Systematic structural studies on cobalt(II) complexes of tricyclohexylphosphine oxide and related ligands

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Abstract
The new cobalt(II) phosphine oxide complexes $Co(Cy_3PO)_2Cl_2$ (**1**), $Co(Cy_3PO)_2Br_2$ (**2**), $Co(Cy_3PO)_2I_2$ (**3**), $Co(Ph_2CyPO)_2Cl_2$ (**4**), $Co(Ph_2CyPO)_2Br_2$ (**5**), $Co(Ph_2CyPO)_2I_2$ (**6**), $Co(Ph_2EtPO)_2Br_2$ (**7**), $Co(Cy_3PO)_2(NCS)_2$ (**8**) and $Co(Cy_3PO)_2(NO_3)_2$ (**9**) have been prepared by the reaction of anhydrous CoX_2 (X = Cl, Br, I, NCS, NO_3) with the appropriate phosphine oxide. The complexes were characterised by single-crystal X-ray crystallography supported by IR and UV/visible absorption spectroscopy. The structural analyses show that the cobalt(II) centre adopts a distorted tetrahedral coordination geometry except for **9** which displays an octahedral geometry. Systematic structural features of these complexes are explained within this paper.

Keywords
Phosphine oxide, cobalt (II) complex, X-ray structures, tetrahedral

1. Introduction

We previously reported the structures of the cobalt(II) complexes $Co(Ph_3PO)_2Cl_2$, $Co(Ph_3PO)_2Br_2$, $Co(Ph_3PO)_2I_2$, $Co(Ph_3AsO)_2Br_2$ and $Co(Ph_3AsO)_2(NO_3)_2$ [1]; all exhibited distorted tetrahedral coordination of cobalt. Clear trends were seen in metal-halogen bond lengths in $Co(Ph_3PO)_2X_2$ (X = Cl, Br, I), whilst the cobalt-oxygen bond length was relatively insensitive to the nature of the halogen. We wished to establish whether such patterns might be found in other simple transition metal complexes and we therefore prepared analogous complexes with other phosphine oxides, which to our knowledge, have not been reported previously, particularly those of tricyclohexylphosphine oxide. In this paper, we report the syntheses and structure of 2:1 complexes of Cy_3PO and Ph_2CyPO with CoX_2 (X = Cl, Br, I); of the analogous complex of Ph_2EtPO with $CoBr_2$; and also the 2:1 complexes of Cy_3PO with $Co(NCS)_2$ and $Co(NO_3)_2$.

2. Experimental

2.1 Material and methods
Tricyclohexylphosphine oxide was synthesised [2] by hydrogen peroxide oxidation of tricyclohexylphosphine. Cobalt salts and the other phosphine oxides were obtained as commercial products and were used without further purification.

2.2 Synthesis of the complexes

[Co(Cy_3PO)$_2$$Cl_2$] (**1**) was prepared by mixing warm ethanolic solutions of anhydrous $CoCl_2$ (0.12 g; 0.92 mmol) and Cy_3PO (0.60 g; 2.0 mmol). Blue crystals formed on cooling. Compounds **2, 4, 5, 7, 8** and **9** were obtained similarly; all formed blue crystals, except **9** which is violet. Compounds **3** and **6** were prepared in a similar procedure, but the initial products of the reactions of CoI_2 with Cy_3PO and Ph_2CyPO were dark green crystals; their exact composition has not been established. However, on leaving the solutions for several weeks to crystallize further, a few green-blue crystals of Co(Cy_3PO)$_2$$I_2$ **(3)** and Co(Ph_2CyPO)$_2$$I_2$ (**6**) formed; these were insufficient for analysis except for X-ray diffraction.

2. 3 X-ray crystallography

Crystals were obtained from the mother liquor and mounted on a glass fibre with oil and transferred to a diffractometer. The crystal data, data collection parameters, and structure solution and refinement details for the crystal structures determined are summarised in Table 1 and 2.

Data collections were carried out using either Bruker Nonius Kappa CCD diffractometers, equipped with an Oxford Cryostream cooling apparatus [3] or using an Oxford Diffraction Gemini A Ultra, equipped with a CryojetXL cooling device. In all cases graphite monochromated Mo Kα radiation was used. The structures were solved using Sir92 [4], SHELX-86 [5] and refined by full-matrix least-squares F^2 using SHELXL-97 [6]. All non-hydrogen atoms were refined with anisotropic displacement parameters and H-atoms were placed in idealised positions and allowed to ride on the relevant C-atom. Isotropic displacement parameters were set at 1.2 U_{eg}. Refinements were continued until convergence was reached and the residual electron density maps showed no significant residual features.

Table 1 Crystal data, data collection parameters and refinement parameters for the complexes **1-5**

Compound reference	**(1)**	**(2)**	**(3)**	**(4)**	**(5)**
Chemical formula	$C_{36}H_{66}Cl_2CoO_2P_2$	$C_{36}H_{66}Br_2CoO_2P_2$	$C_{36}H_{66}CoI_2O_2P_2$	$C_{36}H_{42}Cl_2CoO_2P_2$	$C_{36}H_{42}Br_2CoO_2P_2$
Formula Mass	722.66	811.58	905.56	698.47	787.39
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
a/Å	16.2750(2)	16.3730(2)	20.1463(14)	9.3230(1)	9.4690(2)
b/Å	18.3150(2)	18.4280(3)	9.6082(3)	16.5790(3)	16.6590(5)
c/Å	25.6890(3)	25.8840(3)	20.3167(7)	22.3780(4)	22.3690(4)
α/°	90	90	90	90	90
β/°	90	90	90	99.634(1)	98.702(2)
γ/°	90	90	90	90	90
Unit cell volume/Å^3	7657.29(15)	7809.76(18)	3932.7(3)	3410.10(9)	3487.96(14)
Temperature/K	150(2)	150(2)	150(2)	150(2)	150(2)
Space group	*Pcab*	*Pcab*	$Pca2_1$	$P2_1/n$	$P2_1/n$
No. of formula units per unit cell, Z	8	8	4	4	4
Size	0.40 0.40 0.35	0.5 0.2 0.2	0.17 0.14 0.11	0.80 0.35 0.25	0.40 0.35 0.30
Diffractometer	Kappa	Kappa	Gemini	Kappa	Kappa
No. of reflections measured	110431	94571	29957	55284	51344
No. of independent reflections	11623	10964	12549	9357	9551
R_{int}	0.0544	0.0999	0.0413	0.1015	0.1378
Final R_1 values ($I > 2\sigma(I)$)	0.0407	0.0587	0.0292	0.0551	0.0486
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1028	0.1094	0.037	0.1255	0.1087
Final R_1 values (all data)	0.0599	0.1251	0.0539	0.1285	0.1117
Final $wR(F^2)$ values (all data)	0.1195	0.1331	0.0391	0.1837	0.1562
Flack parameter			-0.030(8)		

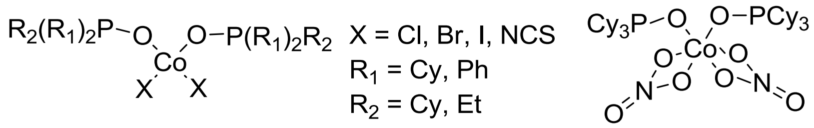
Table 2 Crystal data, data collection parameters and refinement parameters for the complexes **6-9**

Compound reference	**(6)**	**(7)**	**(8)**	**(9)**
Chemical formula	$C_{36}H_{42}CoI_2O_2P_2$	$C_{28}H_{30}Br_2CoO_2P_2$	$C_{38}H_{66}CoN_2O_2P_2S_2$	$C_{36}H_{66}CoN_2O_8P_2$
Formula Mass	881.37	679.21	767.92	775.78
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
a/Å	9.6375(3)	9.6940(2)	9.4220(4)	9.2520(1)
b/Å	16.8434(5)	14.6690(3)	12.2400(3)	21.2490(4)
c/Å	22.3267(7)	20.5910(4)	19.5100(7)	20.3010(4)
α/°	90	90	101.628(2)	90
β/°	97.296(3)	96.856(1)	96.622(2)	95.318(1)
γ/°	90	90	109.748(2)	90
Unit cell volume/Å^3	3594.91(19)	2907.13(10)	2032.74(12)	3973.91(12)
Temperature/K	150(2)	150(2)	150(2)	150(2)
Space group	$P2_1/n$	$P2_1/n$	$P\text{-}\bar{1}$	$P2_1/c$
No. of formula units per unit cell, Z	4	4	2	4
Size	0.19 0.15 0.08	0.55 0.5 0.5	0.35 0.30 0.30	0.3 0.2 0.2
Diffractometer	Gemini	Kappa	Kappa	Kappa
No. of reflections measured	51076	46751	36201	66958
No. of independent reflections	12367	8688	10817	10954
R_{int}	0.0408	0.167	0.1302	0.1049
Final R_1 values ($I > 2\sigma(I)$)	0.0333	0.0663	0.0592	0.0509
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.076	0.1619	0.1185	0.0985
Final R_1 values (all data)	0.0631	0.0826	0.1386	0.1216
Final $wR(F^2)$ values (all data)	0.0803	0.1772	0.1462	0.1183

3. Results and Discussion

3.1 Preparation

The new cobalt(II) phosphine oxide complexes $Co(Cy_3PO)_2Cl_2$ (**1**), $Co(Cy_3PO)_2Br_2$ (**2**), $Co(Cy_3PO)_2I_2$ (**3**), $Co(Ph_2CyPO)_2Cl_2$ (**4**), $Co(Ph_2CyPO)_2Br_2$ (**5**), $Co(Ph_2CyPO)_2I_2$ (**6**), $Co(Ph_2EtPO)_2Br_2$ (**7**), $Co(Cy_3PO)_2(NCS)_2$ (**8**) and $Co(Cy_3PO)_2(NO_3)_2$ (**9**) were prepared by the reaction of anhydrous CoX_2 (X = Cl, Br, I, NCS, NO_3) with the appropriate phosphine oxide using a method previously described for the synthesis of $Co(Ph_3PO)_2X_2$ (X = Cl, Br, I) [1] (Scheme 1). The were initially characterised by IR spectroscopy (see supplementary information) and by comparison with the data reported for $Co(Ph_3PO)_2X_2$.



Scheme 1

3.2 X-ray structures of the compounds 1-9

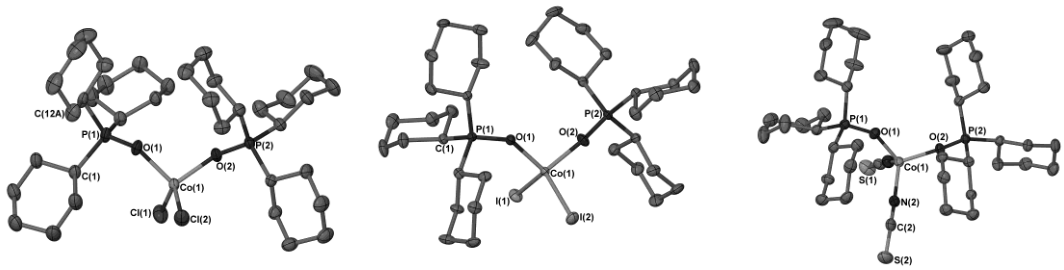


Fig. 1: a) Structures of **1**, b) **3** and c) **8** with hydrogens and disorder in **1** removed for clarity and ellipsoids set at 50 % probability

In the four complexes with tricyclohexylphosphine oxide (**1-3, 8**), cobalt has distorted tetrahedral coordination, being bound to the oxygen atoms of two tricyclohexylphosphine oxides and two halogens or thiocyanate ligands. An analysis of the packing in these four structures showed no short intermolecular interactions, the molecules being separated by normal van-der-Waals distances. Compounds **1-2** crystallize in the orthorhombic space group *Pcab*, with one molecule per asymmetric unit and the structures are isomorphous and isostructural (Fig.1a). Compound **3**, on the other hand, crystallizes in the orthorhombic space group $Pca2_1$, again with one molecule per asymmetric unit (Fig. 1b). The structure of **1** displays disorder in one of the cyclohexyl rings (C12-C17) in a ratio of ca. 90:10, which is not found within the other two structures. It is treated as a disorder model with the total occupancy of each atom being summed to unity. Only the major compound is refined with anisotropic displacement parameters. The closely related thiocyanate complex, $Co(Cy_3PO)_2(NCS)_2$ **8**, crystallizes in the triclinic space group *P*-1 with one molecules in the asymmetric unit (Fig. 1c).

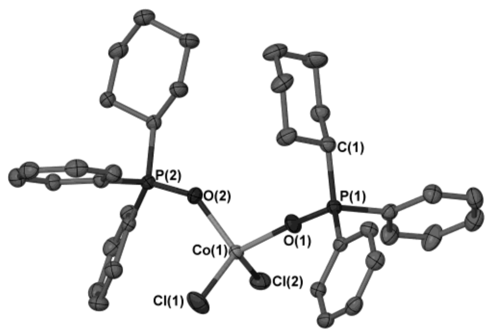


Fig. 2: Structure of **4** with hydrogens and disorder removed for clarity and ellipsoids set at 50 % probability

The three structures **4-6** are isomorphous and isostructural and crystallize in the monoclinic space group $P2_1/n$, with one molecule per asymmetric unit (Fig. 2).

Again the molecules are separated by normal van-der-Waals distances and there is no indication of any significant intermolecular interactions. The distorted tetrahedral Co(II) centre is coordinated by two phosphine oxide ligands and two halogen atoms.

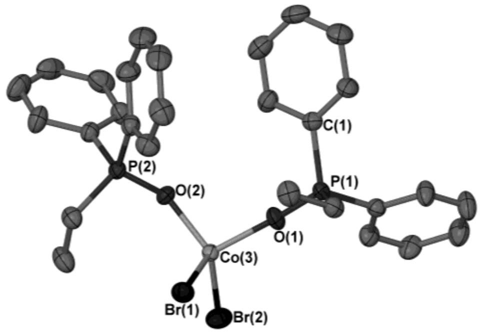


Fig. 3: Structure of **7** with hydrogens and disorder removed for clarity and ellipsoids set at 50 % probability

Compound **7** crystallizes in the monoclinic space group $P2_1/n$. The structure shows no obvious intermolecular packing interactions in the crystal. The distorted tetrahedral cobalt centre is bound to two phosphine oxide ligands and two bromides (Fig.3).

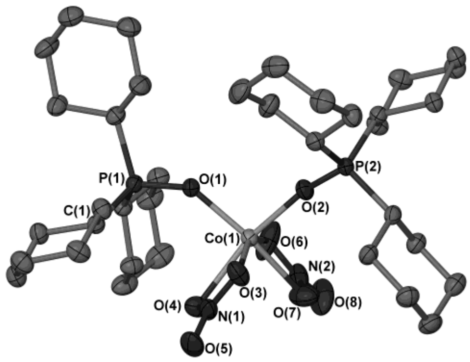


Fig. 4: Structure of **9** with hydrogens and disorder removed for clarity and ellipsoids set at 50 % probability

The complex $Co(Cy_3PO)_2(NO_3)_2$ (**9**) crystallizes in the monoclinic space group $P2_1/c$ with one molecule per asymmetric unit. The cobalt ion in is bound to two bidentate oxygens of each nitrate group and to the two oxygens of the phosphine oxides. **9** has octahedral coordination of cobalt, with the phosphine oxide ligands adopting a *cis* arrangement, as also found in $Co(Ph_3PO)_2(NO_3)_2$ [7] and $Ni(NO_3)_2(Cy_3PO)_2$ [8], but in contrast to tetrahedral $Co(Ph_3AsO)_2(NO_3)_2$ [1], where the nitrate groups exhibit a monodentate coordination mode. The molecules within the crystal structure are separated by normal van-der-Waals distances and there is no evidence for any significant intermolecular interactions.

*3.3 Comparison of bond parameters across the series **1-9***

Table 3 Principal bond lengths and angles for the coordination sphere of the complexes **1-9**

	(1)	**(2)**	**(3)**	**(4)**	**(5)**	**(6)**	**(7)**	**(8)**	**(9)**
Co-X	2.2464(5)	2.3847(6)	2.5530(4)	2.2462(11)	2.3830(6)	2.5915(4)	2.3808(6)	1.947(2)	2.1077(16)
	2.2562(5)	2.3964(7)	2.5543(4)	2.2559(11)	2.3884(7)	2.5915(4)	2.3940(7)	1.957(3)	2.1171(19)
									2.1916(18)
									2.2461(17)

Co-O	1.9648(12)	1.960(2)	1.9461(17)	1.961(2)	1.954(3)	1.9422(16)	1.937(3)	1.9413(19)	1.9703(15)
	1.9827(12)	1.968(2)	1.9601(17)	1.966(2)	1.964(3)	1.9655(16)	1.957(3)	1.9660(18)	1.9996(14)
X-Co-X	116.58(2)	114.22(3)	120.68(1)	117.97(4)	119.16(3)	115.99(1)	109.10(3)	111.9(1)	
O-Co-O	101.85(5)	102.7(1)	104.12(8)	102.6(1)	103.5(1)	104.24(7)	102.9(1)	107.22(8)	99.75(6)
O-Co-X	109.21(4)	108.98(8)	106.68(6)	111.58(8)	110.32(9)	109.13(6)	108.67(10)	108.22(9)	
	111.35(4)	111.48(8)	113.72(5)	107.81(8)	107.58(8)	107.23(5)	113.24(9)	110.08(9)	
	109.74(4)	111.61(8)	107.61(6)	106.38(8)	105.58(8)	105.01(5)	110.94(10)	110.25(9)	
	107.09(4)	107.26(8)	107.78(5)	109.41(8)	109.65(9)	109.47(5)	111.81(9)	109.10(9)	

For the chloride complexes, average Co-O bond lengths of 1.974 Å in **1** and 1.964 Å in **4** are similar to the values of 1.972 Å and 1.971 Å in $Co(Me_3PO)_2Cl_2$ [9] and $Co(Ph_3PO)_2Cl_2$ [1] respectively; similarly average Co-Cl bond lengths of 2.251 Å in both **1** and **4** are likewise comparable to the respective values of 2.262 Å and 2.227 Å in $Co(Me_3PO)_2Cl_2$ and $Co(Ph_3PO)_2Cl_2$. The Cl-Co-Cl angles of 116.58(2)° in **1** and 117.97(4)° in **4** are rather greater than the values of 113.6(1)° and 112.76(6)° in $Co(Me_3PO)_2Cl_2$ and $Co(Ph_3PO)_2Cl_2$, respectively, whilst the O-Co-O angles of 101.85(5)° in **1** and 102.6(1)° in **4** are intermediate between the values of 105.6(2)° and 97.86(16)° in $Co(Me_3PO)_2Cl_2$ and $Co(Ph_3PO)_2Cl_2$, respectively.

For the bromide complexes, average Co-O bond lengths of 1.964 Å in **2**, 1.959 Å in **5** and 1.947 Å in **7** are very comparable with the values of 1.957 Å and 1.970 Å in $Co((Me_2N)_3PO)_2Br_2$ [10] and $Co(Ph_3PO)_2Br_2$ [1], respectively. Similarly average Co-Br bond lengths of 2.391 Å in **2**, 2.386 Å in **5** and 2.387 Å in **7** are likewise close to the respective values of 2.404 Å and 2.385 Å in $Co(Me_3PO)_2Br_2$ and $Co(Ph_3PO)_2Br_2$. The O-Co-O angles of 102.7(1)° in **2**, 103.5(1)° in **5** and 102.9(1)° in **7** are similar to that in $Co(Ph_3PO)_2Br_2$ (103.9(2)°), but much less than the value of 110.7(3)° in $Co((Me_2N)_3PO)_2Br_2$. There is in most cases very significant deviation from regular tetrahedral geometry in the Br-Co-Br bond angles of 114.22(3)° in **2**, 119.16(3)° in **5** and 109.10(3)° in **7**, as in $Co(Ph_3PO)_2Br_2$ (113.72(5)°) and 117.97(6)° in $Co((Me_2N)_3PO)_2Br_2$.

For the iodide complexes, average Co-O bond lengths of 1.953 Å in **3** and 1.954 Å in **6** are virtually identical to the values of 1.952 Å and 1.958 Å in $Co(Ph_2{}^iPrPO)_2I_2$ [11] and $Co(Ph_3PO)_2I_2$ [1], respectively. Similarly, average Co-I bond lengths of 2.554 Å in **3** and 2.591 Å in **6** are closely comparable to the respective values of 2.576 Å and 2.578 Å in $Co(Ph_2{}^iPrPO)_2I_2$ and $Co(Ph_3PO)_2I_2$. The I-Co-I angles of 120.68(1)° in **3** and 115.99(1)° in **6** reveal considerable distortion from the tetrahedral ideal; values for $Co(Ph_2{}^iPrPO)_2I_2$ and $Co(Ph_3PO)_2I_2$ are 117.11(5)° and 112.46(3)° respectively. The O-Co-O angles of 104.12(8)° in **3** and 104.24(7)° in **6** are similar to the values of 102.7(3)° and 105.12(12)° in $Co(Ph_2{}^iPrPO)_2I_2$ and $Co(Ph_3PO)_2I_2$, respectively.

The structure of $Co(Cy_3PO)_2(NCS)_2$ (**8**) is also slightly distorted tetrahedral, with an O-Co-O angle of 107.2(1)° and an N-Co-N angle of 111.9(1)°. The Co-O distance averages 2.034 Å, whilst the average Co-N bond is 1.952 Å, similar to the value of 1.939 Å in Co(3,5-dimethylpyrazole)$_2$(NCS)$_2$ [12] and 1.964 Å in $K_2[Co(NCS)_4]\cdot H_2O\cdot 2CH_3NO_2$ [13]. The IR spectrum of **8** has the characteristic C-N stretching vibration at 2062 cm^{-1}. The molecular structure of $Co(Cy_3PO)_2(NCS)_2$ contrasts with $Co(Ph_3PO)_2(NCS)_2$, which, in the solid state at least, adopts an "auto-ionised" structure, $[Co(OPPh_3)_4]^{2+}$ $\{[Co(OPPh_3)(NCS)_3]^-\}_2$ [14]. The identity of the complex isolated is due to a balance of many factors, not least the solubility of each species present in solution, as well as its concentration.

The average distances in the complex **9** are 2.166 Å for the metal-oxygen (nitrate) and 1.985 Å for the metal-oxygen (phosphine oxide) distances, similar to those in $Co(Ph_3PO)_2(NO_3)_2$; comparison is difficult, because of the large standard deviations in $Co(Ph_3PO)_2(NO_3)_2$. The metal-oxygen (phosphine oxide) distances average 1.985 Å in $Co(Cy_3PO)_2(NO_3)_2$ and 1.984 Å in the nickel analogue, $Ni(Cy_3PO)_2(NO_3)_2$, with metal-oxygen (nitrate) distances of 2.166 Å and 2.106 Å, respectively. There is a close correspondence between the ν_3 (asymmetric stretching) vibration of coordinated nitrate in the IR spectra of the two cobalt complexes ($Co(Cy_3PO)_2(NO_3)_2$ and $Co(Ph_3PO)_2(NO_3)_2$); ν_3 occurs as two strong bands centred on 1284 and 1484 cm^{-1} in the spectrum of $Co(Cy_3PO)_2(NO_3)_2$, very similar to those at 1282 cm^{-1} and a split band (1490, 1482 cm^{-1}) in the spectrum of $Co(Ph_3PO)_2(NO_3)_2$. In both compounds ν_1 lies at ca.1010 cm^{-1}.

3.4 Electronic spectra of [$Co(R_3PO)_2X_2$] complexes

The electronic spectra can be found in the Supporting Information. The spectrum of **1** in chloroform is typical of tetrahedrally coordinated Co^{2+}; having a maximum ~667 nm with ε value of 450, significantly higher than the value for octahedral coordination, due to the $^4A_2 \rightarrow {}^4T_1(P)$ transition with splitting due to either spin-orbit coupling effects or to doublet state transitions [15]. Similar spectra are obtained from the other tetrahedral $Co(R_3PO)_2X_2$ complexes in chloroform. On dissolution of these tetrahedral complexes in ethanol, the absorptions due to the tetrahedral species remain, but with substantially reduced extinction coefficients and extra absorptions in the "octahedral region" ~500 nm can often be seen, notably in the spectra of **1** and **2**. We ascribe this to additional coordination of solvent ethanol, leading to complexes of the type $Co(R_3PO)_2X_2(EtOH)_2$. Similarly in the spectrum of **8** in ethanol, the peaks at 641 and 601 nm may be associated with a tetrahedral species and those at 524 and 480 nm with an octahedral species. Thus an ethanolic solution of **5** has absorptions at 668, 639(sh); 624(sh); 583(sh) and 526nm, in both the "octahedral" and "tetrahedral" regions. The absorptions in the spectrum of **4** in chloroform have very low extinction coefficients for a tetrahedral complex. When the chloroform solution was prepared, a significant amount of pale violet coloured insoluble material remained; this is probably an insoluble chloride bridged polymer with an octahedral geometry about the cobalt, which presumably crystallizes from the tetrahedral form in chloroform solution.

The spectrum of **9** in ethanol is typical of octahedral coordinated Co^{2+}, with a maximum at ~520 nm with ε value of 18, due to the $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transition ~19000 cm^{-1}. The high-frequency shoulder may be due to spin-orbit coupling effects or to transitions to doublet states [15].

4. Conclusions

Within the three families of $Co(R_3PO)_2X_2$ complexes (R_3 = Ph_3, Cy_3, Ph_2Cy**;** X = Cl, Br, I), certain patterns are clear. In all three series, the Co-X bond lengths increase with increasing size of the halogen roughly in line with size of the halogen [16]. Again, in all three series the Co-O distance decreases slightly with increasing atomic number of the halogen. Individually each trend is not statistically meaningful, but we believe that the same trend in all three families of compounds is significant, and can be explained as follows: As Group 7 is descended and as the σ-donor power of the halogen decreases, the phosphine oxide ligand can donate electrons more strongly and therefore the Co-O distance shortens.

There is no pattern in ∠X-Co-X or ∠X-Co-O, but in all three series, ∠O-Co-O increases as the halogen becomes heavier. This may be a genuine trend reflecting a greater cone angle of the larger halogens, as simple estimates of the cone angles 2θ of the halogens (based on θ = radius X^- / Co-X distance) do indicate a slight increase in the order Cl^- (146.2º), Br^- (149.2º) and I^- (155.6º). This calculation relies on the use of the ionic radii of the halide ions in six-coordination [16].

Overall in these families it is clear that there is relatively little variation in bond length for similar complexes, but that bond angles can vary substantially, in the solid state. This in turn may mean that the potential energy well has relatively steep sides with respect to stretching along the Co-O and Co-X coordinates, but shallow sides with respect to deformation.

5. Supplementary material

Crystallographic supplementary data are available from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk) quoting the deposition numbers CCDC 834053 - 834061.

6. Acknowledgements

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References

[1] S. A. Cotton, J. Fawcett and V. Franckevicius, Transition Met. Chem., 27 (2002) 38-41.

[2] A. P. Hunter, A. M. J. Lees and A.W.G. Platt, Polyhedron, 26 (2007) 4865-4876.

[3] http://www.oxfordcryosystems.co.uk/cryostream/700series.htm

[4] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori and M. Camalli, J. Appl. Cryst., 27 (1994) 435.

[5] G. M. Sheldrick, Acta Crystallogr., Sect.A, 46 (1990) 467-473.

[6] G. M. Sheldrick, SHELXL97, a program for crystal structure refinement, University of Goettingen. 1997.

[7] A. M. G. Dias Rodriguez, R. H. P. Francisco and J. R. Lechat, Acta Crystallogr., Sect. C., 11 (1982) 847-852.

[8] A. R. Kennedy, S. W. Sloss and M. D. Spicer, Acta Crystallogr. Sect. C., 53 (1997) 292-293.

[9] M.-J. Menu, M. Simard, A.L. Beauchamp, H. König, M. Dartiguenave, Y. Dartiguenave and H.-F. Klein, Acta Crystallogr. Sect. C., 45 (1989) 1697-1699.

[10] H. Suzuki, Y. Abe and S-I. Ishiguro, Acta Crystallogr. Sect. C., 57, (2001) 721-722.

[11] S. K. Bauer, C. J. Willis and N. C. Payne, Acta Crystallogr. Sect. C., 51 (1995) m586-m587.

[12] X.-F. Chen, S.-H. Liu, X.-Z. You, H.-K. Fun, K. Chinnakali and I. A. Razak, Acta Crystallographica. Sect. C, 55 (1999) 22-24.

[13] J. S. Wood and R. K. McMullan, Acta Crystallogr. Sect C., 40 (1984) 1803-1806.

[14] D. Y. Sun, D. H. Jiang, Y. H. Yang and J. L. Shen., Chinese Chem. Letts., 4 (1993) 469-472.
[15] D. Nicholls, Complexes and First Row Transition Elements, Basingstoke, Macmillan, 1974, pp 96-97.
[16] R. D. Shannon, Acta Crystallogr., Sect. A, 32 (1976) 751-767.

Graphical Abstract

Systematic structural studies on cobalt(II) complexes of tricyclohexylphosphine oxide and related ligands

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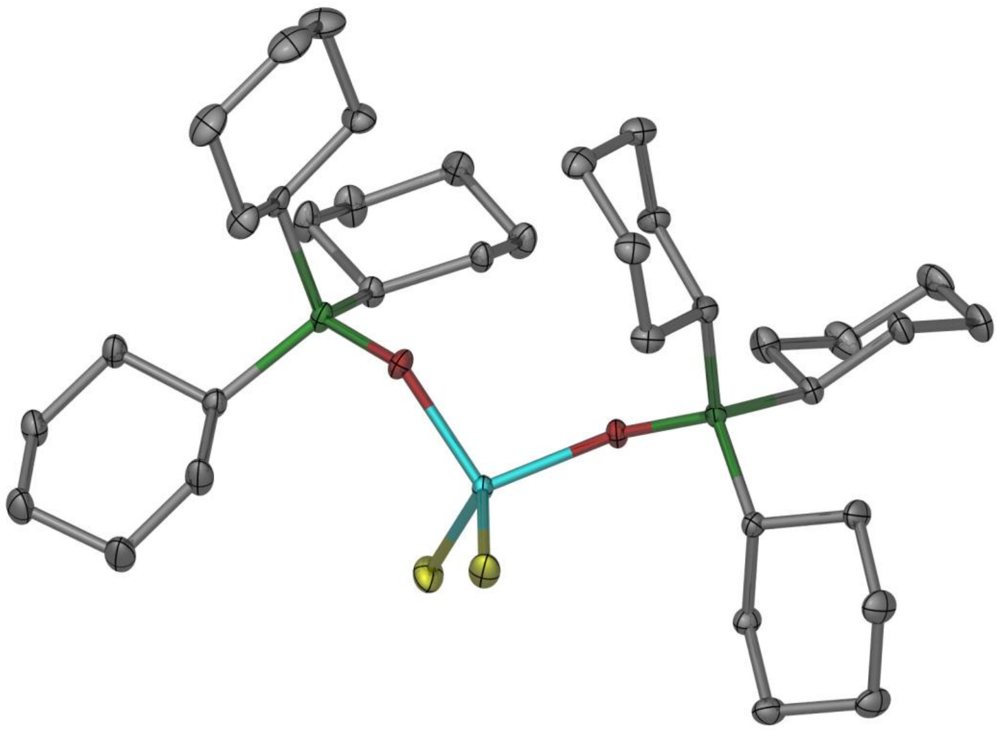

A series of 9 cobalt(II) phosphine oxide complexes, supported by halide, thiocyanate or nitro groups have been prepared and structurally characterised. Trends in the molecular bond parameters have been analysed.