Reactivity of Cobalt(II) Complexes $[Co(OEPh_3)_2X_2]$ (E = P or As; X = Cl, Br, I or NCS) with SO_2 under Aerobic and Anaerobic Conditions. Crystal Structure of Cocrystallised $[Co(OPMe_3)_3(OH_2)_2]I_2$ and $[Co(OPMe_3)_3(OH_2)_3]I_2$†

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Pseudo-tetrahedral complexes $[Co(OEPh_3)_2X_2]$ (E = P or As; X = Cl, Br, I or NCS) and $[Co(OPMe_3)_2I_2]$ have been isolated by conventional synthesis from ethanolic solutions of the appropriate hydrated metal salt and Ph_3EO. Their reactivity with sulfur dioxide has been examined in the solid state (anaerobic conditions) and for toluene slurries or solutions (aerobic and anaerobic conditions). The $[Co(OEPh_3)_2X_2]$ (X = Cl or Br) complexes show no reactivity and are recovered unchanged from all forms of exposure to SO_2. However, $[Co(OEPh_3)_2X_2]$ (E = P or As, X = I or NCS) reacted slowly with SO_2 in the solid state to form 1 : 1 adducts, as evidenced by elemental analyses and mass changes. The visible spectra of the precursor complexes and their adducts are similar, suggesting that SO_2 is ligand-bound. On exposure to air, SO_2-saturated toluene slurries and solutions of $[Co(OPPh_3)_2I_2]$ underwent a complex oxidation process resulting in the quantitative isolation of $CoSO_4{\cdot}H_2O$, $(Ph_3PO)(Ph_3POH)(HSO_4)$ and I_2. Visible spectroscopy indicates at least one iodine-containing intermediate, which may be analogous to the cocrystallised $[Co(OPMe_3)_3(OH_2)_2]I_2$ and $[Co(OPMe_3)_3(OH_2)_3]I_2$ recovered from the reaction of $[Co(OPMe_3)_2I_2]$ with SO_2 and air. SO_2-Saturated solutions of $[Co(OAsPh_3)_2I_2]$ afforded $(Ph_3AsOH)(HSO_4)$, I_2, Ph_3AsI_4 and $CoSO_4{\cdot}H_2O$ in the presence of air, although I_2 and Ph_3AsI_4 appear to be produced even under anaerobic conditions. Aerobic reactivity was also observed for $[Co(OEPh_3)_2(NCS)_2]$ (E = P or As); $CoSO_4{\cdot}H_2O$ and ligand derivatives of sulfuric acid were again isolated, however, the fate of the thiocyanate anion remains unclear. The inactivity of $[Co(OPPh_3)_2(NCS)_2]$ under anaerobic conditions contrasts with its subsequent aerobic reactivity and suggests that simple adduct formation and oxidation of SO_2 to sulfuric acid are not closely linked processes.

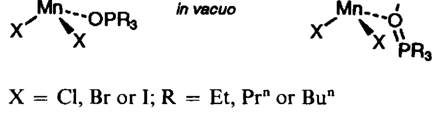
The diversity of bonding and reactivity observed between sulfur dioxide and metal complexes has stimulated numerous studies which have predominantly focused on second- and third-row organometallic complexes, such as the palladium and platinum systems extensively examined by Mingos and co-workers.[1] In the past decade acceptance of the environmental damage caused by acid rain and recognition of the part played by metal-catalysed autoxidation of S^{IV} to S^{VI} have provided further impetus to the study of sulfur dioxide co-ordination.

We are currently investigating the reactivity of first-row transition-metal complexes containing phosphine- and arsine-oxide ligands with sulfur dioxide, and have already characterised systems which may prove effective in the removal of SO_2 from industrial gas streams. This work was initiated by the novel reactivity of the co-ordinatively saturated complex $[Mn(OPPh_3)_4\{OS(O)I\}_2]$.[2] Co-ordination of SO_2 in this air-stable complex is partially reversible, with a single SO_2 moiety being lost at reduced pressures or elevated temperatures.

The systems appear finely balanced since $[Mn(OPPh_3)_4(NCS)_2]$ also binds two SO_2 moieties but exhibits completely reversible co-ordination,[3] whilst $[Mn(OAsPh_3)_4I_2]$ loses one ligand on co-ordination of SO_2 to form an unstable adduct. On heating the solid, or in solution at ambient temperature, the adduct undergoes redox reactivity involving the $OAsPh_3$ ligands which results in the isolation of Ph_3AsI_2, Ph_3AsI_4 and $[(Ph_3AsO)_2H]I_3$.[4-6] Our studies have been carried out in rigorously moisture- and oxygen-free conditions, but on deliberate exposure to air we have observed further unusual behaviour. Prolonged exposure of SO_2-saturated toluene solutions of $[Mn(OPPh_3)_4(NCS)_2]$ to air resulted in the isolation of a remarkable sulfuric acid derivative, $(Ph_3PO)(Ph_3POH)(HSO_4)$.[3]

The $OPPh_2(OPh)$ analogues of $[Mn(OPPh_3)_4I_2]$ and $[Mn(OPPh_3)_4(NCS)_2]$ show markedly different behaviour; the former gives an unstable SO_2 adduct in solution and binds only 1 equivalent of the gas in the solid state, whilst the latter appears to be totally inert to SO_2.[7] Moreover, analogous trialkylphosphine oxide complexes display completely different reactivity, undergoing reversible co-ordination of SO_2 in which the gas is bonded to the phosphine oxide ligand rather than the metal centre.[8] No oxidation of SO_2 occurs with these adducts, behaviour which is typical of ligand-bound SO_2 (Scheme 1).

We have now extended our investigations to cobalt(II) complexes containing $OPPh_3$ and $OAsPh_3$ with the intention of providing further specific information concerning the reactivity of these first-row metal systems, principally addressing the following two questions: (*i*) is insertion of SO_2 limited to complexes of d^5 electronic configuration, or to octahedral geometries?; (*ii*) can systems other than high-spin d^5 complexes catalyse oxidation of SO_2, and can a multicomponent process



Scheme 1 X = Cl, Br or I; R = Et, Pr^n or Bu^n

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

such as oxidation of SO_2 to sulfuric acid be further elucidated using a d^7 metal the electronic spectrum of which is more sensitive to the ligand donor set and geometry than are high-spin d^5 systems?

Results

Synthesis of Complexes.—The complexes $[Co(OEPh_3)_2X_2]$ (E = P or As; X = Cl, Br, I or NCS) have been readily synthesised by several groups using the facile combination of hot ethanolic solutions of the appropriate hydrated cobalt(II) salt and a similar solution containing 2 equivalents of Ph_3EO.[9-11] This method yields deep blue crystalline $[Co(OEPh_3)_2X_2]$ complexes with the exception of $[Co(OAsPh_3)_2(NCS)_2]$ which forms as an oil and requires the addition of light petroleum to produce a solid complex.[12] Previous characterisation, including several crystallographic studies,[13-15] indicate the complexes have pseudo-tetrahedral geometries. Elemental analyses and physical characterisation of the complexes employed here are listed in Table 1.

Solid-state Reactivity with Sulfur Dioxide.—Solid-state coordination of SO_2 was determined for the $[Co(OEPh_3)_2X_2]$ (E = P or As; X = Cl, Br, I or NCS) complexes by monitoring the mass increase occurring when the solid complexes were exposed to gaseous SO_2 under anaerobic conditions. The sulfur dioxide atmospheres were replenished daily and mass readings were taken until a consistent plateau was achieved. Results obtained over a *ca.* 28 d period, Table 2, indicated the formation of 1:1 adducts for $[Co(OEPh_3)_2I_2]$ (E = P or As) and $[Co(OAsPh_3)_2(NCS)_2]$. This is a most interesting result; the fact that $[Co(OPPh_3)_2(NCS)_2]$ does not bind SO_2 shows a complex ligand/anion dependence for binding of SO_2 in these systems. The remaining complexes showed minimal mass increases which can be attributed to surface coverage by SO_2.

Adduct formation was confirmed by elemental analysis for $[Co(OPPh_3)_2I_2(SO_2)]$ [Found (Calc.): C, 46.6 (46.3); H, 3.3 (3.2)%] and $[Co(OAsPh_3)_2(NCS)_2(SO_2)]$ [Found (Calc.): C, 51.3 (51.6); H, 3.6 (3.6); N, 2.8 (3.2)%]. However, attempts unequivocally to define the mode of bonding of SO_2 have been unsuccessful; infrared spectra of the sulfur dioxide adducts of $[Co(OPPh_3)_2I_2]$ and $[Co(OAsPh_3)_2(NCS)_2]$ show new bands at 1260 and 912, and at 880 and 850 cm^{-1}, respectively. The former can be assigned to a symmetric ν(S–O) stretch, but lies in a region which could indicate pyramidal SO_2 bonding, metal–halogen insertion or ligand binding.[16] Iodo complexes develop a green tinge on exposure to SO_2 and $[Co(OAsPh_3)_2(NCS)_2]$ appears to become a deeper blue; however, solid-reflectance spectra of the latter show only a general increase on absorbance in the visible region rather than changes in specific bands. Thus, direct $Co–SO_2$ interation may be excluded, since more pronounced spectral changes would result from such binding; therefore, SO_2–anion or –ligand interaction must occur.

Anaerobic Reactivity with Sulfur Dioxide in Solution.—The complexes $[Co(OEPh_3)_2X_2]$ (E = P or As; X = Cl, Br, I or NCS) complexes were slurried in dry SO_2-saturated toluene and isolated after *ca.* 7 d by standard Schlenk techniques. The solvent was removed in a flow of nitrogen without heating or application of a vacuum. Chloro- and bromo-complexes were recovered unchanged from such reactions and complete characterisation indicates no change from the data presented in Table 1.

Slurries and solutions of $[Co(OPPh_3)_2I_2]$ show a slight blue to green change on exposure to SO_2. Once again elemental analysis indicates the formation of a 1:1 adduct [Found (Calc.): C, 46.5 (46.3); H, 3.4 (3.2)%]. Reaction also occurs for $[Co(OAsPh_3)_2I_2]$ under the same conditions, but whilst an adduct of this complex with SO_2 may initially form, the complex appears to undergo further irreversible reactivity. Solutions develop red colourations which, from the characterisation of the material derived from aerobic reactivity, is likely to result from the formation of I_2 or Ph_3AsI_4. Despite numerous careful attempts to exclude air from such reactions it has proved impossible to isolate a simple adduct without signs of irreversible reactivity.

The thiocyanate complexes appear to follow the pattern established for solid-state activity; $[Co(OPPh_3)_2(NCS)_2]$ once

Table 1 Elemental analyses and physical characterisation for the $[Co(OEPh_3)_2X_2]$ complexes

					Analysis (%)[c]				
Complex	Colour	M.p./ °C	μ_{eff}/μ_B[a]	$\tilde{\nu}$(EO)[b]/ cm^{-1}	C	H	P	Co	X or N
$[Co(OPPh_3)_2Cl_2]$	Pale blue	232	4.60	1151s	63.0 (63.0)	4.3 (4.4)	8.9 (9.0)	8.1 (8.6)	10.4 (10.3)
$[Co(OPPh_3)_2Br_2]$	Pale blue	222	4.65	1153s	56.0 (55.7)	4.1 (3.9)	7.9 (8.0)	7.1 (7.5)	20.6 (20.6)
$[Co(OPPh_3)_2I_2]$	Blue	233	4.80	1148s	49.5 (49.7)	3.4 (3.4)	6.6 (7.1)	6.5 (6.7)	29.1 (29.2)
$[Co(OPPh_3)_2(NCS)_2]$	Blue	232	4.50	1141s[d]	62.3 (62.4)	4.0 (4.1)	8.2 (8.5)	7.6 (8.1)	3.9 (3.8)
$[Co(OAsPh_3)_2Cl_2]$	Pale blue	224	4.65	840, 895s	55.7 (55.8)	3.8 (3.9)		7.2 (7.6)	9.2 (9.2)
$[Co(OAsPh_3)_2Br_2]$	Pale blue	204	4.65	860, 895s	50.2 (50.1)	3.8 (3.5)		6.3 (6.8)	18.5 (18.5)
$[Co(OAsPh_3)_2I_2]$	Blue	212	4.70	875, 895s	45.1 (45.1)	3.4 (3.5)		6.5 (6.2)	26.5 (26.5)
$[Co(OAsPh_3)_2(NCS)_2]$	Blue	230	4.50	862s[e]	55.9 (55.7)	3.7 (3.7)		6.8 (7.2)	3.1 (3.4)
$[Co(OPMe_3)_2I_2]$	Blue	174	4.71	1100, 1135s	14.2 (14.5)	3.6 (3.6)	11.2 (11.7)	10.9 (11.1)	50.9 (51.1)

[a] $\mu_B \approx 9.27 \times 10^{-24}\ J\ T^{-1}$. [b] E = P or As. [c] Calculated values in parentheses. [d] Also ν(CN) 2060s cm^{-1}. [e] Also ν(CN) 2060s cm^{-1}.

Table 2 Uptake of $[Co(OEPh_3)_2X_2]$ (E = P or As; X = Cl, Br, I or NCS) complexes exposed to gaseous SO_2

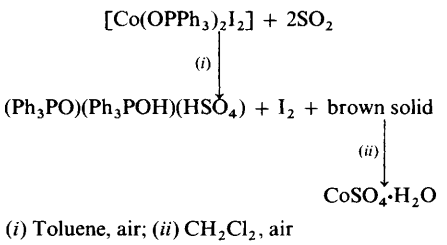
	Mass				Mass SO_2 absorbed		
Complex	g	10^4 mol	Increase in mass/g	Ar/SO_2 correction/g	g	10^4 mol	$Co:SO_2$ ratio
$[Co(OPPh_3)_2Cl_2]$	0.1531	2.23	0.0243	0.0233	0.0010	0.16	1: < 0.1
$[Co(OPPh_3)_2Br_2]$	0.1328	1.71	0.0109	0.0096	0.0007	0.11	1: < 0.1
$[Co(OPPh_3)_2I_2]$	0.5727	6.59	0.0557	0.0167	0.0333	6.09	1:0.93
$[Co(OPPh_3)_2(NCS)_2]$	0.4716	6.45	0.0146	0.0126	0.0020	0.31	1: < 0.1
$[Co(OAsPh_3)_2Cl_2]$	0.4929	6.37	0.0101	0.0096	0.0005	0.08	1: < 0.1
$[Co(OAsPh_3)_2Br_2]$	0.3937	8.34	0.0131	0.0126	0.0005	0.08	1: < 0.1
$[Co(OAsPh_3)_2I_2]$	0.2744	2.87	0.0329	0.0167	0.0162	2.53	1:0.88
$[Co(OAsPh_3)_2(NCS)_2]$	0.3937	4.81	0.0378	0.0077	0.0301	4.70	1:0.98

again showed no co-ordination of SO_2, whilst an adduct is formed by $[Co(OAsPh_3)_2(NCS)_2]$. Binding of SO_2 can be confirmed for the latter complex, as similar infrared shifts were observed in the ν(As–O) region to those noted for the solid-state adduct $[Co(OAsPh_3)_2(NCS)_2(SO_2)]$. However, the extent of co-ordination of SO_2 in toluene for the latter complex cannot be established by elemental or thermogravimetric analysis, since exposure to SO_2 results in the formation of a solvent-rich oil.

Aerobic Reactivity with Sulfur Dioxide in Solution.—The complexes $[Co(OEPh_3)_2X_2]$ (E = P or As; X = Cl, Br, I or NCS) were slurried in dry SO_2-saturated toluene. Once prepared these slurries were either immediately exposed to air, or filtered using standard Schlenk techniques, after which the resulting solutions could be exposed to air. No reactivity was observed under these conditions for the chloro- and bromo-complexes over *ca.* 28 d.

In contrast, the blue-green solutions or slurries of $[Co(OPPh_3)_2I_2]$ turned red over *ca.* 7 d, Fig. 1. The red chromophore is readily identified as diiodine by UV/VIS spectroscopy, a conclusion which is confirmed by HPLC analysis, Table 3. In addition, a white crystalline solid and brown material precipitate from solution in a process which occurs concurrently with the observed colour change. Elemental analysis indicates the crystalline solid to be $(Ph_3PO)(Ph_3POH)(HSO_4)$, whilst the brown solid on work-up in air yields pink $CoSO_4{\cdot}H_2O$. Relatively poor elemental analyses were obtained for the latter; however, the predominance of $CoSO_4{\cdot}H_2O$ within the material is confirmed by X-ray powder studies.[17] The reactivity is thus in accord with Scheme 2.

Moreover, yields for all three products were as expected, Table 3, consistent with the quantitative oxidation process outlined in Scheme 3. The multicomponent nature of such a reaction suggests that several intermediate steps may be involved in the formation of the final products, and this is reflected in the visible spectra obtained from the exposure of an SO_2-saturated toluene solution of $[Co(OPPh_3)_2I_2]$ to air, Fig. 2. Whilst the only chromophores present during aerobic oxidation appear to be $[Co(OPPh_3)_2I_2]$ and I_2, slight



Scheme 2 (*i*) Toluene, air; (*ii*) CH_2Cl_2, air

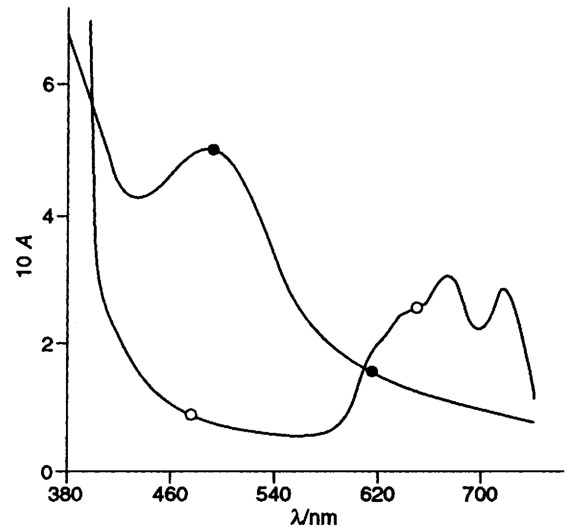


Fig. 1 Visible spectra recorded for a 2.53 × 10^{-4} mol dm^{-3} solution of $[Co(OPPh_3)_2I_2]$ in SO_2-saturated toluene under anaerobic conditions (○) and 7 d after exposure to air (●)

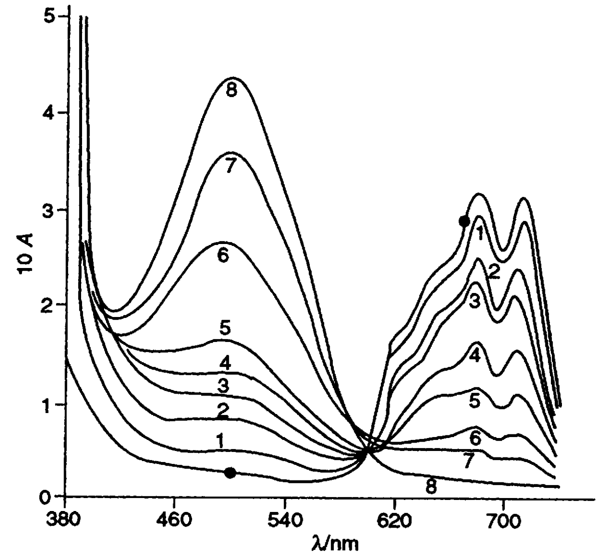


Fig. 2 Visible spectra recorded for a 3.34 × 10^{-4} mol dm^{-3} solution of $[Co(OPPh_3)_2I_2]$ in SO_2-saturated toluene under anaerobic conditions (●) and *n* days after exposure to air

Table 3 Products obtained by the exposure of $[Co(OEPh_3)_2X_2]$ (E = P or As; X = I or NCS) to SO_2 and air in toluene slurries and solutions

Complex	Product	Colour	M.p./°C	Characterisation[a]
$[Co(OPPh_3)_2I_2]$	I_2	Red	—	UV/VIS λ = 500 nm; yield = 98%; HPLC R_f = 195 s.[b]
	$(Ph_3PO)(Ph_3POH)(HSO_4)$	White	186	C, 65.8 (66.1); H, 4.7 (4.9); S, 4.9 (4.9).
	$CoSO_4{\cdot}H_2O$	Pink	> 250	SO_4^{2-}, 50.5 (55.5); IR ν(SO_4^{2-}) 1200, 620s (br).
$[Co(OAsPh_3)_2I_2]$	I_2	Red	—	UV/VIS λ = 500 nm; HPLC R_f 190 s.[b]
	$(Ph_3AsOH)(HSO_4)$	White	154	C, 51.1 (51.5); H, 3.9 (4.0); S 7.4 (7.6).
	$CoSO_4{\cdot}H_2O$	Pink	> 250	SO_4^{2-}, 48.6 (55.5); IR ν(SO_4^{2-}) 1200, 620s (br).
	Ph_3AsI_4	Ruby red	140	UV/VIS λ_1 = 360 nm, λ_2 = 290 nm, λ_2/λ_1 = 2.0: C, 26.6 (26.5); H, 1.8 (1.8); I, 62.2 (62.4).
$[Co(OPPh_3)_2(NCS)_2]$	$(Ph_3PO)(Ph_3POH)(HSO_4)$	White	190	C, 66.0 (66.1); H, 4.8 (4.9); S, 4.8 (4.9)
	$CoSO_4{\cdot}H_2O$	Pink	> 250	SO_4^{2-}, 50.5 (55.5); IR ν(SO_4^{2-}) 1200, 620s(br).
$[Co(OAsPh_3)_2(NCS)_2]$	$(Ph_3AsOH)(HSO_4)$	White	139	C, 51.2 (51.4); H, 3.8 (4.0); S, 7.8 (7.6).
	$CoSO_4{\cdot}H_2O$	Pink	> 250	SO_4^{2-}, 50.5 (55.5); IR ν(SO_4^{2-}) 1200, 620s (br).

[a] Elemental analysis, given as Found (Calc.) %. [b] R_f for standard = 180 s.

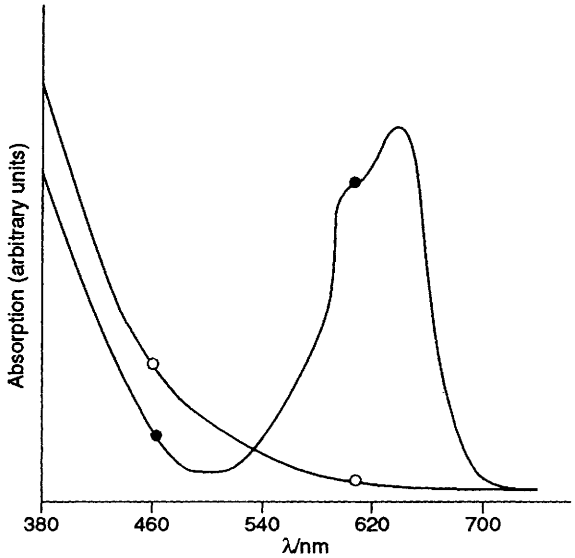


Fig. 3 Visible spectra recorded for an SO_2-saturated toluene solution of $[Co(OPPh_3)_2(NCS)_2]$ under anaerobic conditions (●) and *ca.* 7 d after exposure to air (○)

$$[Co(OPPh_3)_2I_2] + 2SO_2 + \tfrac{3}{2}O_2 + 2H_2O \longrightarrow$$
$$I \longrightarrow CoSO_4\cdot H_2O + (Ph_3PO)(Ph_3POH)(HSO_4) + I_2$$

Scheme 3

deviations from isosbestic behaviour are apparent. Moreover, calculation of the total iodine present, as $[Co(OPPh_3)_2I_2]$ and I_2, falls to 60–80% of the iodine initially observed as $[Co(OPPh_3)_2I_2]$ and finally isolated as I_2. Clearly, at least one iodine-containing intermediate, **I**, must occur (Scheme 3).

The reactivity of $[Co(OAsPh_3)_2I_2]$ is very similar to that of $[Co(OPPh_3)_2I_2]$; once again a sulfuric acid–ligand adduct is formed as well as I_2 and $CoSO_4\cdot H_2O$, Table 3. However, it differs in two important respects. (*i*) The susceptibility of SO_2-saturated toluene slurries and solutions of $[Co(OAsPh_3)_2I_2]$ to irreversible reactivity is more pronounced than that of $[Co(OPPh_3)_2I_2]$. Even the most diligent attempts to exclude moisture and oxygen produced solutions with significant red colourations. However, whilst the behaviour is mechanistically interesting, it is not quantitative and the oxidation products and quantitative yields recorded in Table 3 are the result of deliberate exposure to air. (*ii*) An additional product, in the form of Ph_3AsI_4, is isolated from the reaction of SO_2 and air with $[Co(OAsPh_3)_2I_2]$. The compound crystallises from solution on standing, with commensurate reductions in the yield of I_2.

Surprisingly, both $[Co(OPPh_3)_2(NCS)_2]$ and $[Co(OAsPh_3)_2(NCS)_2]$ react with SO_2 in the presence of air, despite the former's apparent inability to co-ordinate sulfur dioxide. Blue solutions become pale yellow and cobalt(II) sulfate and a ligand derivative of sulfuric acid are precipitated, Table 3. The thiocyanate anion also appears to undergo some form of reactivity, as evidenced by the loss of the deep blue chromophore from $[Co(OAsPh_3)_2(NCS)_2]$ during aerobic oxidation, Fig. 3; however, it was not possible to characterise the species formed. Reactivity analogous to that of the iodo-complexes would result in anion oxidation to thiocyanogen $(NCS)_n$, and whilst the latter is known to form as a brick-red polymer, it is sensitive to moisture giving uncharacterised degradation products.[18]

Aerobic Reactivity of $[Co(OPMe_3)_2I_2]$ *and Crystal Structures of* $[Co(OPMe_3)_3(OH_2)_2]I_2$ *and* $[Co(OPMe_3)_3(OH_2)_3]I_2$.—The complex $[Co(OPMe_3)_2I_2]$ is an air-stable deep blue pseudo-tetrahedral species. Its toluene solutions or slurries can be indefinitely exposed to air with no apparent oxygen or moisture sensitivity. Moreover, anaerobically prepared toluene solutions can be exposed to sulfur dioxide with only minor changes in UV/VIS spectra, which can be attributed to weak SO_2–anion interactions. However, on exposure to air, SO_2-saturated toluene slurries of the complex precipitate pale purple-pink crystals over *ca.* 12 h. The latter material is stable in air, but on heating to 79 °C it decomposes and a blue colouration develops, typical of tetrahedral cobalt(II). When left in solution in the presence of SO_2 and air, slow decomposition occurs to afford a series of oxidation products. These prove harder to separate than those formed from the aerobic reaction of $[Co(OPPh_3)_2I_2]$; however, infrared spectra suggest the presence of cobalt(II) sulfate and, possibly, a ligand derivative of sulfuric acid.

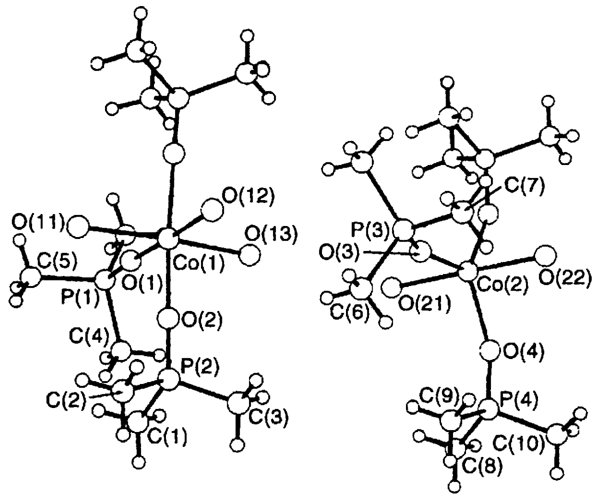


Fig. 4 Single-crystal structures of cocrystallised $[Co(OPMe_3)_3(OH_2)_2]I_2$ and $[Co(OPMe_3)_3(OH_2)_3]I_2$ (iodide anions omitted)

The purple-pink crystals proved suitable for X-ray analysis, and the structural determination indicated the material contained cocrystallised five- and six-co-ordinated $[Co(OPMe_3)_3(OH_2)_2]I_2$ and $[Co(OPMe_3)_3(OH_2)_3]I_2$, Fig. 4. The formation of such complexes from the normally air-stable $[Co(OPMe_3)_2I_2]$ has important mechanistic implications which are discussed below; however, in themselves, the compounds also exhibit several interesting structural features. Both lie on crystallographic mirror planes, with a consequent increase in the number of symmetrically equivalent bonds. The octahedral complex contains *mer*-$[Co(OPMe_3)_3(OH_2)_3]^{2+}$ cations with all three water molecules and a single $OPMe_3$ ligand lying in the mirror plane; $[Co(OPMe_3)_3(OH_2)_2]^{2+}$ is trigonal bipyramidal with the axial aqua ligands and one $OPMe_3$ again lying in the mirror plane. The iodide counter ions for each complex are non-bonded and lie within the crystal lattice. Selected bond angles and lengths are given in Table 4 and indicate significant differences in $OPMe_3$ bonding both within each complex and between the two cocrystallised species. Fractional atomic coordinates are contained in Table 5.

Within the octahedral cation one $OPMe_3$ ligand interacts strongly with the metal centre giving a short Co(1)–O(1) distance of 1.87(6) Å and a long O(1)–P(1) bond of 1.62(6) Å. This ligand lies along the plane of symmetry *trans* to a water molecule. The Co–O distance is comparable with those for two distinct structural determinations of $[CoCl_2(OPMe_3)_2]$ and with the distances observed in $[CoCl_2(OPPh_3)_2]$ and $[CoCl_2\{OP(CH_2Ph)_3\}_2]$.[12,13,19,20] Whilst elongation of the P–O distance on co-ordination is a normal feature of phosphine oxide bonding, the shift from the free oxide distance of 1.489(6) Å[21] appears large in comparison to the 1.508(3)–1.513(6) Å distances obtained for $[CoCl_2(OPMe_3)_2]$. What is certainly clear is that this $OPMe_3$ ligand interacts more strongly with the metal centre than the second crystallographically observed

Table 4 Selected bond lengths (Å) and angles (°) for [Co(OPMe$_3$)$_3$(OH$_2$)$_2$]I$_2$·[Co(OPMe$_3$)$_3$(OH$_2$)$_3$]I$_2$

Co(1)–O(1)	1.87(6)	Co(2)–O(3)	1.92(5)
Co(1)–O(2)	2.03(2)	Co(2)–O(4)	2.03(2)
Co(1)–O(11)	2.16(4)	Co(2)–O(21)	2.18(3)
Co(1)–O(12)	2.17(4)	Co(2)–O(22)	2.09(3)
Co(1)–O(13)	2.18(4)	P(3)–O(3)	1.54(5)
P(1)–O(1)	1.62(6)	P(4)–O(4)	1.45(2)
P(2)–O(2)	1.42(2)		
Co(1)–O(1)–P(1)	175(4)	O(11)–Co(1)–O(13)	169(2)
Co(1)–O(2)–P(2)	172(4)	O(12)–Co(1)–O(13)	92(2)
O(1)–Co(1)–O(2)	97(1)	Co(2)–O(3)–P(3)	158(3)
O(1)–Co(1)–O(11)	80(2)	Co(2)–O(3)–P(4)	148(2)
O(1)–Co(1)–O(12)	178(2)	O(3)–Co(2)–O(4)	119.8(7)
O(1)–Co(1)–O(13)	89(2)	O(3)–Co(2)–O(21)	87(2)
O(2)–Co(1)–O(11)	89(2)	O(3)–Co(2)–O(22)	95(2)
O(2)–Co(1)–O(12)	83(2)	O(4)–Co(2)–O(21)	89(2)
O(2)–Co(1)–O(13)	91(2)	O(4)–Co(2)–O(22)	89(2)
O(2)–Co(1)–O(2′)	166(2)	O(4)–Co(2)–O(4′)	120(2)
O(11)–Co(1)–O(12)	97(2)	O(21)–Co(2)–O(22)	177(2)

Primed atoms are related by the operation $x, \frac{1}{2} - y, z$.

Table 5 Positional parameters

Atom	x	y	z
I(1)	0.704 09(9)	0.118 1(1)	0.295 4(4)
I(2)	0.961 00(8)	0.130 39(9)	−0.242 7(5)
Co(1)	1.048 8(2)	$\frac{1}{4}$	0.279(1)
P(1)	1.121 1(6)	$\frac{1}{4}$	0.631(3)
P(2)	1.043 4(4)	0.088 8(3)	0.256(2)
O(1)	1.090(2)	$\frac{1}{4}$	0.462(8)
O(2)	1.045 2(9)	0.155(1)	0.252(5)
O(11)	1.117(1)	$\frac{1}{4}$	0.154(5)
O(12)	1.003(1)	$\frac{1}{4}$	0.062(5)
O(13)	0.987(1)	$\frac{1}{4}$	0.446(5)
C(1)	1.076(2)	0.060(2)	0.423(6)
C(2)	1.072(2)	0.059(2)	0.088(7)
C(3)	0.987(1)	0.061(1)	0.263(7)
C(4)	1.112(1)	0.178(2)	0.760(7)
C(5)	1.183(2)	$\frac{1}{4}$	0.58(1)
Co(2)	0.806 4(3)	$\frac{1}{4}$	0.663(1)
P(3)	0.855 1(5)	$\frac{1}{4}$	0.279(3)
P(4)	0.791 1(3)	0.099 1(3)	0.770(2)
O(3)	0.844(1)	$\frac{1}{4}$	0.465(7)
O(4)	0.788 9(7)	0.167 3(8)	0.773(3)
O(21)	0.874(1)	$\frac{1}{4}$	0.798(5)
O(22)	0.740(1)	$\frac{1}{4}$	0.543(5)
C(6)	0.888(1)	0.178(2)	0.223(6)
C(7)	0.806(2)	$\frac{1}{4}$	0.150(7)
C(8)	0.822(1)	0.071(1)	0.941(6)
C(9)	0.822(2)	0.070(2)	0.602(8)
C(10)	0.734(1)	0.070(1)	0.790(6)

OPMe$_3$. The latter, which lies out of the mirror plane and thus generates two crystallographically equivalent *trans*-OPMe$_3$ ligands, exhibits a long Co(1)–O(2) bond of 2.03(2) Å and O(2)–P(2) distance close to that of the free phosphine oxide.

Perhaps the most remarkable feature of both ligands within the [Co(OPMe$_3$)$_3$(OH$_2$)$_3$]$^{2+}$ cation is the approximate linearity of the Co–O–P bond, being 175(4) and 172(4)°, respectively. Bent M–O–P bonding is a normal feature of phosphine oxide co-ordination and has been justified on the basis of a partially sp^2-hybridised oxygen centre which offers a sp^2 lone pair for metal co-ordination and a full p$_\pi$ orbital for p$_\pi$–d$_\pi$ bonding to phosphorus.[22] Thus the almost linear Co–O–P angles in [Co(OPMe$_3$)$_3$(OH$_2$)$_3$]$^{2+}$ contrast with angles of 140–129° in [CoCl$_2$(OPMe$_3$)$_2$] and [Co(NO$_3$)$_2$(OPMe$_3$)$_2$],[23] and with numerous bent bonding modes for OPPh$_3$ ligands. Linear OPR$_3$ bonding is known, having been structurally characterised for Ph$_3$PO·ECl$_3$ adducts (E = Al or Ga);[24] however, such bonding has not previously been observed at transition metals.

The geometry of the trigonal-bipyramidal cation [Co(OPMe$_3$)$_3$(OH$_2$)$_2$]$^{2+}$ is closer to those published for other OPMe$_3$ complexes. The Co–O distances are 1.92(5) and 2.03(2) Å for the equatorial OPMe$_3$ ligands and the O–P distances of 1.54(5) and 1.45(2) Å are close to those of the free phosphine oxide. Moreover, the Co–O–P bond angles of 158(3)° and 148(2)° are much closer to the conventional angles recorded for other phosphine oxide complexes than the almost linear bonds of the [Co(OPMe$_3$)$_3$(OH$_2$)$_3$]$^{2+}$ cation. Clearly the bonding angle is critically dependent on the cobalt(II) geometry, but could such linear bonding be typical of octahedral cobalt(II) complexes? Few structural determinations of OPMe$_3$ complexes have been reported; however, a single example of an octahedral cobalt(II) complex exists, [Co(MeCN)$_2$(OPMe$_3$)$_4$][BPh$_4$]$_2$.[25] This shows normal bent OPMe$_3$ co-ordination with Co–O and O–P bond distances of 2.065, 2.050 Å and 1.490, 1.489 Å, respectively, and Co–O–P angles of 133.8 and 140.2°. Thus, it must be concluded that the [Co(OPMe$_3$)$_3$(OH$_2$)$_3$]$^{2+}$ cation exhibits a unique co-ordination environment for the OPMe$_3$ ligand which is generated both by the co-ordination geometry of the complex and the ligand donor set.

Discussion

Numerous forms of sulfur dioxide co-ordination to metals are known, and, moreover, the metal-facilitated oxidation of SO$_2$ to various higher oxidation states has been extensively reported,[16,17] and we have provided several examples of novel co-ordination and oxidation of SO$_2$ to discrete forms of sulfuric acid.[2–8,26,27] Thus, it is the intention of the present work to elucidate the structure–reactivity relationships associated with co-ordination of SO$_2$ and to investigate the mechanism of its oxidation to sulfuric acid, rather than simply to provide further examples of phosphine- and arsine-oxide complexes which display such behaviour.

Characterisation suggests that when adducts of SO$_2$ are formed by the d^7 cobalt(II) complexes binding occurs at the anions or ligands, rather than directly to the metal. Sulfur dioxide insertion into metal–halide bonds can occur with both manganese(II) and iron(III) complexes,[2–4] but clearly not for cobalt(II). Since the latter differ in both electronic configuration and co-ordination number, it is not possible to distinguish the critical effect. However, insertion of SO$_2$ is clearly not a general process for phosphine- and arsine-oxide complexes. Whilst we strongly believe that a different mode of bonding of SO$_2$ occurs for cobalt(II) relative to that of iron(III) and manganese(II), there are, nonetheless, strong parallels between the observed anion and ligand influences in these systems,[2–4] which warrant further investigation.

Since the facile oxidation of sulfur dioxide to sulfuric acid discovered by us[2–8,26,27] is a novel process, can the d^7 systems reported here provide an insight into the mechanisms involved? Studies of the aerobic reactivity of [Co(OPPh$_3$)$_2$I$_2$] and SO$_2$ have proved particularly valuable. The quantitative isolation of I$_2$, CoSO$_4$·H$_2$O and (Ph$_3$PO)(Ph$_3$POH)(HSO$_4$) provides a clear indication of the fate of each component of the starting complex. Clearly, iodine and sulfur undergo oxidation: from I^{-I} to I^0 and S^{IV} to S^{VI}, respectively. Notably, even though cobalt(III) complexes are common, no permanent metal oxidation occurs.

Clearly, the complexity of the oxidation process suggests several steps. The UV/VIS spectroscopic studies of the aerobic reaction of SO$_2$ and [Co(OPPh$_3$)$_2$I$_2$] provide further evidence for the presence of reaction intermediates. The conversion of iodine from [Co(OPPh$_3$)$_2$I$_2$] into I$_2$ is accurately observed during oxidation, and the overall process is quantitative. However, even though no other species is observed during the reaction the total iodine present represents only 60–80% of the expected value. Therefore, an intermediate must be involved which contains iodine and has a weak UV/VIS spectrum. An octahedral cobalt(II) complex would be an obvious candidate; however, no such complex can be isolated from $[Co(OPPh_3)_2I_2]$ reactions in this study.

The isolation of cocrystallised $[Co(OPMe_3)_3(OH_2)_2]I_2$ and $[Co(OPMe_3)_3(OH_2)_3]I_2$ from the aerobic reaction of $[Co(OPMe_3)_2I_2]$ and SO_2 is potentially significant. The geometries of the complexes are in accord with the required UV/VIS properties of an aerobic oxidation intermediate, and, although no SO_2 is present in the complexes, they cannot be formed in its absence. Thus, SO_2 must play a vital role in the formation of the complexes.

If it is assumed that mixed aqua–phosphine oxide complexes similar to those observed with $OPMe_3$ are involved in the aerobic oxidation of $[Co(OPPh_3)_2I_2]$, what could their role be?

The reactants SO_2, H_2O, O_2 and $OPPh_3$ are required for the formation of $(Ph_3PO)(Ph_3POH)(HSO_4)$, and to provide a low-activation-energy pathway most or all must be simultaneously present in the metal co-ordination sphere. In addition, the ligands must be substitution labile to allow reactants to enter and products to leave, and the co-ordination number of the complex must be sufficient to stabilise the metal after $(Ph_3PO)(Ph_3POH)(HSO_4)$ is lost. Does $[Co(OPMe_3)_3(OH_2)_2]I_2$ or $[Co(OPMe_3)_3(OH_2)_3]I_2$ possess any of these properties? Only SO_2 and O_2 are not co-ordinated in either complex and SO_2 does react readily with co-ordinated water or hydroxyl groups to form bound sulfito species.[28] Thus, the transient co-ordination of O_2 would bring together all the necessary reactants. The cocrystallisation of the five- and six-co-ordinate complexes indicates the lability of one water moiety; moreover, further water is lost at 79 °C to afford a tetrahedral species. Thus sufficient lability is present within the complex to allow O_2 binding. Loss of $(Ph_3PO)(Ph_3POH)(HSO_4)$ from the five- or six-co-ordinate complexes would leave unstable two- or three-co-ordinate cobalt(II). However, the iodide anions readily co-ordinate to cobalt(II) in $[Co(OPPh_3)_2I_2]$ and would therefore be able to generate a stable tetrahedral species. Whilst such arguments do not fully explain the oxidation process they are in accord with the observed behaviour.

Whilst the available evidence does not fully explain the reactivity of $[Co(OAsPh_3)_2I_2]$ and SO_2, it does appear that ligand and halide reactivity may be involved in the irreversible formation of I_2 and Ph_3AsI_4 rather than contamination by traces of air and moisture. It is clear that aerobic reactivity can also occur since the final isolated products, $(Ph_3AsO)(HSO_4)$ and $CoSO_4{\cdot}H_2O$, must be derived from the action of oxygen and moisture.

Experimental

Reagents.—Hydrated cobalt(II) salts (X = Cl or Br, BDH; X = I, Alfa) were used as received; $OPPh_3$ and $OPMe_3$ were obtained from Fluka and Strem, respectively, whilst $OAsPh_3$ was prepared by oxidation of $AsPh_3$ (Lancaster) with H_2O_2.

Preparation of Complexes.—The following synthesis of $[Co(OPPh_3)_2Cl_2]$ is typical. The compound $CoCl_2{\cdot}6H_2O$ (1.50 g, 6.30 mmol) was dissolved in ethanol (*ca.* 10 cm^3) and warmed to reflux, whilst a similar solution was prepared containing $OPPh_3$ (3.50 g, 12.60 mmol). The solutions were combined and allowed to cool. After *ca.* 1 h deep blue crystalline $[Co(OPPh_3)_2Cl_2]$ (> 90% yield) was filtered off, washed with Et_2O and dried *in vacuo*. A similar preparation of $[Co(OAsPh_3)_2(NCS)_2]$ resulted in a deep blue oil which was solidified by vigorous shaking with light petroleum (b.p. 60–80 °C).

Reactions with Sulfur Dioxide.—Techniques for aerobic and anaerobic reactions with sulfur dioxide have been previously reported.[27] Solutions of $[Co(OEPh_3)_2X_2]$ complexes were prepared using the same techniques as those employed for toluene slurries with the added provision that precise quantities of solvent and complex were used. Samples were removed for UV/VIS spectroscopy in an argon-filled dry-box and transferred to silica cells (path length 1 cm) fitted with polytetrafluoroethylene seals.

Table 6 Crystallographic data for $[Co(OPMe_3)_3(OH_2)_2]I_2{\cdot}[Co(OPMe_3)_3(OH_2)_3]I_2$

Molecular formula	$C_{18}H_{64}Co_2I_4O_{11}P_2$
M	1268.0
System	Orthorhombic
Space group	*Pnma*
a/Å	27.774(9)
b/Å	21.262(5)
c/Å	8.108(2)
U/Å^3	4788
Z	4
D_c/g cm^{-3}	1.759
μ(Mo-Kα)/cm^{-1}	34.79
F(000)	2464
Crystal dimensions/mm	0.35 × 0.3 × 0.2
R	0.067
R'	0.051
ρ of $w = 1/[\sigma^2(F_o) + \rho(F_o)^2]$	0.03

Elemental analyses were carried out at UMIST by the Microanalytical Service. Infrared spectra for Nujol mulls on KBr discs were recorded in the 4000–200 cm^{-1} region on a Perkin-Elmer 598 spectrophotometer, UV/VIS spectra on a Varian Cary 210 machine. Magnetic susceptibilities were recorded using a Johnson Matthey balance and corrected for diamagnetism. X-ray powder patterns were recorded using a Scintag 2000 diffractometer and Cu-Kα radiation (λ = 1.5418 Å) in the 2θ range 5–70°. The HPLC studies were performed using a normal phase column and compared to a 1 mmol solution of I_2 in toluene.

X-Ray Crystallography.—Measurements were made using a Nicolet R3m/V diffractometer and graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å). Data were collected in ω–2θ scan mode with a scan width of 0.80 + 0.35 tan θ and speed 0.5–5.0° min^{-1}; three intensity standards were measured regularly and showed no decay in intensity. 2710 Unique reflections were collected ($0 < \theta < 24°$) of which 1054 had $I > 3\sigma(I)$. Lorentz-polarisation corrections were applied but absorptions were ignored.

Standard heavy-atom techniques were used to locate the iodine atoms, and remaining non-hydrogen atoms were detected from Fourier-difference maps. Full-matrix least-squares refinement was carried out using TEXSAN[29] crystallographic software on a Vax 5760 computer. Later refinements assigned anisotropic parameters to all iodine and cobalt atoms and three of the four phosphorus centres. The remaining phosphorus, P(1), as well as the oxygen and carbon atoms, were refined isotropically. Hydrogen atoms were constrained to chemically reasonable positions, except those of the co-ordinated water molecules which were ignored. Final R = 0.067 and R' = 0.051. Maximum and minimum peaks in the final difference map were 0.94 and −0.92 e Å^{-3}, respectively. Neutral atom scattering factors and anomalous dispersion effects were taken from standard sources.[30,31] Full crystal data are given in Table 6.

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

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References

1 A. D. Burrows, J. C. Machell, M. P. Mingos and H. R. Powell, *J. Chem. Soc., Dalton Trans.*, 1992, 1521 and refs. therein.

2 G. A. Gott, J. Fawcett, C. A McAuliffe and D. R. Russell, *J. Chem. Soc., Chem. Commun.*, 1988, 1095.

3 K. Al-Farhan, B. Beagley, O. El-Sayrafi, G. A. Gott, C. A. McAuliffe, P. P. Mac Rory and R. G. Pritchard, *J. Chem. Soc., Dalton Trans.*, 1990, 1243.

4 B. Beagley, O. El-Sayrafi, G. A. Gott, D. G. Kelly, A. G. Mackie, P. P. Mac Rory, C. A. McAuliffe and R. G. Pritchard, *J. Chem. Soc., Dalton Trans.*, 1988, 1095.

5 B. Beagley, C. B. Colburn, O. El-Sayrafi, G. A. Gott, D. G. Kelly, A. G. Mackie, P. P. Mac Rory, C. A. McAuliffe and R. G. Pritchard, *Acta Crystallogr., Sect. C*, 1988, **44**, 38.

6 C. A. McAuliffe, B. Beagley, G. A. Gott, A. G. Mackie, P. P. Mac Rory and R. G. Pritchard, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 264.

7 S. Abbas, B. Beagley, S. M. Godfrey, D. G. Kelly, C. A. McAuliffe and R. G. Pritchard, *J. Chem. Soc., Dalton Trans.*, 1992, 1915.

8 S. M. Godfrey, D. G. Kelly and C. A. McAuliffe, *J. Chem. Soc., Dalton Trans.*, 1992, 1305.

9 R. H. Holm and F. A. Cotton, *J. Chem. Phys.*, 1960, **32**, 1168.

10 F. A. Cotton, D. M. L. Goodgame, M. Goodgame and A. Sacco, *J. Am. Chem. Soc.*, 1961, **83**, 4157.

11 D. M. L. Goodgame, M. Goodgame and F. A. Cotton, *Inorg. Chem.*, 1962, **2**, 239.

12 F. Edelmann and U. Behrens, *Acta Crystallogr., Sect. C*, 1986, **42**, 1715.

13 M. M. Mangion, R. Smith and S. G. Shore, *Cryst. Struct. Commun.*, 1976, **5**, 493.

14 P. J. M. W. L. Birker, P. Prick and P. T. Beurskens, *Cryst. Struct. Commun.*, 1976, **5**, 135.

15 P. Prick, P. T. Beurskens and P. J. M. W. L. Birker, *Cryst. Struct. Commun.*, 1977, **6**, 437.

16 R. R. Ryan, G. J. Kubas and P. G. Eller, *Struct. Bonding (Berlin)*, 1981, **46**, 48.

17 Z. Pistorius, *Z. Kristallogr.*, 1961, **115**, 303.

18 *The Chemistry and Biochemistry of Thiocyanic Acid and Its Derivatives*, ed. A. A. Newmann, Academic Press, New York, 1975.

19 M.-J. Menu, M. Simend, A. L. Beauchamp, H. Konig, M. Dartiguenave, Y. Dartiguenave and H. F. Klein, *Acta Crystallogr., Sect. C*, 1989, **45**, 1697.

20 R. H. DeSantos and A. Mascarenhas, *J. Coord. Chem.*, 1979, **9**, 59.

21 L. M. Engelhardt, C. L. Raston, C. R. Whitaker and A. H. White, *Aust. J. Chem.*, 1986, **39**, 2151.

22 F. A. Cotton, R. D. Barnes and E. Bannister, *J. Chem. Soc.*, 1960, 2199.

23 F. A. Cotton and R. H. Soderberg, *J. Am. Chem. Soc.*, 1963, **85**, 2402.

24 N. Burford, B. W. Royan, R. E. H. Spence, T. S. Cameron, A. Linden and R. G. Rodgers, *J. Chem. Soc., Dalton Trans.*, 1990, 1521.

25 M. Dartiguenave, Y. Dartiguenave, M. J. Oliver and A. L. Beauchamp, *J. Coord. Chem.*, 1990, **21**, 275.

26 S. M. Godfrey, D. G. Kelly, C. A. McAuliffe and G. C. Ranger, *J. Chem. Soc., Dalton Trans.*, 1993, 2809.

27 B. Beagley, D. G. Kelly, P. P. Mac Rory, C. A. McAuliffe and R. G. Pritchard, *J. Chem. Soc., Dalton Trans.*, 1990, 2657.

28 R. van Eldik, J. von Jouanne and H. Kelm, *Inorg. Chem.*, 1982, **21**, 2818 and refs. therein.

29 TEXSAN-TESRAY Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1985.

30 D. T. Cromer and J. T. Waber, *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.

31 J. A. Ibers and W. C. Hamilton, *Acta. Crystallogr.*, 1964, **17**, 781.

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