$(S_1 \cdot S_2)^2$ can be multiplied by $S_{1z}{}^2$, $S_{3z}{}^2$, $S_{1z}S_{2z}$, $S_{1z}S_{3z}$, and $S_{3z}S_{4z}$. The last two terms will have vanishing expectation values as will all terms which are linear in a spin operator for one of the atoms. The first two are equal to $S(S+1)\langle(S_1 \cdot S_2)^2\rangle_0/3$ since $\langle(S_1 \cdot S_2)^2S_{1z}{}^2\rangle_0 = \langle(S_1 \cdot S_2)^2S_{1x}{}^2\rangle_0 = \langle(S_1 \cdot S_2)^2S_{1y}{}^2\rangle_0 = \langle(S_1 \cdot S_2)^2S_1{}^2\rangle_0/3$. In our basis the diagonal part of $(S_1 \cdot S_2)^2$ is

$$S_{1z}{}^2S_{2z}{}^2 + (S_{1+}S_{1-}S_{2-}S_{2+} + S_{1-}S_{1+}S_{2+}S_{2-})/4 =$$
$$S_{1z}{}^2S_{2z}{}^2 + [S^2(S+1)^2 - S(S+1)(S_{1z}{}^2 + S_{2z}{}^2) +$$
$$S_{1z}{}^2S_{2z}{}^2 - S_{1z}S_{2z}]/2$$

We now see

$$\langle(S_1 \cdot S_2)^2S_{1z}{}^2\rangle_0 = \langle(S_1 \cdot S_2)^2S_{3z}{}^2\rangle_0 = S^3(S+1)^3/9$$

which could also be determined from symmetry considerations. The diagonal part of $(S_1 \cdot S_2)^2$ also allows us to determine

$$\langle(S_1 \cdot S_2)^2S_{1z}S_{2z}\rangle_0 = -S^2(S+1)^2/18$$

The only remaining contributions from $W^2S_z{}^2$ are from

$$\langle(S_1 \cdot S_2)(S_1 \cdot S_3)S_{2z}S_{3z}\rangle_0 = \langle S_{1z}{}^2S_{2z}{}^2S_{3z}{}^2\rangle = S^3(S+1)^3/27$$

By similar considerations we find the results

$$\langle S_z{}^2\rangle_0 = nS(S+1)/3$$

$$\langle S_z{}^4\rangle_0 = (5n-2)nS^2(S+1)^2/15 - nS(S+1)/15$$

$$\langle W\rangle_0 = 0$$

$$\langle WS_z{}^2\rangle_0 = -2S^2(S+1)^2 \Sigma'J_{ij}/9$$

$$\langle WS_z{}^4\rangle_0 = -[4(5n-4)S^3(S+1)^3 - 8S^2(S+1)^2]\Sigma'J_{ij}/45$$

$$\langle W^2\rangle_0 = 2S^2(S+1)^2\Sigma'J_{ij}{}^2/3$$

$$\langle W^2S_z{}^2\rangle_0 = 2S^2(S+1)^2[nS(S+1) - 1]\Sigma'J_{ij}{}^2/9 + 8S^3(S+1)^3\Sigma'J_{ij}J_{ik}/27$$

$$\langle W^3\rangle_0 = 2S^2(S+1)^2 \Sigma'J_{ij}{}^3/3 - 8S^3(S+1)\Sigma'J_{ij}J_{ik}J_{jk}/9$$

$$\langle W^3S_z{}^2\rangle_0 = -4[2S^4(S+1)^4/15 - (4/45 + n/18) \times S^3(S+1)^3 + 4S^2(S+1)^2/45]\Sigma'J_{ij}{}^3 - 8[2S^4(S+1)^4 - S^3(S+1)^3]\Sigma'J_{ij}{}^2J_{ik}/9 - 8[nS^4(S+1)^4 - S^3(S+1)^3]/27\Sigma'J_{ij}J_{ik}J_{ki} - 4\Sigma'J_{ij}{}^2J_{kl}S^4(S+1)^4/9 - 8\Sigma'J_{ij}J_{jk}J_{kl}S^4(S+1)^4/27$$

Four-, Five-, and Six-Coordinate Metal Complexes of Di(2-pyridyl) Disulfide and 1,2-Di(2'-pyridyl)ethane.   Further Studies of the Infrared Spectra of Pyridine–Metal Complexes

BY M. KEETON AND A. B. P. LEVER*

Complexes of cobalt(II), nickel(II), zinc(II), and mercury(II) with the ligands di(2-pyridyl) disulfide and 1,2-di(2'-pyridyl)-ethane are described. The cobalt complexes are tetrahedral, while tetrahedral, square-planar, and five-coordinate complexes of nickel are characterized. Utilization is made of electronic spectra, vibrational spectra (conventional and far-infrared), and magnetism in structural diagnosis. A detailed comparison of the bonding characteristics of the two closely related ligands is made. It is shown that in the five-coordinate complexes, the ligands span equatorial and axial sites. The sulfur atoms of the disulfide ligand are not involved in coordination except in the mercury complex.

There has been extensive interest[1] in the chemistry of ligands formed by the linkage of two pyridine residues, in the ortho position, by various groups such as $-CH_2-$, $-NH-$, $-CH_2NHCH_2-$, $-CO-$, $-S-$, $-CH{=}CH-$, $-SO_2-$, $-CH_2CH_2XCH_2CH_2-$ (X = S, NH), $-N{=}N-$, etc.

In most cases the bridging atom(s) is (are) not involved in coordination to the metal and the ligand behaves essentially as a sterically hindered 2-substituted pyridine. When coordination by the bridging group does occur, as for example with $-CH_2CH_2SCH_2CH_2-{}^2$ or with $-N{=}N-$,[3] complexes of interesting stereochemistry are obtained.

The complexing ability of di(2-pyridyl) disulfide (LS) was investigated in the hope that this very simple ligand would give rise to five-coordinate complexes. This in fact it does although, surprisingly, the sulfur atoms are not involved.

As a model for comparison purposes, the pyridine analog of ethylenediamine, 1,2-di(2'-pyridyl)ethane (LE) was also studied.

LN

LS

LE
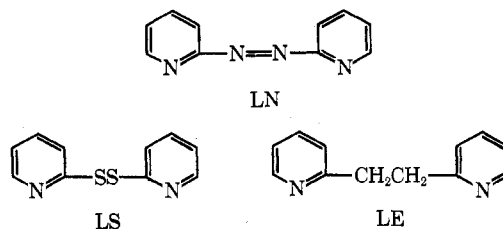
* To whom correspondence should be addressed.
(1) W. R. McWhinnie, *Coord. Chem. Rev.*, in press
(2) S. M. Nelson and J. Rodgers, *Inorg. Chem.*, **6**, 1390 (1967).
(3) D. A. Baldwin, A. B. P. Lever, and R. V. Parish, *ibid.*, **8**, 107 (1969).

Vibrational (conventional and far-infrared) (Tables I and II) and electronic spectroscopy (Table III) and

TABLE I

INFRARED CHARACTERISTICS[a]

Region, cm^{-1}	Assignment	No. of bands in each region					
		Series 1		Series 2		Series 3	
		LS	LE	LS	LE	LS	LE
380–450	ϕ(C–C)	2	2	2	2	2 (3)	3 (4)
630–660	α(C–C–C)	1	1	2	2	1 (2)	2
700–810	ϕ(C–C), γ(C–H)	3 (4)	3 (4)	4	4	4–6	4–6
990–1040	Ring, A$_1$	1 (2)	1 (2)	1 (2)	1	2	2 (3)
1400–1500	ν(C–C, C–N)	3	2 (3)	2 (3)	3	4–6	6
1500–1650	ν(C–C, C–N)	2 (3)	2	2 (3)	2 (3)	3	35

[a] Series 1: CoLBr$_2$, CoLI$_2$, CoL(NCS)$_2$, Ni(LE)Br$_2$, NiLI$_2$, Hg$_2$(LE)Cl$_4$. Series 2: CoLCl$_2$, Ni(LE)$_2$(ClO$_4$)$_2$. Series 3: NiLCl$_2$, NiL(NCS)$_2$, Ni(LS)Br$_2$, ZnLCl$_2$ (L = LE and LS).

magnetism (Experimental Section) were employed to identify the products obtained. Complexes of cobalt-(II), nickel(II), copper(II), zinc(II), and mercury(II) have been characterized. The two ligands behave very

12 spectrophotometer. Metal and halogen analyses were by the authors and C, H, and N analyses were by Galbraith Laboratories, Inc., Knoxville, Tenn. 37921. Magnetic measurements were obtained by the Faraday method using an Alpha (4-in.) variable-temperature magnetic balance, calibrated with mercury tetrathiocyanatocobaltate(II). A Wayne Kerr B221A universal bridge was employed for the conductivity determinations.

Complexes of Di(2-pyridyl) Disulfide.—The ligand was obtained commercially from Aldrich under the trade name 2,2'-Aldrithiol.

Ni(LS)Cl$_2$.—Equimolar solutions of hydrated nickel chloride and di(2-pyridyl) disulfide in ethyl alcohol (absolute) were mixed while hot and stirred on the steam bath. After 15 min the yellow-green product had crystallized out and was removed by filtration from the hot solution. It was recrystallized from ethyl alcohol (yield 90%). *Anal.* Calcd for C$_{10}$H$_8$Cl$_2$N$_2$NiS$_2$: C, 34.3; H, 2.3; Cl, 20.3; Ni, 16.8. Found: C, 34.1; H, 2.15; Cl, 19.9; Ni, 16.6.

Ni(LS)Br$_2$.—This was prepared by the method used above for the dichloride giving a yellow-green crystalline product (yield 90%). *Anal.* Calcd for C$_{10}$H$_8$Br$_2$N$_2$NiS$_2$: C, 27.4; H, 2.1; Br, 36.4; Ni 13.4. Found: C, 27.2; H, 1.8; Br, 36.1; Ni, 13.4.

Ni(LS)(NCS)$_2$.—Equimolar solutions of nickel thiocyanate and

TABLE II

FAR-INFRARED SPECTRA (450–190 CM^{-1})

Complex	Ligand bands						M–N (L)				M–X			Unassigned	
LS (free ligand)	437 w	428 m	402 s	347 s	255 m		...				...				
LE (free ligand)	401 s	(392)	277 m				...				...				
Co(LS)Cl$_2$	427 m	416 s	336 s	(252)			242 ms	231 mw			(325)	297 s			
Co(LE)Cl$_2$	432 s	415 s	277 w				252 s				333 s	309 s		360 m	
Co(LS)Br$_2$	427 m	416 s	344 m	323 s			245 ms				267 s	217 s			
Co(LE)Br$_2$	430 s	403 mw	266 s				247 ms				273 s	229 s		343 m	
Co(LS)I$_2$	421 m	418 s	351 w	335 m	253 m		232 m				208 s				
Co(LE)I$_2$	431 s	404 mw	271 m				251 ms	231 s			211 ms			345 s	
Co(LE)(NCS)$_2$	427 s	407 mw	(270)				262 s				320 s	300 s		350 s	
Ni(LS)Cl$_2$	432 m, b	421 m	(350)	335 ms	260 s, b^a		(230)				(278)				
Ni(LE)Cl$_2$	444 m	(437)	426 s	401 s	(260)		(245)	236 m			300 s	293 s	ϵ		
Ni(LS)Br$_2$	440 w	427 m	413 m	340 w	328 s	261 m	237 ms				212 ms				
Ni(LE)Br$_2$	430 s	405 mw	(265)				251 s				270 s	219 s			
Ni(LS)I$_2$	428 s	407 mw	268 m				253 m	225 s			207 m				
Ni(LS)(NCS)$_2$	430 m	422 m	414 m	345 w	334 m	253 m	253 m^b				(280)	267 s	217 s		
Ni(LE)(NCS)$_2$	437 s	(432)	422 m	403 m	265 s		252 s				321 s	218 s, b		298 mw	
Ni(LE)$_2$(ClO$_4$)$_2$	437 m	428 m	410 m	260 w			463 s				...			(345)	326 m^c
														303 m	282 m
Zn(LS)Cl$_2$	427 m	415 s	(345)				240 m				323 s	291 s		220 mw	229 mw
Zn(LE)Cl$_2$	427 m	415 m	405 m	351 m	273 m		252 w	230 m	225 m		314 s	(308)	298 s		
Hg(LS)Cl$_2$	431 m	403 s	357 s	277 mw			225 mw?				328 s, b			300 w	
Hg$_2$(LE)Cl$_4$	426 s	410 s					245 m?				295 s			275w	

[a] Probably contains ν(M–N).   [b] Ligand and ν(M–N).   [c] Bands near 300 cm^{-1} are probably N–Ni–N deformation modes z.

similarly toward cobalt(II) and zinc(II), less so toward nickel(II), and have quite different behavior toward copper(II) and mercury(II). Both the metal ions and the ligands will have preferred bonding characteristics; it would appear that in the case of cobalt, for example, the requirement of the metal overrides that of the ligands, while for the stereochemically much more adaptable copper ion, the ligands dictate what kind of complex will be formed. This paper describes the complexes of cobalt(II), nickel(II), zinc(II), and mercury-(II); the chemistry of the copper(II) ion with these ligands will be published elsewhere.[4]

Experimental Section

Electronic (visible and near-infrared) spectra were recorded with an Applied Physics Cary 14 spectrophotometer, using a Beckman VLT-2 variable-temperature cell (with quartz windows) for the low-temperature work. Infrared and far-infrared data were obtained as Nujol or HCBD mulls with a Beckman IR

(4) M. Keeton, A. B. P. Lever, and B. S. Ramaswamy, *Can. J. Chem.*, in press.

di(2-pyridyl) disulfide in ethanol were mixed while hot and stirred while being allowed to cool. The product separated out as small pale green crystals and was recrystallized from ethanol (yield 90%). *Anal.* Calcd for C$_{12}$H$_8$N$_4$NiS$_4$: C, 36.5; H, 2.0; Ni, 14.85. Found: C, 36.0; H, 2.1; Ni, 14.6.

Co(LS)Cl$_2$.—Equimolar solutions of cobalt chloride and the ligand in ethyl alcohol were mixed while hot; the product separated almost immediately as large blue crystals. It was recrystallized from ethyl alcohol (yield 95%). *Anal.* Calcd for C$_{10}$H$_8$Cl$_2$CoN$_2$S$_2$: C, 34.3; H, 2.3; Cl, 20.25; Co, 16.8. Found: C, 34.1; H, 2.2; Cl, 20.6; Co, 16.8.

Co(LS)Br$_2$.—The same method was used for the dibromide as was used for the dichloride giving a royal blue crystalline product (yield 95%). *Anal.* Calcd for C$_{10}$H$_8$Br$_2$CoN$_2$S$_2$: C, 27.35; H, 1.8; Br, 36.4; Co, 13.4. Found: C, 27.4; H, 1.9; Br, 36.2; Co, 13.3.

Co(LS)I$_2$.—The procedure followed that of the other cobalt halide complexes. The product was microcrystalline and colors ranged from light green to dark green depending on the size of crystals making up the individual sample. It was recrystallized from ethyl alcohol (yield 85%). This complex was exceedingly difficult to analyze for C and H. *Anal.* Calcd for C$_{10}$H$_8$-CoI$_2$N$_2$S$_2$: Co, 11.05; I, 47.6. Found: Co, 11.0; I, 47.9.

TABLE III

ELECTRONIC SPECTRA (CM^{-1})

(a) Mull Transmittance Spectra[a]

Ni(LS)Cl$_2$	rt 7140, (11,760), 13,790, 23,530
	lt 6890, 8500, (11,630), 12,050, 13,890, 19,050 w, 23,530
Ni(LS)Br$_2$	rt 6990, (8000), (11,430), 13,440, 22,980
Ni(LS)(NCS)$_2$	rt 8170, 15,150, (25,000)
	lt 8475, (13,790), 15,750, (25,000)
Co(LS)Cl$_2$	rt 6890, 9260, (16,000), 16,390, (17,390), (20,000 w)
	lt (6600), 7520, 9300, (14,810), (15,380), 16,390, 17,390, 20,000 w
Co(LS)Br$_2$	rt 6450, 8560, 15,380, (15,870), 16,950, (18,050 w), (20,410 w)
	lt 6670, 8810, 15,380, 15,920, 16,810, 19,050 w, 20,620 w
Co(LS)I$_2$	rt (6060), (6890), 8000, (12,820), (14,600), 15,150, 16,000
	lt (6050), (7080), 8165, (12,740), (14,600), 15,040, 16,000, (23,260)
Ni(LE)Cl$_2$	rt 5200,[b] (9855), (11,760), 12,930, (16,670 w), (19,230)
	lt 5525,[b] (9760), 10,425, (11,760), 13,070, 17,240 w, 20,410, 23,260
Ni(LE)Br$_2$	rt 8000 w, 10,260, 11,360, 14,930, 18,500, 23,260 w
	lt 8340,[c] 10,750, 11,760, 15,750, 18,520, 23,260
Ni(LE)I$_2$	rt 7810 w, 10,150, 10,810, 14,550, (16,600), 17,670, 21,980, 23,530
	lt 7970,[c] 10,260, 10,910, 14,390, (16,950), 17,700, 21,510, 25,320
Ni(LE)$_2$(ClO$_4$)$_2$	rt 25,000
Ni(LE)(NCS)$_2$	rt (6025), (6580), 9525 w, (11,560), (12,800), 15,150
	lt 6625, (7025), 9850 w, 11,560 w, 12,500, 15,380, (17,390), (19,190)
Co(LE)Cl$_2$	rt 6390, 7690, 9570, 16,390, 17,390, (18,870 w), (21,050)
	lt 6390, 7690, 9645, 16,260, 16,670, (17,390), 19,230 w, 20,000 w, 21,280 w
Co(LE)Br$_2$	rt (6370), 6710, 8890, 15,620, (16,000), 17,090, (19,050), 20,410 w, etc.
	lt 6310, (6580), 8850, 15,620, (15,380), 17,090, 18,520 w, 19,050 w, etc.
Co(LE)I$_2$	rt (6150), 6760, 8510, 14,810, 15,620, (16,180), 18,870 w, 19,420 w, etc.
	lt (6150), 6670, 8510, 12,120 w, 14,600, 15,620, (16,260), 17,390 w, etc.
Co(LE)(NCS)$_2$	rt (7690), 8510, (9090), 16,810, (17,700), (20,410), (25,000)
	lt 7840, 8620, 9090, 16,670 (17,040), 19,610 w, 20,280 w, etc.

(b) Solution Spectra in Acetonitrile (Extinction Coefficients in Parentheses Immediately Following Energies)

Co(LS)Cl$_2$	7100 (47), 8770 (31), (15,770), 16,385 (406), 17,390 (311)
Ni(LS)(NCS)$_2$	9420 (14), 15,900 (20)
Co(LE)Cl$_2$	6450 (45), 7620 (69), 9645 (54), (15,845), 16,480 (593), 17,420 (379)
Co(LE)Br$_2$	6300 (49), 7270 (81), 9270 (74), 15,570 (897), (16,000), 16,920 (494)
Ni(LE)(NCS)$_2$	6415 (E = 0.6),[d] 10,460 (E = 0.4),[d] 15,315 (E = 1)[d]
Ni(LE)Br$_2$	10,360 (53), (11,430), 11,700 (38), 16,465 (128), 18,340 (113), 22,610 (48)
Ni(LE)I$_2$	10,250 (27), 10,810 (31), 15,180 (80), (16,830), 17,920 (95), (22,200), 27,600 (4140)

[a] rt, room temperature: lt, liquid nitrogen temperature. Parentheses indicate shoulders; etc. refers to a large number of weak spin-forbidden transitions which are exceptionally well resolved at low temperature. [b] Number of shoulders observed on the high-frequency edge of this band probably derive from ligand overtones. [c] Weak multiple absorption in this region, probably vibrational modes of the ligand. [d] Insufficiently soluble for an accurate determination of the extinction cofficients, optical densities are quoted.

Hg(LS)Cl$_2$.—This complex was prepared in high yield as a white solid of very low solubility by reaction of stoichiometric proportions of the ligand with mercuric chloride in hot ethanol. *Anal.* Calcd for C$_{10}$H$_8$Cl$_2$HgN$_2$S$_2$: C, 24.4; H, 1.6; Cl, 14.4. Found: C, 24.3; H, 1.8; Cl, 14.1.

Zn(LS)Cl$_2$.—This was prepared in a similar manner to the mercury complex. *Anal.* Calcd for C$_{10}$H$_8$Cl$_2$N$_2$S$_2$Zn: C, 33.7; H, 2.3; Cl, 19.9. Found: C, 34.2; H, 2.3; Cl, 19.9.

Preparation of 1,2-Di(2'-pyridyl)ethane.—1,2-di(2'-pyridyl)ethylene (5.46 g, 0.03 mol) was dissolved in 250 ml of ethyl acetate and hydrogenated with palladium charcoal (5 mg) as catalyst. The intake of hydrogen was very fast in the initial stage of the reaction but slowed down later and further hydrogenation was very slow. When very little or no hydrogen was being absorbed (about 48 hr), the palladium charcoal was filtered off and the solvent was removed to give 1,2-di(2'-pyridyl)ethane (3.0 g, 90% yield). Crystallization from ethyl acetate gave a white crystalline product melting at 49.5–51° (lit.[5] mp 49–51°).

Ni(LE)Cl$_2$.—Equimolar solutions of 1,2-di(2'-pyridyl)ethane and the metal salt in ethanol were mixed and the complex formed as yellow-green crystals on cooling; it was recrystallized from ethanol (yield 90%). *Anal.* Calcd for C$_{12}$H$_{12}$Cl$_2$N$_2$Ni: C, 45.9; H, 3.85; Cl, 22.6; Ni, 18.7. Found: C, 45.7; H, 3.8; Cl, 22.85; Ni, 18.9.

Ni(LE)Br$_2$.—The same method was used as for the dichloride.

The product, however, was blue (yield 90%). *Anal.* Calcd for C$_{12}$H$_{12}$Br$_2$N$_2$Ni: C, 35.8; H, 3.0; Br, 39.7; Ni, 14.6. Found: C, 35.5; H, 3.0; Br, 40.0; Ni, 14.8.

Ni(LE)I$_2$.—The method used for the chloride and bromide complexes was used for the diiodide. The product was green and highly crystalline (yield 80%). *Anal.* Calcd for C$_{12}$H$_{12}$I$_2$N$_2$Ni: C, 29.0; H, 2.4; I, 51.1; Ni, 11.8. Found: C, 28.8; H, 2.4; I, 50.9; Ni, 11.9.

Ni(LE)(NCS)$_2$.—Equimolar solutions of the metal salt and ligand in ethanol were mixed and allowed to stand at room temperature for several days. Deep green crystals formed and were collected and recrystallized from ethanol (yield 50%). *Anal.* Calcd for C$_{14}$H$_{12}$N$_4$NiS$_2$: C, 46.8; H, 3.4; Ni, 16.3. Found: C, 47.0; H, 3.2; Ni, 16.4.

Ni(LE)$_2$(ClO$_4$)$_2$.—Ethanolic solutions of metal salt and ligand in a 1:2 molar ratio were mixed while hot and the yellow microcrystalline product formed immediately. It was recrystallized from ethanol (yield 95%). *Anal.* Calcd for C$_{24}$H$_{24}$Cl$_2$N$_4$NiO$_8$: C, 46.0; H, 3.85; Ni, 9.4. Found: C, 46.1; H, 4.0; Ni, 9.6.

Co(LE)X$_2$ (X = Cl, Br, I, NCS).—Equimolar solutions of the cobalt salt and ligand in ethanol were mixed. The crystalline product formed immediately for X = Cl, Br, and I; crystals were obtained on standing for X = NCS. All the salts were approximately the same royal blue color and were obtained in high yield. *Anal.* Calcd for C$_{12}$H$_{12}$CoCl$_2$N$_2$: C, 45.9; H, 3.85; Cl, 22.6; Co, 18.8. Found: C, 45.8; H, 3.9; Cl, 22.9; Co, 18.6. Calcd for C$_{12}$H$_{12}$Br$_2$CoN$_2$: C, 35.8; H, 3.0; Br, 39.65; Co, 14.6;

(5) G. Bianchetti, *Farmaco, Ed. Sci.*, **11**, 346 (1956).

mol wt 403. Found: C, 35.9; H, 3.2; Br, 39.55; Co, 14.4; mol wt 460 (ebullioscopically in acetonitrile). Calcd for $C_{12}H_{12}$-CoI_2N_2: C, 29.0; H, 2.4; Co, 11.85; I, 51.1. Found: C, 28.9; H, 2.5; Co, 11.6; I, 51.15. Calcd for $C_{14}H_{12}CoN_4S_2$: C, 46.8; H, 3.4; Co, 16.4. Found: C, 46.6; H, 3.5; Co, 16.25.

$Hg_2(LE)Cl_4$.—This was prepared by the method used for Hg-(LS)Cl₂ using the appropriate stoichiometric proportions. *Anal.* Calcd for $C_{12}H_{12}Cl_4Hg_2N_2$: C, 19.8; H, 1.7; Cl, 19.5. Found: C, 19.5; H, 1.8; Cl, 19.3.

$Zn(LE)Cl_2$.—This was prepared in the same manner as Zn-(LS)Cl₂. It is rather more soluble than the LS derivative and may be recrystallized from ethanol. *Anal.* Calcd for $C_{12}H_{12}$-Cl_2N_2Zn: C, 45.0; H, 3.8; Cl, 22.1. Found: C, 44.8; H, 3.8; Cl, 22.4.

Magnetic Data (20°).—The molar susceptibilities (x'_M) are corrected for the diamagnetism of all the ligands [LE, 120×10^{-6} cgsu; LS, 126×10^{-6} cgsu] through Pascal's constants. The data are as follows: complex, x_g (10^6 cgsu), x'_M (10^6 cgsu), μ_{eff} (BM): Co(LE)Cl₂, 25.73, 8072, 4.39; Co(LE)Br₂, 23.11, 9488, 4.71; Co(LE)I₂, 18.32, 9315, 4.67; Co(LE)(NCS)₂, 27.59, 10074, 4.86; Ni(LE)Cl₂, 15.29, 4955, 3.41; Ni(LE)Br₂, 15.67, 6488, 3.90; Ni(LE)I₂, 11.17, 5755, 3.67; Ni(LE)(NCS)₂, 12.49, 4652, 3.30; Ni(LE)₂(ClO₄)₂, diamagnetic; Co(LS)Cl₂, 24.15, 8614, 4.49; Co(LS)Br₂, 19.27, 8641, 4.50; Ni(LS)Cl₂, 12.88, 4668, 3.31; Ni(LS)Br₂, 9.425, 4332, 3.19; Ni(LS)(NCS)₂, 10.336, 4175, 3.13. In view of the difficulty in obtaining satisfactory C and H analyses for Co(LS)I₂, its magnetic properties are not reported.

Results and Discussion

Infrared Spectra (380–4000 cm⁻¹).—It is well known that the infrared spectra of complexes containing pyridine residues may be reliably used as a guide to pyridine coordination and the criteria employed have been adequately discussed (see ref 3 and references therein). The earlier study[3] of 2,2'-azopyridine (LN) had shown that the complexes prepared could be divided into two series, on the basis of their infrared spectra. Series A, of general formula $(LN)(MX_n)_2$, has structures in which both pyridine residues are coordinated, while series B, of general formula $(LN)_2MX_2$, has structures involving both coordinated and uncoordinated pyridine.

Most of the complexes to be discussed here fall into a general class of complexes of formula LMX_2 (we shall use L when no distinction between LS and LE is implied) and these may be further subdivided into *three* rather than two series according to their infrared spectra (Table I).

Complexes belonging to series I have relatively simple spectra indicative of the presence of a ligand having both pyridine residues coordinated to the metal. Moreover the simplicity of the spectra suggests that the pyridine groups are chemically equivalent and probably related by a symmetry operation. The series II complexes have slightly more complex spectra than those belonging to series I, both pyridine residues again being coordinated. In this series it is suggested that the pyridine residues are essentially equivalent but are not related by a symmetry operation (see further discussion of this point for the cobalt(II) complexes).

The series III complexes have much more complex spectra in which many of the key bands indicative of metal coordination are doubled. Since these bands are, for the most part, significantly shifted from their positions in the free ligand spectrum, the implication is that

both pyridines are coordinated but are not chemically equivalent.

This point is exemplified by consideration of the out-of-plane deformation frequencies near 400 cm⁻¹. Pyridines and substituted pyridines generally exhibit one band near 400 cm⁻¹ which increases in frequency upon coordination of the ligand to a metal. The frequency increase depends upon the metal, and, in general, the more strongly bound the metal ion, the greater the increase in frequency.[6,7]

In the azopyridine series, the complexes involving coordination by only one pyridine residue exhibited two bands in this region attributable to the presence of both coordinated and uncoordinated pyridine. It is relevant that the lower energy band fell within 3–6 cm⁻¹ of the position of the single band in the free ligand.

The series I and II complexes of LS and LE exhibit two bands in the 400-cm⁻¹ region (Table II). This is construed to arise through coupling of the deformation vibrations, the ligands being constrained (in the complexes) to adopt a cis or gauche, but not trans, configuration (with respect to the bridging atoms, see below). The azopyridine complexes, on the other hand, are all believed to involve a trans arrangement about the bridging atoms. In the series III complexes three or four bands may be discerned in this region, the *lowest* of which occurs 7 cm⁻¹ above the free ligand value. Thus the series III complexes are considered to involve coordination by both pyridine residues but with a marked difference in the chemical nature of the two metal–pyridine bonds.

It is pertinent that the complex[4] $Cu_2(LE)(OAc)_4$ exhibits only one band (very slightly split) near 400 cm⁻¹ and is believed to involve the ligand in a trans conformation bridging dimer copper acetate units.

Magnetism.—Magnetic data at room temperature are reported in the Experimental Section. The cobalt-(II) complexes, of empirical formula $LCoX_2$ (X = Cl, Br, I, NCS), have moments in the range 4.39–4.86 BM implying a tetrahedral stereochemistry.[8] This is confirmed by their far-infrared (Table II) and electronic spectra (Table III). The nickel(II) complexes (LE)-NiI₂ and (LE)NiBr₂ have moments of 3.90 and 3.67 BM, respectively; these very high values imply tetrahedral stereochemistry[8] which is confirmed below.

It is convenient to discuss the remaining data in terms of the individual complexes.

Cobalt(II) Complexes.—All of these blue complexes appear to have a tetrahedral stereochemistry, on the basis of their magnetism and far-infrared and electronic spectra. The cobalt–halogen stretching frequencies may readily be picked out from their infrared spectra; these fall within the ranges expected for such compounds[9] and imply covalent metal–halogen bonds. Their electronic spectra (Table III) include the intense multicomponent bands in the near-infrared region

(6) N. S. Gill, R. H. Nuttall, D. E. Scaife, and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, **18**, 79 (1964).

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

(8) J. Lewis, *Sci. Progr.*, **51**, 452 (1963).

(9) R. J. H. Clark, "Halogen Chemistry," Vol. 3, V. Gutman, Ed., Academic Press, New York, N. Y., 1968, p 85.

near 8000 cm^{-1} and in the visible region near 16,000 cm^{-1} as expected.[10]

The complexes $LCoX_2$ (X = Br, I, NCS) fall into series I according to their infrared spectra, while the chloride derivatives both fall into series II. The above data imply a monomeric formulation and in one case this was confirmed by a molecular weight determination. The other complexes are insufficiently soluble. Moreover the solution electronic spectra are closely similar in band energies to the mull spectra of the solid compounds (Table III). The species in the solid state and in solution must be the same. The complexes are assumed therefore to involve the ligand coordinated in a bidentate fashion to the cobalt atom (structure V of ref 3).

Both ligands (LS and LE) are related conformationally to ethylenediamine and may be expected in principle to exist in a cis, trans, or gauche form.[11] In these bidentate cobalt complexes, the trans form is excluded since it would place the pyridine nitrogen atoms too far apart. The cis form would be expected to have a more simple infrared spectrum than the gauche form since in the former case there is a plane of symmetry bisecting the ligand (the complex would also contain a twofold axis of rotation if it adopts a regular form). Molecular models reveal that interaction between the bridging methylene (or sulfur) atoms and the halogen atoms is less in the cis form than in the gauche form. We propose that the series I complexes contain the ligand in its cis conformation while the series II complexes adopt the gauche conformation (which lacks any symmetry elements). It is significant that the larger halogens appear to adopt the conformation offering minimum *interligand* repulsion (cis) while the smallest halogen, chloride, adopts the gauche conformation which is that with the minimum *intraligand* repulsion (within L). Such infrared arguments have not always been successful even with the simpler ethylenediamine ligand, but such an approach seems a useful working hypothesis. To date it has not been possible to obtain any nmr data to use as a means of conformational analysis.

Nickel Complexes.—The nickel complexes have the general formulas $NiLX_2$ (X = Cl, Br, I, NCS) and $Ni(LE)_2(ClO_4)_2$ but unlike the cobalt series, the stereochemistries are not always the same for both ligands.

The intensely colored complexes $Ni(LE)X_2$ (X = Br, I), having moments indicative of a tetrahedral stereochemistry, have electronic spectra (Table III, Figure 1) also consistent with this formulation although the first absorption band (ν_2 in T_d symmetry) is split, an unusual observation for tetrahedral (or pseudotetrahedral) nickel(II).[10] The splitting is believed to be caused by mixing with spin-forbidden transitions (^1E, $^1T_2$) expected in the same region. The positions of the nickel–halogen stretching frequencies in the far-infrared spectrum (Table II) however leave little doubt that a pseudotetrahedral structure is correct.[3,9] In-
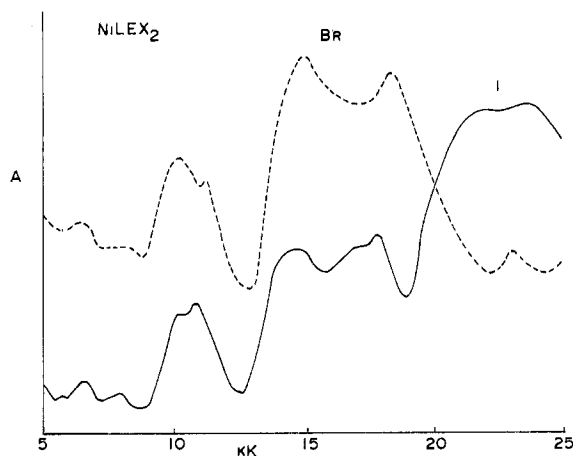

Figure 1.—The electronic spectra of tetrahedral Ni(LE)Br$_2$ and Ni(LE)I$_2$.

deed between 200 and 350 cm^{-1} the infrared spectrum of Ni(LE)Br$_2$ is virtually identical with that of Co(LE)-Br$_2$, and Ni(LE)I$_2$ is almost the same as Co(LE)I$_2$. The chlorides and thiocyanates differ however (see below). The absence of strong absorption bands in the electronic spectrum of the bromide derivative between 19,000 and 30,000 cm^{-1} excludes a five or six or square-planar four-coordinate formulation.[10] Calculation[12] of Dq and B using the center of gravity of the observed multiplets yields $Dq = 583$ and $B = 838$ cm^{-1} for the bromide and $Dq = 565$ and $B = 818$ cm^{-1} (all data ±3 cm^{-1}) for the iodide. These are acceptable values for a tetrahedral NiN_2X_2 chromophore. The band near 22,000 cm^{-1} in the iodide spectrum is a ligand to metal charge-transfer transition split, as expected, by spin–orbit coupling.[13] Calculation of the optical electronegativity of the nickel atom on the basis of the mean band position and the energies of the d–d bands leads[14] to $\chi_{opt}(Ni) = 2.0$ in excellent agreement with that expected for tetrahedral nickel.[10,14] These complexes fit into series I analogous with the corresponding tetrahedral cobalt derivatives and are assumed to involve the bidentate ligand in the cis conformation. The green complex Ni(LS)I$_2$ also belongs to series I and has an analogous tetrahedral stereochemistry; however it was extremely difficult to obtain a pure sample of this complex. Yellow Ni(LS)Br$_2$ is clearly different, belonging to series III with far-infrared and electronic spectra quite inconsistent with tetrahedral nickel(II). Indeed the complexes NiLX$_2$ (L = LS, LE; X = Cl, NCS) and the complex Ni(LS)Br$_2$ all belong to series III.

Comparison of the far-infrared spectra of each complex leads to the fairly ready identification of the metal–halogen or metal–thiocyanate stretching frequencies (Table II, Figure 2). The metal–chloride vibrations occur between 270 and 290 cm^{-1}, while the metal–bromide stretch is observed at 212 cm^{-1}. These values are too low to be associated with a tetrahedral complex and are too high to be associated with an octahedral

(10) A. B. P. Lever, "Inorganic Electronic Spectroscopy," Elsevier, Amsterdam, 1968, p 322.

(11) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Complexes," Wiley, New York, N. Y., 1963, p 186.

(12) A. B. P. Lever, *J. Chem. Educ.*, **45**, 711 (1968).

(13) P. Day and C. K. Jørgensen, *J. Chem. Soc.*, 6226 (1964).

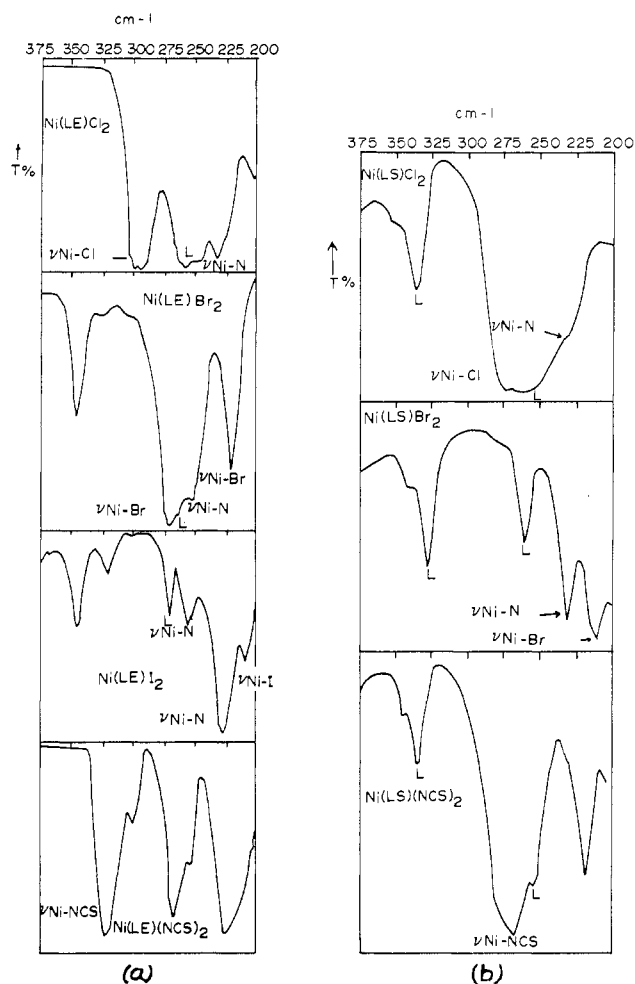(14) C. K. Jørgensen, *Solid State Phys.*, **13**, 376 (1962).

Figure 2.—(a) The far-infrared spectra of the five-coordinate complexes Ni(LE)(NCS)₂ and Ni(LE)Cl₂ and the tetrahedral complexes Ni(LE)Br₂ and Ni(LE)I₂. (b) The far-infrared spectra of the five-coordinate Ni(LS)X₂ (X = Cl, Br, NCS). Note that at liquid nitrogen temperature the broad band envelope in the Ni(LS)Cl₂ complex is clearly resolved into bands at 224 and 231 cm⁻¹ assigned to the nickel–nitrogen stretching modes, 253 cm⁻¹ assigned to the ligand, and 274 cm⁻¹, with a shoulder at 265 cm⁻¹, assigned to nickel–chlorine stretching.

complex.[3,9] While the metal–ligand stretching frequencies in five-coordinate metal complexes have not been systematically studied, it does seem reasonable to suppose that for most metal ions they would lie intermediate in energy between the values observed for four- and six-coordinate complexes in the same spin state. Evidence for this contention is available.[15–18] Thus the far-infrared data exclude both tetrahedral and octahedral formulations for chlorides and bromides and infer a five-coordinate stereochemistry. Their electronic spectra are fully consistent with such a formulation being similar to those of known five-coordinate nickel complexes.[2,10,19]

The position of the metal–thiocyanate stretching

(15) D. J. Bryson and R. H. Nuttall, *Inorg. Nucl. Chem. Lett.*, **5**, 347 (1969).
(16) C. Postmus, J. R. Ferraro, and W. Wozniak, *Inorg. Chem.*, **6**, 2030 (1967).
(17) P. Bamfield, R. Price, and R. G. J. Miller, *J. Chem. Soc.*, 1447 (1969).
(18) V. L. Goedken, J. V. Quagliano, and L. M. Vallarino, *Inorg. Chem.*, **8**, 2331 (1969); *J. Amer. Chem. Soc.*, **92**, 303 (1970).
(19) C. Furlani, *Coord. Chem. Rev.*, **3**, 141 (1968).

frequency is less sensitive to changes in stereochemistry. However the presence of only one strong band assignable to this vibration in the NiL(NCS)₂ complexes precludes a tetrahedral NiL(NCS)₂ covalent formulation. Indeed any tetrahedral formulation, such as an ionic polymer NiLNCS⁺NCS⁻, is eliminated by the electronic spectra of these compounds which are quite dissimilar from those of tetrahedral nickel derivatives.[10] The high energy of the nickel–thiocyanate stretching frequency in the LE complex would also exclude an octahedral formulation for this compound.[3] The electronic spectrum of the Ni(LE)(NCS)₂ complex is closely related to that of the corresponding chloride derivative, but the bands are shifted to higher energies (Figure 3).
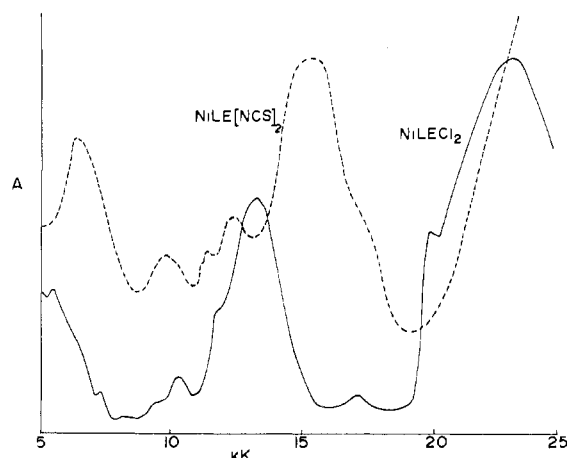

Figure 3.—The electronic spectra of the five-coordinate Ni(LE)Cl and Ni(LE)(NCS)₂ at −196°.

Nevertheless the lowest energy band is seen near 6600₂ cm⁻¹, certainly too low to be attributed to an octahedral nickel complex involving nitrogen ligands. In the infrared spectrum there are several widely separated $\nu(CN(NCS))$ stretching frequencies (2051 (s), 2079 (w), 2116 (s), and 2130 cm⁻¹ (s)) indicating the presence of both bridging and terminal thiocyanate groups. Bands at 461 and 817 cm⁻¹ are assigned to the bending and C–S stretching modes of a terminal N-bonded thiocyanate group, respectively. Unfortunately the corresponding vibrations of a bridging thiocyanate group are obscured by organic ligand absorption. The presence of both types of thiocyanate group confirms a five-coordinate stereochemistry for this complex.

The complex Ni(LS)(NCS)₂ differs in not having two widely separated $\nu(CN(NCS))$ infrared absorption frequencies but merely a broad ill-resolved band at 2100 cm⁻¹ (s) (2108 cm⁻¹ (sh)), and the ν(Ni–NCS) frequency occurs at much lower energy (Table II). The presence of at least one terminal N-bonded thiocyanate group is implied by the presence of bands at 470 and 818 cm⁻¹.

Both thiocyanate complexes exhibit a strong band near 220 cm⁻¹ absent from the spectrum of the tetrahedral CoL(NCS)₂. This band has been observed in other complexes involving bridging thiocyanate groups[20]

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

and is probably assignable to a metal–sulfur stretching vibration. Thus the complex may be five-coordinate but with an unexpectedly low nickel–thiocyanate stretching frequency, or it may be octahedral involving one thiocyanate bridge and a tridentate (using a sulfur atom) LS. This latter possibility may be excluded by consideration of the electronic spectrum.

The lowest energy band occurs near 8000 cm^{-1}, too low to be attributed to an octahedral NiN_4S_2 chromophore.[10] Although the spectrum has the general appearance of an octahedral nickel complex, the ratio of the energies of the first two bands, 1.85, is above the range expected theoretically[12] for octahedral nickel complexes.

Thus an octahedral formulation for $Ni(LS)(NCS)_2$ is excluded and a five-coordinate formulation is necessarily required. In the absence of further information it is not possible to explain the difference in the nickel–thiocyanate stretching frequencies in the two thiocyanate complexes but it is possible that they represent extremes of stereochemistry in that one is essentially a square pyramid and the other essentially trigonal bipyramidal.

In view of the close similarity between the spectra of $Ni(LE)Cl_2$ and $Ni(LS)Cl_2$ and the existence of thiocyanate bridging in the thiocyanate complexes, the five-coordinate halides achieve five-coordination by halogen bridging. This is clearly a necessity in the LE compounds, but it is not necessarily so in the LS compounds since the sulfur atom could be involved. We believe however that it is not.

The electronic spectra show a considerable amount of structure, especially at liquid nitrogen temperature. A distinction between the spectra anticipated for square-pyramidal nickel and for trigonal-bipyramidal nickel is not readily drawn;[19] moreover the complexes are likely to be very distorted. Both thiocyanates show marginal solubility in polar organic solvents, the LS complex being more soluble. However comparison of the solution and solid-state spectra reveals that, while the LE complex dissolves unchanged, the LS complex decomposes. It is suggested therefore that the LE complex is probably dimeric, with thiocyanate bridges, while the LS complex may involve polymerization through the lattice, being broken down on dissolution.

If the basic hypothesis that the presence of more than one out-of-plane deformation frequency (near 400 cm^{-1}) in the infrared spectra of these derivatives infers a cis (or gauche) rather than trans conformation for the ligand, then the ligand must be bidentately coordinated to one metal atom rather than act as a bridge. The existence of a series III spectrum for these five-coordinate derivatives then requires that the two pyridine residues be chemically nonequivalently coordinated to the same metal atom. *It follows that one of the pyridine residues must be coordinated axially and one equatorially in the five-coordinate stereochemistry.* The lower energy out-of-plane deformation frequency in the five-coordinate LE complexes lies some 7–9 cm^{-1} above that of the free ligand inferring that the axial interaction is

very weak, although it certainly exists. In the complex $Cu(LE)Cl_2$ which possesses a six-coordinate tetragonal structure,[4] with the LE bridging equatorial and axial sites, the lower energy deformation band is only 1 cm^{-1} higher than the free ligand. The electronic and vibrational spectra of this compound confirm however that axial coordination is taking place.

In the five-coordinate LS complexes the relevant band occurs some 12–19 cm^{-1} above the free ligand comparable to the increase in the tetrahedral complexes. Evidently the axial interaction is strong in these cases. The difference in behavior between LS and LE may be related to the "bite" of the ligand, which would be greater for the sulfur ligand, thus enabling it to coordinate in axial sites more readily. The complex $Ni(LE)_2(ClO_4)_2$, like the closely related $Cu(LE)_2(ClO_4)_2$ complex,[4] has a square-planar structure based on its electronic spectrum and diamagnetism. The infrared spectrum implies the presence of bidentately coordinated ligands probably in the gauche conformation. However the spectra of these two derivatives differ somewhat from those of the other series II complexes perhaps because of coupling through the metal atom, the metal–nitrogen bonds in these cases being particularly strong.

Zinc and Mercury Complexes.—The $Zn(LS)Cl_2$ complex has a far-infrared spectrum in which the Zn–Cl stretching vibrations may readily be identified (Table II). They fall in the region expected for a tetrahedral zinc complex. Similar peaks may be identified in the far-infrared spectrum of the $Zn(LE)Cl_2$ complex. Both complexes have a series III spectrum which is somewhat surprising. Following our earlier arguments a simple bidentate tetrahedral structure is ruled out. The possibility that the complexes are really five-coordinate seems excluded in view of the far-infrared data. Five-coordinate zinc complexes exhibit $\nu(Zn–Cl)$ vibrations at somewhat lower frequencies[16] than those observed here. The complexes may be polymeric through the organic ligand generating a molecule of very low symmetry.

It was rather disappointing that the sulfur atoms did not coordinate in the complexes described above, and reaction with mercury(II) was tried as a last resort. The complexes $Hg(LS)Cl_2$ and $Hg_2(LE)Cl_4$ were synthesized. The latter complex was obtained from various stoichiometric ratios of the starting materials, no evidence being found for the existence of $Hg(LE)Cl_2$. The infrared spectrum of this binuclear complex was not of very good quality presumably because of the large inorganic content of the complex. However it does appear to belong to series I. Certainly both pyridine residues are coordinating. Molecular models suggest that the obvious formulation, namely, the bidentate ligand bridging an Hg_2Cl_4 unit, is quite feasible. This would parallel the behavior of azopyridine toward the binuclear unit Cu_2Cl_4 as reported by Beadle, *et al.*[21] (see Figure IV of ref 21). A polymeric structure in

(21) P. J. Beadle, R. Grzeskowiak, M. Goldstein, and D. M. L. Goodgame, *J. Chem. Soc. A*, 305 (1970).

which the ligand bridged $HgCl_2$ units (see Figure II of ref 21) seems excluded by the infrared spectrum of the complex. Our earlier conclusions would require that such a structure have a series III spectrum which can be definitely ruled out. The infrared spectrum while poor at higher energies is good in the 400-cm^{-1} region. A tetrahedral formulation about the mercury atom is supported by the position of the mercury–chlorine stretching frequency (295 cm^{-1}).[22]

The $Hg(LS)Cl_2$ complex has what might be termed a series 0 spectrum in that it differs little from the spectrum of the free ligand LS. While for the LE complex the lower energy vibration near 400 cm^{-1} is increased by 18 cm^{-1} relative to the free ligand, in the LS complex the increase is but 1 cm^{-1}. Even in the complex $(py)_2HgCl_2$ where the mercury–pyridine bonds are known[23] to be long (2.60 Å) there is considerable perturbation of the infrared spectrum of the pyridine ligand as a consequence of coordination. Coordination by the pyridine residues in the LS complex is therefore eliminated, and coordination by sulfur is required.

The ν(Hg–Cl) stretching vibrations fall at a much higher frequency in this complex (Table II) relative to the tetrahedral ethane ligand complex above. They are in the region expected for a linear Cl–Hg–Cl species.[24] The complex is therefore construed to have linear Cl–Hg–Cl molecules linked to the ligand by long and weak Hg–S bonds.

Electronic Spectra.—The similarity between the spectra of the cobalt derivatives and those of substituted pyridine derivatives $Co(R-py)_2X_2$ is such that it is possible to estimate the extent of interligand repulsion (between L and the halogen) by correlating the cobalt–halide stretching frequency with the position of the highest energy component of the ν_2 absorption in the near-infrared spectrum.[25] Using this method the interligand repulsion in the bromides and chlorides is found to be less than that experienced by a 2-alkyl-substituted pyridine but more than that experienced by a 3-alkyl-substituted pyridine. This observation is quite understandable on the basis that the substituents on the pyridine rings being linked together as a bridge are pinned back out of the way of the metal–halogen bonds, in a manner which cannot be emulated by two isolated 2-substituted pyridines. Interligand repulsion in the iodide complexes on the other hand appears to be greater than in the corresponding pyridinecobalt iodides.

Little more can be said of the electronic spectra of the nickel complexes. The evident distortion of the stereochemistry would render a detailed analysis of the electronic spectra of little benefit.

Far-Infrared Spectra.—The tetrahedral chloro and bromo complexes of both cobalt and nickel each show two well-defined strong bands in the region 200–400

cm^{-1} attributable to the symmetric and asymmetric stretching vibrations of the metal–halogen bonds. Additional bands in these complexes are then unambiguously assigned to ligand and M–N vibrations (Table II). $Ni(LE)I_2$ and $Co(LE)I_2$ exhibit four strong bands below 300 cm^{-1}, while $Co(LS)I_2$ shows only three. The highest energy band in each case must be assigned to a ligand vibration, while the lowest is assuredly a metal–iodide stretch. The complex $Co(LS)I_2$ exhibits one remaining band (at 232 cm^{-1}) which must necessarily be assigned to a metal–nitrogen stretching vibration. It appears to follow that the band observed near 230 cm^{-1} in the other two complexes must be a metal–nitrogen vibration rather than a metal–iodide stretch and that these iodide complexes only exhibit one metal–iodide stretching vibration above 200 cm^{-1}. In the five-coordinate compounds, the metal–nitrogen stretching vibrations can generally be identified after subtraction of the ligand vibrations (not greatly different from those in the free ligand) and the metal–halogen or –thiocyanate vibrations (generally very strong and obviously anion dependent). The LS ligand and all the complexes exhibit one or two bands near 350 cm^{-1}. A similar band is seen in all the tetrahedral complexes of LE but not in the free LE ligand itself nor in complexes of other stereochemistry. These bands must evidently be ligand in origin and undoubtedly reflect the symmetry or conformation of the ligand. However their assignment is obscure (none of the complexes of the azopyridine ligand shows these bands) and we cannot as yet use the absorption in a diagnostic manner.

Behavior in Solution.—The tetrahedral cobalt complexes are sparingly soluble in acetonitrile yielding solutions of low conductivity [35–40 mhos/mol cm^2 at 10^{-3} M concentration]. Comparison of their solution and transmittance spectra reveals that they dissolve essentially unchanged, no solvolysis occurring. The tetrahedral nickel complexes are also soluble in acetonitrile but while the bromide gives a solution of low conductivity [44 mhos/mol cm^2 at 10^{-3} M], the conductivity of the iodide solution [235 mhos/mol cm^2 at 10^{-3} M] implies extensive solvolysis. The I→M charge-transfer band is almost totally absent in acetonitrile solutions of $Ni(LE)I_2$.

Evidently the equilibrium

$$Ni(LE)_2I_2 + 2CH_3CN \rightleftharpoons Ni(LE)_2(CH_3CN)_2 + 2I^-$$
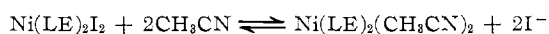
lies predominantly to the right. Interestingly the d–d spectrum in acetonitrile is similar to the solid showing that the solvolyzed species is tetrahedral and that the field strength of CH_3CN is similar to that of I^-.

The nickel–thiocyanate complexes dissolve in acetonitrile giving essentially nonconducting solutions [$(LE)Ni(NCS)_2$, $\Lambda = 17$ mhos/mol cm^2 and $(LS)Ni(NCS)_2$, $\Lambda = 31$ mhos/mol cm^2, both at approximately 10^{-3} M concentration in acetonitrile].

Summary—The stereochemistries of the various complexes are summarized in Table IV as a function of metal ion and ligand.

The formation of five-coordinate nickel complexes

(22) G. E. Coates and D. Ridley, *J. Chem. Soc.*, 166 (1964).
(23) D. Grdenic and I. Krstanovic, *Ark. Kemi*, **27**, 143 (1955).
(24) D. M. Adams, "Metal-Ligand and Related Vibrations," Edward Arnold, London, 1967, p 52.
(25) M. Keeton, A. B. P. Lever, and B. S. Ramaswamy, *Spectrochim. Acta*, in press.

TABLE IV

| Four-coordinate tetrahedral | Co(LS)X₂ | Co(LE)X₂ |

Four-coordinate tetrahedral	Co(LS)X₂ (X = Cl, Br, I)	Co(LE)X₂ (X = Cl, Br, I, NCS)
		Ni(LE)Br₂
	Ni(LS)I₂	Ni(LE)I₂
	Zn(LS)Cl₂	Zn(LE)Cl₂
		Hg₂(LE)Cl₄
Four-coordinate square		Ni(LE)₂(ClO₄)₂
Five-coordinate	Ni(LS)Cl₂	Ni(LE)Cl₂
	Ni(LS)Br₂	
	Ni(LS)(NCS)₂	Ni(LE)(NCS)₂
Linear	Hg(LS)Cl₂	

with bidentate pyridine ligands requires some comment. Five-coordination with d^8 species is expected when the oxidation number of the central species is low (say 0 or 1), as a consequence of the decreasing separation of the nd and $(n + 1)p$ orbitals.[26]

In the case of nickel(II), with a formal charge of $+2$, five-coordination will be favored with the more polarizable ligands, where the effective nuclear charge and therefore the 3d–4p separation may be reduced. In agreement many five-coordinate complexes of nickel(II) involve ligands with arsenic, phosphorus, sulfur, or selenium atoms as donors and are magnetically low spin. However a series of high-spin five-coordinate complexes are known (see ref 2 and references therein) which involve polydentate pyridine ligands. In these cases five-coordination must arise principally through the steric requirements of the ligand. The ligands under discussion here represent very simple examples of these polydentate pyridine ligands. They are suffi-

ciently sterically crowded that six-coordination is inhibited, while their polarizability is small such that four-coordinate tetrahedral nickel(II) derivatives are only produced with the more polarizable counterions. Thus five-coordinate and high-spin complexes are produced by the exclusion of other less favorable stereochemistries. The existence of five-coordinate nickel complexes with LE and LS but not with azopyridine (LN) is probably due to the fact that while azopyridine cannot coordinate in a bidentate fashion to a single metal atom but can utilize its bridge atoms for coordination, the reverse is true for the LS and LE ligands.

Very recently Sacconi[27] discussed the spin state of five-coordinate nickel(II) and cobalt(II) complexes in terms of the electronegativity of the donor atoms as determined by Allred and Rochow.[28] Sacconi summed the electronegativities of the donor atoms and demonstrated the existence of a crossover point below which the complexes were low spin and above which they were high spin. For the tri- and tetradentate ligands he discussed the crossover came at about 13 (sum of donor atom electronegativities) for nickel(II). For the five-coordinate complexes discussed in this paper the sum exceeds 14 so that high-spin behavior is expected and is observed.

(26) G. A. Barclay, R. S. Nyholm, and R. V. Parish, *J. Chem. Soc.*, 4433 (1961); R. S. Nyholm and M. L. Tobe, *Advan. Inorg. Chem. Radiochem.*, **5**, 1 (1963).

(27) L. Sacconi, *J. Chem. Soc. A*, 248 (1970).

(28) A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.*, **5**, 264 (1958).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MICHIGAN STATE UNIVERSITY, EAST LANSING, MICHIGAN 48823

Substituted Group VI Metal Carbonyl Complexes of Dimethyl Methylphosphonite and Bis(dimethylamino)methylphosphine

BY CHRISTOPHER E. JONES AND K. J. COSKRAN*

The synthesis of substituted metal carbonyls of the types M(CO)₆₋ₓLₓ, where M = Cr, Mo, or W, where x = 1, 2, or 3 for L = CH₃P(OCH₃)₂, and where x = 1 or 2 for L = CH₃P(N(CH₃)₂)₂ are described. The infrared data in the CO stretching region and CO stretching force constants are discussed and an order is proposed for the π-acceptor strength of the ligands: P(OCH₃)₃ > CH₃P(OCH₃)₂ > (CH₃)₃P > CH₃P(N(CH₃)₂)₂ > P(N(CH₃)₂)₃. The proton nmr data are also discussed for these complexes and tentative assignment is made for the sign of ²J_{PH} (coupling of phosphorus to the methyl protons). In the di- and trisubstituted complexes, phosphorus–phosphorus coupling is observed in the proton nmr spectra with the absolute value of ²J_{PP} being larger in the trans isomer than in the cis isomer for a given compound and larger in Mo and W compounds than in analogous Cr compounds. These spectral data are used to help interpret the nature of the metal–phosphorus bond.

Introduction

Many substituted metal carbonyl complexes of the types M(CO)₆₋ₓLₓ, where M = Cr, Mo, or W, x = 1, 2, or 3, and L = tertiary phosphorus ligands, have

been prepared and studied before. In particular, complexes of P(OCH₃)₃,[1] P(CH₃)₃,[1,2] and P(N(CH₃)₂)₃[3] have been previously investigated using infrared tech-

* To whom correspondence should be addressed.

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