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Antiferromagnetic Complexes of Cobalt(II) and Nickel(II) with 2-Substituted Pyridine N-Oxides

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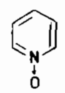
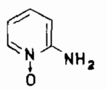
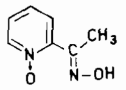
There appears to be a gap in the coordination chemistry of pyridine N-oxide (I, po) in that, whilst very many N-oxide-bridged antiferromagnetic complexes of copper(II) are known [1, 2], there are very few reports of such antiferromagnetic complexes of other transition metals with pyridine N-oxide. We have found that it is possible to readily obtain pyridine N-oxide-bridged antiferromagnetic complexes of nickel(II) and cobalt(II), by using ligands based on pyridine N-oxide with donor groupings in the 2-position.



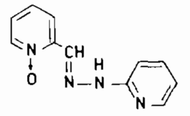
(I, po)



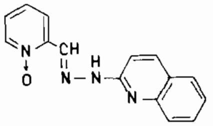
(II, Hapo)



(III, pxo)



(IV, poph)



(V, poqh)

Results and Discussion

In the table we show the magnetic data for a series of nickel(II) and cobalt(II) complexes with the ligands Hapo (II), pxo (III), poph (IV) and poqh (V).

The complexes in group I in the table are all markedly antiferromagnetic and are, therefore, considered to be N-oxide-bridged, since the alternative anion-bridging does not appear to produce marked magnetic interaction in complexes [3–5] of the type $M(ligand)_nX_2$ (M = Co, Ni; X = Cl, Br, NCS). The complexes have large Weiss θ values in the range 46–117 K.

With the nickel complexes, the μ_{eff} values are reduced, at 90 K, to the range 2.1–2.6 B.M., below the usual values of 2.8–3.2 B.M. which are found when magnetic interaction is absent [3, 4]. The magnetic data have been compared with those expected [6] for binuclear nickel complexes, and close agreement was found, using the values of g and J which are listed in the table. The nickel complexes are likely, therefore, to have binuclear structures. For the cobalt (II) complexes, the μ_{eff} values also decrease markedly with decreasing temperature, and the drop of 0.7–1.4 B.M., which occurs, contrasts with the change of *ca.* 0.2–0.6 B.M. found when interaction is absent [3, 4].

As a comparison, we list, in group II of the table, some complexes of these N-oxide ligands in which there is no detectable magnetic interaction and where N-oxide-bridging is probably, therefore, absent. The maximum decrease in μ_{eff} is 0.2 B.M., compared

TABLE. Magnetic Data for Complexes of Pyridine N-oxide and Its 2-Substituted Derivatives.

Group I

Complex	μ_{eff} (B.M.)				
	298 K	89 K	θ (K)	g^b	J $(cm^{-1})^b$
$Ni(Hapo)_2Br_2$	2.97	2.15	-115^c	2.25	−28
$Ni(pxo)Cl_2 \cdot CH_3OH$	2.93	2.28	-67^c	2.15	−19
$Ni(poph)(NCS)_2$	2.93	2.21	-84^c	2.19	−24
$Ni(poqh)(NCS)_2 \cdot ½H_2O$	3.12	2.61	−64	2.26	−16
$Co(Hapo)_2Br_2 \cdot C_2H_5OH$	4.67	3.28	-90^c		
$Co(pxo)Cl_2 \cdot CH_3OH$	4.59	3.89	-46^c		

Group II

Complex	μ_{eff} (B.M.)		
	298 K	89 K	θ (K)^a
$Ni(Hapo)Cl_2 \cdot H_2O$	3.11	2.91	−17
$Ni(pxo)_2Br_2$	3.16	3.10	−5
$Ni(poph)(NO_3)_2 \cdot 2H_2O$	3.32	3.27	−2
$Ni(poqh)(NO_3)_2 \cdot ½H_2O$	3.28	3.18	−8
$Co(Hapo)Cl_2 \cdot C_2H_5OH$	4.84	4.58	−14
$Co(pxo)_2Br_2$	4.77	4.61	−3
$Ni(po)Cl_2 \cdot H_2O$	3.17	3.10	−3
$Ni(po)Br_2 \cdot H_2O$	3.14	2.95	−18
$Co(po)Cl_2 \cdot H_2O$	4.76	4.55	−4

[a] The Curie–Weiss law is taken as $\chi_A^{-1} \propto (T - 1)$. [b] The values of g and J are those which give the best agreement between the experimental magnetic data and those calculated for a binuclear arrangement of nickel(II) ions. [c] The plot of χ_A^{-1} against temperature deviated from linearity at lower temperatures.

to the decrease of 0.5–1.4 B.M. found for the N-oxide-bridged, group I, complexes.

In group II we also list some new magnetic data on the pyridine N-oxide (po) complexes $M(po)(halide)_2 \cdot H_2O$ (M = Ni, Co). The reflectance electronic spectra of the po complexes show that they are six-coordinate [7], and so either N-oxide or halogen-bridging must be present. As can be seen in the table, the complexes exhibit no magnetic interaction and so halogen-bridging is considered likely. A similar halogen-bridged structure was proposed for $Ni(po)Cl_2$ by Karayannis *et al.* [8], on the basis of far-infrared spectra and magnetic data. Similar halogen-bridging has been proposed for 1:1 complexes of cobalt(II) halides with pyridine N-oxides (L); the analogous 2:1 complexes, $CoL_2(halide)_2$, appear to be monomeric and tetrahedral [9]. The complex $Ni(po)_2Br_2$ appears to be the only antiferromagnetic N-oxide-bridged complex of nickel(II) or cobalt(II) which has been reported with pyridine N-oxides [10]. This contrasts with the wide range of analogous 1:1 and 2:1 complexes with copper(II) which are N-oxide bridged and antiferromagnetic [1, 2].

This reluctance by pyridine N-oxide to readily produce N-oxide-bridged complexes with metals other than copper(II) is not shown by the N-oxides of more complicated amines such as diazines. The latter ligands have recently been found to yield N-oxide-bridged antiferromagnetic complexes with a range of transition metal ions [11].

Experimental

The ligand Hapo was prepared by the method of Delarge and Thunus [12]. The remaining ligands were prepared by condensation of relevant N-oxide compounds [13, 14] with appropriate amines. Complexes had satisfactory analyses and were generally obtained by reaction in alcoholic media in the presence of 2,2-dimethyoxypropane. Physical measurements were as previously described [15].

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