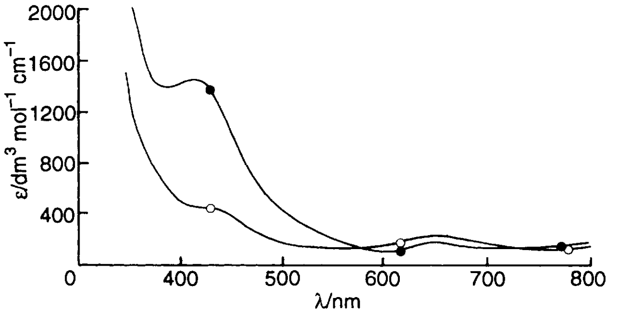

Fig. 6 Visible spectra of [Cu(OPPr$^n{}_3$)$_2$Br$_2$] (●) and [Cu{O(SO$_2$)PPr$^n{}_3$}$_2$Br$_2$] (○) in dichloromethane

ESR Spectra.—Only isotropic ESR spectra could be obtained for [Cu(OPPr$^n{}_3$)$_2$Br$_2$] and [Cu{O(SO$_2$)PPr$^n{}_3$}$_2$Br$_2$] at room temperature in CH$_2$Cl$_2$, a result in accord with powder studies of [Cu(OPPh$_3$)$_2$Cl$_2$].[38] Even at 77 K [Cu(OPPr$^n{}_3$)$_2$Br$_2$], as a CH$_2$Cl$_2$ glass, gives an isotropic signal of g_i = 2.16, Fig. 7. However, under the same conditions, fine detail can be observed in the [Cu{O(SO$_2$)PPr$^n{}_3$}$_2$Br$_2$] spectrum at g = 2.20 and 2.61. Interpretation of such results is difficult; however, the difference between the spectra of the precursor complex and the adduct is not inconsistent with the presence of different metal geometries which was asserted from the electronic spectra of the compounds. Firm conclusions cannot be drawn from the spectra, but they do suggest that binding of SO$_2$ significantly affects the copper(II) electronic environment.

Conclusion

A reversible interaction between sulfur dioxide and trialkylphosphine oxides co-ordinated to first-row transition metals occurs independently of the metal present for Mn^{II}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}. Phosporus-31 NMR spectroscopy suggests that considerable competition occurs between the co-ordinated SO$_2$ and metal for the trialkylphosphine oxide ligand. The metal geometry of the distorted four-co-ordinate copper complexes probably changes on co-ordination of SO$_2$, but those of the C_{2v} pseudo-tetrahedral cobalt complexes do not.

Experimental

Metal salts and sulfur dioxide were supplied by BDH Chemicals and used as received. The OPEt$_3$ and OPr$^n{}_3$ ligands were obtained from Strem Chemicals and dried at 100 °C *in vacuo* for 8 h. The dried ligands were stored under dinitrogen.

Preparation of Complexes.—Unco-ordinated trialkylphosphine oxides are hygroscopic. Hence, the complexes were

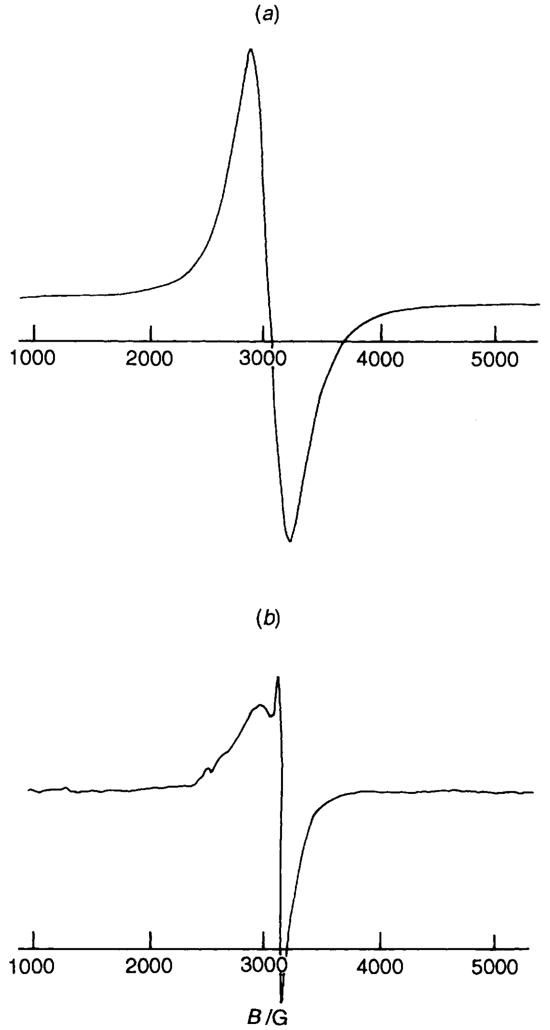

Fig. 7 ESR spectra of (*a*) $[Cu(OPPr^n{}_3)_2Br_2]$ and (*b*) $[Cu\{O(SO_2)PPr^n{}_3\}_2Br_2]$ as dichloromethane glasses; G = 10^{-4} T

synthesised using dry distilled solvents in an inert atmosphere. The final products are air stable. The preparation of $[ZnBr_2(OPEt_3)_2]$ is typical. A predried round-bottomed flask (250 cm^3) was charged with $ZnBr_2$ (0.435 g, 1.93 mmol) against a flow of dinitrogen. The flask was then evacuated, flame dried and allowed to cool. The compound $OPEt_3$ (0.518 g, 3.86 mmol) and toluene (25 cm^3) were then added against a flow of dinitrogen. The flask was re-evacuated and the vacuum let down with dinitrogen, after which the reactants were stirred for *ca.* 7 d and finally isolated by standard Schlenk techniques. Where products formed as oils the solution produced after *ca.*7 d was concentrated and hexane (25 cm^3) added. The solvent was then decanted from the reaction vessel and the oil washed with hexane (3 × 5 cm^3) before being dried *in vacuo* for 24 h.

Reactions with Sulfur Dioxide.—Exposure to sulfur dioxide was carried out by observing the increase in mass of a sample (*ca.* 0.1–0.5 g) of complex 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 SO_2 was added over several days until a constant mass was achieved. Full details of this procedure have been published previously.[8]

Samples for ESR, ^{31}P NMR and visible spectroscopy were prepared in a dinitrogen-filled glove-box. In each case the glassware was adapted for connection to a vacuum line, where the solvents could be saturated with SO_2 under anaerobic conditions.

Thermogravimetric 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 was monitored for samples (*ca.* 0.025 g) of $[ZnBr_2(OPEt_3)_2]$ using a series of temperature/partial pressure programmes. Equilibration was rapid in all cases (< 0.2 h), but samples were maintained at constant temperatures and partial pressures of SO_2 for > 1 h.

Elemental analyses were performed by the UMIST Microanalytical Service. Infrared spectra were obtained on KBr plates as Nujol mulls for solids and as neat samples for oils using Perkin Elmer 598 and Nicolet PC5 FT-IR spectrophotometers in the 4000–250 cm^{-1} range. Electronic spectra were recorded for dichloromethane solutions using 1 cm path length silica cells on a Cary 210 spectrophotometer, ESR spectra for *ca.* 10^{-3} mol dm^{-3} CH_2Cl_2 solutions at 298 and 77 K on a Varian E9 machine. Decoupled ^{31}P NMR spectra were recorded as $CDCl_3$ solutions for the zinc complexes using a Bruker AC200 spectrometer at 81.0 MHz. Free-ligand spectra were obtained from CCl_4 solutions, relative to an 80% H_3PO_4 external lock on a Bruker WP80 spectrometer at 81.0 MHz. Magnetic moments were measured at room temperature using an Oxford Instruments Faraday balance with a 5 in (0.1016 m) Newport N100 electromagnet.

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