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Metal Complexes of 2-Pyridinecarboxamide N-Oxide and 2-Pyridinecarbothioamide N-Oxide

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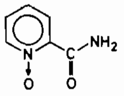
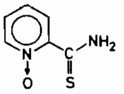
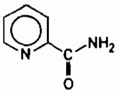
Complexes of 2-pyridinecarboxamide N-oxide (pco) are reported with chromium(III), manganese(II), cobalt(II), nickel(II) and copper(II). The ligand appears to be an O,O donor, via the N-oxide and carboxamide groups, according to evidence from infrared spectra. Mn(pco)Cl_2 appears to be halogen bridged, but the remaining complexes are monomeric, and all are high-spin. Apart from Mn(pco)Cl_2 and [Cr(pco)$_3$]$Cl_3 \cdot 2H_2O$, the pco complexes have structures of the type M(pco)$_2X_2$. With 2-pyridinecarbothioamide (ptco), only Cu(ptco)$_2Cl_2$ and Cu(ptco)$_2Br_2$ could be obtained; these complexes appear to contain ON and OS bonded ptco, respectively. Magnetic measurements and electronic spectra to liquid nitrogen temperature are reported, together with infrared spectra (including deuteration studies) and X-ray powder diffraction spectra.

Introduction

We have been examining metal complexes of pyridine N-oxide ligands which contain donor substituents in the 2-position [1–3]. This paper reports complexes of 2-pyridinecarboxamide N-oxide (I, pco) and 2-pyridinecarbothioamide N-oxide (II, ptco). The only previous complexes prepared with these ligands are some lanthanide complexes of pco, recently reported [4].


(I, pco)


(II, ptco)


(III, pc)

Results and Discussion

Complexes are listed in Table I, with analytical data. Complexes of pco are discussed first.

Complexes of 2-Pyridinecarboxamide N-oxide

The infrared data for the complexes are shown in Table II. The infrared spectrum of pco resembles the spectrum [5] of 2-pyridinecarboxamide (III, pc) with additional bands, assigned to the N-oxide ν(NO) and δ(NO) modes, at 1233 and 851 cm^{-1}, respectively. The ν(NO) frequency of pco decreases by *ca.* 8–36 cm^{-1} upon complex formation, whereas δ(NO) remains approximately constant. This indicates N-oxide coordination by pco [6].

The amide ν(CN) and ν(CO) bands in pco occur at 1374 and 1675 cm^{-1}, respectively, similar to their positions in pc and in related carboxamides [5, 7, 8]. In the pco complexes, the ν(CN) frequency (not detected in the chromium complex) is *ca.* 8–34 cm^{-1} higher than the free ligand value. The ν(CO) mode (or its average) is *ca.* 3–22 cm^{-1} lower than the free ligand value (except in the copper halide complexes). These frequency shifts indicate O-bonded carboxamide in the complexes [5, 7, 8], because O-coordination should increase the contribution of amide canonical form (IV) and decrease that of form (V). The only exception to the above frequency shifts is with the copper halide complexes, where a rise of ν(CO) occurs. This effect occurs with some other O bonded carboxamide complexes [5, 7–9]. It has been attributed to the effects of hydrogen-bonding in the free ligand, which lowers the ligand ν(CO) frequency. When complex formation occurs, the effects of oxygen-coordination, and the concomitant breaking of hydrogen-bonding, may approximately cancel each other out, leading to no marked change in ν(CO) or even to a moderate rise [7, 9].


(IV) (V)

As a check upon the above assignments, deuteration studies have been carried out on pco and on the copper halide complexes. The results are shown in Table III, and are generally similar to those for pc and its complexes, which are included for comparison

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TABLE I. Analytical Data on the Complexes.

Compound	Analyses % Calculated and Found				Colour
	C	H	N	M	
Mn(pco)Cl_2	27.3	2.3	10.6	20.8	yellow
	27.8	2.3	10.7	20.6	
$Cr(pco)_3Cl_3 \cdot 2H_2O$	35.5	3.6	13.1	8.1	dark green
	35.5	4.1	10.9	7.8	
$Ni(pco)_2Cl_2$	35.1	2.9	13.6	14.5	bright-green
	35.4	3.1	13.0	14.6	
$Ni(pco)_2Br_2$	29.1	2.4	11.3	11.9	green-yellow
	29.3	2.6	10.9	11.6	
$Co(pco)_2Cl_2$	35.5	3.0	13.8	14.5	green
	35.7	3.0	13.6	14.3	
$Co(pco)_2Br_2$	29.1	2.4	11.3	11.9	green
	29.4	2.7	10.8	12.2	
$Co(pco)_2(NO_3)_2 \cdot H_2O$	30.2	3.0	17.6	12.4	light pink
	30.4	2.9	17.0	12.1	
$Cu(pco)_2Cl_2$	35.1	2.9	13.6	11.2	light-green
	34.7	3.2	13.0	10.9	
$Cu(pco)_2Br_2$	28.9	2.4	11.2	12.7	yellow
	29.0	2.5	10.9	12.9	
$Cu(pco)_2(NO_3)_2 \cdot 0.5H_2O$	30.5	2.7	17.8	13.4	blue-green
	30.3	2.9	17.0	13.1	
$Cu(pco)_2(ClO_4)_2 \cdot CH_3OH$	27.4	2.8	9.8	11.1	blue
	27.0	3.1	9.6	11.0	
$Cu(ptco)_2Cl_2$	32.6	2.7	12.7	14.4	dark-red
	32.4	2.9	11.5	14.6	
$Cu(ptco)_2Br_2$	27.1	2.3	10.5	12.0	yellow-brown
	26.8	2.4	10.0	11.6	
Deuterated compounds (assuming 100% exchange on the carboxamide group).					
pco	51.4	5.8	20.0		
	51.1	5.4	19.3		
$Cu(pco)_2Cl_2$	34.8	3.9	13.5		
	34.5	3.7	11.5		
$Cu(pco)_2Br_2$	28.6	3.2	11.1		
	29.0	3.2	12.0		

TABLE II. Infrared Spectra (cm^{-1}) of pco Complexes.

Compound	ν(CO)	$\Delta\nu$(CO)^a	ν(CN)	$\Delta\nu$(CN)^a	ν(NO)	δ(NO)
pco	1675vs	–	1374vs	–	1233vs	851vs
Mn(pco)Cl_2	1672s	–3	1391w	+17	1225vs	853vs
$Cr(pco)_3Cl_3 \cdot 2H_2O$	1660vs	–15	^{b}	–	1202m	852m
$Ni(pco)_2Cl_2$	1658vs	–17	1399s	+25	1209vs	851vs
$Ni(pco)_2Br_2$	1653vs	–22	1402s	+28	1208vs	850vs
$Co(pco)_2Cl_2$	1663vs	–12	1401s	+27	1204vs	849vs
$Co(pco)_2Br_2$	1658vs	–17	1398s	+24	1202vs	849vs
$Co(pco)_2(NO_3)_2 \cdot 2H_2O$	1663vs	–12	*ca.* 1408sh	*ca.* +34	1197vs	843vs
$Cu(pco)_2Cl_2$	1689vs	+14	1393m	+19	1207vs	848vs
$Cu(pco)_2Br_2$	1688vs	+2*	1382s	+8	1198vs	848vs
	1666vs					840vs

(continued on facing page)

TABLE II. *(continued)*

Compound	ν(CO)	$\Delta\nu$(CO)[a]	ν(CN)	$\Delta\nu$(CN)[a]	ν(NO)	δ(NO)
$Cu(pco)_2(NO_3)_2 0.5H_2O$	1662s	−13	1387s	+13	1199s	848vs
$Cu(pco)_2(ClO_4)_2 \cdot CH_3OH$	1684s 1661vs	−3*	1408w 1362m	+11*	1217m 1203m	859m 849m

*Average shift. [a] Shift of the band upon complex formation. [b] Band not detected.

TABLE III. Infrared Spectra of Deuterated pco and pc Systems (cm^{-1}).

Compound[b]	$\nu(NH_2)$ or $\nu(ND_2)$	ν(CO)	$\delta(NH_2)$ or $\delta(ND_2)$	ν(CN)	ν(NO)	δ(NO)
pco	3250mbr	1675vs	[c]	1374vs	1233vs	851vs
pco (KBr disc)	3260mbr, 3100wbr	1685sh 1673vs	[c]	1377vs	1229vs	848vs
deuterated pco (KBr disc)	2464m, 2370wbr	1710vs	1230w, 1181w 1168w	1392s	1248m	840vs
$Cu(pco)_2Cl_2$	3335m, 3170w *ca.* 3080wbr	1689vs	1565mbr[d]	1393m	1207vs	848vs
deuterated $Cu(pco)_2Cl_2$	2510m, 2460w *ca.* 2350wbr	1713m	1178w, 1188w 1218w	1395m	1202m	843vs
$Cu(pco)_2Br_2$	3430w, 3318m, 3230w, 3180w	1688vs 1666vs	1562m[d]	1382s	1198vs	848vs 840vs
deuterated $Cu(pco)_2Br_2$	2570w, 2505m 2455w, 2370mbr	1678sh 1658sh	1215w, 1172w	1393s	1198m	848s 842vs
pc[a]	3420s, 3155s	1659s	1602m	1391s	–	–
deuterated pc[a]	2550s, 2360s	1650s	1204m	1400s	–	–
$[Ni(pc)_2(H_2O)_2]Cl_2$[a]	3300s, 3120s	1664s	1616w	1434s	–	–
deuterated $[Ni(pc)_2(H_2O)_2]Cl_2$[a]	2490s, 2300s	1636s	1221m	1438s	–	–

[a] Data on pc systems are from reference [4]. [b] Mull spectra, unless otherwise indicated. [c] Obscured by aromatic ν(CC/CN) modes. [d] Band is overlapped with aromatic ν(CC/CN) absorption, however on deuteration the band is observed to decrease in intensity.

TABLE IV. Reflectance Spectra.

Complex	Absorption Maxima ($cm^{-1} \times 10^{-3}$)
$Cr(pco)_3Cl_3 \cdot 2H_2O$	15.8, 22.4
$Ni(pco)_2Cl_2$	
RT	7.0, 7.6, 8.8sh; 13.7
83 K	6.7, 7.7, 9.3sh; 13.2sh, 14.3
$Ni(pco)_2Br_2$	
RT	6.8, 9.1; 13.0sh, 14.0
83 K	7.0, 9.4; 12.7sh, 14.6
$Co(pco)_2Cl_2$	
RT	6.4, 8.8; 15.0sh, 17.1, 18.7
83 K	6.5, 9.1; 15.5sh, 17.5, 18.9

(continued overleaf)

TABLE IV. *(continued)*

Complex	Absorption Maxima (cm^{-1} × 10^{-3}
$Co(pco)_2Br_2$	
RT	6.1, 8.8; 16.8, 18,4
83 K	6.2, 9.0; 17.2, 18.5,
$(Co(pco)_2NO_3)_2 \cdot H_2O$	8.4; 18.9
$[Co(H_2O)_4Cl_2]Cl_2 \cdot 2H_2O$	
RT	6.8, 7.8; 18.5, 20.0, 21.8sh
83 K	6.8, 8.2; 11.4m; 16.0sh, 18.6, 20.6, 22.2
$Cu(pco)_2Cl_2$	11.9
$Cu(pco)_2Br_2$	9.9
$Cu(pco)_2(NO_3)_2 \cdot 0.5H_2O$	10.0sh, 13.9
$Cu(pco)_2(ClO_4)_2 \cdot CH_3OH$	9.5sh, 13.3

TABLE V. Magnetic Data for pco and ptco Complexes.

Compound	μ_{eff} (BM)		θ^a (K)
	294 K	89 K	
$Mn(pco)Cl_2$	5.75	5.75	0
$Cr(pco)_3Cl_3 \cdot 2H_2O$	4.24	4.17	−2
$Ni(pco)_2Cl_2$	3.27	3.25	−2
$Ni(pco)_2Br_2$	3.29	3.21	−4
$Co(pco)_2Cl_2$	4.81	4.59	−14
$Co(pco)_2Br_2$	4.78	4.62	−8
$Co(pco)_2(NO_3)_2 \cdot H_2O$	4.99	4.76	−10
$Cu(pco)_2Cl_2$	1.96	1.94	−7
$Cu(pco)_2Br_2$	1.97	1.93	−4
$Cu(pco)_2(NO_3)_2 \cdot 0.5H_2O$	1.92	1.85	−6
$Cu(pco)_2(ClO_4)_2 \cdot CH_3OH$	2.18	2.04	−13
$Cu(ptco)_2Cl_2$	1.02	–	–
$Cu(ptco)_2Br_2$	0.74	–	–

[a] Curie–Weiss law taken as $\chi_A^{-1} \propto (T - \theta)$.

[5]. The usual large shifts in the NH_2 modes occur, with small shifts in the CO, CN and NO modes.

In summary, the infrared spectra indicate that pco coordinates as an O,O ligand. Reflectance spectra for the complexes are given in Table IV. The magnetic properties of the complexes (Table V), over a temperature range, are normal for monomeric complexes, except with $Mn(pco)Cl_2$ which has a somewhat low μ_{eff} value of 5.75 B.M. A bridged structure is proposed for $Mn(pco)Cl_2$. Halogen-bridging rather than N-oxide-bridging is likely, because the ν(NO) frequency in the complex is not lower than those for the other monomeric pco complexes [6]. Similar halogen-bridged structures have been proposed for some pyridine N-oxide, and substituted pyridine N-oxide, complexes of the type $MnLCl_2$, which have low room-temperature moments of *ca.* 5.5 B.M. [10].

For $Cr(pco)_3Cl_3 \cdot 2H_2O$, the ν(CN) band could not be detected. The band may be obscured by ligand absorption, as a result of a larger than normal shift, caused by coordination to the trivalent cation. The ν(NO) and ν(CO) frequencies indicate O,O bonded pco, as with the other complexes. The structure $[Cr(pco)_3]Cl_3 \cdot 2H_2O$ is therefore proposed, with a CrO_6 chromophore. The reflectance spectrum contains bands at 15,700 and 22,000 cm^{-1}, attributed to the $^4T_{2g} \leftarrow {}^4A_{2g}$ (ν_1) and $^4T_{1g} \leftarrow {}^4A_{2g}$ (ν_2) transitions of octahedral chromium(III). This spectrum resembles the spectra of some $[Cr(po)_6]^{3+}$ complexes with substituted pyridine N-oxides, which have ν_1 and ν_2 absorptions at *ca.* 16,000 and 23,000 cm^{-1}, respectively [11]. The complex was insoluble in common solvents, so conductivity measurements were not possible.

The electronic spectra of the $Ni(pco)_2Hal_2$ complexes indicate six-coordinate structures, with marked tetragonal distortion. Asymmetric bands occur in the approximate regions of $\nu_1(^3T_{2g} \leftarrow {}^3A_{2g})$ and $\nu_2(^3T_{1g} \leftarrow {}^3A_{2g})$ of six-coordinate nickel(II) (ν_3 is obscured by ligand absorption). Using the 'centre of gravity' of the bands, the ν_2/ν_1 ratios for the chloride and bromide are *ca.* 1.8 and 2.05 respectively. These are outside the range of 1.55–1.65 for regular octahedral nickel(II) complexes, and are typical of tetragonally distorted systems. In addition, the bands have pronounced shoulders or components at room temperature, which are further resolved at liquid nitrogen temperature [12–14]. The tetragonal distortion indicates structures of the type *trans*-$[Ni(pco)_2Hal_2]$, with bidentate ligand, containing the *trans*-NiO_4Hal_2 chromophore.

TABLE VI. X-Ray Powder Diffraction Spectra.

d-spacings (Å)			
$Ni(pco)_2Cl_2$	$Co(pco)_2Cl_2$	$Ni(pco)_2Br_2$	$Co(pco)_2Br_2$
8.42s	6.86s	7.00vs	7.00vs
6.86w	6.33m	6.34s	6.36s
6.40m	5.96vs	5.89m	5.89m
5.85vs	5.57m	5.64m	5.66m
5.57m	5.03m	5.11m	5.13m
5.03s	4.80m	4.88vs	4.86vs
4.80w	4.26w	4.10m	4.11m
4.22w	4.04w	3.76w	3.76w
3.50m	3.50m	3.60m	3.58m
3.41m	3.43w	3.46m	3.46m
3.22s	3.25w	3.34w	3.32w
3.08w	3.13s	3.23m	3.25m
2.92w	2.93m	3.18vs	3.18vs

In $Co(pco)_2(NO_3)_2 \cdot H_2O$, the anion infrared bands (1428vs, 1312vbs, 1042s, 817m, 732w, cm^{-1}) indicate that the nitrate ions are coordinated, and probably unidentate [15–17]. This suggests a six-coordinate CoO_6 structure, with bidentate pco ligands. The reflectance spectrum of the complex (8,400 and 18,900 cm^{-1}) and the magnetic moment (4.98 B.M.) are both typical of octahedral cobalt(II), in agreement with the proposed structure [13, 18].

The reflectance spectra of the cobalt(II) complexes $Co(pco)_2Cl_2$ and $Co(pco)_2Br_2$ are more complicated than those of the nitrate, as distinct components of the main bands are present. This suggests *trans*-CoO_4Hal_2 structures [13, 19]. In keeping with this, X-ray powder patterns (see Table VI) show that $Co(pco)_2Br_2$ is isostructural with $Ni(pco)_2Br_2$, which we consider to be a *trans*-compound. The cobalt and nickel chloride complexes are not isostructural, but $Co(pco)_2Cl_2$ has a similar reflectance spectrum to that of $[Co(H_2O)_4Cl_2](H_2O)_2$, which has a *trans*-CoO_4Cl_2 structure [20]. Both spectra show low-symmetry components of the main bands (see Table IV).

The compounds $Cu(pco)_2(NO_3)_2 \cdot 0.5H_2O$ and $Cu(pco)_2(ClO_4)_2 \cdot CH_3OH$ have, respectively, nitrate infrared bands (at 1425vs, 1313vs, 1045m, and 827vs, cm^{-1}) and perchlorate infrared bands (at 1128vs, 1060vs, 932m, cm^{-1}) which are in keeping with coordinated, unidentate, anions [15, 21, 22]. Six-coordinate CuO_6 structures are proposed for the compounds. The reflectance spectra, with a main band at *ca.* 13,500 cm^{-1}, and a shoulder at 10,000 cm^{-1}, are similar to those for other CuO_6 systems [23, 24].

The halide complexes $Cu(pco)_2X_2$ (X = Cl, Br) have symmetric reflectance bands at 11,900 and 9.900 cm^{-1} respectively. This excludes planar CuO_4 structures, since bands at much higher frequency would be expected [23]. The spectra are consistent with *trans*-CuO_4Hal_2 structures. For example, Cu(biuret)$_2$Cl$_2$, with a *trans*-CuO_4Cl_2 chromophore, has a reflectance band at 12,900 cm^{-1} [25–27]. The tetragonal distortion in the ligand field would be greater with such *trans*-CuO_4Hal_2 chromophores than with related CuO_6 systems. Increasing tetragonal distortion tends to shift the lower band ($^2A_{1g} \leftarrow {}^2B_{1g}$ in D_{4h}) to relatively higher frequency in tetragonal complexes, *i.e.* closer to the main absorption band [22, 24, 28, 29]. This could account for the narrower reflectance band in the halide complexes, in contrast to the broader more asymmetric band in the nitrate and perchlorate complexes.

The complex $Cr(pco)_3Cl_3 \cdot 2H_2O$ appears to be the only one with uncoordinated anions. If our structural assignment is correct, then a Dq value of 1580 cm^{-1} for $[Cr(pco)_3]^{3+}$ may be derived from the electronic spectrum of $Cr(pco)_3Cl_3 \cdot 2H_2O$, taking ν_1 = 10 Dq. This is similar to the Dq values of 1558–1613 cm^{-1} for $[Cr(po)_6]^{3+}$ complexes with some 3- and 4-substituted pyridine N-oxides [6]. The complex $[Cr(bipyO_2)_3]^{3+}$ with 2,2′-bipyridine-1,1′-dioxide, has ν_1 as a doublet at 14,950 and 15,850 cm^{-1}, in its electronic spectrum, so an approximate Dq value of 1540 cm^{-1} is obtained, similar to that for the pco complex [30]. Other N-oxide O,O ligands give higher Dq values with $[CrL_3]^{3+}$ complexes, *e.g.* 2-acetylpyridine N-oxide (Dq = 1640 cm^{-1}) [31] and 2-ethylsulfinylpyridine N-oxide (Dq = 1667 cm^{-1}) [32]. Also 2-pyridylcarbinol N-oxide (LH) produces a Dq of 1667 cm^{-1} in $[Cr(L)_2LH]^+$ and 1710 cm^{-1} in $[CrL(LH)_2]^{2+}$ [33].

Complexes of 2-Pyridinecarbothioamide N-oxide

In contrast to the situation with pco, the only complexes which could be isolated with ptco were the cupric halide complexes $Cu(ptco)_2X_2$ (X = Cl, Br). The complexes have low magnetic moments indicating bridged structures, which probably involve bridging N-oxide. Although bridging carbothioamide is known (*e.g.* in $Ni(thiourea)_2(NCS)_2$), it is much less common than N-oxide bridging [6, 34]. Halogen bridging would not be expected to produce the low magnetic moments which are observed. If N-oxide bridging is present, it is expected to be ‘in-plane’ as in $[Cu(po)_2Cl_2]_2$, which has a μ_{eff} of *ca.* 0.6 B.M. [6, 35], rather than ‘out of plane’ as in $[Cu(po)_2(NO_3)_2]_2$ (po = pyridine N-oxide), since the latter bridging leads to very weak interaction [36]. The reflectance spectra of both ptco complexes were uninformative, because the ligand field bands were masked by strong ligand or charge transfer absorptions. Conductivity measurements were not possible because of the low solubility of the complexes.

TABLE VII. Infrared Spectra for ptco Complexes

Compound	ν(CN)	ν(NO)	'ν(CS)'
ptco	1372m	1208s	822
$Cu(ptco)_2Cl_2$	1334m	1199m	858s, 848m
$Cu(ptco)_2Br_2$	1392m	1212m	815s

Infrared data for ptco and its copper(II) complexes are given in Table VII. Band assignments were made by comparison with the spectra of pco, 2-pyridinecarbothioamide and other carbothioamides. The ν(NO) modes in the ptco complexes (1199 and 1212 cm^{-1}) are similar to those in other N-oxide complexes, consistent with N-oxide coordination [6]. The ν(NO) frequency in free ptco (1208 cm^{-1}) is rather similar to the ν(NO) frequencies in the complexes and is below usual values for uncoordinated pyridine N-oxides. This may be a result of hydrogen bonding in the free ligand. A similar situation has been found for 2-methylaminopyridine N-oxide and its complexes [37]. The criteria used for determining the mode of bonding of the carbothioamide group in the complexes are those of Goodwin *et al.* [38]. Bands at 1372 and 822 cm^{-1} in ptco are assigned as the ν(CN) and one of the ν(CS) 'mixed vibrations', respectively. For $Cu(ptco)_2Cl_2$, a drop of ν(CN) and a rise of ν(CS), compared to the free ligand values, suggest O,N coordination, whereas for the bromide complex a rise in the ν(CN) mode and a drop in ν(CS) indicate O,S coordination. It is remarkable that a similar situation, with both N- and S-bonded carbothioamide, was observed by Sutton for copper(II) complexes of 2-pyridinecarbothioamide [39].

Experimental

Ligands

The ligand pco was prepared by oxidation of 2-pyridinecarboxamide [40]. The compound ptco was prepared by the method of Leonard and Wajngurt [41].

Metal Complexes

The complexes were generally prepared by mixing hot ethanol or methanol solutions of the ligand and metal salt in 1:1 molar ratios. The complexes were deposited by allowing the resulting solutions to cool, or to stand for several days, or by concentration of the solution. All complexes were dried under vacuum over anhydrous calcium chloride.

$Cu(pco)_2Cl_2$

A warm ethanol (40 ml) solution of ligand (1.0 g) was added to a warm solution of cupric chloride dihydrate (1.25 g) in ethanol (35 ml). The resulting solution was warmed for 10 min and the complex deposited on cooling.

$Cu(pco)_2Br_2$

A boiling methanol solution (40 ml) of ligand (1.0 g) was added to a boiling methanol solution of anhydrous cupric bromide (0.84 g). The solution was stirred vigorously and a complex was deposited; the solution was allowed to cool and the product was filtered off.

$Cu(pco)_2(NO_3)_2\cdot 0.5H_2O$

A boiling ethanol (35 ml) solution of ligand (1.20 g) was added to a boiling solution of cupric nitrate trihydrate (1.5 g) in ethanol (40 ml) and 2,2-dimethoxypropane (12 ml). The solution was concentrated to approximately 40 ml and left to stand in a desiccator for several days, whereupon the complex was deposited.

$Cu(pco)_2(ClO_4)_2\cdot CH_3OH$

A boiling solution of ligand (1.0 g) in methanol (30 ml) and ethanol (30 ml) was added to a warm ethanol (30 ml) solution of cupric perchlorate hexahydrate (1.5 g). The solution was concentrated to approximately 40 ml and left to stand in a desiccator for several days whereupon the complex was deposited.

$Ni(pco)_2Cl_2$

The ligand (1.0 g) was dissolved in boiling ethanol (35 ml) and was added to a boiling ethanol (40 ml) solution of nickel(II) chloride hexahydrate (1.78 g). The solution was concentrated till a bright green powder appeared, then allowed to cool and the product filtered off.

$Ni(pco)_2Br_2$

The complex was prepared in analogous manner to the chloride complex. The following quantities were employed: nickel(II) bromide trihydrate 1.1 g, ethanol 40 ml, ligand 1.1 g and ethanol 35 ml.

$Co(pco)_2Cl_2$

A boiling mixture of ligand (1.4 g) and ethanol (40 ml) and 2,2-dimethoxypropane (5 ml) was added to a boiling solution of cobalt(II) chloride hexahydrate (1.0 g) in ethanol (30 ml) and 2,2-dimethoxypropane (10 ml). The mixture was warmed for several minutes and upon allowing to cool the complex was deposited.

$Co(pco)_2Br_2$

The complex was prepared in an analogous manner to $Co(pco)_2Cl_2$.

$Co(pco)_2(NO_3)_2 \cdot H_2O$

The ligand (1.1 g) was dissolved in boiling ethanol (30 ml) and added to a boiling ethanol (20 ml) solution of cobalt(II) nitrate hexahydrate (1.0 g). The solution was concentrated to approximately 30 ml and left to stand overnight. Cooling the solution in an ice bath resulted in the complex being deposited.

$Cr(pco)_3Cl_3 \cdot 2H_2O$

A boiling solution of ligand (1.5 g) in ethanol (30 ml) and 2,2-dimethoxypropane (5 ml) was added to a boiling solution of chromium(III) chloride hexahydrate dissolved in ethanol (25 ml) and 2,2-dimethoxypropane (8 ml). The solution was concentrated to approximately 30 ml and the complex was deposited after standing for several hours.

$Mn(pco)Cl_2$

A boiling solution of manganese(II) chloride tetrahydrate (1.0 g) dissolved in ethanol (35 ml) was added slowly and with vigorous stirring to a boiling ethanol (25 ml) solution of ligand (1.40 g). The complex was deposited immediately, the solution was allowed to cool and the product was filtered off.

$Cu(ptco)X_2$ ($X = Cl, Br$)

The above complexes were prepared by combining the ligand and appropriate metal salt in a 2:1 molar ratio, using ethanol as a solvent. The complexes appeared to decompose after several weeks and were insoluble in common solvents.

Attempts at preparing complexes of deprotonated pco, using sodium methoxide as a base and alcohol as solvent for both the ligand and metal salt, were unsuccessful. In addition, attempts at isolation of ptco complexes with many of the above metal salts, using ethanol as a solvent, were unsuccessful.

Deuterated Compounds

N-deuterated pco was prepared by recrystallisation of the ligand from D_2O. Complexes of N-deuterated pco were prepared by reaction between the ligand and anhydrous metal salts, in O-deuterated methanol [42]. Atmospheric moisture was excluded from all operations.

Analyses and Physical Measurements

These were as previously described [2].

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