nickel in the EDTA complexes is to increase the k_2 value by a factor of 260. The effect of using EDTA in place of CyDTA with the cobalt complexes is to increase the k_2 value by a factor of 1.2×10^5. On the basis of these ratios, the k_2 value for NiCyCN^{3-} can be predicted to be 3.5×10^{-5} M^{-2} sec^{-1} if direct proportionality is valid. A very small value of k_2 is in agreement with the observation[17] that over a period of 2 months no displacement of CyDTA from nickel occurred using 0.01 M cyanide ion and, in fact, k_2 must be less than 3×10^{-5} M^{-2} sec^{-1}.

Ligand replacement reactions for EDTA complexes compared to CyDTA complexes are much faster in general. The rate constants of the polyamine reactions of CuEDTA^{2-} were found[20] to be about 5×10^4 greater than for the corresponding reaction with CuCyDTA.$^{2-}$

The diminished reactivity of the CyDTA complexes

(20) J. D. Carr, R. A. Libby, and D. W. Margerum, *Inorg. Chem.*, **6**, 1083 (1967).

is attributed in part to steric effects due to interference of the cyclohexane ring and in part to the greater initial stability of the complexes. In the case of cobalt(II) log $K_1 = 19.6$ for CyDTA[21] compared to log $K_1 = 16.3$ for EDTA[22] at 20°. The greater thermodynamic and kinetic stability is due to the more basic nitrogen atoms and the cagelike structure of the CyDTA complex.

In each of these polyaminocarboxylate systems, an over-all third-order cyanide dependence was found in contrast to the fourth-order dependence found for the formation of tetracyanonickelate(II) from the aquonickel ion[23] and from triethylenetetraminenickel(II).[24]

(21) G. Anderegg, *Helv. Chim. Acta*, **46**, 1833 (1963).
(22) G. Schwarzenbach, R. Gut, and G. Anderegg, *ibid.*, **37**, 937 (1954).
(23) G. B. Kolski and D. W. Margerum, *Inorg. Chem.*, **7**, 2239 (1968).
(24) G. B. Kolski and D. W. Margerum, *ibid.*, **8**, 1125 (1969).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WOOLWICH POLYTECHNIC, NORTHERN POLYTECHNIC, AND IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON, ENGLAND

Metal Complexes of Azopyridines. II. Complexes of Bivalent Cobalt, Nickel, and Copper with 3,3'- and 4,4'-Azopyridines

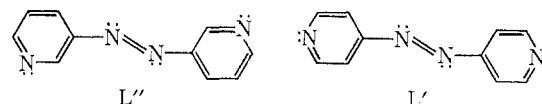By P. J. BEADLE,[1a] M. GOLDSTEIN,[1b] D. M. L. GOODGAME,[1c] AND R. GRZESKOWIAK[1a]

4,4'-Azopyridine (L') and 3,3'-azopyridine (L'') have been used to prepare complexes of the type MX$_2$·L (L = L' or L''; M = Co, X = Cl, Br, I; M = Ni, Cu, X = Cl, Br), of the type MSO$_4$·nH$_2$O·L' (M = Cu, n = 4; M = Co, n = 2, 6), and CuSO$_4$·L'. Structures are suggested on the basis of diffuse reflectance spectra, infrared spectra (450–80 cm^{-1}), and magnetic properties. Except for CoBr$_2$·L', CoI$_2$·L', and CoI$_2$L'' which are pseudotetrahedral, the halide complexes have distorted octahedral structures involving halogen and azopyridine bridges. The oxyanion complexes appear to have the metal atom in a tetragonal environment.

Introduction

The base 2,2'-azopyridine and its 3,3' and 4,4' isomers are stable in solution in their *trans* configurations.[2] Models show that of the three isomers only 2,2'-azopyridine will chelate without undue strain. Preliminary experimental work showed that 2,2'-azopyridine could form more than one type of complex when different mole ratios of reactants were used, but that the other two organic bases always gave 1:1 complexes. A brief report on the preparation of some of the 2,2'- and 4,4'-azopyridines has been made previously.[3]

The work has now been extended and a clearer picture of the coordination behavior of these ligands has been obtained. We report here the results for the complexes of 3,3'-azopyridine (=L'') and 4,4'-azopyridine (=L')

(1) (a) Woolwich Polytechnic; (b) Northern Polytechnic; (c) Imperial College.
(2) D. J. Bullock, C. W. N. Cumper, and A. I. Vogel, *J. Chem. Soc.*, 5316 (1965).
(3) P. J. Beadle and R. Grzeskowiak, *Inorg. Nucl. Chem. Letters*, **3**, 245 (1967).

L''   L'

Experimental Section

Preparation of Compounds.—The 3,3'- and 4,4'-azopyridines were prepared from 3- and 4-aminopyridine, respectively, by a modified method of Kirpal and Reiter and the products[4] were purified by partition chromatography.[5]

Recrystallization of 3,3'-azopyridine from petroleum ether (bp 60–80°) gave orange needles, mp 142°, and the 4,4' isomer formed yellow-brown needles, mp 109°.

The complexes were prepared by mixing ethanolic solutions of metal salts and ligands. The precipitates were isolated by centrifugation, washed with ethanol and then with dry ether, and dried *in vacuo* at room temperature over silica gel. Attempts to obtain complexes other than the 1:1 type failed. Analytical results are given in Table I.

Physical Measurements.—Magnetic susceptibility measurements at room temperature were made by the Gouy method using HgCo(NCS)$_4$ as the calibrant. The diamagnetic correction for

(4) A. Kirpal and E. Reiter, *Chem. Ber.*, **60**, 664 (1927).
(5) N. Campbell, A. W. Henderson, and D. Taylor, *J. Chem. Soc.*, 1281 (1953).

TABLE I

COLORS AND ANALYTICAL DATA FOR SOME 3,3'-AZOPYRIDINE
(=L'') AND 4,4'-AZOPYRIDINE (=L') COMPLEXES

| | | Analytical data | | | | | |
| | | %Calcd | | | %Found | | |
Compound	Color	M	X	C	M	X	C
CuCl₂·L''	Green	19.9	22.2	37.7	19.7	22.3	37.7
CuBr₂·L''	Green	15.6	39.2	29.5	15.5	39.0	30.0
CoCl₂·L''	Brown	18.8	22.6	38.2	19.0	22.7	38.4
CoBr₂·L''	Brown	14.6	39.7	29.8	14.7	39.6	30.5
CoI₂·L''	Green	11.9	51.1	24.2	11.6	50.4	24.8
NiCl₂·L''	Yellow	18.7	22.6	38.2	18.5	22.4	38.4
NiBr₂·L''	Yellow	14.6	39.7	29.8	14.6	39.7	29.8
CuCl₂·L'	Gray-green	19.9	22.2	37.7	19.6	22.0	37.6
CuBr₂·L'	Yellow-green	15.6	39.2	29.5	15.6	39.0	30.0
CuSO₄·L'	Brown	18.5		34.9	18.5		34.4
CuSO₄·4H₂O·L'	Green	15.3		28.9	15.3		29.1
CoCl₂·L'	Brown	18.8	22.6	38.2	18.9	22.3	38.8
CoBr₂·L'	Turquoise	14.6	39.7	29.8	14.2	39.5	30.3
CoI₂·L'	Green	11.9	51.1	24.2	12.0	50.9	25.0
CoSO₄·2H₂O·L'	Orange	15.0		32.0	15.0		31.7
CoSO₄·6H₂O·L'	Red-orange	13.2		26.9	13.3		27.2
NiCl₂·L'	Brown	18.7	22.6	38.2	19.1	22.4	37.7
NiBr₂·L'	Brown	14.6	39.7	29.8	14.7	39.3	29.7

3,3'-azopyridine (-90×10^{-6} cgsu) and 4,4'-azopyridine (-60×10^{-6} cgsu) were obtained experimentally[6] and those of metal salts were calculated from Pascal's constants.

Infrared spectra in the region 4000–400 cm^{-1} were recorded with a Perkin-Elmer 337 spectrometer using Nujol mulls on potassium bromide plates or by preparing potassium bromide disks. The far-infrared (450–80 cm^{-1}) spectra were obtained from pressed disks in polythene using a Research and Industrial Instruments Co. Ltd. FS-520 Michelson interferometer, as described previously.[7]

Electronic spectra were obtained using a Beckman DK2 spectrometer. Measurements were restricted to the solid state by the poor solubility of the complexes in solvents other than those which caused decomposition.

Results and Discussion

Electronic Spectra and Magnetic Moments.—Identification of the d–d bands (Table II) was restricted to the region below *ca.* 20 kK by the more intense parity-allowed bands at higher energy.

The spectra show that the compounds MX₂·L'' (M = Co, Ni; X = Cl, Br), CoCl₂·L', and NiX₂·L' (X = Cl, Br) have *trans*-octahedral configurations as in Figure 1. The low-symmetry components of the ligand fields are sufficient to split the T₂g (in Oₕ) levels (such that $^3E_g > {}^3B_{2g}$ for Ni and $^4B_{2g} > {}^4E_g$ for Co, both in D₄ₕ). However, for the nickel complexes the band at 14 kK (due to $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ in Oₕ) showed no detectable splitting (we assign the very weak shoulder on the low-energy side to a spin-forbidden transition). The *Dt* values for the cobalt and nickel complexes lie in the range 200–300 cm^{-1} (Table II, *cf.* 275 cm^{-1} for Ni(py)₂Cl₂ and 305 cm^{-1} for the polymeric, octahedral form of Co(py)₂Cl₂).

The spectra of CoI₂·L'' and CoX₂·L' (X = Br, I) are typical of cobalt(II) in a distorted tetrahedral ligand field. Since the azopyridines cannot chelate, the pseudotetrahedral CoN₂X₂ units are presumably linked by azopyridine bridges. The $^4T_1(F)$ and $^4T_1(P)$ levels are both split, but only for CoI₂·L'' are the three expected components of $^4T_1(F)$ resolved, and two of them are quite close in energy (6.58 and 5.81 kK). For the

TABLE II

DIFFUSE REFLECTANCE SPECTRA AND ROOM-TEMPERATURE
MAGNETIC MOMENTS OF SOME COMPLEXES WITH
3,3'-AZOPYRIDINE (=L'') AND 4,4'-AZOPYRIDINE (=L')

| Compound	μ, BM	Dt, cm^{-1} [a]	νmax, kK
L''	...	...	46.5 sh, 44.0 sh, 35.0, 27.0, 22.4
CuCl₂·L''	1.86	...	46.0 sh, 38.0 sh, 30.0, 20.5 sh, 13.9
CuBr₂·L''	1.81	...	46.0 sh, 38.0 sh, 30.0, 23.0 sh, 13.51
CoCl₂·L''	5.20	250	45.0 sh, 38.0 sh, 34.5, 29.7, 26.3 sh, 22.0 sh, 16.81, 14.8 sh, 8.51 sh, 6.33
CoBr₂·L''	5.11	270	45.0, 42.7, 38.0 sh, 30.0, 21.5 sh, 18.3 sh, ~17.2 sh, 15.82, 8.26, 5.90
CoI₂·L''	4.46	...	45.0, 34.5, 23.5 sh, 22.4 sh, 19.25 sh, 15.7, 15.04, 14.39, 9.01, 6.58, 5.81 sh
NiCl₂·L''	3.31	215	43.0, 37.5 sh, 32.0, 25.0 sh, 21.5 sh, 14.29, 12.42 sh, 8.68, 6.73
NiBr₂·L''	3.27	230	43.0 sh, 38.0 sh, 30.0, 21.5 sh, 13.8, 8.30, 6.30
L'	...	...	45.0 sh, 39.5 sh, 30.0, 27.0, 21.7
CuCl₂·L'	1.81	...	30.0 sh, 37.0, 29.0 sh, 23.5 sh, 13.99
CuBr₂·L'	1.81	...	38.5 sh, 37.0 sh, 30.0 sh, 23.4, 13.99
CuSO₄·L'	1.89	...	39.0, 37.25, 30.0 sh, 21.05, 12.12
CuSO₄·H₂O·L'	1.86	...	38.5, 35.4, 29.5, 21.0, 13.79
CoCl₂·L'	5.32	300	44.5 sh, 38.0 sh, 26.0 sh, ~19.24 sh, 17.8 sh, 16.67 sh, 14.5 sh, 8.70, 6.06
CoBr₂·L'	4.73	...	44.0 sh, 37.0, 31.5, 26.5, 16.67, 15.2, 9.09, 6.06
CoI₂·L'	4.57	...	44.5, 36.0, 30.5, 23.5 sh, 15.87, 15.06, 14.15, 8.62, 5.87
CoSO₄·2H₂O·L'	5.14	...	44.5 sh, 36.5, 21.05, 8.26
CoSO₄·6H₂O·L'	5.07	...	44.0 sh, 37.5, 30.0, 21.05, 8.62
NiCl₂·L'	3.30	260	44.0 sh, 35.5, 29.0, 21.5 sh, 14.18, 12.4 sh, 8.66, ~6.39 b
NiBr₂·L'	3.30	235	44.0 sh, 35.5, 30.0, 22.0 sh, 13.6, 11.5 sh, 8.20, 6.15

[a] To the nearest 5 cm^{-1}.
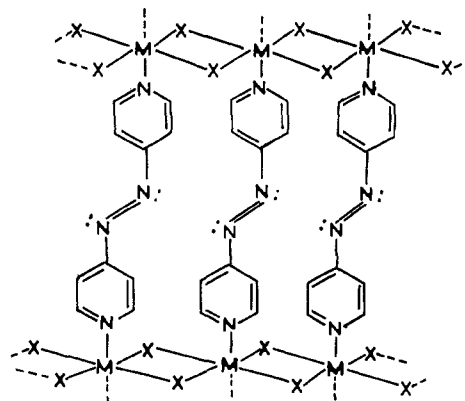
Figure 1.

4,4'-azopyridine compounds the lowest energy band probably contains two overlapping absorptions corresponding to those which are resolved in CoI₂·L''.

The spectra of the hydrated complexes of cobalt sulfate with L' show only one d–d band below 20 kK (Table II), and this is of low intensity (0.2–0.3 OD unit). We conclude that the cobalt ions are in each case six-coordinate, but the electronic spectra provide no details concerning the relative dispositions of the donor atoms.

The magnetic data for the cobalt and nickel complexes (Table II) are in accord with the structural conclusions drawn above. The nickel compounds have moments close to 3.3 BM at room temperature, but those of cobalt fall into two distinct groups: (a) those with moments in the range 5.1–5.3 BM typical of octahedral complexes and (b) those assigned pseudotetra-

hedral structures above, which have moments below 4.75 BM.

The electronic spectra of the cupric halide complexes (Table II) are similar to those of $Cu(py)_2Cl_2$ and Cu-(quin)Cl_2,[8] and, in agreement with the conclusions from the far-infrared data (see below), these compounds most probably have polymeric structures as in Figure 1. The copper sulfate complexes appear, from their electronic spectra, to be quite analogous to the corresponding quinoxaline compounds described by Underhill.[9] The magnetic moments are as expected for tetragonal copper(II) compounds.

Far-Infrared Spectra.—A structure of the type shown in Figure 1, in which azopyridine ligands link planar $[MX_2]_n$ chains, has a factor group isomorphous with point group D_{2h}. The $\nu(MX)$ modes reduce to $2a_g + 2a_u$ while the $\nu(MN)$ modes are represented by $a_g + a_u$; only the a_u modes will be infrared active. Any distortion from this symmetry, such as nonlinearity of the azopyridine bridges or nonplanarity of the $[MX_2]_n$ chains, is likely to cause activation of the a_g modes. Furthermore, some coupling between $\nu(MX)$ and $\nu(MN)$ modes of the same symmetry can take place, as is reasonable where such vibrations are close in frequency. The result will be three to six infrared absorption bands all of which will involve some metal–halogen and –nitrogen stretching character and hence show halogen and metal dependence to greater or lesser extents.

The spectra of the complexes $CoCl_2 \cdot L'$, $NiX_2 \cdot L'$ (X = Cl, Br), and $MX_2 \cdot L''$ (M = Co, Ni; X = Cl, Br) are in accord with these predictions (see, for example, Figure 2). In each case, besides the internal modes of the organic ligands (Table III), four or five bands can be identified and correlated from compound to compound. The general regions of these absorptions, for which the only reasonable assignment is $\nu(MX) + \nu(MN)$, indicate that in each case the metal is six-coordinate.[10] We conclude that all of the compounds listed in Table III have structures of the type shown in Figure 1.

Not all of the $MX_2 \cdot L'$ and $MX_2 \cdot L''$ complexes have spectra of this type. In $CuX_2 \cdot L'$ and $CuX_2 \cdot L''$, the $\nu(Cu-X)$ and $\nu(Cu-N)$ modes can be distinguished (Table IV). The spectra (Figure 3) closely resemble those of the corresponding compounds $CuX_2 \cdot 2py$,[11] $CuX_2 \cdot tsc$,[7,12] and $CuCl_2 \cdot sc$[7,12] (tsc = thiosemicarbazide, sc = semicarbazide), and these compounds appear also to have structures as represented by Figure 1; bridging by the ligands L' and L'' along $[CuX_2]_n$ chains is stereochemically unlikely. The marked differences between the spectra of the copper compounds and those of the corresponding cobalt and nickel analogs probably
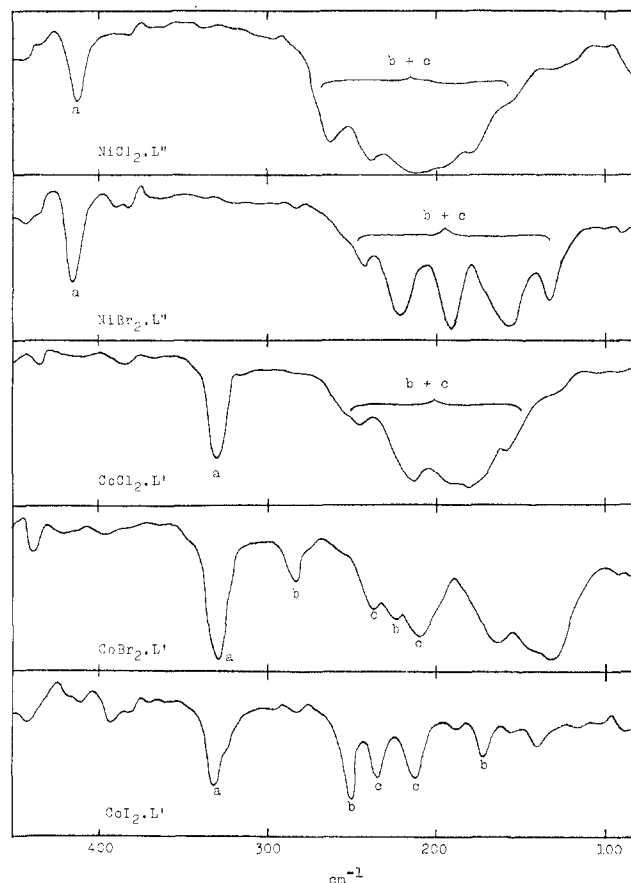

Figure 2.—Far-infrared spectra of some cobalt and nickel halide complexes of 3,3'-azopyridine (=L'') and 4,4'-azopyridine (=L'). Assignments are as follows (see also Tables III and V): a, internal mode of ligand, $\nu(L)$; b, $\nu(MX)$; c, $\nu(MN)$.

TABLE III

FAR-INFRARED SPECTRA[a] OF OCTAHEDRAL COBALT AND NICKEL HALIDE COMPLEXES OF 3,3'-AZOPYRIDINE (=L'') AND 4,4'-AZOPYRIDINE (=L')

Compound	Internal $\nu(L)$[b]	$\nu(MX) + \nu(MN)$
L''	400 m	. . .
$CoCl_2 \cdot L''$	409 m	250 m, 220 s, 200 s, 182 s, 172 ush
$CoBr_2 \cdot L''$	411 ms	234 ush, 212 s, 166 s, 147 s, 126 m
$NiCl_2 \cdot L''$	413 m	263 mw, 239 m, 212 vs, b, 180 sh
$NiBr_2 \cdot L''$	416 ms	245 mw, 223 s, 191 s, 159 s, b, 133 m
L'	304 s	. . .
$CoCl_2 \cdot L'$	331 s	250 w, 215 m, 185 s, b, 160 ush
$NiCl_2 \cdot L'$	340 s	265 mw, 230 m, 200 vs, b, 168 ush
$NiBr_2 \cdot L'$	340 vs	251 w, 220 s, 185 ms, 158 vs, b, 137

[a] For this and subsequent tables, frequencies are in cm^{-1} and abbreviations are: vs, very strong; s, strong; m, medium; w, weak; b, broad; ush, unresolved shoulder. [b] Here and in subsequent tables, this is probably the ν_{15} (X-sensitive) mode of the substituted pyridine rings: J. H. S. Green, W. Kynaston, and H. M. Paisley, *Spectrochim. Acta*, **19**, 549 (1963).

TABLE IV

FAR-INFRARED SPECTRA OF CUPRIC HALIDE COMPLEXES $CuX_2 \cdot L''$ AND $CuX_2 \cdot L'$

Compound	Internal $\nu(L)$	$\nu(CuX)$	$\nu(CuN)$	$\delta(CuX)$	$\pi(CuX)$	$\delta(CuN)$
$CuCl_2 \cdot L''$	417 ms	302 vs, 220 s	255 s	172 s	100 s	191 m
$CuBr_2 \cdot L''$	416 ms	249 vs, 200 vs	257 s	128 m	<80	188 ush
$CuCl_2 \cdot L'$	350 s	301 vs, 224 s	252 s	170 s	92 s, b	190 ush
$CuBr_2 \cdot L'$	349 s	252 vs,[a] 204 s	252 vs[a]	129 s	<80	183 m

[a] Overlapping bands.

(8) D. E. Billing, A. E. Underhill, D. M. Adams, and D. M. Morris, *J. Chem. Soc., A*, 902 (1966).

(9) A. E. Underhill, *ibid.*, 4336 (1965).

(10) R. J. H. Clark and C. S. Williams, *Inorg. Chem.*, **4**, 350 (1965).

(11) M. Goldstein, E. F. Mooney, A. Anderson, and H. A. Gebbie, *Spectrochim. Acta*, **21**, 105 (1965).

(12) M. J. Campbell, M. Goldstein, and R. Grzeskowiak, *Chem. Commun.*, 778 (1967).
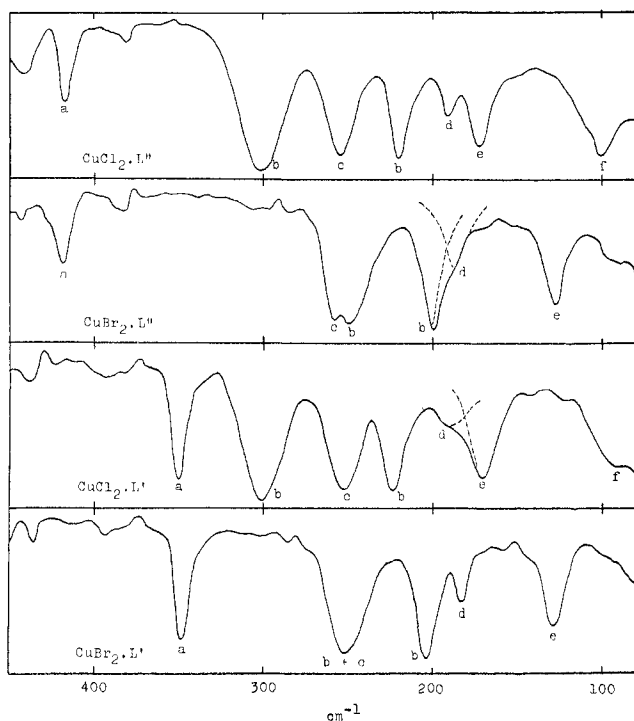
Figure 3.—Far-infrared spectra of cupric halide complexes of 3,3'-azopyridine (=L'') and 4,4'-azopyridine (=L'). Assignments are as follows (see also Table IV): a, internal mode of ligand, ν(L); b, ν(CuX); c, ν(CuN); d, δ(CuN); e, δ(CuX); f, π(CuX).

reflect the unsymmetrical nature of the copper–halogen bridges as found[13] in the CuCl$_2$·2py.

The band at 284 cm^{-1} in the spectrum of CoBr$_2$·L' has no counterpart in the spectrum of the corresponding chloride (Figure 2). This frequency is consistent with assignment to ν_{as}(CoBr) of a tetrahedral structure (*cf.* 271 cm^{-1} in tetrahedral CoBr$_2$·2py[10]). The complexes CoI$_2$·L' and CoI$_2$·L'' also have spectra which are readily interpreted in terms of tetrahedral geometry. The assignments of ν(Co–N) in these compounds (Table V) follow those given for the bis-pyridine analogs[10] if allowance is made for a lowering of the frequency due to the larger mass of the organic ligand. These conclusions agree with those drawn from the electronic spectral and magnetic measurements above.

The spectra of the sulfate complexes of cobalt and

(13) J. D. Dunitz, *Acta Cryst.*, **10**, 307 (1957).

TABLE V

FAR-INFRARED SPECTRA OF TETRAHEDRAL COBALT HALIDE COMPLEXES CoX$_2$·L'' AND CoX$_2$·L'

Compound	Internal ν(L)	ν(CoX)	ν(CoN)	Others
CoI$_2$·L''	417 ms	249 vs, 177 m	224 s	159 m, 137 w
CoBr$_2$·L'	330 vs	284 m, 224 m	238 m, 211 ms	166 m, 134 s, b
CoI$_2$·L'	333 s	252 s, 173 mw	236 m, 214 m	140 w

copper with 4,4'-azopyridine show very broad, diffuse absorption between 300 and 150 cm^{-1} and are less easily interpreted. The strong bands at 260 cm^{-1} in CuSO$_4$·L' and at 254 cm^{-1} in CuSO$_4$·4H$_2$O·L' might arise from metal–oxygen stretching modes of coordinated sulfate ligands,[7] and this would agree with mid-infrared studies on these compounds (see Conclusions). However, there are similar bands in the spectra of CoSO$_4$·2H$_2$O·L' (260 cm^{-1} s, vb) and CoSO$_4$·5H$_2$O·L' (260 cm^{-1} m, b) which appear, from the SO$_4$ internal modes, to contain ionic sulfate groups so that the validity of the ν(M–OSO$_3$) assignment is questionable.

Conclusions

The metal halide complexes fall into two structural groups in which the metal is in either (i) a distorted octahedral environment in which metal–halogen chains are linked together by the azopyridine ligand or (ii) a pseudotetrahedral environment, as in the case of CoBr$_2$·L', CoI$_2$·L', and CoI$_2$·L'', in which structure a metal atom is linked to two adjacent metal atoms *via* the azopyridine ligand.

The interpretation of the results for oxyanions is less positive. Mid-infrared spectra show that in the cases of CuSO$_4$·L' (608 s, 618 s, 645 s, 980 m, 1075 s, 1120 s, 1225 cm^{-1}) and CuSO$_4$·4H$_2$O·L' (604 m, 620 s, 650 m, 970 s, 1030 vs, 1070 sh, 1140 vs cm^{-1}) the sulfate groups have C$_{2v}$ symmetry with the group being chelating in the former case and bridging in the latter.[14] Both cobalt sulfate complexes give two unresolved bands in the 1100- and 625-cm^{-1} regions characteristic of sulfate group in T$_d$ symmetry, and according to electronic spectra the cobalt is six-coordinated.

(14) J. R. Hall, C. H. L. Kennard, and R. A. Plowman, *J. Inorg. Nucl. Chem.*, **28**, 467 (1966); R. Eskenazi, J. Raskovan, and R. Levitus, *ibid.*, **28**, 521 (1966).