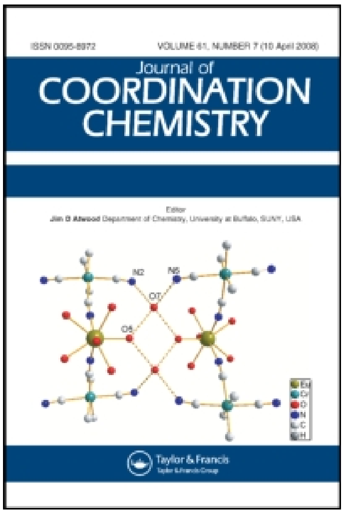

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COBALT(II) COMPLEXES WITH PHOSPHINE OXIDES

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Solid complexes of tribenzylphosphine oxide (tbpo), dibenzylphenylphosphine oxide (dbppo) and benzyldiphenylphosphine oxide (bdppo) with Cobalt(II) chloride, bromide, iodide, thiocyanate, nitrate and perchlorate are reported and characterized. The compounds have the general formulas $[CoL_2X_2]$ and $[CoL_4](C\ell O_4)_2$, where L is the phosphine oxide and X = Cℓ, Br, I, NCS or NO_3. They are characterized and identified by chemical analysis and physical measurements. Analogous complexes of triphenylphosphine oxide (tppo) reported in the literature were also prepared in order to compare the spectral data. The chloride, bromide, iodide, thiocyanate and perchlorate complexes are tetrahedral and the nitrate ones are octahedral, like those with tppo. The crystal field parameters for the complexes of the four phosphine oxides are very similar and they are placed in a common position in the spectrochemical and nephelauxetic series. The molar absorptivities measurements of the tetrahedral complexes in dichloroethane solutions indicate that this property increases according to the following order: tbpo $<$ dbppo $<$ bdppo $<$ tppo. This order indicates that phenyl radical produces an increase in the molar absorptivity when it is compared with the benzyl radical. The difference could also indicate that phenyl radical produces a higher degree of covalence in the metal–ligand bond than the benzyl radical. The infrared spectra of the complexes have been examined. The characteristic frequencies of the P–O bond, coordinated nitrate and thiocyanate and ionic perchlorate are reported.

INTRODUCTION

In a previous communication[1] we reported the synthesis and some properties of the following Cobalt(II) complexes with tbpo: $[CoC\ell_2(tbpo)_2]$, $[Co(NO_3)_2(tbpo)_2]$ and $[Co(tbpo)_4](C\ell O_4)_2$. In this work we have prepared and studied the analogous complexes with dbppo and bdppo and others involving bromide, iodide and thiocyanate of Cobalt(II) and the three mentioned phosphine oxides. The properties of all complexes, mainly the spectroscopic ones, are compared with those of the known tppo complexes studies by Cotton and co-workers[2-7] in order to obtain information about the structure of the new complexes and about the influence, in those properties, of the progressive substitution of the phenyl radical by the benzyl radical.

EXPERIMENTAL

Materials

The ligands bdppo and dbppo were prepared by a Grignard reaction, starting with chlorodiphenylphosphine or dichlorophenylphosphine and benzyl chloride,[8,9] tbpo was prepared as previously described.[1] Benzene and ethanol were the solvents used in the recrystallizations. The white products have the following melting points:[10] bdppo 194–6°C, dbppo 175–7°C and tbpo 215–7°C; tppo was obtained from Koch-Light Laboratories Ltd. (m.p. 153–5°C). Cobalt(II) chloride and nitrate were used in the hydrated form and they were reagent grade chemicals from Baker and BDH respectively.

Cobalt(II) perchlorate, bromide and iodide were prepared starting with $2CoCO_3 \cdot 3Co(OH)_2 \cdot nH_2O$ (Carlo Erba) in excess and the corresponding diluted acid.

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Cobalt(II) thiocyanate was prepared starting with $CoC\ell_2$ and KNCS in ethanolic solution.

The solvents used in the preparations of the complexes and in conductance and spectra measurements were purified by the usual methods.

Synthesis

All the complexes were prepared by the same general procedure. The salt and the ligand were mixed in the required proportions in boiling absolute ethanol and the solution was concentrated and cooled. In many cases good crystals were obtained. In some other cases it was necessary to recrystallize the solid complexes from benzene or other solvent like 1,2-dichloroethane or a mixture of them. 2,2-dimethoxy-propane was also used, in some preparations, for dehydration. The reaction between Cobalt(II) perchlorate and dbppo gave an oil that did not solidify, even up on addition of a number of other solvents such as methanol, acetone, isopropylalcohol, benzene, light petroleum, etc.

The tppo complexes were prepared by the methods described by Cotton and co-workers[2-7] with some modifications.

Analysis

The complexes were dried in the Abderhalden apparatus (P_4O_{10}, 78°C and 1 mm Hg), dissolved in a small quantity of ethanol and decomposed by deionized water. The ethanol was evaporated and the solution was cooled in an ice bath. The insoluble phosphine oxides were filtered and weighed. The filtrates were analysed for Co(II) by complexometric titration.[11]

The perchlorate ion was determined by an ion exchange resin technique (Amberlite IR-120) and the nitrate by a gravimetric procedure with nitron.[12] Halides and thiocyanate were determined gravimetrically as their silver salts.

Physical Measurements

Electrolytic conductance measurements were made in 10^{-3} M nitromethane solutions of the complexes at 25 ± 1°C on a "Metrohm" Model E-182 conductometer using a cell previously calibrated with aqueous solutions of $KC\ell$.

Magnetic susceptibilities were determined at 25 ± 1°C by the Faraday method. The equipment consisted of a Brucker electromagnet and a Sartorius balance. Magnetic moments were corrected

TABLE I

Analytical data and some physical properties for bdppo, dbppo and tbpo complexes

Complex	% Ligand		% Metal		% Anion		Colour	m.p. °C	ΛM $\Omega^{-1}\cdot cm^2/Mol$	μ_{eff} B.M. ±0.02
	Calcd.	Exp.	Calcd.	Exp.	Calcd.	Exp.				
$[Co(bdppo)_2C\ell_2]$	81.82	80.4	8.25	8.2	9.93	10.0	blue	205–6	8.0	4.67
$[Co(bdppo)_2Br_2]$	72.77	72.1	7.34	7.3	19.90	19.8	blue	221–3	8.0	4.71
$[Co(bdppo)_2I_2]$	65.14	64.5	6.56	6.6	28.29	27.8	green	205–6	10.0	4.75
$[Co(bdppo)_2(NO_3)_2]$	76.15	75.7	7.67	7.7	16.17	16.1	violet	196–7	6.0	4.82
$[Co(bdppo)_2(NCS)_2]$	76.93	75.7	7.76	7.8	15.29	15.5	blue	179–80	10.0	4.55
$[Co(bdppo)_4](C\ell O_4)_2$	81.69	79.8	4.12	4.0	14.19	13.8	blue	189–90	166.0	4.78
$[Co(dbppo)_2C\ell_2]$	82.51	81.2	7.94	8.0	9.55	9.6	blue	135–6	5.0	4.85
$[Co(dbppo)_2Br_2]$	73.68	72.7	7.09	7.1	19.23	18.8	blue	158–60	5.0	4.87
$[Co(dbppo)_2I_2]$	66.19	65.0	6.37	6.4	27.43	27.2	bluish-green	173–4	6.0	4.86
$[Co(dbppo)_2(NO_3)_2]$	77.00	76.1	7.41	7.4	15.59	15.4	violet	134–6	4.0	4.73
$[Co(dbppo)_2(NCS)_2]$	77.76	77.9	7.48	7.6	14.75	14.5	blue	96–7	9.0	4.57
$[Co(tbpo)_2C\ell_2]$	83.16	83.7	7.64	7.6	9.19	9.0	blue	223–4	1.0	4.66
$[Co(tbpo)_2Br_2]$	74.56	74.0	6.84	6.7	18.58	18.1	blue	177–9	3.0	4.68
$[Co(tbpo)_2I_2]$	67.23	67.5	6.17	6.1	26.60	25.6	green	172–5	7.0	4.76
$[Co(tbpo)_2(NO_3)_2]$	77.80	76.6	7.15	7.2	15.05	15.3	violet	149–51	5.0	4.81
$[Co(tbpo)_2(NCS)_2]$	78.54	77.4	7.22	7.0	14.23	14.0	blue	146–50	11.0	4.41
$[Co(tbpo)_4](C\ell O_4)_2$	83.36	82.7	3.82	3.8	12.92	12.6	blue	189–91	154.0	4.67

for diamagnetism, which was estimated from Pascal's constants. Precision was such that reproducibility of magnetic moments is ± 0.02 B.M.

Visible and near infrared spectra of 10^{-1} to 10^{-3} M solutions in dichloroethane were obtained at 25 ± 1°C on Cary 17 and Cary 14 recording spectrophotometers.

Infrared spectra of the ligands and of the complexes were determined as Nujol mulls between KBr plates on a Perkin Elmer Model 457 spectrophotometer.

RESULTS AND DISCUSSION

The analytical data for all complexes and some of their physical properties are listed and summarized in Table I. We also included the tbpo complexes previously described,[1] for comparative purpose. From the electrical conductivity measurements and analytical data we concluded that the chloride, bromide, iodide, thiocyanate and nitrate complexes are non-electrolytes and the perchlorates are 1:2 electrolytes;[13] thus the general formulas are $[CoL_2X_2]$ and $[CoL_4](C\ell O_4)_2$ where L = bdppo, dbppo or tbpo and X = $C\ell$, Br, I, NCS or NO_3.

Electronic spectra and magnetic moments of the new complexes are very similar to the tppo corresponding complexes studied by Cotton and coworkers.[2-7]

The chloride, bromide, iodide, thiocyanate and perchlorate complexes are clearly tetrahedral and the results obtained for the crystal field parameters Δ, B and β are given in Table II.

In agreement with the results found for the nitrates of other Cobalt(II) phosphine oxide complexes[6,14] the nitrate complexes with bdppo, dbppo and tbpo are found to be octahedral. The spectral data are given in Table III.

Cotton and Soderberg[15] have shown from an X-ray structure determination that $[Co(tmpo)_2(NO_3)_2]$ (tmpo = trimethylphosphine oxide) is octahedral with

TABLE II
Visible and near infrared spectral data for the chloride, bromide, iodide, thiocyanate and perchlorate complexes

Complex	ν_3 kK(ϵ)	ν_2 kK	Δ cm^{-1}	Bcm^{-1}	β
$[Co(tppo)_2C\ell_2]$	15.5(471)	5.5	3,150	770	0.79
$[Co(bdppo)_2C\ell_2]$	15.6(433)	5.5	3,140	780	0.80
$[Co(dbppo)_2C\ell_2]$	15.6(405)	5.6	3,200	770	0.79
$[Co(tbpo)_2C\ell_2]$	15.6(376)	5.5	3,140	780	0.80
$[Co(tppo)_2Br_2]$	15.2(564)	5.5	3,150	750	0.77
$[Co(bdppo)_2Br_2]$	15.2(522)	5.4	3,090	760	0.78
$[Co(dbppo)_2Br_2]$	15.2(480)	5.4	3,090	760	0.78
$[Co(tbpo)_2Br_2]$	15.3(463)	5.4	3,090	760	0.78
$[Co(tbpo)_2Br_2]$ (nujol)	15.15	5.6	3,210	740	0.76
$[Co(tppo)_2I_2]$	14.8(660)	5.5	3,150	720	0.74
$[Co(bdppo)_2I_2]$	14.9(562)	5.4	3,090	740	0.76
$[Co(dbppo)_2I_2]$	14.9(525)	5.4	3,090	740	0.76
$[Co(tbpo)_2I_2]$	14.9(504)	5.4_5	3,120	730	0.75
$[Co(tppo)_4]C\ell O_4)_2$	16.5(351)	6.2	3,560	800	0.82
$[Co(bdppo)_4](C\ell O_4)_2$	16.7(279)	6.0	3,430	830	0.85
$[Co(tbpo)_4](C\ell O_4)_2$	17.0(183)	6.3	3,610	830	0.85
$[Co(tppo)_2(NCS)_2]$	16.1(859)	6.8	3,930	740	0.76
$[Co(bdppo)_2(NCS)_2]$	16.1(804)	6.5	3,740	760	0.78
$[Co(dbppo)_2(NCS)_2]$	16.0(749	6.4_5	3,720	750	0.77
$[Co(tbpo)_2(NCS)_2]$	16.2(741)	6.5	3,740	770	0.79

TABLE III
Visible and near infrared spectra data for the nitrate complexes

Complex	ν_1 kK	ν_2 kK	ν_3 kK(ϵ)	Δcm^{-1}	Bcm^{-1}	β
$[Co(tppo)_2(NO_3)_2]$	7.1	14.9	18.1(114)	7,710	800	0.82
$[Co(bdppo)_2(NO_3)_2]$	7.0	14.5	18.2(143)	7,590	810	0.83
$[Co(dbppo)_2(NO_3)_2]$	7.0	14.5	18.1(143)	7,590	805	0.83
$[Co(tbpo)_2(NO_3)_2]$	7.0_5	14.7	18.1(132)	7,650	800	0.82

each nitrate group acting as a bidentate ligand. A similar arrangement was presumed to exist in the [Co(tppo)$_2$(NO$_3$)$_2$].[7] Figures 1 and 2 show the visible and near infrared spectra of the [CoL$_4$] (CℓO$_4$)$_2$ (tetrahedral) and [CoL$_2$(NO$_3$)$_2$] (octahedral) complexes.

The values of the crystal field parameters for all complexes were determined, using the modifications suggested by Reedijk and co-workers.[16] The ν_1, ν_2 and ν_3 transition energies used in the calculations and indicated in Tables II and III correspond with the centres of gravity of the multiple bands.[6,14] The values obtained for the parameters of the complexes of the four phosphine oxides in a given geometry (either tetrahedral or octahedral) are very similar and they are thus best placed in a common position in the spectrochemical and nephelauxetic series. In some cases, like in the thiocyanate ones, the Δ values obtained suggest that tppo gives higher values than the other phosphine oxides, for this parameter.

So, the parameters Δ, B and β are not good indicators of the influence of the progressive substitution of the phenyl radical by the benzyl radical on the metal–ligand bond. A better indication can be obtained from the molar absorptivities[17] of the ν_3 bands ($^4T_{1g}(P) \longleftarrow {}^4A_2$) of the tetrahedral complexes.

For this kind of complexes, there is a general relationship between the oscillator strength of the ν_3 transition and the B value.[14] The higher the oscillator strength (the higher the intensity) of the ν_3 band, the lower is B. So, the most covalent complexes give the most intense spectra.

Sheka and co-workers[17] compared the covalent character of the bonds between Co(II) and the oxygen of the phosphoryl group by studying the increase in the intensity of the ν_3 band in tetrahedral complexes. They used CoCℓ_2, several phosphine oxides and solvents like acetone and tetrahydrofuran. They found that the covalent character of the bonding in the complexes CoCℓ_2(R$_3$PO)$_2$ is greater in bdppo than in tppo. They also concluded that the

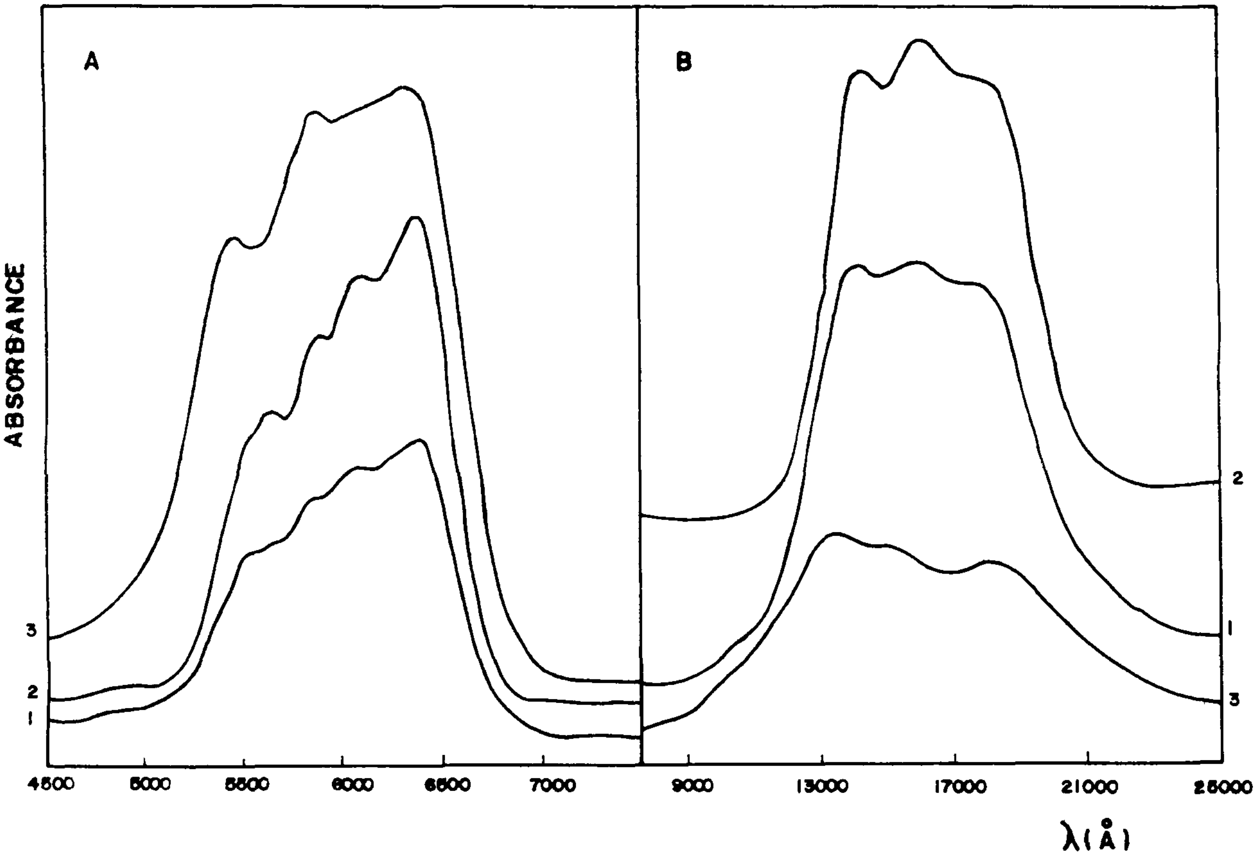

FIGURE 1 Visible (A) and near infrared (B) spectra of the perchlorate complexes in dichloroethane. (1) [Co(bdppo)$_4$(ClO$_4$)$_2$; (2) [Co(tppo)$_4$](ClO$_4$)$_2$ and (3) [Co(tbpo)$_4$](ClO$_4$)$_2$.

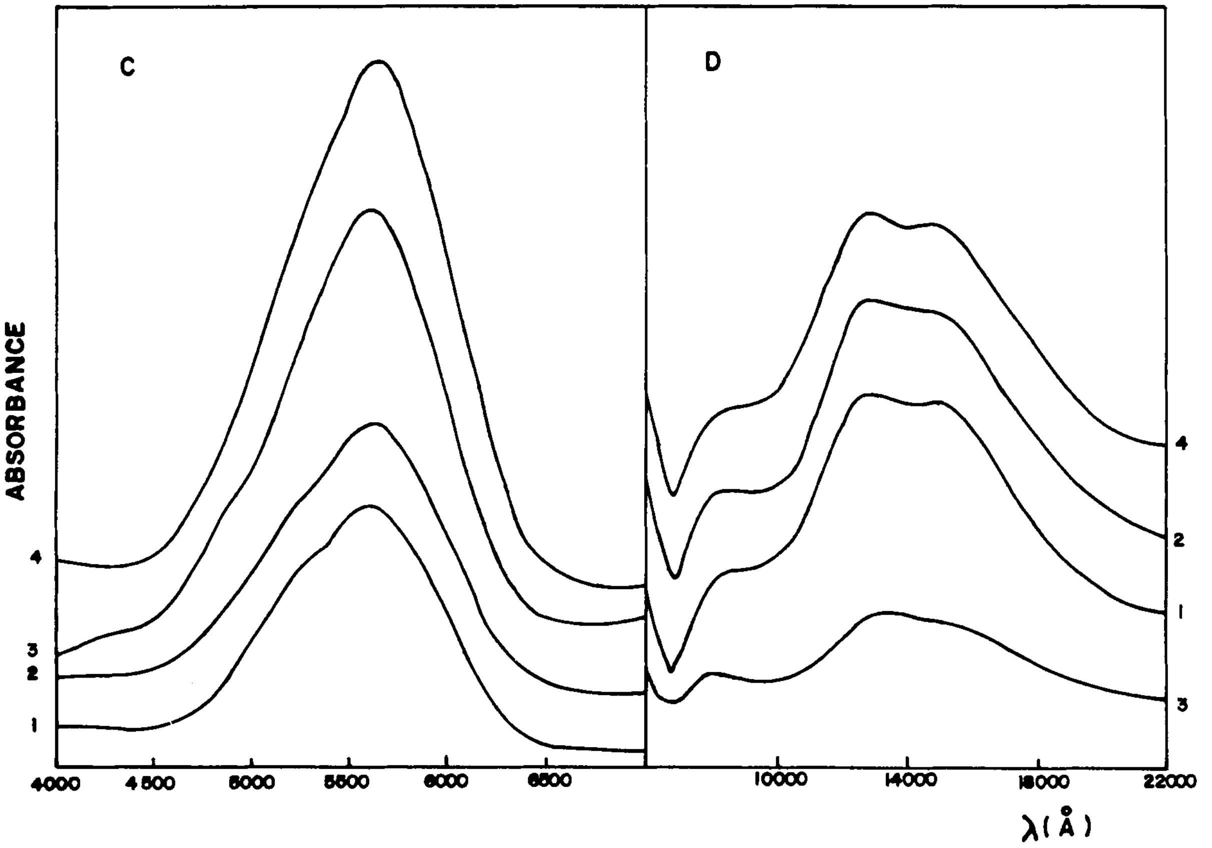

FIGURE 2 Visible (C) and near infrared (D) spectra of the nitrate complexes in dichloroethane.
(1) $[Co(tbpo)_2(NO_3)_2]$; (2) $[Co(bdppo)_2(NO_3)_2]$; (3) $[Co(tppo)_2(NO_3)_2]$ and (4) $[Co(dbppo)_2(NO_3)_2]$.

intensity of the absorption depends on the substituents in the ligand molecules and decreases with increase their electronegativity.

We determined the molar absorptivities in the centre of gravity of the ν_3 bands of all complexes in dichloroethane, a non-coordinating solvent. The results are given in Table II. From these data, we can conclude that benzyl radicals decrease the molar absorptivity and consequently the degree of covalence of the Co–O bond. This result is evidently in disagreement with the one found by Sheka and co-workers.

It is interesting to note that there are some differences between our determinations and those of Sheka and co-workers. They used acetone and tetrahydrofuran, two coordinating agents, and we used 1,2 dichloroethane. They worked with solutions of $CoC\ell_2$ and phosphine oxides with alkyl and aryl substituents, including tppo and bdppo and we worked with complexes of five salts and four ligands with gradative substitution of phenyl by benzyl radical.

Furthermore, in solvents like acetone and tetrahydrofuran, equilibria have been shown to occur[18,19] and it would be necessary to know the degree of dissociation of the complexes. In our case this problem is probably eliminated as the solid complexes were dissolved in a non-coordinating solvent. This assumption is supported by the fact that for the $[Co(tbpo)_2(NCS)_2]$ complex we obtained the same value for the molar absorptivity even using a metal : ligand molar proportion of 1:6. Finally it is worth noting that the correlation between the molar absorptivities and the degree of covalence of the Co–O bond will be best understood when structural data for the complexes become available. X-ray structure determinations of the four chloride complexes are currently in progress.[20] There are some effects that must be considered, like the steric hindrance, the change in the electronic density of the phosphoryl oxygen atom, the possibility of existence of a hydrogen bond involving CH_2 benzyl groups, the Co–O–P angles and the change in the π bonding between phosphorus and oxygen.

It was also possible to calculate the contribution of each phosphine oxide, or anion, in the molar absorptivity of the tetrahedral complexes of Co(II). The mean values are: $C\ell = 145$, $Br = 189$, $I = 216$, $NCS = 329$, tppo = 88, bdppo = 70, dbppo = 56 and tbpo = 46.

The i.r. absorption frequencies are given in Table IV for the P–O, nitrate, thiocyanate and perchlorate groups. For tppo the values are in good agreement (± 5 cm^{-1}) with the literature values.[3,7,21]

The frequencies for the anions are compatible with the ones for ionic perchlorate, coordinated nitrate and N-coordinated thiocyanate.[21]

The values for the P–O groups are somewhat uncertain due to the presence of a large number of bands in the 1000–1200 cm^{-1} region. It does appear however that the P–O stretching frequency falls, as expected, to lower values in the complexes and that the largest shifts are found in the perchlorate complexes.

The presence of two or more bands in the region of P–O stretching frequencies could be related to the existence of non-equivalent ligands in the crystal.[3] In this connection, it is also interesting to note that the X-ray structure determination of the dibromobis (triphenylphosphine oxide) copper II complex $[Cu(tppo)_2Br_2]$ has been reported recently.[22] The occurrence of two P–O stretching frequencies for this complex (*i.e.*, 1145 and 1169 cm^{-1}) was associated to the existence of different Cu–O–P angles (144.0° and 154.8°).

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TABLE IV
Vibrational spectral data for the phosphine oxides and their complexes

	ν(P–O)cm^{-1}	Anion frequencies (cm^{-1})
tppo	1195[a]	–
$[Co(tppo)_2C\ell_2]$	1155[a]	–
$[Co(tppo)_2Br_2]$	1153[a]	–
$[Co(tppo)_2I_2]$	1153[a]	–
$[Co(tppo)_2(NCS)_2]$ [b]	1148, 1170	2025(sh) 2070(s,shp) 2090(sh)
$[Co(tppo)_2(NO_3)_2]$	1160	1497(s,b) 1290(s,shp) 1024(m,shp) 812(w,shp)
$[Co(tppo)_4](C\ell O_4)_2$	1146[a]	1085(s,b) 625(s,shp)
bdppo	1185	–
$[Co(bdppo)_2C\ell_2]$	1133, 1172	–
$[Co(bdppo)_2Br_2]$	1130, 1155, 1172	–
$[Co(bdppo)_2I_2]$	1130, 1155, 1172	–
$[Co(bdppo)_2(NCS)_2]$	1128, 1158, 1165	2080(s,b) 2090(sh)
$[Co(bdppo)_2(NO_3)_2]$	1170	1485(s,b) 1285(s,b) 1024(s–m,shp) 812(m,shp)
$[Co(bdppo)_4](C\ell O_4)_2$	1135	1100(s,b) 628(s,shp)
dbppo	1185	–
$[Co(dbppo)_2C\ell_2]$	1158	–
$[Co(dbppo)_2Br_2]$	1155, 1170	–
$[Co(dbppo)_2I_2]$	1158	–
$[Co(dbppo)_2(NCS)_2]$	1132, 1152	2080(s,b) 2090(sh)
$[Co(dbppo)_2(NO_3)_2]$	1130, 1158, 1168	1475(s,b) 1285(s,b) 1022(s–m,shp) 812(m,shp)
tbpo	1190	–
$[Co(tbpo)_2C\ell_2]$	1145, 1175	–
$[Co(tbpo)_2Br_2]$	1150	–
$[Co(tbpo)_2I_2]$	1150	–
$[Co(tbpo)_2(NCS)_2]$	1150	2075(s,shp) 2090(s,shp)
$[Co(tbpo)_2(NO_3)_2]$	1155	1475(vs,b) 1290(vs,b) 1020(s–m,shp) 812(m–w,shp)
$[Co(tbpo)_4](C\ell O_4)_2]$	1152	1105(s,b) 625(s–m,shp)

[a] Ref. 3.
[b] Ref. 5.
[c] Ref. 4.

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