acid-independent k_1 values of the three complexes should be equal. For the aniline and *p*-toluidine complexes this is found to be the case. The slightly lower k_1 value of the *m*-toluidine complex might be due to a steric or some other unknown factor. Substituent effects are expected to be more significantly reflected in the k_2 values of these complexes, since the nature and position of the substituent in the phenyl ring would make the Co–N π bond less or more effective. Higher k_2K_a values for the chloro-*p*-toluidine complex might be the result of higher k_2 values, which might again be due to the *para*-orienting effect of the methyl group. However, with the approximately estimated values of k_2 this aspect need not be discussed further.

While this work was in progress, the aquation rate of chloro(aniline)bis(ethylenediamine)cobalt(III) chloride was reported by Jones, *et al.*[9] The rate of chloride

(9) M. M. Jones, N. K. Chawla, and D. G. Lambert, *J. Am. Chem. Soc.*, **89**, 557 (1967).

release was followed by them conductometrically presumably in the absence of added acid. The rate constant for chloride release at 40° was reported to be 2.1×10^{-4} sec^{-1}. In the absence of acid with the perchlorate salt we obtained a rate constant of 1.8×10^{-4} sec^{-1} at 40°. With the aged aquo complex they reported to have observed very slow release of aniline with the formation of the diaquo complex. With the chloro complexes under acid conditions up to about 60% reaction (chloride release) no aniline release could be detected by us. In view of the similarity in the method of preparation and on analogy with the ir findings of Baldwin[10] with a number of similar ethylenediamine complexes, we prefer the *cis* configuration for these arylamine complexes though all attempts to isolate the other isomer have proved unsuccessful.

(10) M. E. Baldwin, *J. Chem. Soc.*, 4369 (1960).

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

Complexes of 2,2'-Azopyridine with Iron(II), Cobalt(II), Nickel(II), Copper(I), and Copper(II). An Infrared Study

BY D. A. BALDWIN,[1a] A. B. P. LEVER,[1b] AND R. V. PARISH[1a]

Vibrational spectroscopy in both the conventional and far-infrared regions, electronic spectroscopy, and magnetism are used to characterize a series of coordination complexes of 2,2'-azopyridine. Complexes of the title ions with ligand to metal ratios of 3:1, 2:1, or 1:2 are described. The nickel(II) and iron(II) derivatives are six-coordinate, while both six-coordinate and four-coordinate tetrahedral complexes of cobalt(II) and copper are reported. Evidence is presented indicative of a very strong interaction between the spin-paired iron(II) atom and the ligand.

Metal complexes involving the aza group are frequently intensely colored and find extensive use as dyestuffs. Much has been published[2] concerning these dyestuffs, which often involve large complicated aza ligands. Few fundamental papers dealing with simple aza ligands have appeared, although some interest has been shown recently.[3] A short note[4] on 2,2'-azopyridine appeared during this investigation.

Highly colored complexes are also formed by diimine ligands with oxidizable metal ions, and it is of interest to compare the two systems N=C—C=N in the diimines and N=C—N=N—C=N in the aza ligands. We have therefore investigated the complexes formed by 2,2'-azopyridine (L) and salts of metals of the first transition series.

The ligand 2,2'-azopyridine is capable, in principle, of several modes of coordination. Those shown as I–IV are the most likely; there is no evidence for coordination as in V. The ligand cannot function as a tridentate without considerable angular strain. We find that three coordination modes occur: series a, coordination mode I—L(CuCl)$_2$, L(CuI)$_2$, L(CuCl$_2$)$_2$, and L(CoCl$_2$)$_2$; series b, coordination mode II—ML$_2$-(NCS)$_2$ (M = Fe, Co, Ni), CoL$_2$X$_2$ (X = Cl, Br), and NiL$_3$(ClO$_4$)$_2$. The binuclear complex L(Cu(O$_2$-CCH$_3$)$_2$)$_2$ is thought to involve mode IV.

(1) (a) University of Manchester; (b) York University.

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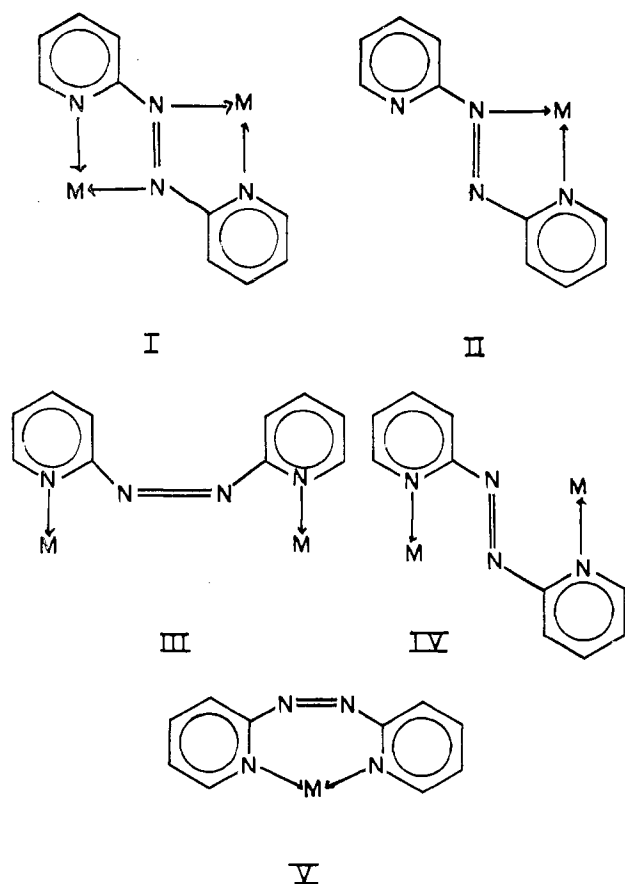
Experimental Section

Materials.—All of the metal salts were reagent grade and were used without further purification. Methyl cyanide, purchased from Hopkins and Williams Ltd., was dried over phosphorus pentoxide and fractionated from fresh phosphorus pentoxide; the fraction at 81° was used.

Carbon, hydrogen, and nitrogen analyses were carried out by the Institute's analytical laboratory under the direction of Mr. Manohin. Metal analyses were carried out gravimetrically using standard methods.[5]

Magnetic Measurements.—The magnetic susceptibility data were obtained with a Newport magnetic (Gouy) balance with 1.5-in. pole pieces. The tube was calibrated using mercury tetrathiocyanatocobaltate(II).[6] The data are believed accurate to ±3%.

Spectra.—The infrared spectra were run in the 4000–650-cm^{-1} region as Nujol and hexachlorobutadiene mulls on a Perkin-Elmer 21 instrument. The region 650–400 cm^{-1} was obtained as Nujol mulls between KBr plates on a Perkin-Elmer 137 instrument provided with KBr optics. The region 450–200 cm^{-1} was run as Nujol mulls between polythene plates on a Grubb-Parsons DM4 instrument. The instrument was flushed out with dry nitrogen during use.

Electronic spectra were recorded in solution on an Optika CF4 double-beam grating instrument using matched silica cells. Solution data were obtained in the concentration range 10^{-2}–10^{-4} M, and, except where otherwise stated in the text, the solution obeyed Beer's law. Reflectance spectra were obtained between 350 and 750 mμ on the Optika CF4 and above 650 mμ on a Beckman DK 2A instrument.

Preparation of 2,2'-Azopyridine.—The ligand can be prepared by the method of Kirpal and Reiter.[7] The yield from this preparation is low and an improved procedure was sought. The

following method is very quick and easy and the yield (about 30%) is improved on that of Kirpal and Reiter.[7]

2-Aminopyridine (10 g) was dissolved in water (80 ml) and cooled by the use of a solid CO_2–methylated spirits bath. Sodium hypochlorite (500 ml, 12.5 wt %) was cooled in the solid CO_2–methylated spirits bath until a small amount of solid began to separate out. The cold 2-aminopyridine solution was then added. Rapid stirring and cooling for 10 min gave a deep red solution and a brown solid began to separate. Upon appearance of the solid, the mixture was immediately extracted with two portions of 250 ml of diethyl ether. The extract was dried and reduced in volume to give a red crystalline solid which was recrystallized from petroleum ether; yield about 30%.

Preparation of Complexes.—All of the complexes were dried *in vacuo* at 75–100°.

Tetraacetato(2,2'-azopyridine)dicopper(II).—Cupric acetate monohydrate (0.59 g) was dissolved in methyl cyanide (70 ml) and the ligand (0.25 g) dissolved in methyl cyanide (10 ml) was added. After cooling the solution for 24 hr in a refrigerator a dark green precipitate was obtained. The solid was filtered off and washed with methyl cyanide and ether. *Anal.* Calcd for $C_{18}H_{20}Cu_2N_4O_8$: C, 39.6; H, 3.7; N, 10.3; Cu, 23.2. Found: C, 39.9; H, 3.7; N, 10.5; Cu, 22.8.

Dichloro-μ-(2,2'-azopyridine)-dicopper(I).—Cupric chloride dihydrate (1.45 g, 2 equiv) was dissolved in water (80 ml) and 2,2'-azopyridine (0.55 g, 1.1 equiv) dissolved in a minimum quantity of water was added. The solution was filtered and 5 drops of hypophosphorous acid (50% w/w) were added. On standing for 0.5 hr a black-blue precipitate was obtained. The complex was filtered and washed thoroughly with water, methanol, and diethyl ether. *Anal.* Calcd for $C_{10}H_8Cl_2Cu_2N_4$: C, 31.4; H, 2.1; N, 14.7; Cu, 30.1. Found: C, 31.6; H, 2.4; N, 14.7; Cu, 30.0.

Diiodo-μ-(2,2'-azopyridine)-dicopper(I).—Cupric chloride dihydrate (1.45 g, 2 equiv) was dissolved in water (80 ml) and the ligand (0.55 g, 1.1 equiv) dissolved in a minimum quantity of water was added. When a concentrated solution of potassium iodide was added dropwise with stirring, a black precipitate was obtained. This was filtered and washed very well with water to remove any excess potassium iodide. The complex was further washed with methanol and anhydrous ether to remove iodine. *Anal.* Calcd for $C_{10}H_8Cu_2I_2N_4$: C, 21.7; H, 1.4; N, 9.9; Cu, 22.9. Found: C, 22.0; H, 1.6; N, 9.8; Cu, 22.8.

Tetrachloro-μ-(2,2'-azopyridine)-dicopper(II).—A concentrated solution of the ligand in methyl cyanide was added dropwise to a solution of excess anhydrous cupric chloride in methyl cyanide to give a red-brown precipitate. The solid was filtered off and washed with methyl cyanide and anhydrous ether. *Anal.* Calcd for $C_{10}H_8Cl_4Cu_2N_4$: C, 26.5; H, 1.8; N, 12.4; Cu, 28.0. Found: C, 26.4; H, 2.1; N, 12.6; Cu, 27.8.

Tetrachloro-μ-(2,2'-azopyridine)-dicobalt(II).—Anhydrous cobaltous chloride (0.35 g, 2 equiv) was dissolved in dry methyl cyanide (70 ml) and the ligand (0.25 g, 1 equiv) dissolved in a minimum quantity of dry methyl cyanide was added. The black precipitate was filtered under dry nitrogen and washed thoroughly with methyl cyanide and anhydrous ether. The solid was dried *in vacuo* at 40° for 2 hr. *Anal.* Calcd for $C_{10}H_8Cl_4Co_2N_4$: C, 27.0; H, 1.8; N, 12.6. Found: C, 26.9; H, 2.0; N, 12.9.

Dithiocyanatobis(2,2'-azopyridine)copper(II).—Cupric chloride dihydrate (0.32 g, 1 equiv) was dissolved in water (20 ml) and the ligand (0.5 g, 2 equiv) dissolved in a minimum quantity of water was added. Excess solid ammonium thiocyanate was introduced to give an immediate yellow precipitate. The solid was filtered and washed very well with water to remove any excess thiocyanate and then with a small quantity of ethanol and anhydrous ether. *Anal.* Calcd for $C_{22}H_{16}CuN_{10}S_2$: C, 48.3; H, 2.9; N, 25.6; Cu, 11.6. Found: C, 48.1; H, 2.9; N, 25.5; Cu, 11.5.

The following thiocyanates were similarly prepared: dithiocyanatobis(2,2'-azopyridine)cobalt(II) [*Anal.* Calcd for $C_{22}H_{16}$-$CoN_{10}S_2$: C, 48.7; H, 2.9; N, 25.8. Found: C, 48.8; H, 3.1; N, 26.0] and **dithiocyanatobis(2,2'-azopyridine)nickel(II)**

(5) I. Vogel, "Quantitative Inorganic Analysis," Longmans, Green and Co., New York, N. Y., 1962.

(6) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

(7) A. Kirpal and E. Reiter, *Chem. Ber.*, **60B**, 664 (1927).

[*Anal.* Calcd for $C_{22}H_{18}N_{10}NiS_2$: C, 48.7; H, 2.9; N, 25.8; Ni, 10.3. Found: C, 48.4; H, 3.2; N, 26.0; Ni, 10.4].

Dichlorobis(2,2'-azopyridine)cobalt(II).—Anhydrous cobalt chloride (0.176 g, 1 equiv) was dissolved in a minimum quantity of methyl cyanide and the ligand (0.5 g, 2 equiv) dissolved in methyl cyanide was added. After cooling the solution in a refrigerator, a red to purple crystalline solid was obtained. The complex was filtered and washed with a small amount of methyl cyanide and ether. *Anal.* Calcd for $C_{20}H_{16}Cl_2CoN_8$: C, 48.2; H, 3.2; N, 22.5. Found: C, 48.5; H, 3.3; N, 22.8.

Prepared similarly was **dibromobis(2,2'-azopyridine)cobalt(II)**. *Anal.* Calcd for $C_{20}H_{16}Br_2CoN_8$: C, 41.0; H, 2.7; N, 19.2. Found: C, 41.0; H, 2.7; N, 19.1.

Tris(2,2'-azopyridine)nickel(II) Perchlorate.—Nickel perchlorate hexahydrate (0.51 g, 1 equiv) was dissolved in methanol (10 ml) and the ligand (0.77 g, 3 equiv) dissolved in methanol (10 ml) was added. The dark yellow-green solution was refluxed for 1 hr, filtered hot, and allowed to cool slowly to give yellow-green crystals. These were filtered off, washed with a small amount of methanol and ether, and recrystallized from methanol. *Anal.* Calcd for $C_{30}H_{24}Cl_2N_{12}NiO_8$: C, 44.6; H, 3.0; N, 20.8; Ni, 6.9. Found: C, 44.3; H, 3.0; N, 20.5; Ni, 7.0.

Dithiocyanatobis(2,2'-azopyridine)iron(II).—Ferrous chloride solution was prepared by refluxing ferrous chloride tetrahydrate (0.4 g, 1 equiv) with iron powder (1 g) for 1 hr in methanol under dry nitrogen. The colorless solution was filtered under nitrogen. To this solution was added the ligand (1 g, 3 equiv) dissolved in methanol and the solution was refluxed for 0.5 hr under nitrogen. A concentrated aqueous solution of ammonium thiocyanate was added dropwise to the hot solution until it became darker. The solution was then maintained at 90° on a water bath for 10 min and subsequently cooled. The blue-black solid which was obtained was filtered off, washed with methanol–water (50:50), methanol, and ether. The solid was recrystallized three times by Soxhlet extraction with methanol. *Anal.* Calcd for $C_{22}H_{16}FeN_{10}S_2$: C, 48.8; H, 3.0; N, 25.9. Found: C, 48.9; H, 3.2; N, 26.1.

Results and Discussion

Infrared Spectra.[8]—The ligand is basically a 2-substituted pyridine and extensive infrared correlations have been made for compounds of this type.[9-18] The vibrations of interest are the four $\nu(C{=}C)$, $\nu(C{=}N)$ bands observed between 1430 and 1610 cm^{-1}, the $\nu(N{=}N)$ band near 1420 cm^{-1}, the ring-breathing mode near 1000 cm^{-1}, an out-of-plane CH deformation near 800 cm^{-1}, a skeletal mode near 740 cm^{-1}, and an out-of-plane deformation near 400 cm^{-1}.

The complexes may be divided into two series, A and B, on the basis of their infrared spectra.

Series A.—The series A complexes, all of the general formula $(MX_n)_2L$, exhibit the four $\nu(C{=}C)$, $\nu(C{=}N)$, skeletal frequencies[8] in the following ranges: band I, 1590–1603 cm^{-1}; band II, 1569–1580 cm^{-1}; band III,

(8) Infrared data supplementary to this article have been deposited as Document No. NAPS-00129 with the ASIS National Auxiliary Publication Service, c/o CCM Information Sciences, Inc., 22 West 34th St., New York, N. Y. 10001. A copy may be secured by citing the document number and by remitting $1.00 for microfiche, or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS-NAPS.
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(14) N. S. Gill and H. J. Kingdon, *Australian J. Chem.*, **19**, 2197 (1966).
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1449–1488 cm^{-1}; band IV, 1435–1439 cm^{-1}. The presence of these four bands (rather than eight) suggests that both pyridine residues are approximately equivalent. Band I is increased significantly in frequency from the free-ligand value of 1581 cm^{-1}, an indication of the coordination of pyridine to a metal atom.[11] The ring-breathing mode observed at 990 cm^{-1} in the free ligand disappears in the series A complexes and is replaced by a band at 1005–1020 cm^{-1}. This shift is also indicative of pyridine coordination.[12]

Two strong bands are observed in the spectrum of the free ligand at 796 and 736 cm^{-1}. These bands are assigned[13] to $\gamma(C{-}H)$ and $\phi(C{-}C)$, respectively. The 736-cm^{-1} band splits into two components lying between 719 and 754 cm^{-1}. This splitting is also believed to be an indication of pyridine to metal coordination.[12,14] The band observed at 796 cm^{-1} in the free ligand is observed as a single band lying between 785 and 806 cm^{-1}.

The uncoordinated ligand exhibits a band at 405 cm^{-1} assigned to the C–C out-of-plane deformation,[13,18] while series A complexes exhibit a single band between 408 and 423 cm^{-1}. An increase in frequency upon coordination is to be expected[19] (see below).

The data leave little doubt that in the series A complexes both pyridine residues are coordinated to metal atoms.

The N=N stretching mode in 2,2'-azopyridine occurs at 1424 cm^{-1} and is in the range observed by Bassignana and Cogrossi[20] in their study of azo compounds. This assignment has been confirmed by Raman studies.[17] The N=N stretching mode is forbidden in the *trans* form of the ligand but allowed in the *cis*.[17] The intensity of the band provides an indication of the conformation of the ligand, or more accurately an indication of whether the molecule has a center of symmetry passing through the center of the N=N bond. In the series A complexes the $\nu(N{=}N)$ band is observed as a very weak band or shoulder between 1395 and 1410 cm^{-1}, suggesting that the complexes do possess a center of symmetry. The decrease in the frequency, relative to the free ligand, implies an aza to metal bond and mode I as the structural type for the series A complexes. The reduction in the $\nu(N{=}N)$ frequency upon coordination is in contrast to the increase in the $\nu(C{=}N)$ frequency observed in some diimine derivatives.[11]

Series B.—The infrared spectra of the series B complexes, which contain two or three ligand molecules per metal atom, differ from the series A in a number of respects. Five to eight bands may be picked out between 1429 and 1603 cm^{-1}, suggesting the presence of two nonequivalent pyridine residues. With the exception of the iron thiocyanate derivative, to which we shall return later, these complexes show two bands near 1000 cm^{-1}, one between 990 and 999 cm^{-1} and one between 1008 and 1017 cm^{-1}, suggesting the pres-

(19) N. S. Gill, R. H. Nuttall, D. E. Scaife, and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, **18**, 79 (1961).
(20) P. Bassignana and C. Cogrossi, *Tetrahedron*, **20**, 2361 (1964).

ence of both coordinated and uncoordinated pyridine. The 790–740-cm^{-1} region of the spectrum is also more complex than in the series A derivatives, with two, three, or even four bands being observed for each vibration.

Two bands are observed between 400 and 440 cm^{-1}. The lower energy band, which lies at almost the same frequency as in the uncomplexed ligand, is almost independent of the metal while the higher energy band is not. Its energy increases with decreasing size of the metal ion, Fe(II) < Co(II) < Ni(II) < Cu(II), an effect which has been noted previously.[19,21] In the series A complexes the single band increases in the sequence Cu(I) < Co(II) < Cu(II) as would be anticipated.

The multiplicity of bands may arise through (a) coupling of the ligand vibrations through the metal when more than one ligand is attached to the metal ion, (b) chemical inequivalence of the several ligands attached to the metal, and (c) the presence of both coordinated and uncoordinated pyridine residues on the same ligand molecule.

In general the presence of more than one 2-substituted pyridine ligand attached to the metal atom does not split[11,14] the four pyridine bands observed between 1430 and 1610 cm^{-1} although splitting does occur in some dipyridyl derivatives.[12] There is no reason to assume that the several ligands are chemically inequivalent.

In the thiocyanate complexes the metal–thiocyanate bond is covalent (from infrared studies). The ligand must be bidentate since a tridentate mode of bonding is energetically unfeasible and in this case would lead to eight-coordination which is considered unlikely. Since the $\nu(N=N)$ band is decreased in energy relative to the free ligand, bonding to the aza group is inferred. Hence only one of the two pyridine residues can be coordinated. The multiplicity of bands is wholly consistent with the view that the series B complexes involve only one coordinated pyridine residue.

The $\nu(N=N)$ frequency is observed between 1410 and 1418 cm^{-1} for all of the complexes other than the iron thiocyanate derivative where it appears to have decreased to 1393 cm^{-1}. In most cases the band is of medium to strong intensity suggesting that these complexes lack a center of symmetry. The data point to mode II as the structural type for the series B complexes. The observation that the $\nu(N=N)$ frequencies in the series B complexes lie at a higher energy than those in the A series is also consistent with the suggestion that while both aza nitrogen atoms are used for coordination in the A series, only one is used in the B series.

Infrared Spectra of the Anionic Groups (3000–600 Cm^{-1}). (a) **Acetate Group.**—The symmetry of the acetate group is low (C$_{2v}$) and coordination does not alter the selection rules or resolve any degeneracies.[22] The complex L(Cu(OAc)$_2$)$_2$ exhibits bands at 1421

(21) R. J. H. Clark and C. S. Williams, *Inorg. Chem.*, **4**, 350 (1965).
(22) K. Nakamoto, F. Fujita, S. Tanaka, and M. Kobayashi, *J. Am. Chem. Soc.*, **79**, 4909 (1957).

and 1623 cm^{-1} attributed to the symmetric and antisymmetric carboxyl stretching frequencies, respectively. The magnetic moment of our complex, 1.4 BM at 293°K, compares favorably with the moment of py$_2$-Cu$_2$(OAc)$_4$[23] reported[24] to be 1.39 BM at 309°K. Since L(Cu(OAc)$_2$)$_2$ is a series A complex, it is likely that it possesses a polymeric structure in which the ligand is linking Cu$_2$(OAc)$_4$ units, using mode IV.

(b) **Thiocyanate Group.**—The infrared spectrum of the thiocyanate group has been studied by many workers[25–28] and reviewed by Burmeister.[29] The thiocyanate group can coordinate through the nitrogen or sulfur atoms or act as a bridge. Infrared data may be used to distinguish the modes of bonding of the thiocyanate group according to the assignments (in cm^{-1}) given below which should however be used with

	ν_1 (C–N str)	ν_2 (N–C–S bend)	ν_3 (C–S str)
N-Bonded thiocyanate	2040–2100	450–490	780–860
S-Bonded thiocyanate	2080–2120	410–470	690–720
Bridging thiocyanate	2075–2150	...	775–790

some caution. The position of the ν_1 frequency is the least reliable guide to the nature of the bonding. The wide separation in the C–S frequencies for N and S bonding makes ν_3 a much more useful guide when the band can be unequivocally assigned. Table I lists the

Table I

Thiocyanate Group Infrared Frequencies^a (cm^{-1})

Complex	ν_1	ν_2	ν_3
FeL$_2$(NCS)$_2$	2102 vs	491 m	815 m
	2079 s	484 m	
CoL$_2$(NCS)$_2$	2075 vs	479 m	807 sh
		470 sh	
NiL$_2$(NCS)$_2$	2088 vs	479 m	803 sh
		471 w	
CuL$_2$(NCS)$_2$	2092 s	473 w	...

^{a} Nujol mull.

bands observed in the thiocyanate complexes described here. All of the complexes are believed to be six-coordinate, being nonconductors in methyl cyanide. Their comparatively low solubility precluded molecular weight determination. The cobalt, nickel, and copper complexes are presumably *trans* (with respect to the thiocyanate groups) since they only exhibit a single C–N stretching frequency. Although the iron complex exhibits two $\nu(C–N)$ bands in the solid, only one is observed in solution (chloroform) at 2100 cm^{-1}. It is therefore believed to have a *trans* configuration. All of the complexes contain N-bonded thiocyanate and bidentate azopyridine groups bonded as in II. The possibility that the ligand is monodentate and the complexes four-coordinate is eliminated on the basis of their magnetism and electronic spectra (below).

(23) D. P. Graddon, *J. Inorg. Nucl. Chem.*, **17**, 222 (1961).
(24) E. Kokot and R. L. Martin, *Inorg. Chem.*, **3**, 1306 (1964).
(25) P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 1912 (1960).
(26) F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and T. E. Haas, *Inorg. Chem.*, **1**, 565 (1962).
(27) A. Turco and C. Pecile, *Nature*, **191**, 66 (1961).
(28) J. Lewis, R. S. Nyholm, and P. W. Smith, *J. Chem. Soc.*, 4590 (1961).
(29) J. L. Burmeister, *Coord. Chem. Rev.*, **1**, 205 (1966); **3**, 225 (1968).

TABLE II

| Complex | Color | Magnetic moment, BM (25°) | Absorption spectra, wave-numbers (log ε) | Far-infrared spectra (400–200 cm⁻¹) | | | |
				M–NCS str	M–N (ligand str)	M–X (Cl or Br)	Unassigned
L(CuCl)₂	Blue-black	0	16,370,[a] 24,450,[a] 28,010,[a] 16,250[b] (2.85), 31,350[c] (4.11)			215 vs	
L(CuI)₂	Blue-black	0	15,950,[a] 16,460[b] (2.76), 31,350[c] (3.92)				
L(CuCl₂)₂	Red-brown	1.87	7350 sh,[a] 9570,[a] 22,830,[a] 17,900[e] (2.05), 21,890[e] (2.75), 29,900[e] (3.63), 39,220 sh,[e] 44,840[e] (3.6)			324 vs, 278 vs	
L₂Cu(NCS)₂	Yellow	1.80	15,160,[a] 20,150 sh,[a] 31,150[e] (4.43), 45,150[e] (4.29)	325 vs, 295 sh	256 m, 229 m		452 m
LCu₂(OAc)₄	Green	1.42	14,410 sh,[a] 22,170 sh,[a] 25,480,[a] 14,880[e] (2.45), 22,750[e] (2.47), 32,150[e] (3.76), 39,290[e] (3.94), 45,050[e] (3.93)				351 s, 263 vs, 234 vs
L₃Ni(ClO₄)₂	Yellow-green	3.25	10,470 sh,[a] 15,270,[a] 27,930,[a] 29,240[e] (4.62)		264 m, 247 sh, 225 s		
L₂Ni(NCS)₂	Yellow	3.17	10,930,[a] 15,850,[a] 23,700,[a] 24,980 sh,[a] 26,550 sh,[a] 29,670[e] (4.48), 44,640[e] (4.51)	265 vs	257 vs, 240 vs		367 w
L(CoCl₂)₂	Blue	4.18	4640,[a] 5980,[a] 12,050,[a] 16,370,[a] 22,720,[a] 31,300[f] (3.82)		241 m, 217 s	310 vs, 274 vs	
L₂CoBr₂	Rust	4.75	8300,[a] 14,040,[a] 17,330 sh,[a] 19,340 sh,[a] 23,580 sh,[a] 26,490,[a] 30,580[e] (4.34), 45,550[e] (4.40)		257 m, 234 s	203 vs	380 vw, 363 w
L₂CoCl₂	Rust	4.70	8510,[a] 14,330,[a] 17,610,[a] 20,790,[a] 31,350[e] (4.24), 38,760[e] (4.05), 45,150[e] (4.34)		250 s	268 vs	367 w
L₂Co(NCS)₂	Red-brown	4.69	10,450,[a] 17,730 sh,[a] 24,010,[a] 30,490[e] (4.44), 45,450[e] (4.52)	258 vs	238 vs, 217 sh		357 w, 337 w
L₂Fe(NCS)₂	Blue	0	13,950,[a] 17,860 sh,[a] 14,170[e] (3.74), 17,960[e] (3.32), 31,100[e] (4.33), 42,020[e] (4.40)	341 s	377 m, 374 sh		454 m
Azopyridine	Red	0	21,880[e] (2.53), 32,100[d] (4.15), 45,450[g] (4.07)				

[a] Diffuse reflectance spectrum. [b] Pyridine solution (1.25 g/1.). [c] Probably Cu(I)→py charge transfer. [d] Pyridine solution (2.8 g/1.). [e] CH₃CN solution. [f] CH₃SOCH₃ solution. [g] Fine structure observed between 38,160 and 41,160 cm⁻¹.

Far-Infrared Spectra (600–200 Cm⁻¹).

No bands were observed between 400 and 200 cm⁻¹ in the spectrum of the uncoordinated ligand.

The spectrum of the NiL₃(ClO₄)₂ complex exhibits two bands and a shoulder between 264 and 225 cm⁻¹. These lie in the general region expected for metal-nitrogen (pyridine) vibrations.[19,21,30] However, metal-nitrogen (bipyridyl) vibrations are not observed in this region,[31] casting some doubt on this assignment. Clark and Williams[31] have suggested that bands observed in bipyridyl M(II) complexes between 260 and 300 cm⁻¹ and assigned as M–N (bipyridyl) vibrations[9] are ligand bands activated by coordination to the metal ion. This assignment is based on the observation that although the bands disappear when the metal ion is trivalent, or spin-paired divalent (*e.g.*, Fe(II)), they are apparently not replaced by a new band at higher energy. Bands are observed in the azopyridine complexes between 217 and 264 cm⁻¹ for cobalt(II), nickel(II), and copper(II) but not for Fe(II) (spin-paired) or copper(I). In the spectrum of the spin-paired Fe(II) complex additional bands are observed between 300 and 400 cm⁻¹ which could be Fe–N (azopyridine) vibrations. Thus the assignment of bands between 200 and 300 cm⁻¹ in the cobalt(II), nickel(II), and copper(II) derivatives to M–N (azopyridine) absorption, as shown in Table II, is reasonable. The metal–nitrogen vibrations are likely to be extensively coupled together, the multiplicity of bands being due to the low symmetry of the complexes.

Table III summarizes in an approximate manner the frequencies expected for the various metal–ligand vibrations under discussion for both tetrahedral and octahedral complexes of cobalt(II), nickel(II), and copper(II) with pyridine-type ligands.[21,30,32,33] The complex L(CoCl₂)₂, whose color, electronic spectrum,

TABLE III[a]

METAL–LIGAND STRETCHING FREQUENCIES (WAVE NUMBERS)[21,30,32,33]

| Vibration | M | | |
	Co(II)	Ni(II)	Cu(II)
Monomeric Octahedral			
M–Cl	230	240	
M–Br	<200	<200	
M–N (pyridine)	215	235	245–280
M–N (NCS)	270	290	310
Tetrahedral			
M–Cl	320–340	330	
M–Br	270	250–260	
M–N (pyridine)	250	240	
M–N (NCS)	300	310	330

[a] Where more than one band is to be expected only the highest energy is quoted. The band positions are only approximate.

and magnetism leave little doubt that it is tetrahedral, has Co–N (azopyridine) absorption in the region expected for tetrahedral cobalt–pyridine systems. The nickel complexes are clearly octahedral from magnetic and electronic spectral considerations but their Ni–N (azopyridine) absorption is noticeably high when compared with the data in Table III. The L₂CoX₂ complexes have magnetic and electronic spectroscopic behavior which is not clear-cut but which indicates an octahedral rather than a tetrahedral environment about the metal atom. The metal–nitrogen frequencies would be consistent with a tetrahedral formulation and are high for an octahedral formulation. However, if the complexes were tetrahedral, then the complex L₂Co(NCS)₂ would be expected to exhibit two ν(Co–N) (thiocyanate) and two ν(C–N) vibrations, whereas in fact only one of each is observed. The halides would be expected to show two metal–halogen stretching vibrations but only one is observed (see below). Thus the complexes are octahedral (in disagreement with an earlier formulation[4] of L₂CoCl₂). The complex L₂Cu(NCS)₂ has Cu–N (azopyridine) vibrations in the region expected for octahedral (or tetragonal) com-

(30) C. W. Frank and L. B. Rogers, *Inorg. Chem.*, **5**, 615 (1966); J. Burgess, *Spectrochim. Acta*, **24A**, 277 (1968).

(31) R. J. H. Clark and C. S. Williams, *ibid.*, **23A**, 1055 (1967).

(32) R. J. H. Clark and C. S. Williams, *ibid.*, **22**, 1081 (1966).

(33) D. Forster and D. M. L. Goodgame, *Inorg. Chem.*, **4**, 715 (1965).

plexes of copper(II). The complex $L_2Fe(NCS)_2$ does not have any absorption between 200 and 300 cm^{-1} but shows a doublet near 375 cm^{-1} which is probably attributable to the Fe–N (azopyridine) absorption. These bands are strong and quite unlike the weak absorption observed in this region in dipyridyl complexes[31] and assigned as an out-of-plane C–C deformation. ν(Fe–N) vibrations have been assigned[9,34] between 400 and 600 cm^{-1} but with little confirmatory evidence. A strong band appears near 370 cm^{-1} in the low-spin form of Fe(o-phen)$_2$(NCS)$_2$. This was also assigned as an out-of-plane deformation.[35] However, it might be better assigned as a ν(Fe–N) vibration. The thiocyanate complexes show an additional band below 400 cm^{-1} which is attributed, by comparison with Table III, to an M–N (NCS) vibration. The Ni–N (NCS) band is a trifle low, while the Fe–N (NCS) band seems high. Very recently the ν(M–NCS) vibration in tetrahedral Fe(quin)$_2$(NCS)$_2$ has been attributed[36] to a band observed at 295 cm^{-1}. If this is correct, then the vibration in an analogous octahedral complex should occur at a lower frequency. Since such a band does not occur in our spectrum, the tetrahedral assignment is in doubt.

The complexes CoL_2Cl_2 and CoL_2Br_2 exhibit bands at 268 and at 203 cm^{-1}, respectively, which are probably metal–halogen stretching vibrations. These frequencies are rather high for octahedral systems but low for tetrahedral systems. As mentioned above the presence of only one metal–halogen stretching vibration seems to exclude a tetrahedral formulation. The frequencies lie in the ratio 0.76:1 (Br:Cl) confirming their assignment as metal–halogen modes.[21] The complex $L(CoCl_2)_2$ exhibits two bands assigned as Co–Cl vibrations, lying close to the position expected for a tetrahedral molecule. The number and position of the bands both confirm the tetrahedral formulation of this complex.

The complex $L(CuCl)_2$ has a strong band at 215 cm^{-1} which, in view of its intensity, is probably a Cu(I)–Cl stretching vibration; the possibility that it is ν(Cu-(I)–N) (azopyridine) cannot be excluded. The bivalent copper complex $L(CuCl_2)_2$ has an electronic spectrum clearly indicative of tetrahedral stereochemistry (or a distorted form thereof). The bands observed at 278 and 324 cm^{-1} are assigned to Cu(II)–Cl stretching vibrations, since two bands are expected and the Cu–N (azopyridine) band is unlikely to exceed 300 cm^{-1} (by extrapolation within Table III). However, the 278-cm^{-1} band may contain both ν(Cu–Cl) and ν(Cu–N).

The copper acetate complex has absorptions at 234 and 263 cm^{-1} which is quite broad and unlike the M–N (azopyridine) absorption noted in the other complexes. For this reason they are not assigned as Cu–N modes. They are probably attributable, with the

band at 351 cm^{-1}, to both ν(Cu–N) and ν(Cu–O) (acetate). $Cu_2(OAc)_4$ itself[37] has strong absorptions, presumably ν(Cu–O), at 330 and 268 cm^{-1}.

It is perhaps worthwhile stressing here that none of the assigned bands is likely to arise from a pure vibration but will in general be a mixture of metal–ligand modes and other vibrations of the same symmetry.

Magnetic Properties.—The nickel complexes have magnetic moments which are in accord with their formulation as octahedral molecules.[38] The copper(I) complexes are diamagnetic as expected. The complexes $L(CuCl_2)_2$ and $L_2Cu(NCS)_2$ have normal magnetic moments for d^9 ions while the complex $L(Cu(OAc)_2)_2$ has a depressed moment typical of the binuclear copper acetate series[24] (Table II).

The complexes L_2CoX_2 have moments near 4.7 BM. This is in the so-called tetrahedral region[38] for cobalt(II). If the electronic spectra of these complexes are interpreted in terms of a tetrahedral stereochemistry, then Dq may be calculated to be about 500 cm^{-1}. Assuming a value for the spin–orbit coupling coefficient $(-\lambda)$ of about 160 cm^{-1}, the magnetic moments of these complexes are calculated[38] to be not greater than about 4.5 BM. The observed moments are therefore inconsistent with a tetrahedral stereochemistry. The higher magnetic moments observed in octahedral cobalt(II) complexes arise as a consequence of the orbital triplet ground state generating an orbital contribution. If the symmetry of the complex is lower than cubic, the degeneracy of the orbital triplet will be partially or wholly removed and the orbital contribution decreased or eliminated. The moments of about 4.7 BM observed for the complexes under discussion lie at the lower end of the octahedral region[38] and are consistent with a distorted octahedral environment.

The complex $L(CoCl_2)_2$ has a low moment suggestive perhaps of a metal–metal interaction. This is in contrast to the magnetic moment of the apparently analogous $L(CuCl_2)_2$ complex, which is normal. Both complexes are believed to contain a tetrahedral chromophore on the basis of their vibrational and electronic spectra. There are however, significant differences in their –N=N– stretching and pyridine ring breathing frequencies. While the copper complex has ν(N=N) at 1397 cm^{-1} and the breathing mode at 1005 cm^{-1} typical of a series A complex, the corresponding bands lie at 1410 and 1020 cm^{-1} in the cobalt derivative more typical of a series B complex. The exact structure of this cobalt complex remains unknown.

Electronic Spectra. (i) **Transitions within the Ligand.**—The ultraviolet spectrum of the free ligand consists essentially of three bands. Our sample, which is predominantly the *trans* isomer, exhibits a band at 21,880 cm^{-1} attributable to an n–π^* transition, a band at 32,100 cm^{-1} (labeled A) attributed to a π–π^* transition encompassing the whole molecule, and a band at 45,450 cm^{-1} (labeled B) attributed to a π–π^* transi-

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(36) C. D. Burbridge and D. M. L. Goodgame, *J. Chem. Soc., A*, 1074 (1968).
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(38) J. Lewis, *Sci. Progr.* (London), **51**, 452 (1963).

tion localized predominantly on the pyridine rings. These labels and assignments follow those for azobenzene.[39] The data confirm the less detailed information reported in an earlier communication[40] which also considered the *cis* isomer (Table II).

The spectra of all of the complexes in the ultraviolet region are dominated by the two intense bands of the ligand. These lie at approximately the same energies as in the *trans* form of the ligand (the *cis* form has bands at 22,400 and 35,200 cm^{-1}; band B was not reported),[40] suggesting that in all of the complexes, *in solution*, the ligand has a *trans* conformation. Since many of the complexes undergo change in solution, as indicated by their ligand field absorption, this information cannot necessarily be extended to the solid state.

A shift occurs in both the A and B bands on coordination, the shift in the former being the greater. Band A exhibits a bathochromic shift in all of the complexes except in the copper acetate complex which gives a slight, hypsochromic shift. No correlation of the shifts in the A band with the metal ion could be made.[41,42] One result that does stand out is the position of band B in the complex FeL_2NCS_2; the shift is much larger than in the complexes of the other metal ions. Since the band is essentially associated with the pyridine rings, a considerable interaction must occur, in the ferrous complex, between the metal ion and the pyridine rings.

A third intense band occurs in the complex [Cu(OAc)₂]₂L at 39,290 cm^{-1}. This is assumed to be associated with the copper acetate dimer unit. A similar intense band at 40,000 cm^{-1} reported in the spectrum of copper acetate monohydrate has been attributed to charge transfer within the copper acetate dimer unit.[43]

The weak $n-\pi^*$ visible transitions of the ligand cannot be readily distinguished from the d–d transitions and possible charge-transfer bands in the complexes (see below).

(ii) Charge-Transfer Spectra.—Very intense transitions are observed in the visible spectra of cuprous and ferrous complexes of π-acceptor ligands such as bipyridyl, 1,10-phenanthroline,[44–46] and related diamine ligands.[47,48]

These bands have been assigned as metal to ligand charge-transfer transitions involving transfer of an electron from the metal d orbitals to π^* orbitals of the ligand.[41,49,50]

Similar intense absorption is observed in the spectra of cuprous and ferrous azopyridine derivatives. The complexes $L(CuCl)_2$ and $L(CuI)_2$ exhibit bands at 16,370 and 15,950 cm^{-1}, respectively, assigned as $(core)d^{10} \rightarrow (core)d^9\pi^*$ transitions. The bands lie at far too low an energy to be assigned as halogen to metal charge transfer.[51,52]

The complexes appear to be insoluble in all common solvents other than pyridine, in which they are partially solvolyzed. The 16,000-cm^{-1} band appears in pyridine with a molar intensity of 10^2–10^3 M^{-1} cm^{-1} but the species does not obey Beer's law. An intense band assigned as Cu(I)→pyridine (d → π^*) charge transfer appears in pyridine solution at 31,250 cm^{-1} and is observed at almost this identical frequency when cuprous chloride is dissolved in pyridine.

The ferrous complex has charge-transfer absorption with a maximum at 13,950 cm^{-1} and a shoulder at 17,860 cm^{-1}. The band envelope is more characteristic of a bidentate than a tridentate imine ligand.[47,48] The complex is blue rather than the more customary red (of, for example $Fe(dipy)_3^{2+}$)[26] because the band has shifted considerably into the red end of the visible spectrum. In fact, to the authors' knowledge, the azopyridine iron derivative exhibits the lowest energy charge-transfer band ever reported for a diamine ligand coordinated to iron(II). The significance of this is discussed below. In acetonitrile two maxima are observed (Table II) at almost the same energies as the bands observed in the solid state, suggesting that the species dissolves unchanged. Of the two maxima, that at lower energy (14,170 cm^{-1}) is the more intense. The transition responsible for this absorption is $(core)t_{2g}^6 \rightarrow (core)t_{2g}^5\pi^*$. The presence, in solution, of two peaks, rather than a peak and a shoulder, as in the solid, is atypical for a bidentate ligand.[47,48]

(iii) Ligand Field Absorption.—The ligand azopyridine is colored, with $n-\pi^*$ absorption as low as 21,880 cm^{-1}, and only the low-energy ligand field absorption is likely to be useful as a guide to stereochemistry. In class B complexes one of the two aza lone pairs remains essentially unperturbed and should give rise to $n-\pi^*$ absorption in much the same region as the parent ligand. All of the class B complexes show absorption around 20,000–22,000 cm^{-1} which is generally poorly resolved and is likely to arise from both ligand-field and $n-\pi^*$ absorption. The complexes $L(CuCl)_2$ and $L(CoCl_2)_2$ each show a band just below 23,000 cm^{-1} which is probably attributable to the $n-\pi^*$ ligand transition. If both the aza nitrogen atoms are coordinating to metals, we might have expected the band to move to a somewhat higher energy than this.

No electronic absorption is noted below 10,000 cm^{-1} in the spectra of the two yellow-green nickel(II)

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complexes confirming that these complexes are not tetrahedral.[51,52] The band observed near 10,900 cm^{-1} in each complex can safely be attributed to the $^3T_{2g} \leftarrow$ $^3A_{2g}$ transition of an octahedral nickel ion. This transition has an energy equal to $10Dq$. The crystal field strength of azopyridine, toward nickel(II), is seen to be comparable to that of other aromatic amines[51,53] though perhaps a trifle low.[53] Because of the perturbing effect of the ligand visible absorption, it would not be reasonable to calculate the Racah parameter B from the positions of the higher energy d–d bands or, indeed, even to assign them.

The complex $L(CoCl_2)_2$, which is intensely colored in the solid state, absorbs well below 10,000 cm^{-1} indicating an essentially tetrahedral rather than octahedral environment about the cobalt atom.[51,52] The solution spectrum of the complex is in general different from the solid-state spectrum. Indeed in many solvents, the initial blue color changes to red over a period of hours.

The complexes CoL_2X_2 absorb at higher energies than $L(CoCl_2)_2$. The lowest energy band lies at 8300, 8510, and 10,450 cm^{-1} in the chloride, bromide, and thiocyanate, respectively. This is consistent with an octahedral rather than tetrahedral environment about the cobalt atom. The band is assigned to the transition $^4T_{2g} \leftarrow {}^4T_{1g}$ and may be compared[54] with 8655 cm^{-1} for the corresponding band in the octahedral $Co(py)_4(CCl_3CO_2)_2$.

The solution spectra of these derivatives are complicated and differ from the solid, and it seems likely that a tetrahedral–octahedral equilibrium is set up.

The complex $L(CuCl_2)_2$ exhibits a broad band below 10,000 cm^{-1} clearly indicative of a tetrahedral (or distorted tetrahedral) rather than square or octahedral environment[55] about the copper atom. This low-energy band disappears when the complex is dissolved in acetonitrile, to be replaced by a single band at 17,900 cm^{-1} indicative of a square configuration about the copper atom.[51,52] A band observed at 21,800 cm^{-1} in this solution is presumably the ligand n–π^* transition. The ligand is still coordinated to the copper atom since the ultraviolet spectrum of the solution differs from that of the free ligand. It seems probable that the acetonitrile has broken the aza nitrogen to copper bonds.

The complex $CuL_2(NCS)_2$ does not absorb below 10,000 cm^{-1} and cannot therefore be tetrahedral.[55] The band observed at 15,160 cm^{-1} in the diffuse reflectance spectrum of the solid is consistent with an octahedral (or tetragonal six-coordinate) environment about the copper atom.

The complex $L(Cu(OAc)_2)_2$ has a band at 14,410 cm^{-1} which may be compared with 14,750 cm^{-1} exhibited[23] by $Cu_2(OAc)_4py_2$.

Back-Donation in $FeL_2(NCS)_2$.—Extensive delocalization of the $t_{2g}{}^6$ electrons of a spin-paired iron(II) atom is believed to occur when it is coordinated by an

unsaturated polydentate amine.[11,35,56–58] There is evidence that a strong interaction also occurs with azopyridine. The following data may be interpreted in this context.

(a) The Fe–N (azopyridine) stretching frequency being some 100 cm^{-1} higher than the other divalent ions studied is indicative of a strong iron–ligand interaction. The spin-paired ion is smaller and has a higher effective nuclear charge than the other divalent species under consideration and its greater polarizing power may be the reason for the greater interaction. The presence of any delocalization, by increasing the bond order of the metal–nitrogen bond, would also increase the observed stretching frequency.

(b) The –N=N– stretching frequency is significantly lower than observed in the other complexes. Overlap of iron t_{2g} orbitals with π-antibonding orbitals associated with the aza linkage would lead to just such a reduction. Considerable reduction of the C=N stretching frequency in spin-paired iron complexes of diimine ligands has been previously noted.[56]

(c) The Fe–N (NCS) stretching frequency is also higher in energy than any of the other metal thiocyanate stretches observed. The small size of the iron atom and/or enhanced back-donation of electrons to the azopyridine group leading to an increased positive charge on the iron atom and therefore a greater ionic interaction with the thiocyanate group would cause this effect.

(d) No ring-breathing mode is observed above 1000 cm^{-1}. The increase in the frequency of this mode upon coordination (free ligand, 990 cm^{-1}) may be viewed as a tightening of the ring caused by the metal ion draining out some electron density. No such increase is observed in the case of iron. Instead a single band is observed at 992 cm^{-1} presumably arising from both the coordinated and uncoordinated pyridine residues. Apparently the release of electron density back into the ring by a π mechanism compensates for the drainage of electrons out by a σ mechanism, and the band does not move. The $Fe(dipy)_3{}^{2+}$ ion exhibits the same phenomena but to a less marked extent. The ring-breathing mode is observed at 995 cm^{-1} in dipyridyl, near 1020 cm^{-1} in tris-dipyridyl complexes of cobalt(II), nickel(II), and copper(II), but at 1008 cm^{-1} in the corresponding spin-paired iron(II) complex.[9]

(e) The considerable decrease in energy of band B in the ultraviolet spectrum of the iron complex has already been cited as an indication of a strong interaction between iron and ring. This is not necessarily a π interaction since the ligand π orbitals which combine with the metal t_{2g} functions do not necessarily correspond with those responsible for the ultraviolet absorption.[59]

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(f) The iron to azopyridine charge-transfer band lies at an exceptionally low energy. Other things being equal, the difference in energy between the metal t_{2g} orbitals and the empty ligand orbitals into which they are delocalized (which are higher in energy than the metal t_{2g} orbitals) will be smaller in this case than in the imine ligands previously investigated. This situation will favor extensive delocalization. We might anticipate that the extent of π delocalization will increase with decreasing energy of the iron to ligand charge-transfer band.

All of the items are indicative of a remarkably strong interaction between the iron atom and azopyridine. The items (b) and (d) seem especially indicative of a π-delocalization mechanism playing an important role in this interaction.[58] If item (d) is correctly interpreted, we may infer that the iron atom should act as an electron-donating substituent in determining, for example, the substitution pattern of the ligand. Experiments to see if this is so are being undertaken.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF PITTSBURGH, PITTSBURGH, PENNSYLVANIA 15213

Circular Dichroism of Cobalt(III) Complexes with Ethylenediamine-N,N'-diacetic Acid and a Carbonate, Oxalate, or Malonate Anion[1]

By CAROLYN W. VAN SAUN AND BODIE E. DOUGLAS

Preparation and resolution procedures are reported for a series of cobalt(III) complexes with the tetradentate ligand ethylenediamine-N,N'-diacetic acid (EDDA) and a carbonate, oxalate, or malonate anion. Proton magnetic resonance was used to establish the *trans* coordination of the oxygens of EDDA in isomers studied. Absolute configurations of the new complexes are assigned by comparison of their CD curves with that of $(+)_{589}$-*trans*-Co(EDDA)en$^+$, for which the absolute configuration is known. Rotational strengths of the d–d transitions were found to be determined largely by the EDDA and to be quite insensitive to the bidentate ligand used.

Introduction

While the relationship between the absolute configuration of cobalt(III) complexes containing chelate rings and the sign of the Cotton effects of their d–d transitions has received considerable attention,[2] the magnitude of the rotational strengths of these transitions has not been studied systematically. Reasons for variations in intensities of circular dichroism (CD) bands within and between series of related complexes are not known.

With the aim of assessing the influence of ring size on rotational strength, a new series of cobalt(III) complexes has been prepared with each complex containing the tetradentate ligand ethylenediamine-N,N'-diacetate (EDDA) and a carbonate or a dicarboxylate anion. The anions used were carbonate, oxalate (ox), and malonate (mal) giving four-, five-, and six-membered chelate rings, respectively. The geometrical isomers studied were those with the coordinated oxygens of the EDDA *trans* to one another.

For the previously studied complexes containing these bidentate anions, no consistent relationship between ring size and rotational strength has been found.

For the complex ions Co(en)(ox)$_2^-$ and Co(en)(mal)$_2^-$, it was found that the rotational strength in the visible region for the malonato complex was approximately twice that for the oxalato complex.[3] On the other hand, for the ions Co(gly)(ox)$_2^{2-}$ and Co(gly)(mal)$_2^{2-}$, the rotational strength in the visible region for the oxalato complex is about twice that for the malonato complex.[4] For the series Co(en)$_2$X$^+$, where X = CO$_3^{2-}$, ox, or mal, the carbonato complex gave the highest rotational strength and the malonato complex gave the lowest, but it was thought that complete resolution was not achieved for the malonato complex.[5] More circular dichroism data are needed to determine whether it is ring size or some other property of these anions which is important for determining the rotational strengths of the d–d transitions of these complexes.

Experimental Section

The optically active isomers of the new complexes are characterized by (+) or (−), the sign of the lowest energy CD maximum.

Ethylenediamine-N,N'-diacetic acid was obtained from K & K Laboratories, Inc., or from Pfaltz and Bauer, Inc., and used without further purification.

(1) This work was supported, in part, by a research grant (GM 10829-10) from the Division of General Medical Studies, Public Health Service.
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