1995 (m), and 1985 (w) cm^{-1}, which resemble the carbonyl bands for 1. An absorption at 721 cm^{-1} is assignable to the N–S stretching band. Two absorptions at 755 and 682 cm^{-1} are the CH out-of-plane deformation bands for the monosubstituted benzene. In the far-infrared region were observed absorptions at 642 (m), 617 (s), 583 (s), 561 (s), ~475 (w, b), 445 (w), and 397 (w, b) cm^{-1}.

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CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF THE UNIVERSITY OF MANCHESTER INSTITUTE OF SCIENCE AND TECHNOLOGY, MANCHESTER, ENGLAND, AND YORK UNIVERSITY, DOWNSVIEW, ONTARIO, CANADA

Some Aspects of the Stereochemistry of Amine Oxide Metal Complexes

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Vibrational and electronic spectra and magnetic data are correlated to show that complexes of the type $M(R\text{-}PyO)_6{}^{n+}(ClO_4)_n$ (R–PyO = pyridine N-oxide or a substituted derivative) do not have octahedral (O_h) symmetry. Similarly the copper complexes $Cu(R\text{-}PyO)_4(ClO_4)_2$ do not have D_{4h} symmetry. The argument employs data from the literature as well as some novel vibrational (infrared) and low-temperature electronic spectroscopic data. A new five-coordinate derivative $Co(2\text{-}CH_3PyO)_5(ClO_4)_2$ (2-CH_3PyO = 2-picoline N-oxide) is characterized.

Complexes of type $ML_6{}^{n+}$, where L is a polyatomic monodentate ligand, generally have electronic, vibrational, and magnetic properties close to those anticipated for an octahedral complex even though such a molecule will not, in general, belong to the point group O_h.[2] The *effective* symmetry of the molecule is determined not only by the geometric site symmetry of the ion but also by the electronic symmetry, governed by the degree of interaction between the metal ion wave functions and the ligand wave functions. This is particularly marked with bidentate ligands where the properties of species such as $ML_3{}^{n+}$, where L is an unsaturated molecule such as bipyridyl, deviate considerably from octahedral behavior;[3] with saturated systems such as ethylenediamine, the deviation is very much smaller.[2,4] Pyridine N-oxide and its substituted derivatives are known to react with a wide range of metal ions forming complexes of considerable current interest.[5,6]

This ligand appears to be one of the very few monodentate ligands whose hexakis complexes have properties indicative of a marked variation from regular octahedral symmetry. This variation from the expected octahedral behavior is the main topic of discussion in this paper. During the course of our investigation a novel five-coordinate cobalt(II) complex of 2-picoline N-oxide was synthesized. This is also discussed.

Experimental Section

Electronic diffuse reflectance spectra were recorded with a Beckman DK2A instrument. The low-temperature transmittance spectra were obtained, by the method outlined by Rowley and Drago,[7] using a Cary 14 instrument. Vibrational spectra were recorded with Perkin-Elmer Models 21 and 257 spectrophotometers. Magnetic moments were determined using the Gouy method with a 1.5-in. pole piece Newport electromagnet. Mercury tetrathiocyanatocobaltate(II) was used as calibrant.

The new complexes reported in this paper were prepared by the following general technique. The metal salt (1 g) and the ligand (1 g) were each dissolved in hot alcohol (20 ml). The solutions were filtered and mixed. The mixture was then kept at 0° for 24 hr. The products were recrystallized from the same solvent, washed with diethyl ether, and dried under reduced pressure. Table I lists the analytical data and also the alcohol (methanol or ethanol) used for each synthesis. In the case of the complex $Fe(4\text{-}NO_2PyO)_6(ClO_4)_2$ 1 g each of the metal salt and ligand were refluxed in ethanol (10 ml) for 5 min. *Note: This complex may detonate* and care should be taken in handling it. The other complexes described here were not observed to be liable to explosion. The unusually intense color of this complex and of the corresponding manganese(II) complex is due to the presence of a relatively low-energy charge-transfer band and to the absorption of the $-NO_2$ group. The detailed nature of the charge-transfer absorption in pyridine N-oxide metal complexes, which has been briefly commented upon,[8] is the subject of a future paper.[9]

The five-coordinate complex $Co(2\text{-}CH_3PyO)_5(ClO_4)_2$ was prepared using a total of 25 ml rather than 40 ml of solvent as in the general method. Prolonged cooling at 0° is required to induce crystallization. This cobalt complex has a conductivity of 207 mhos mol^{-1} cm^{-2} at an approximately 5×10^{-5} *M* concentration in nitromethane. This may be compared with the conductivities of $(C_2H_5)_4N^+Br^-$ and $Co(3\text{-}CH_3PyO)_6(ClO_4)_2$ being 127 and 206 mhos mol^{-1} cm^{-2} at similar temperature and concentration, in nitromethane. A value of about 200 mhos mol^{-1}

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[1] (a) Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester, England; (b) Department of Chemistry, York University, Downsview, Ontario, Canada.

[2] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Metal Compounds," Pergamon Press, Inc., New York, N. Y., 1960; C. K. Jørgensen, *Advan. Chem. Phys.*, **5**, 33 (1963).

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Table I

Experimental and Analytical Data

Complex[a]	Solvent[b]	Color	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found	% metal Calcd	% metal Found
$Co(PyO)_6I_2$	A	Pink	40.7	41.0	5.4	3.7	9.5	9.7		
$Co(3\text{-}CH_3PyO)_6(ClO_4)_2$	A	Pink	47.4	47.1	4.6	4.8	9.25	9.3	6.7	6.6
$Co(2\text{-}CH_3PyO)_5(ClO_4)_2$	A	Violet	45.0	45.5	4.4	5.0	8.75	8.9	7.35	7.3
$Cu(2\text{-}CH_3PyO)_4(ClO_4)_2$	B	Blue	40.8	40.8	4.4	4.3	8.0	8.25	9.1	9.2
$Cu(2,6\text{-}(CH_3)_2PyO)_4(ClO_4)_2$	B	Blue	44.4	44.8	4.8	4.9	7.4	7.4	8.4	8.4
$Cu(2,4,6\text{-}(CH_3)_3PyO)_4(ClO_4)_2$	B	Green	47.5	47.2	5.4	5.7	6.9	6.6	7.8	7.7
$Mn(4\text{-}NO_2PyO)_6(ClO_4)_2$	A	Bright red	32.6	32.6	2.2	2.4	15.3	15.1	5.0	5.1
$Mn(4\text{-}CH_3PyO)_6(ClO_4)_2$	A	Yellow	47.5	47.6	4.4	4.7	9.25	9.5	5.8	6.1
$Fe(4\text{-}NO_2PyO)_6(ClO_4)_2$	A	Black	32.8	32.6	2.7	2.7	15.9	15.8		

[a] Abbreviations: 2-CH_3PyO, 2-picoline N-oxide; 3-CH_3PyO, 3-picoline N-oxide; 4-CH_3PyO, 4-picoline N-oxide; 4-CH_3OPyO, 4-methoxypyridine N-oxide; 4-NO_2PyO, 4-nitropyridine N-oxide; 2,6-$(CH_3)_2$PyO, 2,6-lutidine N-oxide; 2,4,6-$(CH_3)_3$PyO, 2,4,6-collidine N-oxide. [b] Solvent used in preparation: A, ethanol; B, methanol.

cm^{-2} at infinite dilution in nitromethane is fully consistent with the presence of a 1:1 electrolyte.[10]

Results and Discussion

Six-Coordinate Complexes. Electronic Spectra.—The complexes $(PyO)_6M^{n+}$ would have O_h symmetry if only the metal to oxygen bonds are considered. However the electronic spectra of the chromium(III), nickel(II), and cobalt(II) complexes provide definitive evidence of symmetry lower than O_h. The first absorption band in complexes of Cr(III) and Ni(II) corresponding to the transition $T_{2g} \leftarrow A_{2g}$ is split into at least two components (Table II) revealing that the degeneracy of the T_{2g} state has been lifted, almost certainly by a lower symmetry component of the ligand field. The splitting, which had been noted previously[11] but not discussed, is resolved into two distinct peaks at −196°. The second absorption band, $T_{1g}(F) \leftarrow A_{2g}$ in O_h, is also split (Figure 1).

Table II

Electronic Spectroscopic Data[a] (24,000–4000 cm^{-1})

Complex	Temp, °C	Electronic spectra, cm^{-1}
$Cr(PyO)_6(ClO_4)_3$[b]		15,150, (17,700), (21,300), 23,260
	−196	15,400, 17,650, 22,200, 23,250
$Co(PyO)_6(ClO_4)_2$[b]		(7250), 8300, 17,700, (18,590), (20,410)
	−196	7280, 8333, 17,950, 18,870, 20,000
$Co(3\text{-}CH_3PyO)_6(ClO_4)_2$		(7250), 8600, 18,600, (21,300)
$Ni(4\text{-}CH_3PyO)_6(ClO_4)_2$[b]		(7400), 8475, (12,500), 14,200
	−196	(7280), 8060, 9000, (12,350), 13,800, 14,500
$Cu(PyO)_6(ClO_4)_2$[b]		(9615), 12,250
	−196	10,150, 12,900
$Cu(PyO)_4(ClO_4)_2$[b]		14,800 b[d]
$Cu(2\text{-}CH_3PyO)_4(ClO_4)_2$		14,900 b
$Cu(2,6\text{-}(CH_3)_2PyO)_4(ClO_4)_2$		15,550 b
$Cu(2,4,6\text{-}(CH_3)_3PyO)_4(ClO_4)_2$		15,700 b
$Fe(4\text{-}NO_2PyO)_6(ClO_4)_2$		7700, 9100
$Co(2\text{-}CH_3PyO)_5(ClO_4)_2$[c]		(11,430), 12,660 (19), 18,400 (56), (20,000)
	−196	(11,480), 12,790, (15,380 w), 18,590, (26,670)

[a] Room-temperature data were recorded as diffuse reflectance spectra; low-temperature data were obtained by transmittance through Nujol mulls. [b] Agreement with previously reported[11] room-temperature data is good. Shoulders in parentheses. [c] In CH_3NO_2. [d] b = broad.

We have already observed that monodentate polyatomic ligands, which cannot have cylinderical symmetry about the bonding axis, nevertheless yield six-coordinate complexes whose ligand field (d–d) spectra are consistent with octahedral symmetry. The splitting observed in these examples must arise through the presence of the nonlinear N–O–M bond sequence. This nonlinearity is a necessary requirement of the electronic distribution about the oxygen atom and has been confirmed by a recent X-ray structure of a copper pyridine N-oxide complex[12] and by an nmr study of bis(pyridine-N-oxide)bis(2,4-pentanedionato)cobalt(II).[13] The true (local or effective) symmetry influencing the metal ion must be lower than O_h, and the degeneracy of the orbital triplet states will be partially or wholly lifted. Moreover there is the implication that the metal d-orbital wave functions must combine, at least to some small extent, with wave functions involving the ligand N–O bond. The alternative possibility that the bonding is entirely ionic and the splitting is due to an asymmetric charge distribution about the metal ion seems most unlikely.

The actual symmetry of the molecule is uncertain. The most symmetrical orientation of the ligand groups will give rise to D_{3d} symmetry. In such a molecule there are two sets of three M–O–N bonds, one set pointing up the C_3 (S_6) axis and one set pointing down this axis. The symmetry planes containing each M–O–N bond bisect the angle O–M–O generated by the two other M–O–N bonds in the set. An alternative structure has S_6 symmetry. The M–O–N bonds have rotated so that the C_3 and S_6 axes are retained but the planes of symmetry are lost. Recently an infrared study of the dimethyl sulfoxide complexes $M(DMSO)_6^{n+}$ has been reported.[14] The nonlinear S–O–M bonds introduce the same structural problem as described here. The authors concluded that the dimethyl sulfoxide complexes have S_6 rather than D_{3d} symmetry.

In S_6 symmetry the (octahedral) orbital triplets T_{1g} and T_{2g} will both transform as $A_g + E_g$. Thus the observed splitting of the lower excited states in the spectra of the chromium(III) and nickel(II) pyridine N-oxide

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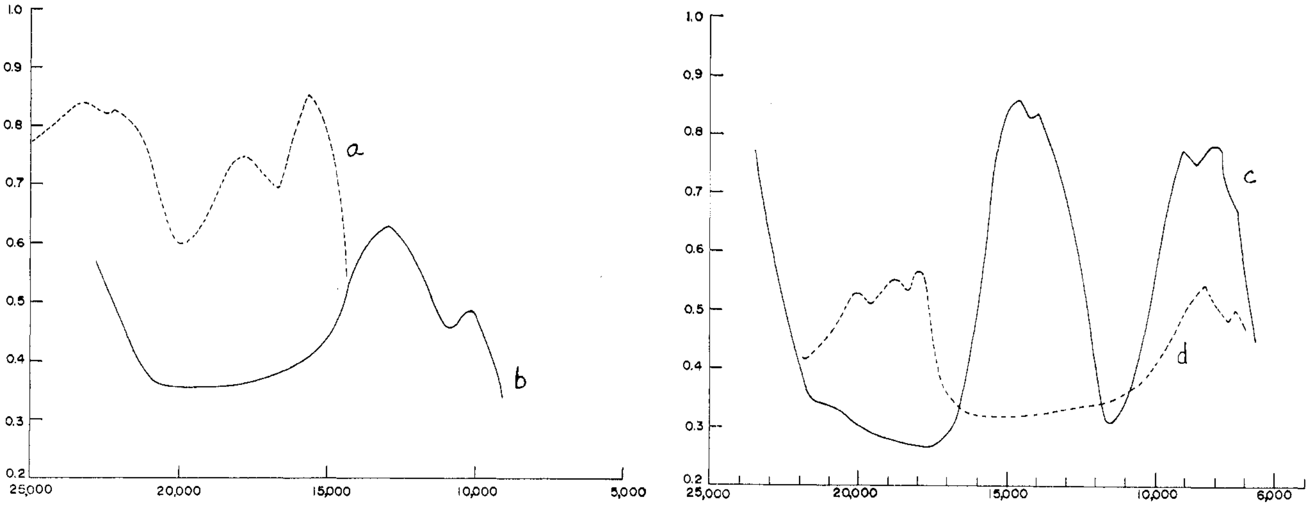

Figure 1.—Mull transmittance spectra of (a) $Cr(PyO)_6(ClO_4)_3$, (b) $Cu(PyO)_6(ClO_4)_2$, (c) $Ni(4\text{-}CH_3PyO)_6(ClO_4)_2$, and (d) $Co(PyO)_6(ClO_4)_2$ at −196°.

derivatives is consistent with S_6 symmetry (as indeed it would be with D_{3d}). The first band in the spectra of the cobalt complexes (${}^4T_{2g} \leftarrow {}^4T_{1g}$ in O_h) is definitely composite with a shoulder at low energy, at room temperature. At −196°, this shoulder is resolved into a second peak (Figure 2). This transition always appears as a single band in regular octahedral molecules. Evidence for the lower symmetry is also reflected in the electronic spectra of the six-coordinate complexes of iron(II) and copper(II). The iron complex exhibits a pronounced splitting of the ${}^5E_g \leftarrow {}^5T_{2g}$ (in O_h) transition (Table II). This is consistent with the lower symmetry although regular octahedral iron complexes also exhibit a split band as a consequence of a Jahn–Teller distortion of the excited ${}^5E_g$ level.[15]

The six-coordinate copper complex $Cu(PyO)_6{}^{2+}\cdot 2ClO_4{}^-$ has a peak at 12,350 cm^{-1} with a pronounced shoulder at 9615 cm^{-1}. At low temperature (−196°) this spectrum is resolved into two distinct peaks at 12,900 and 10,150 cm^{-1}. In S_6 symmetry the d orbitals transform as $A_g + 2E_g$; thus two transitions would be expected for a d^9 system. The possibility that a tetragonal distortion is involved cannot however be excluded.

The electronic spectroscopic evidence leaves no doubt that the metal ion is experiencing a ligand field of symmetry lower than O_h. Alternative explanations of the observed splittings may generally be eliminated. The separation between the components of the multiple bands is too large to be due to vibrational phenomena. Certainly in the case of chromium and cobalt it is too large for the bands to be attributed to spin–orbit components of the same electronic transition. Although the spin–orbit coupling coefficient for copper(II) is fairly large, it is unlikely that we would see two spin–orbit components of the same electronic band separated by nearly 3000 cm^{-1}.

Only in the case of nickel(II) where the spin–orbit coupling coefficient is moderately large and the splitting moderately small, the possibility of attributing the components to spin–orbit structure cannot be entirely excluded.

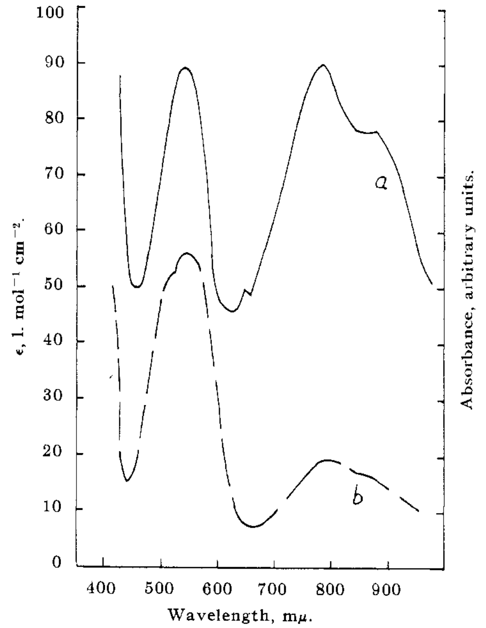

Figure 2.—The electronic spectra of $Co(2\text{-}CH_3PyO)_5(ClO_4)_2$: (a) mull transmittance spectrum at −196°; (b) olution spectrum in CH_3NO_2.

The possibility that one of the components is, in each case, a spin-forbidden band which has gained intensity by mixing with the allowed band can be eliminated for all cases except for the transition to the ${}^3T_{1g}(F)$ (in O_h) level in the nickel(II) spectrum. The transition to the ${}^1E_g$ (in O_h) level may lie close to this spin-allowed band and is believed to gain intensity thereby.[16] However, it is likely that the shoulder near 12,350 cm^{-1} (in the low-temperature spectrum) can be assigned to this forbidden transition.

Infrared Data.—The distortion is also reflected by the infrared data. If the effective symmetry of the molecule was O_h, only one nitrogen–oxygen stretching frequency would be observed in the infrared region near

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1200 cm^{-1}. The six-coordinate pyridine N-oxide complexes of copper(II), cobalt(II), iron(II), and chromium(III) all show multiple bands near 1200 cm^{-1} which we attribute to ν(N–O) frequencies (Table III).

TABLE III[a]

INFRARED SPECTRA SHOWING ν(N–O) FREQUENCIES (CM^{-1})

M^{n+}	PyO	4-CH_3PyO	4-NO_2PyO
	M(R–PyO)$_6^{n+}\cdot ClO_4^-$		
Cr^{3+}	1200		
	(1215)		
Mn^{2+}	1220	1208	1222
		(1225)	1235
Fe^{2+}	(1195)		1220 b
	1215		
Fe^{3+}	1210 b	1206 b	1200 b
Co^{2+}	(1200)	1205	1220 b
	1215	1227	
	(1220)		
Ni^{2+}	1210 b	1205	1225 b
		1212	
		1222	
Cu^{2+}	1210		
	1230		

Cu(R–PyO)$_4^{2+}\cdot 2ClO_4^-$

PyO	4-CH_3PyO	2-CH_3PyO	4-NO_2PyO	2,6-$(CH_3)_2$PyO	2,4,6-$(CH_3)_3$PyO
1202	1210	1205	1208	1197	1205
1206			1228	1220	

[a] For abbreviations see footnote *a*, Table I. Frequencies listed in parentheses are shoulders. b = broad.

The manganese complexes of 4-picoline N-oxide and 4-nitropyridine N-oxide also show two bands while most of the other complexes studied have a single broad band which is very evidently composite in nature. Splitting of the ν(N–O) band has been observed before[17] as indeed has splitting of the N–O bending frequency near 840 cm^{-1}. However the possible significance of these splittings was not discussed.

Some far-infrared studies of pyridine N-oxide complexes have been undertaken.[11,18,19] Two infrared-active metal–oxygen stretching frequencies have been observed in the pyridine N-oxide complexes of chromium(III),[11,19] iron(III),[19] cobalt(II),[11] nickel(II),[11] and aluminum(III)[19] and for most of the corresponding complexes with 4-methyl, 4-chloro, or 4-nitro substituents.[11] If the molecule did have regular octahedral symmetry, only one such band would be expected. Of course the appearance of multiple N–O and M–O bands could arise through various solid-state phenomena decreasing the site symmetry of the molecular species. However, they appear so often that there can be little doubt that they arise as a consequence of the lower symmetry of the molecule. It is unfortunate that most of the complexes dissociate in solution so that solution data cannot be relied upon.[18] A molecule of S_6 symmetry would be expected to give rise to two active ν(N–O) bands and two active ν(M–O) bands of classification $A_u + E_u$.

Magnetic Data.—The magnetic moments of the cobalt(II) derivatives provide supporting evidence for the lower symmetry component of the ligand field. A cobalt(II) atom surrounded by a regular octahedron of oxygen atoms should yield a magnetic moment of the order of 5.2 BM at room temperature as a consequence of the $^4T_{1g}$ ground state providing both a spin and an orbital contribution to the magnetic susceptibility.[20] Pyridine N-oxide cobalt complexes have moments of 4.7–4.8 BM (Table IV). While these moments lie in the so-called "tetrahedral" region for cobalt(II),[20] such low moments are not necessarily indicative of tetrahedral symmetry but are indicative of a loss in orbital degeneracy of the ground state caused by any lower symmetry component.[21]

TABLE IV

MAGNETIC MOMENTS OF M(R–PyO)$_6^{2+}$ COMPLEXES AT 25°

Complex	μ, BM	Ref
Co(PyO)$_6$(ClO$_4$)$_2$	4.84, 4.69	*b* *c*
Co(PyO)$_6$(NO$_3$)$_2$	4.77	*d*
Co(PyO)$_6$I$_2$	4.74 (10.24)[a]	This work
Co(4-CH$_3$PyO)$_6$(ClO$_4$)$_2$	4.71	*b*
Co(3-CH$_3$PyO)$_6$(ClO$_4$)$_2$	4.72 (9.83)[a]	This work
Co(4-CH$_3$OPyO)$_6$(ClO$_4$)$_2$	4.79	*b*
Co(4-ClPyO)$_6$(ClO$_4$)$_2$	4.82	*b*
Co(4-NO$_2$PyO)$_6$(ClO$_4$)$_2$	4.79	*b*
Cu(2,6-(CH$_3$)$_2$PyO)$_4$(ClO$_4$)$_2$	1.92 (1.49)[a]	This work
Cu(2-CH$_3$PyO)$_4$(ClO$_4$)$_2$	1.91 (1.70)[a]	This work
Cu(2,4,6-(CH$_3$)$_3$PyO)$_4$(ClO$_4$)$_2$	1.90 (1.34)[a]	This work
Mn(4-CH$_3$PyO)$_6$(ClO$_4$)$_2$	5.93 (15.85)[a]	This work
Mn(4-NO$_2$PyO)$_6$(ClO$_4$)$_2$	5.92 (13.15)[a]	This work
Fe(4-NO$_2$PyO)$_6$(ClO$_4$)$_2$	5.40 (10.87)[a]	This work

[a] The gram-susceptibility (cgs units) × 10^6 is reported in parentheses for complexes newly described in this work. [b] See ref 11. [c] J. V. Quagliano, J. Fugita, G. Franz, D. J. Phillips, J. A. Walmsley, and S. Y. Tyree, *J. Am. Chem. Soc.*, **83**, 3770 (1961). [d] R. L. Carlin and M. J. Baker, *J. Chem. Soc.*, 5008 (1964).

None of the other ions under consideration has orbitally degenerate ground states (in O_h) so that the effect of the lower symmetry is less obvious. However, the magnetic moments of 3.3 BM, or slightly above, reported[11] for the Ni(R–PyO)$_6^{2+}$ complexes offer an indication of the presence of distortion from an octahedral environment. These moments are high for octahedral nickel[20] and are similar to those reported for tetragonal nickel(II) complexes.[22] Indeed the structurally analogous sulfoxide nickel complexes behave in a similar manner. Hexakis-ligand complexes of nickel(II) with dialkyl sulfoxides[23,24] and with methyl phenyl and diphenyl sulfoxides[24] also exhibit magnetic moments near 3.4 BM, being unusually high for regular octahedral nickel(II) complexes. Some hexakis(sulfinamide)nickel(II) cations also have moments in this region.[25] The high moments are

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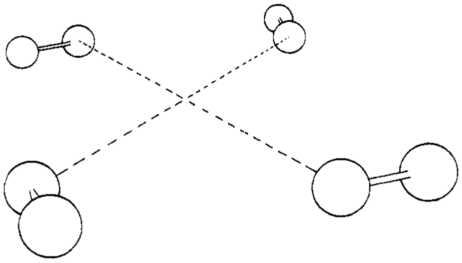
definitely a reflection of some kind of distortion. Detailed temperature range studies of the magnetic susceptibilities of complexes of this nature are being undertaken in order to understand their behavior. Viewed individually these observations provide little information. *In toto*, however, the data presented here provide definitive proof of an interaction between the metal d orbitals and the ligand orbitals such that the effective symmetry of the species is lower than O_h.

Other Complexes. $Cu(R\text{-}PyO)_4(ClO_4)_2$ Derivatives.—There is no evidence in the infrared spectra of these complexes of perchlorate coordination.[26] If only the copper–oxygen bonds are considered, the molecules should have D_{4h} symmetry. Interaction of the copper d-orbital wave functions with the ligand wave functions *via* the nonlinear M–O–N bonds will lead to a lowering of the effective symmetry.



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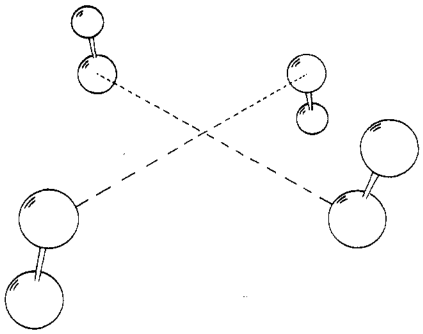

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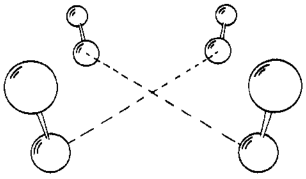

III

There are a number of possible orientations of the pyridine N-oxide groups about the copper atom which will minimize steric interaction between adjacent ligand molecules. The most symmetric structures (I–III) have C_{4h}, D_{2d}, and C_{4v} symmetry, respectively. These structures are expected to exhibit $1(E_u)$, $2(E + B_2)$, and $2(A_1 + E)$ infrared-active N–O stretching frequencies, respectively. A molecule whose effective symmetry was D_{4h} would exhibit one infrared-active (E_u) vibration. In fact, one or two bands are observed (Table III) dependent upon the amine oxide concerned. These bands are narrower and less complex than the bands observed in the $M(R\text{-}PyO)_6{}^{n+}$ series, supporting the view that the multiple nature of the band is due to coupling of the vibrations of the various ligand molecules. Two Cu–O stretching vibrations are reported[11] for the pyridine N-oxide complex but only one is reported for the 4-methyl and 4-nitro derivatives. Unfortunately the infrared data do not permit an unequivocal determination of the structure. However the possibility that the complexes have D_{4h} symmetry can be positively excluded in most of the complexes studied. There is the possibility that the $CuL_4{}^{2+}$ complexes actually contain a polymeric six-coordinate tetragonal structure in which two of the ligands are terminal and two are bridging. The lower of the two infrared ν(N–O) bands could then be assigned to the bridging amine oxide ligands. However such a structure can be excluded since the main d–d band would lie at the same frequency as, or lower than, the main d–d band observed in the $CuL_6{}^{2+}$ complex. In fact, the main d–d band in $Cu(PyO)_4{}^{2+}$ lies some 2500 cm^{-1} higher in energy than the corresponding band in the $Cu(PyO)_6{}^{2+}$ species (Table III).

Finally we report the existence of a five-coordinate complex of cobalt, $Co(2\text{-}CH_3PyO)_5{}^{2+}(ClO_4{}^-)_2$. Its formulation is based on stochiometry, vibrational and electronic spectra, magnetism, and conductivity. The infrared spectrum of this complex reveals that both the perchlorate groups are ionic, there being no splitting[27] of the main $ClO_4{}^-$ absorption band near 1080 cm^{-1}. This is supported by conductivity studies in nitromethane in which the complex is a 1:2 electrolyte (see Experimental Section). Electronic spectroscopy (Figure 2) indicates that the species in the solid state and in nitromethane solution are identical. The infrared spectra show two ν(N–O) bands at 1196 and 1208 cm^{-1} and a doublet at 775 and 787 cm^{-1} assigned to the C–H out-of-plane bending mode.[19] This band is generally a singlet in other 2-picoline N-oxide complexes, there being no coupling between C–H groups of adjacent molecules. The observation of a doublet at 694 and 700 cm^{-1}, which probably corresponds to a singlet observed at 669 cm^{-1} in the free ligand and at 700 cm^{-1} in the complex $Cu(2\text{-}CH_3PyO)_4(ClO_4)_2$, further suggests the presence of two chemically inequivalent sets of ligands.

The electronic spectrum of this complex (Table II, Figure 2) is very closely similar to the spectra of the five-coordinate cobalt(II) complexes reported by Ciampolini[28] and is quite distinguishable from the spectra of either tetrahedral or octahedral cobalt(II).

The complexes described by Ciampolini are known[29] to have a trigonal-bipyramidal configuration. The complex $Co(2\text{-}CH_3PyO)_5(ClO_4)_2$ is also believed to be trigonal bipyramidal. This conclusion is based on the close similarity of its electronic spectrum to the spectra of Ciampolini's derivatives and the poorer relationship with the five-coordinate square-pyramidal

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cobalt(II) complexes described by Lions, *et al.*[30] The magnetic moment of 4.58 BM (20°) is also indicative of trigonal-bipyramidal rather than square-pyramidal symmetry.[30]

This complex is the first example of a five-coordinate derivative of cobalt(II) in which all of the ligands are identical. It is also the first complex to have a trigonal-bipyramidal CoO_5 chromophore.

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Complexes of Aromatic Amine Oxides. 4-Substituted Quinoline 1-Oxide Complexes of Cobalt(II) and Nickel(II) Perchlorates

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The coordinating properties of a series of 4-substituted quinoline 1-oxides toward nickel(II) and cobalt(II) have been investigated. The substituents studied were CH_3O, CH_3, H, Cl, and NO_2. The compounds were assigned octahedral structures with the general formula $M(4\text{-}Z\text{-}C_9H_6NO)_6(ClO_4)_2$ based upon analytical data and the magnetic moments 3.37–3.61 and 4.91–5.25 BM for nickel(II) and cobalt(II), respectively. The electronic spectra were studied and ligand field parameters were determined. The *Dq* values ranged from 790 to 874 cm^{-1} for the nickel(II) complexes and from 955 to 979 cm^{-1} for the cobalt(II) complexes. For comparison purposes, isoquinoline 2-oxide complexes were also studied. Considerable evidence for dπ–pπ back-bonding (synergic bonding) is found and discussed.

Introduction

Many studies have been made with complexes of quinoline and substituted pyridines in order to ascertain what factors determine both the stereochemistry and the physical properties of the resultant complexes.[3–7] From these studies it was concluded that the degree of π overlap between metal and heterocyclic amine was greater for quinoline and isoquinoline than for the pyridines.[3] Further, it has also recently been found that, for $Ni(AA)_2 \cdot L$ and $Co(AA)_2 \cdot L$ complexes[8] (L is pyridine 1-oxide, quinoline 1-oxide, or isoquinoline 2-oxide and AA is 2,4-pentanedionate), more electron spin density is delocalized onto the π system of quinoline 1-oxide and isoquinoline 2-oxide than onto pyridine 1-oxide. Hence, as with the quinolines, the quinoline 1-oxides are better acceptors of π-electron density than the corresponding pyridine 1-oxides.

Not only is there a difference in the π-bonding ability of the pyridine and quinoline 1-oxides, but there also should be a difference in the σ-bonding ability owing to steric interactions. The quinoline 1-oxide series should bear the same steric relation to pyridine 1-oxide that quinoline does to pyridine. Where tetrakispyridine complexes were found,[4,6] only bisquinoline complexes could be isolated.[5] Therefore, if the hexakisquinoline 1-oxide complexes are isolated, the metal–oxygen bonding should be weakened relative to that of the pyridine 1-oxides by a steric interaction, not only between the metal and the bulkier ligand but also by a ligand–ligand repulsion. This weaker bond should manifest itself as a lowering in the *Dq* value for the quinoline 1-oxides relative to that of the corresponding pyridine 1-oxides.

The availability of many 4-substituted pyridine 1-oxides[9] has given rise to several attempts at correlating substituent constants for the various groups with observable properties of either the ligands themselves or their complexes.[10] Quinoline 1-oxide has the same type of resonance forms as does pyridine 1-oxide and thus similar correlations should be possible for this system.

The ease of formation of hexacoordinated complexes of pyridine 1-oxides[11] coupled with our interest in linear free energy relations[10] of aromatic amine oxides prompted us to investigate the ligational properties of a series of 4-substituted quinoline 1-oxides. The ligands $4\text{-}Z\text{-}C_9H_6NO$ (Z = CH_3O, CH_3, H, Cl, and NO_2) and isoquinoline 2-oxide were selected for their constant steric effects and varying basicity. The hexakis complexes of quinoline 1-oxide with nickel(II) and cobalt(II) have previously been reported[12] but have not been extensively characterized.

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