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Metal Complexes of the Schiff Bases of 2-Pyridinylhydrazine and 2-Quinolinylhydrazine with 2-Pyridinecarboxaldehyde N-Oxide, Including some N-Oxide-Bridged Antiferromagnetic Complexes of Cobalt(II) and Nickel(II)

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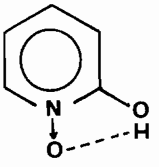
Metal complexes of 2-pyridine carboxaldehyde 2'-pyridinylhydrazone 1-oxide (poph) and 2-pyridinecarboxaldehyde 2'-quinolinylhydrazone 1-oxide (poqh) are reported with copper(II), nickel(II), cobalt(II), iron(II) and manganese(II). Each ligand appears to function as an ONN donor, via *the pyridine N-oxide oxygen, the imine nitrogen, and a pyridine or quinoline nitrogen. The complexes have been characterised by magnetic susceptibility measurements to liquid nitrogen temperature, and also by electronic, infrared, X-ray powder diffraction, and Mössbauer spectra. No magnetic interaction was detected with the copper(II) complexes. All the complexes of metal nitrates appear to be monomers.*

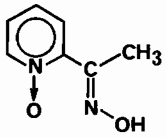
The complexes of poph with the halides and thiocyanates of nickel(II) and cobalt(II) appear to be six-coordinate and N-oxide-bridged; they exhibit varying degrees of antiferromagnetic interaction and the magnetic data for the nickel(II) complexes have been fitted to various models. In contrast, the bulky ligand poqh produces halide-bridged six-coordinate nickel(II) complexes and monomeric five-coordinate cobalt(II) complexes. This behaviour by poqh resembles that of the related NNN ligands paphy and paqhy, which are the Schiff bases of 2-pyridinecarboxaldehyde with 2-pyridinylhydrazine and 2-quinolinylhydrazine, respectively.

Introduction

Complexes of pyridine N-oxide and its substituted derivatives have been extensively studied. Many examples of N-oxide-bridged complexes, displaying magnetic interaction, have been reported with copper(II), but very few complexes of this type have been obtained with other transition metal ions [1]. We have been investigating ligands based on pyridine N-oxide, with donor substituents in the 2-position, to see whether N-oxide-bridging with a wider range of metal ions may be obtained [2]. We have studied ligands (I) to (IV) [3–6] and have obtained antiferromagnetic cobalt(II) and nickel(II) complexes with ligands (II) and (IV).



(I)



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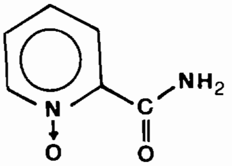

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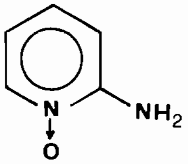

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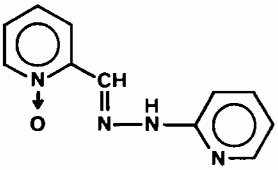
In this paper, we report complexes of 2-pyridinecarboxaldehyde 2'-pyridinylhydrazone 1-oxide (V, poph) and 2-pyridinecarboxaldehyde 2'-quinolinylhydrazone 1-oxide (VI, poqh). Some further examples of N-oxide-bridged cobalt(II) and nickel(II) complexes have been obtained. Some structural differences between complexes of poph and poqh are observed. In particular, the bulky ligand poqh produces five-coordinate cobalt(II) halide complexes, whereas six-coordinate complexes are produced with poph. Part of this work was reported in a preliminary communication [2].



(V, poph)

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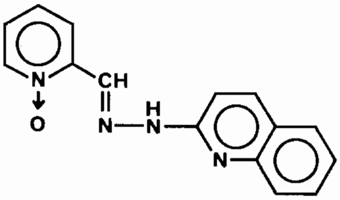
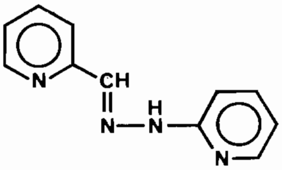
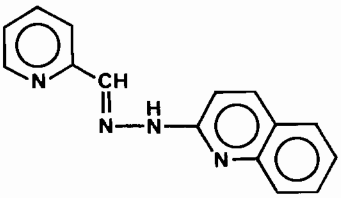

(VI, poqh)

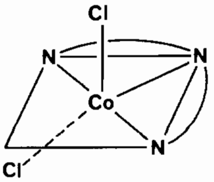
Results and Discussion

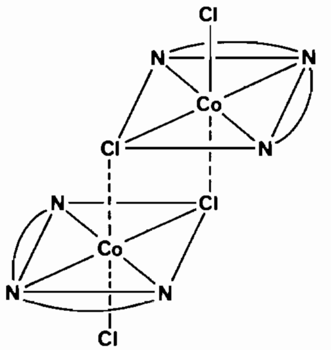
The ligands poph (V) and poqh (VI) are the Schiff bases of 2-pyridinecarboxaldehyde N-oxide with 2-pyridinylhydrazine and with 2-quinolinylhydrazine, respectively. They are N-oxide derivatives of the well known ligands paphy (VII) and paqhy (VIII) [7–11]:


(VII, paphy)


(VIII, paqhy)

Many 1:1 complexes of paphy and paqhy are known in which they coordinate as terdentate ligands [7–11]. A crystal structure determination has shown that the β-form of Co(paphy)Cl_2 has a distorted square-pyramidal structure, illustrated in (IX) [7, 11]. The lattice is built up from units in which two square-pyramidal molecules, related by a centre of symmetry, lie 'base to base'. Other complexes of the type M(paphy)X_2, with M = Mn, Zn, Cd and Hg, are probably five-coordinate, because they are closely related in lattice size and symmetry to β-Co(paphy)-Cl_2 [7, 11].


(IX)


(X)

The α-form of Co(paphy)Cl_2, and the nickel complex Ni(paphy)Cl_2, appear to be six-coordinate, on the basis of their electronic spectra and magnetic properties [7]. X-ray powder diffraction spectra show that the two complexes are isostructural [7]. It has been suggested that the complexes have chloride-bridged dimeric structures, such as (X), and that bridging could be achieved by a lateral displacement of two five-coordinate molecules arranged 'base to base' [7]. The related NNN ligand paqhy also produces a five-coordinate complex with cobalt(II) chloride and a six-coordinate chloride-bridged complex with nickel(II), according to spectroscopic evidence [9].

The complexes of the N-oxide ligands poph and poqh are listed in Table I, with analytical data. They are all 1:1 complexes. Ligand infrared data are given in Table II. The infrared spectrum of poph is fairly similar to the spectrum of paphy, but additional strong bands occur at 1228 cm^{-1} and 851 cm^{-1} for poph, assigned to the ν(NO) and δ(NO) modes, respectively. By comparing poqh with paqhy, the ν(NO) band for poqh is observed at 1231 cm^{-1}, but δ(NO) could not be definitely assigned. The ν(NO) frequencies of poph and poqh decrease by *ca.* 19–36 cm^{-1} upon complex formation, and δ(NO) for poph increases somewhat. This indicates N-oxide coordination by poph and poqh [1]. The imine and heterocyclic nitrogen atoms in poph and poqh are likely to be coordinated, since they are always bonded in 1:1 complexes of paphy and paqhy. We consider, therefore, that poph and poqh behave as terdentate ONN ligands, and the structures of the complexes are all consistent with this, some of them being similar to structures of paphy and paqhy complexes.

We next deal with the infrared spectra of the anions in the complexes. These are given in Table III. The nitrate complexes all exhibit four anion bands in the 1260–1520 cm^{-1} region, indicating coordinated nitrate [12]. In compounds containing ionic nitrate, the ν_3 mode of the ion occurs as a single band at *ca.* 1350–1400 cm^{-1} [12, 13]. It is split when coordination occurs and the extent of splitting is usually, but not always, greater for bidentate (or bridging) nitrate than for unidentate nitrate [13]. For some nickel complexes, splittings of 185–235 cm^{-1} and 105–115 cm^{-1} are found for bidentate and unidentate nitrate, respectively [13]. On this basis, our compounds probably have one unidentate and one bidentate (or bridging) nitrate. The ν_1 mode of an ionic nitrate becomes infrared active when coordina-

TABLE I. Analytical Data.

Compound	Analyses % (Calculated and Found)				Colour
	C	H	N	M	
$poph \cdot 0.33H_2O$	60.0 59.9	4.9 4.9	25.4 23.8		yellow
poqh	68.2 67.9	4.6 4.4	21.2 20.8		yellow
$Cu(poph)Cl_2$	37.9 37.8	2.9 3.0	16.1 15.7	18.2 18.2	green
$Cu(poph)Br_2 \cdot 0.5H_2O$	29.6 29.5	2.5 2.2	12.6 12.2	14.2 14.7	green
$Cu(poph)(NO_3)_2 \cdot H_2O$	31.5 31.5	2.9 3.2	20.0 19.8	15.1 14.9	brown
$Cu(poqh)(NO_3)_2 \cdot 0.5H_2O$	39.1 39.2	2.8 3.1	18.2 17.5	13.8 13.5	brown
$Ni(poph)Cl_2$	38.4 38.4	2.9 3.3	16.3 15.9	17.1 16.8	brown
$Ni(poph)Br_2 \cdot H_2O$	29.3 29.1	2.7 2.6	12.4 11.9	13.0 13.3	brown
$Ni(poph)(NO_3)_2 \cdot 2H_2O$	30.5 30.4	3.3 2.6	19.4 20.3	13.6 13.4	brownish-yellow
$Ni(poph)(NCS)_2$	40.1 39.8	2.6 2.8	21.6 21.0	15.1 14.8	brown
$Ni(poqh)Cl_2 \cdot 0.5H_2O$	44.7 44.7	3.3 3.5	13.9 13.7	14.6 14.7	green
$Ni(poqh)Br_2 \cdot H_2O$	36.0 36.4	2.8 2.9	11.2 11.0	11.7 11.5	brown
$Ni(poqh)Cl_2 \cdot 0.5H_2O$	44.7 44.7	3.3 3.5	13.9 13.7	14.6 14.7	green
$Ni(poqh)Br_2 \cdot H_2O$	36.0 36.4	2.8 2.9	11.2 11.0	11.7 11.5	brown
$Ni(poqh)(NO_3)_2 \cdot 0.5H_2O$	39.5 39.8	2.9 3.2	18.8 18.4	12.9 12.9	brown
$Ni(poqh)(NCS)_2 \cdot 0.5H_2O$	45.6 45.9	2.9 3.2	18.8 18.7	13.1 13.4	brown
$Co(poph)Cl_2$	38.4 38.2	2.9 3.1	16.3 16.3	17.1 17.3	brown
$Co(poph)(NCS)_2$	40.1 40.4	2.6 2.6	21.6 21.3	15.1 15.4	red
$Co(poqh)Cl_2 \cdot 1.5H_2O$	42.8 43.1	3.6 4.1	13.3 12.6	14.0 13.8	greenish-brown
$Co(poqh)Br_2 \cdot H_2O$	36.0 36.0	2.8 3.3	11.2 10.4	11.8 11.5	brown
$Co(poqh)(NO_3)_2 \cdot 0.5H_2O$	39.5 39.2	2.9 2.8	18.4 18.4	12.9 12.7	red
$Mn(poph)Cl_2$	38.9 38.8	3.0 2.8	16.5 16.2	16.2 15.9	yellow
$Fe(poph)Cl_2 \cdot 0.5H_2O$	37.8 37.7	3.5 3.1	16.0 15.0	16.0 16.2	black
$Fe(poqh)Cl_2$	46.1 46.5	3.1 3.3	14.3 14.0	14.3 14.0	greenish-black

TABLE II. Ligand Infrared Spectra (cm^{-1}).

Compound	$\nu(NO)$	$\delta(NO)$
poph	1228vs	851s
$Cu(poph)Cl_2$	1201m	877,868m
$Cu(poph)Br_2 \cdot 0.5H_2O$	1198m	878m
$Cu(poph)(NO_3)_2 \cdot H_2O$	1209w	878m
$Ni(poph)Cl_2$	1202,1193m	878,870m
$Ni(poph)Br_2 \cdot H_2O$	1193s	863m
$Ni(poph)(NO_3)_2 \cdot 2H_2O$	1192m	868m
$Ni(poph)(NCS)_2$	1194m	869m
$Co(poph)Cl_2$	1192s	865m
$Co(poph)(NCS)_2$	1192m	870m
$Fe(poph)Cl_2 \cdot 0.5H_2O$	1208m	873m
$Mn(poph)Cl_2$	1218m	878,869m
poqh	1231s	–
$Cu(poqh)(NO_3)_2 \cdot 0.5H_2O$	1202m	–
$Ni(poqh)Cl_2 \cdot 0.5H_2O$	1208m	–
$Ni(poqh)Br_2 \cdot H_2O$	1211m	–
$Ni(poqh)(NO_3)_2 \cdot 0.5H_2O$	1209,1202m	–
$Ni(poqh)(NCS)_2 \cdot 0.5H_2O$	1202m	–
$Co(poqh)Cl_2 \cdot 1.5H_2O$	1208m	–
$Co(poqh)Br_2 \cdot H_2O$	1205m	–
$Co(poqh)(NO_3)_2 \cdot 0.5H_2O$	1203w	–
$Fe(poqh)Cl_2$	1211m	–

tion occurs, producing a band at *ca.* 1000 cm^{-1}. Most of our complexes have two nitrate bands in this region, consistent with two types of coordinated nitrate being present.

The thiocyanate complexes have a $\nu(CN)$ band occurring in the range 2088–2098 cm^{-1}. This is a region common to N-bonded thiocyanate (usually found at *ca.* 2050–2100 cm^{-1}) and bridging thiocyanate (usually found at *ca.* 2090–2140 cm^{-1}) [14–16]. The $\nu(CS)$ band has been identified for the two nickel thiocyanate complexes (at 822 cm^{-1} and 832 cm^{-1} respectively) and it is the range for N-bonded thiocyanate (780–860 cm^{-1}) [14–16]. The $\nu(CS)$ band is probably too high in frequency for bridging thiocyanate, since this normally produces a band only moderately higher than the free ion value of *ca.* 750 cm^{-1}; many bridged complexes have $\nu(CS)$ at *ca.* 780–790 cm^{-1} [15–17]. N-bonded thiocyanate is, therefore, most likely for the complexes. The splitting of $\nu(CN)$ observed for $Co(poph)(NCS)_2$ may be the result of different environments for the two coordinated anions.

The reflectance spectra and magnetic moments of the complexes are given in Tables IV and V, respectively. The copper(II) complexes have temperature independent μ_{eff} values of *ca.* 1.8–2.0 B.M. This excludes planar N-oxide bridged structures, since these produce strong magnetic interaction [18]. The copper(II) halide complexes have a single reflectance band at *ca.* 14,000 cm^{-1}. This is consistent with halide-bridged six-coordinate structures with CuN_2OHal_3 chromophores, since several CuN_2Hal_4 systems

TABLE III. Infrared Spectra of Anions in Complexes (cm^{-1}).

Complex	Anion absorptions		
	ν_3[a]	ν_1[a]	ν_2[a]
Cu(poph)$(NO_3)_2 \cdot H_2O$	1518s,1425s,1315s,1275sh	1043m,1007m	823w
Ni(poph)$(NO_3)_2 \cdot 2H_2O$	1508s,1460s,1305s,1262s	1022m,1011m	813,803w
Cu(poqh)$(NO_3)_2 \cdot 0.5H_2O$	1475s,1422s,1308sh,1290s	1011s	–
Ni(poqh)$(NO_3)_2 \cdot 0.5H_2O$	1500s,1450s,1305s,1275s	1038m,1018m	–
Co(poqh)$(NO_3)_2 \cdot 0.5H_2O$	1505s,1408s,1347s,1280s	1038m,1023m	–
	ν(CN)	ν(CS)	δ(NCS)
Ni(poph)$(NCS)_2$	2089vs	822w	468vw
Co(poph)$(NCS)_2$	2098vs,2068vs	832w	488w
Ni(poqh)$(NCS)_2 \cdot 0.5H_2O$	2088vs	b	b

[a] The labelling scheme is for ionic (D_{3h}) nitrate. [b] Obscured by ligand absorption.

TABLE IV. Diffuse Reflectance Spectra[a].

Compound	Absorption maxima (cm^{-1} × 10^{-3})
Cu(poph)Cl_2	13.9
Cu(poph)$Br_2 \cdot 0.5H_2O$	14.3
Cu(poph)$(NO_3)_2 \cdot H_2O$	15.3br
Cu(poqh)$(NO_3)_2 \cdot 0.5H_2O$	13.9
Ni(poph)Cl_2	9.1;15.3sh
Ni(poph)$Br_2 \cdot H_2O$	8.5sh,9.9; *ca.* 15.5sh
Ni(poph)$(NO_3)_2 \cdot 2H_2O$	8.0sh,10.9;17.0sh
Ni(poph)$(NCS)_2$	10.0br; *ca.* 17.1sh
Ni(poqh)$Cl_2 \cdot 0.5H_2O$	8.0;15.5
Ni(poqh)$Br_2 \cdot H_2O$	7.1sh,10.3;17.0sh
Ni(poqh)$(NO_3)_2 \cdot 0.5H_2O$	8.0sh,10.6; *ca.* 18.7sh
Ni(poqh)$(NCS)_2 \cdot 0.5H_2O$	9.6; *ca.* 17.5sh
Co(poph)Cl_2	6.0sh,7.8;17.0
Co(poph)$(NCS)_2$	8.5,10.2sh;15.8sh;17.9sh
Co(poqh)$Cl_2 \cdot 1.5H_2O$	4.8sh,5.9;9.8;15.2; *ca.* 19.0sh
Co(poqh)$Br_2 \cdot H_2O$	5.0sh,5.5;9.7;14.4; *ca.* 18.5sh
Co(poqh)$(NO_3)_2 \cdot 0.5H_2O$	9.0; *ca.* 17.5sh,br
Fe(poph)$Cl_2 \cdot 0.5H_2O$	11.0sh
Fe(poqh)Cl_2	10.0sh

[a] Strong ligand/charge transfer absorption obscures any d–d bands beyond about 21.000 cm^{-1}.

TABLE V. Magnetic Data.

Compound		μ_{eff} (B.M.)		θ[a](K)
		298 K[b]	89 K	
Cu(poph)Cl_2		1.91	1.86	–10
Cu(poph)$Br_2 \cdot 0.5H_2O$		1.86	1.84	–3
Cu(poph)$(NO_3)_2 \cdot H_2O$		2.00	1.93	–6
Cu(poqh)$(NO_3)_2 \cdot 0.5H_2O$	(294 K)	1.95	1.91	–2
Ni(poph)Cl_2		2.98	2.62	–37
Ni(poph)$Br_2 \cdot H_2O$		3.17	2.86	–28
Ni(poph)$(NO_3)_2 \cdot 2H_2O$		3.32	3.27	–2
Ni(poph)$(NCS)_2$	(301 K)	2.93	2.21	–84[c]
Ni(poqh)$Cl_2 \cdot 0.5H_2O$		3.33	3.39	+1
Ni(poqh)$Br_2 \cdot H_2O$		3.27	3.17	–9
Ni(poqh)$(NO_3)_2 \cdot 0.5H_2O$		3.28	3.18	–8
Ni(poqh)$(NCS)_2 \cdot 0.5H_2O$		3.12	2.61	–64
Co(poph)Cl_2		4.49	4.15	–22
Co(poph)$(NCS)_2$		4.32	3.86	–37
Co(poqh)$Cl_2 \cdot 1.5H_2O$		4.58	4.36	–4
Co(poqh)$Br_2 \cdot H_2O$		4.49	4.38	–8
Co(poqh)$(NO_3)_2 \cdot 0.5H_2O$		4.64	4.47	–8
Mn(poph)Cl_2		5.85	5.83	0
Fe(poph)$Cl_2 \cdot 0.5H_2O$		5.39	5.14	–9
Fe(poqh)Cl_2	(294 K)	4.98	4.90	–3

[a] Curie–Weiss law taken as $\chi_A^{-1} \propto (T - \theta)$. [b] Some measurements at different temperatures are indicated below. [c] Deviated from linearity at lower temperatures.

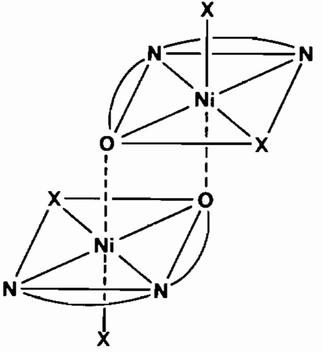
have a reflectance band at *ca.* 14,000 cm^{-1} [19, 20]. Five-coordinate structures with regular or distorted square-pyramidal geometry are also possible, since these can produce spectra similar to six-coordinate complexes [21]. A regular trigonal bipyramidal structure is unlikely, since this should produce absorption at considerably lower frequency. For example, $[Cu(N(CH_2CH_2NMe_2)_3Br]Br$ has a trigonal bipyramidal CuN_4Br structure and has a reflectance band at 10,000 cm^{-1}, and a pronounced shoulder at 12,800 cm^{-1} [22, 23].

As previously discussed, the copper(II) nitrate complexes have infrared spectra which show the presence of two types of coordinated nitrate, probably unidentate and bidentate. This would produce a CuN_2O_4 chromophore. The complexes have a reflectance band in the 14–15,000 cm^{-1} region. Several complexes with CuN_2O_4 chromophores have a main band in this region, with a shoulder at *ca.* 9–10,000 cm^{-1} [24]. Our complexes have no shoulder present, but slight band asymmetry occurs at *ca.* 10–11,000 cm^{-1}.

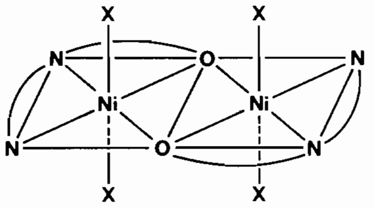
The nickel(II) complexes have reflectance spectra which indicate six-coordinate structures. The reflectance bands are broad and in some cases split. This is in keeping with the relatively unsymmetrical chromophores which are expected. The nickel(II) compounds form two classes on the basis of magnetic properties (Table V, VI). The compounds Ni(poqh)Cl_2·0.5H_2O, Ni(poqh)Br_2·H_2O, Ni(poph)$(NO_3)_2$·2H_2O and Ni(poqh)$(NO_3)_2$·0.5H_2O are simple paramagnets with small θ values and μ_{eff} values largely temperature-invariant. The remaining complexes are antiferromagnetic.

We discuss the simple paramagnetic compounds first. The previously reported six-coordinate complex Ni(paphy)Cl_2 is a simple paramagnet (θ = 0 K), and a chloride-bridged dimeric structure, as in (X), was suggested [7]. Our complexes Ni(poqh)Cl_2·0.5H_2O and Ni(poqh)Br_2·H_2O very likely have this structure or alternatively a polymeric halide-bridged structure. The infrared spectra of the nickel(II) nitrate complexes suggest the presence of unidentate and bidentate nitrate, as previously discussed. This could produce monomeric six-coordinate structures, in keeping with the lack of magnetic interaction found for these complexes.

The remaining nickel(II) complexes are antiferromagnetic. This suggests N-oxide bridged structures, since anion bridging in complexes of the type Ni(ligand)$_n$$X_2$ (X = halide, NCS) does not normally lead to marked antiferromagnetism [25, 26]. The magnetic susceptibility data for the complexes were compared to those predicted for various polynuclear models. In most cases the fits to the different models were similar, probably because of the relatively small interaction. With the most strongly antiferromagnetic compound Ni(poph(NCS)$_2$, the dimeric model gave a substantially better fit (Table VII). In view of this, N-oxide-bridged dimeric structures (possibly as in (XI), or (XII)) are favoured for the antiferromagnetic complexes. The suggested coordination by the thiocyanate groups (terminal N-bonded) in Ni(poph)$(NCS)_2$ and Ni(poqh)$(NCS)_2$·0.5H_2O, deduced from infrared spectra, is in keeping with structures such as (XI).



(XI)



(XII)

TABLE VI. Magnetic Data for Some Antiferromagnetic Complexes.

Ni(poph)Cl_2							
T(K)	298.5	254.6	225.2	176.1	146.6	117.9	88.9
$10^3\chi_A$(cgsu)	3.69	4.24	4.70	5.84	6.73	7.97	9.59
μ_{eff}(B.M.)	2.98	2.95	2.92	2.88	2.82	2.75	2.62
Ni(poph)Br_2·H_2O							
T(K)	298.5	254.6	215.4	176.1	127.4	88.9	
$10^3\chi_A$(cgsu)	4.16	4.78	5.54	6.61	8.67	11.36	
μ_{eff}(B.M.)	3.17	3.13	3.10	3.06	2.98	2.86	
Ni(poph)$(NCS)_2$							
T(K)	301.1	254.6	215.4	176.1	127.4	103.6	88.9
$10^3\chi_A$(cgsu)	3.54	4.00	4.55	5.16	6.10	6.52	6.80
μ_{eff}(B.M.)	2.93	2.87	2.81	2.71	2.50	2.33	2.21
Ni(poqh)$(NCS)_2$·0.5H_2O							
T(K)	298.5	254.6	215.4	176.1	117.9	88.9	
$10^3\chi_A$(cgsu)	4.04	4.56	5.24	6.13	8.05	9.52	
μ_{eff}(B.M.)	3.12	3.06	3.02	2.95	2.77	2.61	
Co(poph)$(NCS)_2$							
T(K)	298.5	254.6	215.4	176.1	127.4	88.9	
$10^3\chi_A$(cgsu)	7.77	8.97	10.38	12.36	15.74	20.80	
μ_{eff}(B.M.)	4.32	4.29	4.25	4.19	4.02	3.86	

TABLE VII. Best Fits of Magnetic Data of Ni(poph)$(NCS)_2$[a].

Model	(Reference)[b]	g	J (cm^{-1})	$\Sigma[(\chi_{obs} - \chi_{calc})T]^2$	$\left\{\frac{\Sigma[(\chi_{obs} - \chi_{calc})T]^2}{\Sigma(\chi_{obs})^2}\right\}$	S.E.[c]
Dimer	(27)	2.19	−24.5	0.11×10^{-3}	0.004	0.007
Linear trimer	(28)	2.27	−26.1	1.40×10^{-3}	0.022	0.030
Equilateral triangle	(28)	2.29	−19.3	1.18×10^{-3}	0.018	0.024
Regular tetrahedron	(29)	2.31	−14.7	1.23×10^{-3}	0.018	0.024
Heisenberg linear polymer	(30)	2.27	−18.6	0.57×10^{-3}	0.011	0.016

[a] Best fits were obtained using a least-squares procedure which minimised $\Sigma[(\chi_{obs} - \chi_{calc})T]^2$. [b] References to the susceptibility equations are given in parentheses. The temperature independent paramagnetism was taken as 200×10^{-6} cgsu. [c] S.E. is the standard error expression $\{\Sigma[\mu_{eff}(obs) - \mu_{eff}(calc)]^2/(NP - k)\}^{1/2}$, where k is the number of parameters used to fit the NP data points (Ginsberg *et al.*, *Inorg. Chem.*, *11*, 2884 (1972)).

The cobalt(II) complexes with poph, and the complex Co(poqh)$(NO_3)_2\cdot0.5H_2O$, have reflectance spectra indicating six-coordinate structures (Fig. 1). The bands are broad, probably because of the unsymmetrical chromophores present. The X-ray powder diffraction pattern (Table VIII) of Co(poqh)$(NO_3)_2\cdot0.5H_2O$ is similar to that of Ni(poqh)$(NO_3)_2\cdot0.5H_2O$, indicating a similar six-coordinate structure, with unidentate and bidentate nitrate.

The six-coordinate structure of Co(poph)$(NCS)_2$ may be produced by either thiocyanate or N-oxide bridging. As we discussed earlier, infrared data suggest that only terminal N-bonded thiocyanate is present, so N-oxide bridging is likely. The compound has a μ_{eff} value of 4.32 BM at room temperature, below the usual range of *ca.* 4.7–5.2 BM for monomeric octahedral complexes [26]. The moment decreases to 3.86 BM at 89 K, giving a θ value of −37 K. A range of magnetically dilute octahedral cobalt(II) complexes had θ values from −11 to −36 K [31]. The depressed μ_{eff} value of the compound suggests significant magnetic interaction, in keeping with the proposed N-oxide-bridged structure. We have found similar antiferromagnetism for N-oxide-bridged cobalt(II) complexes with the pyridine N-oxide ligands (II) and (IV).

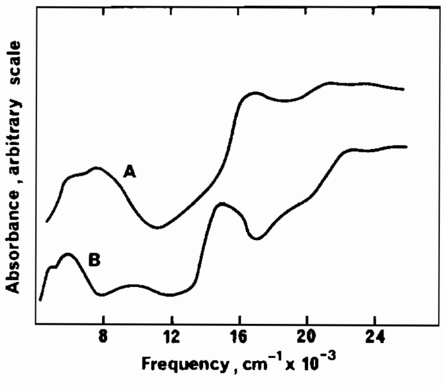


Fig. 1. Diffuse reflectance spectra of Co(poph)Cl_2 (A) and Co(poqh)$Cl_2\cdot1.5H_2O$ (B).

TABLE VIII. Major Lines in X-Ray Powder Diffraction Spectra.

d-spacings (Å)	
Ni(poqh)$(NO_3)_2\cdot0.5H_2O$	Co(poqh)$(NO_3)_2\cdot0.5H_2O$
8.09s	8.09m
7.37m	7.30m
6.95vs	6.95vs
6.20m	6.12w
5.96s	5.89m
5.34m	5.37m
4.86m	4.91m
4.74m	4.72s
4.31s	4.29s
4.06w	4.08s
3.92s	3.93s

Ni(poph)Cl_2	Co(poph)Cl_2	Fe(poph)$Cl_2\cdot0.5H_2O$
10.00s	10.00s	9.8s
7.48vs	7.62vs	7.56vs
7.20w	7.35w	7.15w
6.12m	6.33s	6.47m
5.23m	5.34m	5.43m
5.08w	5.01w	5.13w
4.55w	4.59m	4.65w
–	4.22w	4.22w
3.96s	3.98s	3.92s

The six-coordinate complex Co(poph)Cl_2 has an X-ray powder pattern (Table VIII) similar to that of Ni(poph)Cl_2, for which an N-oxide-bridged structure was proposed above. The cobalt complex has a μ_{eff} value of 4.49 BM at room temperature, somewhat below the usual range for six-coordinate, magnetically dilute, cobalt(II) complexes [26]. This may be a result of antiferromagnetic interaction associated with N-oxide-bridging. The compounds α-Co(paphy)Cl_2 and CoL$Cl_2\cdot0.5H_2O$ (L = 1,10-phenanthroline-2-carboxamide) are considered to have the alternative chloride-bridged structures, and it is interesting that these compounds have room temperature μ_{eff} values of 5.03 BM and 5.00 BM respectively, in the range for magnetically dilute, six-coordinate, cobalt(II) [7, 32].

In contrast to $Co(poph)Cl_2$, the poqh complexes $Co(poqh)Cl_2 \cdot 1.5H_2O$ and $Co(poqh)Br_2 \cdot H_2O$ appear to be five-coordinate. Their electronic spectra (Fig. 1) are similar to the spectrum of the five-coordinate complex β-$Co(paphy)Cl_2$, with bands shifted to lower frequency, in keeping with the NNO coordination of poqh and the NNN coordination by paphy [7]. The spectra are also similar to those of $[Co(Me_5dien)Cl_2]$-(CoN_3Cl_2 structure, Me_5dien = bis(2-dimethylaminoethyl)methylamine) and $[Co(Me_4daeo)Cl_2]$(CoN_2OCl_2 structure, Me_4daeo = bis(2-dimethylaminoethyl)oxide) [33, 34]. All these complexes have spectra with one or two medium bands in the 5–9000 cm^{-1} region, a weak band at *ca.* 10–12,000 cm^{-1}, a strong band at *ca.* 15–17.000 cm^{-1} and a second strong band or shoulder at *ca.* 18–20,000 cm^{-1} [7, 33, 34].

The compounds $Fe(poph)Cl_2 \cdot 0.5H_2O$, $Fe(poqh)Cl_2$ and $Mn(poph)Cl_2$ have magnetic moments which are almost invariant with temperature. The compound $Fe(poph)Cl_2 \cdot 0.5H_2O$ has an X-ray powder diffraction pattern which is very similar to those of $Ni(poph)Cl_2$ and $Co(poph)Cl_2$, so an N-oxide-bridged structure should be present. The lack of evidence for magnetic interaction, found with $Fe(poph)Cl_2 \cdot 0.5H_2O$, could be due to some small distortion of the structure, which does not markedly change the X-ray powder diffraction pattern, but which does reduce the strength of the magnetic interaction in the N-oxide-bridged structure. Both iron(II) complexes have electronic spectra consistent with six-coordinate structures [35]. The Mössbauer spectrum of $Fe(poph)Cl_2 \cdot 0.5H_2O$ has an isomer shift of 1.14 mm s^{-1} and a quadrupole splitting of 2.47 mm s^{-1}, at room temperature. At room temperature $Fe(poqh)Cl_2$ has an isomer shift of 1.24 mm s^{-1} and a quadrupole splitting of 2.36 mm s^{-1}; at liquid nitrogen temperature the corresponding values are 1.38 mm s^{-1} and 2.86 mm s^{-1}, respectively. These Mössbauer spectroscopic data are all similar to values for other high-spin, six-coordinate iron(II) complexes [36].

No d--d spectroscopic bands were observed for $Mn(poph)Cl_2$ so no structural assignments are possible. X-ray powder diffraction patterns were measured for all the compounds, but only cases of similarities are mentioned in this paper.

A range of structures is found with these complexes. The nitrate complexes are six-coordinate, with bidentate and unidentate anion. This is quite common for metal nitrate complexes with terdentate ligands [37–39]. The complexes of poph with nickel(II) and cobalt(II) halides are N-oxide-bridged. If the complexes pack as for β-$Co(paphy)Cl_2$, then N-oxide-bridging could readily be produced by a lateral shift of square-pyramidal molecules packed 'base to base'.

N-oxide-bridging is not found for the poqh complexes with metal halides, possibly because of the bulkier nature of the ligand. The nickel(II) halide complexes with poqh are halide-bridged and six-coordinate, whereas the cobalt(II) halide complexes are five-coordinate. This is similar to the pattern with paphy and other bulky terdentate ligands [7, 40]. All the thiocyanate complexes appear to be N-oxide-bridged. We are not aware of any rationalisation of this. Complexes of the type $ML(NCS)_2$, with terdentate ligands, are very commonly six-coordinate, with one bridging and one N-bonded thiocyanate [6, 37–41].

Experimental

2-Pyridinecarboxaldehyde 2'-Pyridinylhydrazone 1-Oxide (poph)

A warm aqueous (30 ml) solution of 2-pyridylhydrazine (10.0 g) was added with vigorous stirring to a warm aqueous (30 ml) solution of 2-pyridinecarboxaldehyde N-oxide (12.0 g), prepared by the method of Jerchel *et al.* [42]. The yellow Schiff base precipitated immediately and may be recrystallised from boiling ethanol (m.p. 170–1 °C). The compound is moderately light sensitive.

2-Pyridinecarboxaldehyde 2'-Quinolinylhydrazone 1-Oxide (poqh)

An aqueous (30 ml) solution of 2-pyridinecarboxaldehyde N-oxide (11.0 g) was added with stirring to a warm solution of 2-quinolylhydrazine (6.0 g) in water (20 ml) and ethanol (40 ml). The mixture was allowed to cool and the yellow Schiff base was deposited. The ligand is almost insoluble in organic solvents and was purified (m.p. 242 °C) by warming with a 4:1 ethanol–chloroform mixture to remove unreacted hydrazine.

Metal Complexes

Since poqh is so insoluble, its complexes were prepared by heating a suspension of the ligand with excess of the appropriate metal salt dissolved in ethanol. The complexes were dried under vacuum over calcium chloride.

$Cu(poph)Cl_2$, $Cu(poph)Br_2 \cdot H_2O$, $Cu(poph)(NO_3)_2 \cdot H_2O$, $Ni(poph)(NO_3)_2 \cdot 2H_2O$, $Co(poph)Cl_2$, $Co(poph)(NCS)_2$ *and* $Mn(poph)Cl_2$

These complexes were prepared by 1:1 reactions between ligand and metal salt in ethanol; the preparation for $Cu(poph)Cl_2$ is given as an example. A solution of poph (1.2 g) in boiling ethanol (40 ml) was added slowly to a warm ethanol (35 ml) solution of copper(II) chloride dihydrate (1.0 g). The solution was stirred vigorously and the complex was deposited almost immediately.

Ni(poph)Cl$_2$

A boiling solution of poph (1.25 g) in ethanol (50 ml) was added to a warm solution of nickel(II) chloride hexahydrate (1.0 g) in ethanol (30 ml). The solution was filtered and evaporated on a steam bath until crystals formed. The complex was deposited as the solution cooled.

Ni(poph)Br$_2$·H$_2$O and Ni(poph)(NO$_3$)$_2$·2H$_2$O

Both complexes were made by a method of the type shown below. A warm solution of nickel(II) bromide trihydrate (2.0 g) in ethanol (25 ml) was added to a boiling solution of poph (1.0 g) in ethanol (30 ml). The solution was evaporated until crystals appeared, it was removed from the steam bath and petroleum ether (30 ml, 60–80 °C) was slowly added. The complex was deposited after several hours.

Ni(poph)(NCS)$_2$

A bloiling solution of poph (1.3 g) in ethanol (30 ml) was added with stirring to a boiling solution of nickel(II) thiocyanate (1.5 g) in methanol (40 ml).

Fe(poph)Cl$_2$·0.5H$_2$O

A boiling solution of poph (1.2 g) in ethanol (40 ml) was flushed with nitrogen for 15 min. Freshly prepared iron(II) chloride tetrahydrate (1.3 g) was quickly dissolved in ethanol (20 ml) which had been flushed with nitrogen for 10 min. The solutions were quickly combined and stirred vigorously under a nitrogen flush. A fine black powder was deposited.

Cu(poqh)(NO$_3$)$_2$·0.5H$_2$O, Ni(poqh)Cl$_2$·0.5H$_2$O, Ni(poqh)Br$_2$·H$_2$O, Ni(poqh)(NO$_3$)$_2$·0.5H$_2$O, Co(poqh)Cl$_2$·1.5H$_2$O, Co(poqh)Br$_2$·H$_2$O and Co(poqh)(NO$_3$)$_2$·0.5H$_2$O

The complexes were made by the general method illustrated below. A boiling solution of copper(II) nitrate trihydrate (2.0 g) in ethanol (25 ml) was added with stirring to a suspension of poqh (0.9 g) in boiling ethanol (45 ml). The mixture was boiled for several minutes until all the ligand had dissolved. The solution was allowed to cool and the product filtered off.

Ni(poqh)(NCS)$_2$

A boiling solution of nickel(II) thiocyanate (1.5 g) in methanol (45 ml) was added to a boiling suspension of poqh (1.1 g) in absolute ethanol (40 ml). The mixture was boiled until all the ligand had dissolved and a greenish-black powder was deposited.

Fe(poqh)Cl$_2$

A suspension of poqh (0.8 g) in boiling ethanol (50 ml) was flushed with nitrogen for 15 min. Freshly prepared iron(II) chloride tetrahydrate (1.9 g) was quickly dissolved in ethanol (40 ml), which had been flushed with nitrogen, and this solution was quickly added to the suspension. The mixture was stirred vigorously on the steam bath under nitrogen until the ligand had dissolved. A greenish-black powder was deposited.

Analyses and Physical Measurements

These were as previously described [3].

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