

$\times 10^4$ as compared to 7.5×10^4 for the Ni-NTA system. The values of $k_{\text{H}}^{\text{CdL}}$ and k^{CdL} are $2.5 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ and 3.4 sec^{-1} , respectively. No direct comparison can be made between these values and the corresponding Ni-NTA values because of differences in the rate step. The identical ratio, however, shows that the Cd-NTA dissociation follows a similar path to that found in the Ni-NTA dissociation. In the Cd-NTA system a second-order hydrogen ion dependence was also observed at high acidities. Failure to observe this term in the Ni-NTA system might be due to the fact that a high enough acidity was not reached.

Besides comparing the various Ni-NTA intermediates, direct comparison can also be made between the

Ni-NTA and the Ni-EDTA systems on the basis that the rate step is identical in the two systems. Table VI makes this comparison and shows the good agreement obtained. The replacement of an iminodiacetate group by an acetate group does not alter the rate step but does affect the magnitude of the rate constant since the stability of the reaction intermediate is altered. This change in rate constant is quantitatively explained on the basis of the proposed dinuclear reaction intermediates.

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Coordination Compounds of Nickel(II) Salts with Substituted Pyridines. Square-Planar, Tetrahedral, and Octahedral Compounds of 3,4- and 3,5-Dimethylpyridine

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The preparation of a series of new coordination compounds of nickel(II), containing 3,4- and 3,5-lutidine (dimethylpyridines) and various anions (Cl^- , Br^- , I^- , NCS^- , NO_3^- , ClO_4^- , BF_4^-) is reported. Compounds with square-planar, tetrahedral, and octahedral stereochemistry were obtained. Their configurations were deduced from their magnetic and spectral properties. Unusual complexes containing coordinated ClO_4^- and BF_4^- are reported.

Introduction

This work is a continuation of previously reported studies on the coordination compounds of nickel(II) with substituted pyridines.^{1,2} For general information concerning the dimethylpyridines (lutidines) as ligands in metal complexes and in particular the aims of this research, we refer to our paper on the nickel(II) complexes of the α -substituted lutidines.²

Experimental

Starting Materials.—The 3,4- and 3,5-lutidine (3,4-L and 3,5-L or simply L) and the anhydrous nickel(II) halides and thiocyanate were purified as described in the previous paper.² The infrared spectra of the purified lutidines agreed with those reported in the literature.³ The acetonitrile complexes of nickel(II) perchlorate and tetrafluoroborate were obtained from their respective hydrated nickel(II) salts by repeated crystallization from acetonitrile-ethyl ether.

Preparation of the Complexes.—The compounds prepared, together with their colors, melting or decomposition temperatures, and magnetic moments, are listed in Table I.

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TABLE I
FORMULAS AND SOME PHYSICAL PROPERTIES OF SOLID
NICKEL(II)- β -LUTIDINE COMPLEXES

Compound	Color	μ_{eff} , B.M. ^a
$[\text{Ni}(3,4\text{-L})_4\text{Cl}_2]$	Green	3.13
$[\text{Ni}(3,5\text{-L})_4\text{Cl}_2]$	Bluish green	3.19
$[\text{Ni}(3,4\text{-L})_4\text{Br}_2]$	Green	3.32
$[\text{Ni}(3,4\text{-L})_2\text{Br}_2]$	Blue-violet	3.60
$[\text{Ni}(3,5\text{-L})_4\text{Br}_2]$	Bluish green	3.23
$[\text{Ni}(3,4\text{-L})_4\text{I}_2]$	Yellow-brown	Diamag.
$[\text{Ni}(3,5\text{-L})_4\text{I}_2]$	Yellow	3.29
$[\text{Ni}(3,4\text{-L})_4(\text{NCS})_2]$	Light blue	3.18
$[\text{Ni}(3,5\text{-L})_4(\text{NCS})_2]$	Light blue	3.12
$[\text{Ni}(3,4\text{-L})_4(\text{NO}_3)_2]$	Blue	3.25
$[\text{Ni}(3,5\text{-L})_4(\text{NO}_3)_2]$	Blue	3.20
$[\text{Ni}(3,4\text{-L})_4(\text{ClO}_4)_2]$	Yellow	Diamag.
$[\text{Ni}(3,5\text{-L})_4(\text{ClO}_4)_2]$	Light blue	3.27
$[\text{Ni}(3,4\text{-L})_4(\text{BF}_4)_2]$	Yellow	Diamag.
$[\text{Ni}(3,5\text{-L})_4(\text{BF}_4)_2]$	Light blue	3.26

^a At 20°. Diamagnetic corrections were made.

The complexes of the general formula NiL_4X_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCS}, \text{NO}_3$) were prepared as previously described for the halide, thiocyanate, and nitrate complexes of the other lutidines.³ The complexes of 3,4-L are readily soluble in, and were recrystallized from, dichloromethane; those of 3,5-L are only sparingly soluble and were not recrystallized. Most of the complexes decompose on heating, often without melting, in the range 100–200°. In some cases, a change of color is observed well below the decomposition

TABLE II
 ANALYTICAL DATA FOR THE NICKEL(II) COMPLEXES

Compound	Nickel, %		Carbon, %		Hydrogen, %		Halogen, %	
	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
Ni(3,4-L) ₄ Cl ₂	10.35	10.52	59.73	60.24	6.33	6.50	12.61	12.72
Ni(3,5-L) ₄ Cl ₂			60.28		6.66		12.58	
Ni(3,4-L) ₄ Br ₂			51.72	51.97	5.60	5.61	24.10	24.70
Ni(3,5-L) ₄ Br ₂			51.83		5.72		24.64	
Ni(3,4-L) ₂ Br ₂	13.44	13.56					36.78	36.93
Ni(3,4-L) ₄ I ₂	7.55	7.92	45.09	45.37	4.96	4.89		
Ni(3,5-L) ₄ I ₂	7.43		45.29		5.12			
Ni(3,4-L) ₄ (NCS) ₂			59.77	59.70	6.11	6.01		
Ni(3,5-L) ₄ (NCS) ₂			59.57		5.99			
Ni(3,4-L) ₄ (NO ₃) ₂	9.86	9.60	53.94 ^a	55.01	5.93	5.93		
Ni(3,5-L) ₄ (NO ₃) ₂			54.24 ^a		5.91			
Ni(3,4-L) ₄ (ClO ₄) ₂	8.15	8.55	49.97	49.01	5.41	5.29		
Ni(3,5-L) ₄ (ClO ₄) ₂			48.83		5.31			
Ni(3,4-L) ₄ (BF ₄) ₂	8.60	8.88	50.39	50.88	5.54	5.49		
Ni(3,5-L) ₄ (BF ₄) ₂	8.71		50.41		5.35			

^a Carbon results are low, probably because of difficulty in the combustion.

 TABLE III
 INFRARED ABSORPTION FREQUENCIES (CM.⁻¹) IN THE NaCl REGION OF THE ANIONS IN THE COMPLEXES

Compound	Medium	Absorption bands ^{a,b}
[Ni(3,4-L) ₄ (NCS) ₂]	Solid in KBr and Nujol	2080 vs CN stretching 2090 sh 795 s CS stretching
[Ni(3,5-L) ₄ (NCS) ₂]	Solid in KBr and Nujol	2096 vs CN stretching 795 CS stretching
[Ni(3,4-L) ₄ (NO ₃) ₂]	Solid in KBr	1460-1430 vs, vbr, ^{c,d} NO ₂ asym. stretch. 1295 vs, NO ₂ sym. stretch. ... ^e 815 m, nonplanar rocking
[Ni(3,5-L) ₄ (NO ₃) ₂]	Solid in KBr	1480-1450 vs, vbr, ^{c,d} NO ₂ asym. stretch. 1295 vs, NO ₂ sym. stretch. ... ^e 860 m 810 s, nonplanar rocking 767 m, NO ₂ asym. or sym. bend.
[Ni(3,4-L) ₄ (ClO ₄) ₂]	Solid in KBr and Nujol	1108 vs, vbr, ^c ClO ₄ asym. stretch.
	Soln. in CH ₂ Cl ₂	1105 vs, vbr, ^c ClO ₄ asym. stretch.
[Ni(3,5-L) ₄ (ClO ₄) ₂]	Solid in KBr in Nujol	1135 vs, ClO(Ni) asym. bend. 1030 vs, ClO ₃ sym. stretch. 930 s, ClO(Ni) stretch.
	Soln. in CH ₂ Cl ₂	1120-1090 vs, vbr, ^c ClO ₄ asym. stretch.
[Ni(3,4-L) ₄ (BF ₄) ₂]	Solid in KBr and Nujol	1100-1090 vs, vbr, ^c BF ₄ asym. stretch.
[Ni(3,5-L) ₄ (BF ₄) ₂]	Solid in Nujol	1115 vs, ^c BF(Ni) asym. bend. (tentative) 959 m, ^f ? 925 vs, BF ₄ sym. stretch. (tentative) 765 m, ^f BF(Ni) stretch.
	Solid in KBr (interacts with KBr)	1110-1030 vs, vbr ^c 925 mw 760 sh, w
	Soln. in CH ₂ Cl ₂	1120-1090 vs, vbr, ^c BF ₄ asym. stretch.

^a s, strong; m, medium; w, weak; br, broad; sh, shoulder; v, very. ^b Assignments are made according to previously reported investigations. ^c Overlays strong absorptions of the coordinated lutidine. ^d Shows ill-defined shoulders and splitting. ^e The expected band around 1020 cm.⁻¹, NO(Ni) stretching, could not be observed because of the lutidine absorption in this region. However, the lutidine band had a higher relative intensity than in the other complexes. ^f Not well resolved from strong adjacent absorption.

temperature. For [Ni(3,4-L)₄Br₂] the color change from green to blue-violet is complete after heating for 2 hr. at about 115° under vacuum. The product thus obtained is completely soluble in dichloromethane, from which it separates as blue-violet crystals of the composition Ni(3,4-L)₂Br₂.

The nickel(II) perchlorate and tetrafluoroborate complexes were prepared by treating the corresponding crystalline acetonitrile-nickel(II) complexes with excess lutidine and warming the mixture to 80° under reduced pressure. The products separated as well-formed crystals and were filtered off, washed repeatedly with ethyl ether, and recrystallized from dichloromethane.

Analysis.—C and H were determined by microanalyses, halo-

gens by the Volhard method, and nickel by titration with EDTA. The analytical data are reported in Table II. Analyses of the nitrate complexes gave somewhat low carbon results, probably because of difficulties in the combustion.

Magnetic susceptibility measurements were made by the Gouy method. The values of the magnetic moments, μ_{eff} , of the solid compounds, calculated from the magnetic susceptibilities of the finely powdered solids, are listed in Table I. The measurements in solution were qualitative.

Infrared absorption spectra were taken as described.² The absorption bands arising from the coordinated lutidine were found to be almost identical in all complexes and those of the

TABLE IV
 ELECTRONIC ABSORPTION SPECTRA OF THE OCTAHEDRAL COMPLEXES

Compound	Medium	λ_{\max}^a , m μ	ν_1 , cm. ⁻¹	λ_{\max}^a , m μ	ν_2 , cm. ⁻¹	λ_{\max}^a , m μ	ν_3 , cm. ⁻¹
[Ni(3,4-L) ₂ Cl ₂]	Solid, Nujol mull	... ^b		635	15,750	394	25,380
[Ni(3,4-L) ₂ Br ₂]	Soln., CH ₂ Cl ₂ + 5%L	1180-950	8,470-10,525	635 (6)	15,750	393 (12)	25,445
[Ni(3,5-L) ₂ Cl ₂]	Soln., CH ₂ Cl ₂ + 5%L	... ^b		637	15,700	410	24,390
[Ni(py) ₄ Cl ₂] ^c	Soln.	1176-917	8,500-10,900	629	15,900	389	25,700
[Ni(3,4-L) ₂ Br ₂]	Soln., CH ₂ Cl ₂ + 5%L	1300-975	7,700-10,250	644 (13)	15,530	397 (20)	25,188
[Ni(3,5-L) ₂ Br ₂]	Soln., CH ₂ Cl ₂ + 5%L	... ^b		647	15,450	415	24,095
[Ni(3,4-L) ₂ (SCN) ₂]	Soln., CH ₂ Cl ₂	957 (3.9)	10,450	590 (4.1)	16,950	... ^d	
[Ni(3,5-L) ₂ (SCN) ₂]	Soln., CH ₂ Cl ₂	940	10,630	587	17,035	... ^d	
[Ni(3,4-L) ₂ (NO ₃) ₂]	Soln., CH ₂ Cl ₂	1100 (10)	9,090	623 (22)	16,150	380 (51)	26,315
[Ni(3,5-L) ₂ (NO ₃) ₂]	Soln., CH ₂ Cl ₂	1100 (12)	9,090	623 (32)	16,150	383 (56)	26,100
Ni(3,4-L) ₂ (ClO ₄) ₂	Soln., CH ₂ Cl ₂ + 10%L	... ^b		600 (8.5)	16,660	367 (25)	27,248
Ni(3,5-L) ₂ (ClO ₄) ₂	Soln., CH ₂ Cl ₂ + 10%L	... ^b		605	16,550	365	27,400
[Ni(py) ₆](ClO ₄) ₂ ^e	Soln.	985	10,150	607	16,500	371	27,000

^a Numbers in parentheses represent molar extinction coefficients at band maxima. ^b Absorption was too low for resolution. ^c Reference 2. ^d Covered by charge-transfer band. ^e Reference 12.

 TABLE V
 ELECTRONIC ABSORPTION SPECTRA OF THE TETRAHEDRAL AND SQUARE-PLANAR COMPLEXES

Compound	Medium	Absorption maxima, cm. ⁻¹ ^a
Ni(3,4-L) ₂ Br ₂	Solid, Nujol mull	17,420 (br) 10,415 (br)
	0.001 M CH ₂ Cl ₂ soln.	17,985 (200) 10,362 (67)
Ni(3,4-L) ₂ I ₂	CH ₂ Cl ₂ soln.	26,315 (6500) 16,980 (800) 10,870 (33)
		22,470 (sh) 15,750 (sh) 10,000 (33)
Ni(3,4-L) ₂ (ClO ₄) ₂	Solid, Nujol mull	23,390
	CH ₂ Cl ₂ soln.	22,470 (100)
Ni(3,4-L) ₂ (BF ₄) ₂	Solid, Nujol mull	23,640
	CH ₂ Cl ₂ soln.	22,470 (110)
Ni(3,5-L) ₂ (ClO ₄) ₂	CH ₂ Cl ₂ soln.	22,625 (110)
Ni(3,5-L) ₂ (BF ₄) ₂	CH ₂ Cl ₂ soln.	22,730 (120)

^a For solutions, the numbers in parentheses represent molar extinction coefficients at band maxima; br, broad; sh, shoulder.

bromo complexes are given here in cm.⁻¹. Ni(3,4-L)₂Br₂: 715 vs, 750 m, 820 sh, 830 s, 848 s, 868 s, 920 w, 970 sh, 990 sh, 1005 sh, 1020 vs, 1050 vw, 1075 vs, 1180 s, 1205 vs, 1250 m, 1310 m, 1385 m, 1420 s, 1450 vs, 1490 vs, 1540 sh, 1560 m, 1610 s, 2920 m, 2950 sh, 2980 m, 3015 w, 3045w, 3085 m, and 3125 sh. Ni(3,5-L)₂Br₂: 700 vs, 752 vs, 868 vs, 940 w, 1020 s, 1050 sh, 1155 vs, 1175 s, 1248 m, 1275 vw, 1320 w, 1380 sh, 1410-1480 vs, vbr, 1600 vs, 2865 w, 2920 s, 2965 m, and 3050 w. The bands of the anions are reported in Table III and Fig. 4 and 5. Their assignments were made according to previously reported investigations.⁴⁻⁹

Visible spectra of the solutions and of the solids in Nujol mull were taken with a Cary Model 14 recording spectrophotometer and are reported in Tables IV-VII and Fig. 1-3.

Results

Nickel(II) Chloride and Bromide Complexes.—An excess of 3,4- and 3,5-lutidine reacts with anhydrous nickel(II) chloride and bromide to give blue-green crystalline complexes of formula NiL₄X₂ (X = Cl, Br). Their magnetic moments (Table I) and electronic absorption spectra in the solid state indicate a slightly distorted octahedral structure with the halogen atoms in *trans* positions, similar to the analogous pyridine

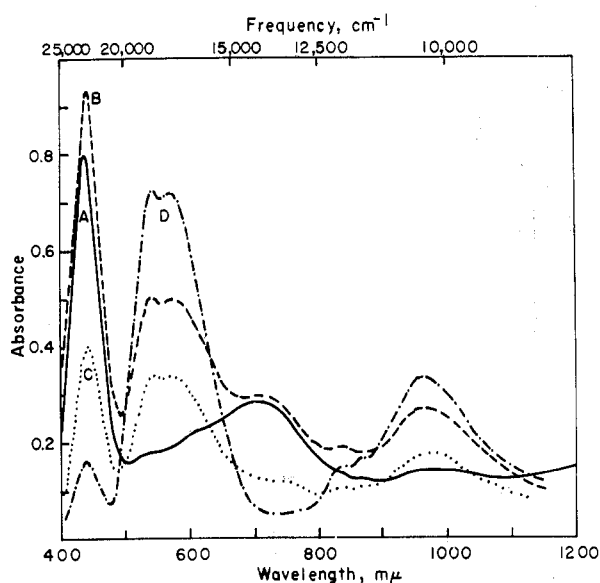


Fig. 1.—Spectra of [Ni(3,4-L)₂Cl₂] in CH₂Cl₂ at various concentrations: A, 0.544 M (cell length 1 mm.); B, 0.02 M (10 mm.); C, 0.008 M (10 mm.); D, 0.0008 M (100 mm.).

complex,¹⁰ [Ni(py)₄Cl₂]. As shown in Table IV, the visible and near-infrared spectra of [Ni(py)₄Cl₂] and [NiL₄Cl₂] are almost identical, and the spectrum

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TABLE VI
 ELECTRONIC ABSORPTION SPECTRA ($m\mu$) OF $[\text{Ni}(\text{3,4-L})_4\text{X}_2]$ IN CH_2Cl_2 SOLUTIONS

Compound	Concn., M	Octahedral bands		Tetrahedral bands	
		λ_{max}^a	λ_{max}^b	λ_{max}^c	λ_{max}^d
$\text{Ni}(\text{3,4-L})_4\text{Cl}_2$	0.544 (1) ^f	690 (0.28) ^e	412 (0.80) ^e	950 (0.14) ^e	553 (0.18) ^e 519 (0.19)
	0.02 (10)	690 (0.29)	416 (0.92)	945 (0.27)	553 (0.50) 519 (0.50)
	0.008 (10)	690 (0.12)	416 (0.40)	945 (0.17)	553 (0.34) 519 (0.34)
	0.0008 (100)	690 (0.05)	416 (0.16)	945 (0.34)	553 (0.73) 519 (0.72)
$\text{Ni}(\text{3,4-L})_4\text{Br}_2$	0.02 (1)	644 (0.33)	417 (0.60)	975 (0.16)	560 (0.11)
	0.006 (10)	644 (0.30)	425 (0.34)	965 (0.26)	560 (0.66)
	0.0004 (100)	644 (0.03)	425 (0.05)	965 (0.20)	560 (0.52)

^a Correspond to ν_2 region. ^b Correspond to ν_3 region. ^c Correspond to ν_2 region. ^d Correspond to ν_3 region. ^e Numbers in parentheses represent the absorbancies at the band maxima. ^f Numbers in parentheses represent the cell length in mm.

 TABLE VII
 ELECTRONIC ABSORPTION SPECTRA ($m\mu$) OF $\text{Ni}(\text{3,4-L})_4\text{Cl}_2$, 0.02 M CH_2Cl_2 SOLUTION, WITH ADDED AMOUNTS OF LUTIDINE (L) OR $[(\text{C}_6\text{H}_5)_4\text{As}]\text{Cl}$, (Cl^-)

Solution ^a	Octahedral bands		Tetrahedral bands	
	λ_{max}^b	λ_{max}^c	λ_{max}^d	λ_{max}^e
Original solution	690 (0.29) ^f	416 (0.92) ^f	945 (0.27) ^f	553 (0.50), ^f 519 (0.50) ^f
With added lutidine				
0.01 M in L	690 (0.25)	416 (0.80)	945 (0.18)	553 (0.34), 519 (0.34)
0.02 M in L	690 (0.23)	416 (0.70)	945 (0.14)	553 (0.23), 519 (0.23)
0.1 M in L	650 (0.13)	405 (0.34)	945 (0.05)	553 (0.02), 519 (0.02)
With added chloride				
0.005 M in Cl^-	690 (0.32) sh	416 (0.80)	950 (0.23)	567 (0.58), 530 (0.47)
0.02 M in Cl^-		416 (0.73)	975 (0.22)	
			1100 (0.24)	595 (0.90)
0.04 M in Cl^-		416 (0.45)	1100 (0.35)	607 (1.30)

^a Cell length = 10 mm. ^b Corresponds to ν_2 region. ^c Corresponds to ν_3 region. ^d Corresponds to ν_2 region. ^e Corresponds to ν_3 region. ^f Numbers in parentheses represent the absorbancies at the band maxima.

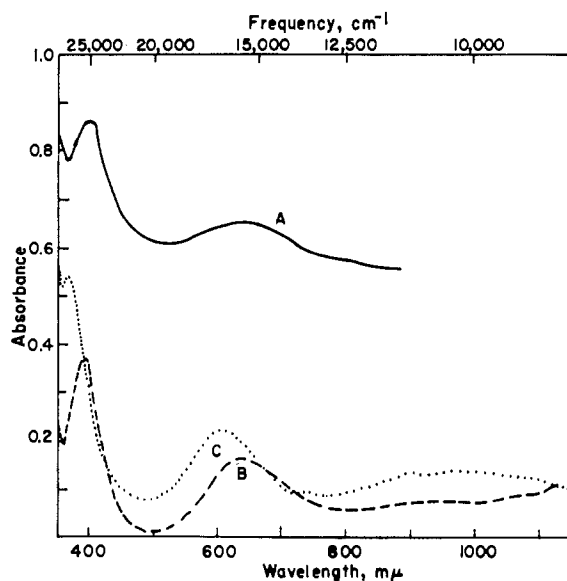


Fig. 2.—Absorption spectra of: A, $[\text{Ni}(\text{3,4-L})_4\text{Cl}_2]$ solid in Nujol mull; B, $[\text{Ni}(\text{3,4-L})_4\text{Cl}_2]$ 0.03 M in CH_2Cl_2 containing excess 3,4-L (1.0 M); C, $[\text{Ni}(\text{3,4-L})_4](\text{ClO}_4)_2$ 0.03 M in CH_2Cl_2 containing excess 3,4-L (1.0 M).

of $[\text{NiL}_4\text{Br}_2]$ is slightly shifted to lower wave numbers as expected for a weaker field.

The $[\text{NiL}_4\text{X}_2]$ complexes are almost insoluble in hydrocarbons and ethyl ether and undergo solvolysis in most of the common organic solvents in which they dissolve, as shown by the spectra of their solutions.

In dichloromethane,¹¹ and also in dichloroethane and chlorobenzene, the complexes dissolve without coordination of the solvent, although the spectra of the solutions indicate that some change takes place. In this respect, the complexes of 3,4-L and 3,5-L are strictly analogous, but since the latter are only very sparingly soluble, we limited our detailed investigation to the 3,4-L complexes.

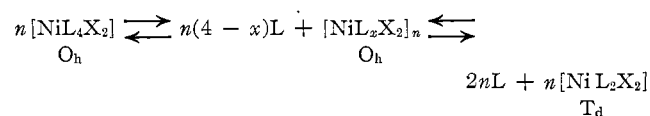
As shown in Table VI and Fig. 1 and 2, the concentrated ($5 \times 10^{-1} M$) solution of $[\text{Ni}(\text{3,4-L})_4\text{Cl}_2]$ in dichloromethane has a spectrum similar to that of the solid but slightly shifted to lower wave numbers, indicating a decrease in the field strength. On dilution Beer's law is not obeyed and at about $1 \times 10^{-2} M$ concentration new bands begin to appear and gradually increase in relative intensity, until at high dilutions (about $10^{-4} M$) they are practically the only bands present in the spectrum. The spectrum of the concentrated solution is very close to that of the octahedral chloro-bridged solid complex,¹² $[\text{Ni}(\text{py})_2\text{Cl}_2]$, whereas the new bands which appear on dilution are typical of tetrahedral nickel(II) compounds. The bromo compound, $[\text{Ni}(\text{3,4-L})_4\text{Br}_2]$, behaves similarly. As expected for the weaker field, the absorption bands of both the octahedral and tetrahedral species formed in solution (Table VI) are shifted to lower wave numbers with respect to the corresponding bands of the

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chloro compounds. The spectrum of the tetrahedral species is identical with that of the complex $[\text{Ni}(3,4\text{-L})_2\text{Br}_2]$, prepared by heating $[\text{Ni}(3,4\text{-L})_4\text{Br}_2]$ under vacuum at about 115° . The complex $[\text{Ni}(3,4\text{-L})_2\text{Br}_2]$ is a well-crystallized blue-violet substance, soluble without decomposition in dichloromethane, and has a magnetic moment of 3.6 B.M. and an electronic spectrum (Table V) typical of a (pseudo)tetrahedral structure. Significant changes in the spectra of the solutions of $[\text{Ni}(3,4\text{-L})_4\text{X}_2]$ are also observed upon addition of lutidine. In the presence of increasing amounts of free lutidine, the spectra of the solutions (Table VII, Fig. 3) gradually approach, and finally become identical with, those of the solid compounds.

The above observations permit us to interpret the behavior of the $[\text{Ni}(3,4\text{-L})_4\text{X}_2]$ complexes in dichloromethane. Upon dissolution, the original complex loses some of the coordinated lutidine and gives a mixture of an octahedral species, very likely polymeric and halogen-bridged, and of the monomeric tetrahedral $[\text{Ni}(3,4\text{-L})_2\text{X}_2]$. The octahedral polymeric species is predominant in concentrated solution but upon dilution breaks down to give the tetrahedral monomer.



The fact that upon addition of free lutidine the spectrum of the solution becomes identical with that of the solid supports this conclusion. It may be noted here that the main absorption band of $[\text{Ni}(3,4\text{-L})_2\text{Cl}_2]$ at $520\text{--}550\text{ m}\mu$ shows a well-marked splitting, whereas the corresponding band of the bromo compound does not. A similar trend is observed in the spectra of other nickel-halide complexes.¹³

Solutions of the complexes $[\text{Ni}(3,4\text{-L})_4\text{X}_2]$ are not only sensitive to an excess of lutidine, as mentioned above, but also to an excess of halide ions (Table VII). When increasing amounts of tetraphenylarsonium or tetrabutylammonium halide are added to a solution of $[\text{Ni}(3,4\text{-L})_4\text{X}_2]$, containing the octahedral and tetrahedral species in equilibrium, the bands of the octahedral species gradually disappear, while those of the tetrahedral species shift gradually to lower wave numbers and then remain constant (Table VII). It seems reasonable to assign to the new tetrahedral species the formula $[\text{Ni}(3,4\text{-L})_3\text{X}_3]^-$. In agreement with this formulation, the shift observed (ν_2 : $965\text{ m}\mu \rightarrow 1137\text{ m}\mu$; ν_3 : $560\text{ m}\mu \rightarrow 631\text{ m}\mu$) upon addition of excess bromide to $[\text{Ni}(3,4\text{-L})_2\text{Br}_2]$ is of the same order as, although somewhat larger than, that observed¹³ between $[\text{Ni}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{Br}_2]$ and $[\text{Ni}\{(\text{C}_6\text{H}_5)_3\text{P}\}_3\text{Br}_3]^-$. Even in the presence of a large excess of halide the spectrum of the tetrahalonickel(II) ion,¹⁴ $[\text{NiX}_4]^{2-}$, was not observed.

Nickel(II) Iodide Complexes.—These complexes have the formula NiL_4I_2 . The complex of 3,4-L is a

brownish yellow well-crystallized diamagnetic substance and that of 3,5-L is a yellow paramagnetic powder (Table I). The spectra of these solid complexes are somewhat different too, but their interpretation is rendered difficult by the presence of the strong charge-transfer bands which partially obscure the ligand field absorptions.

The behavior of the iodo complexes toward organic solvents is similar to that of the corresponding chloro and bromo derivatives. In dichloromethane solution both the 3,4-L and 3,5-L complexes are green and have an identical spectrum (Table V) corresponding to a tetrahedral structure, similar to that of the complex of nickel(II) iodide with β -picoline.¹ In agreement with this assignment a solution of the 3,4-L complex was found to be paramagnetic.

Nickel(II) Thiocyanate Complexes.—These are pale blue crystalline substances of formula $\text{NiL}_4(\text{NCS})_2$, stable to moist air, and soluble without decomposition in dichloromethane. Their magnetic moments (Table I), electronic spectra (Table IV), and infrared spectra (Table III) show that they have an essentially octahedral structure, with the thiocyanate groups in *trans* positions and coordinated through the nitrogen, analogous to the pyridine complex,⁴ $[\text{Ni}(\text{py})_4(\text{NCS})_2]$.

Nickel(II) Nitrate Complexes.—These compounds are blue crystalline substances of formula $\text{NiL}_4(\text{NO}_3)_2$, moderately stable to moisture, and very soluble in many organic solvents. The solids have magnetic moments in the range 3.20–3.25 B.M. (Table I), and the dichloromethane solutions have electronic spectra (Table IV) corresponding to an essentially octahedral structure. The infrared spectra (Table III) confirm that the nitrate groups are coordinated.^{9,15–17}

Nickel(II) Perchlorate and Tetrafluoroborate Complexes.—The 3,4-lutidine forms a yellow crystalline complex with nickel(II) perchlorate of the formula $\text{NiL}_4(\text{ClO}_4)_2$. In the solid state this is diamagnetic and has an electronic absorption spectrum (Table V) similar to that of other diamagnetic square-planar complexes of nickel(II).¹⁸ The compound is not hygroscopic and is only very slowly decomposed by water to give a green solution. It interacts more or less with organic solvents, except dichloromethane, 1,2-dichloroethane, and chlorobenzene in which it dissolves without change in the shape of its spectrum although a shift to lower frequencies is observed. The dichloromethane solution shows no electrical conductivity but this is not surprising as the low dielectric constant of this solvent may favor the formation of ion pairs. The infrared spectra of the solid and of the dichloromethane solution are identical and do not show any change in the symmetry of the free perchlorate ion (Table III). On addition of excess lutidine, the yellow dichloromethane solution becomes blue,

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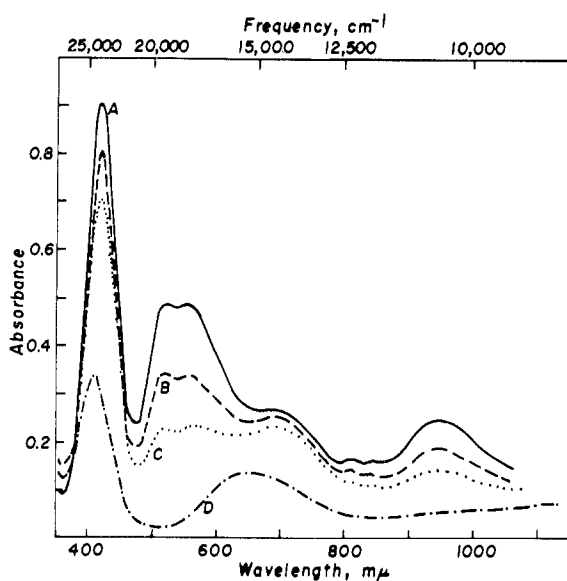


Fig. 3.—Spectra of 0.02 M $[\text{Ni}(3,4\text{-L})_4\text{Cl}_2]$ in CH_2Cl_2 with added 3,4-L, in 10-mm. cell: A, no 3,4-L added; B, 0.01 M 3,4-L; C, 0.02 M 3,4-L; D, 0.10 M 3,4-L.

with a spectrum almost identical with that of the complex¹⁰ $[\text{Ni}(\text{py})_6](\text{ClO}_4)_2$. The same spectrum is observed in nitromethane solution in the presence of excess lutidine. This solution has a conductivity of $162 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ for $10^{-3} M$ concentration at 25° , in the range expected for 2:1 electrolytes,¹⁴ whereas the corresponding dichloromethane solution has a conductivity ($26 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ at $10^{-3} M$) much lower than expected. The electronic spectra of $\text{Ni}(3,4\text{-L})_4(\text{ClO}_4)_2$ (solid, solution, and solution with excess lutidine) are listed in Tables IV and V.

The 3,5-lutidine forms a pale blue crystalline complex with nickel(II) perchlorate of the formula $\text{Ni}(3,5\text{-L})_4(\text{ClO}_4)_2$. The magnetic moment (3.27 B.M.) of the solid complex corresponds to that of octahedral nickel(II) compounds, thereby implying coordination of the perchlorate ion. The infrared spectrum of the solid compound shows (Table III and Fig. 4) that the T_d symmetry of the ClO_4^- ion has been reduced to C_{3v} . The ν_3 mode, which in the free perchlorate ion appears as a very strong broad band at 1100 cm^{-1} , is split into two very strong bands at 1135 and 1030 cm^{-1} , and the ν_1 mode, which in the free ion is infrared inactive and is present as a very weak absorption at 930 cm^{-1} , now appears as a very intense sharp band at the same frequency. Thus the infrared spectrum confirms that the perchlorate ion is coordinated to nickel(II) through one of the oxygen atoms as reported⁶ for the solid $\text{Ni}(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$. The $\text{Ni}(3,5\text{-L})_4(\text{ClO}_4)_2$ complex is soluble in dichloromethane to give a yellow solution, with an electronic spectrum (Table V) nearly identical with that of the corresponding complex of 3,4-L and an infrared spectrum that shows the presence of uncoordinated perchlorate. In the presence of excess lutidine the yellow solution becomes blue and its electronic spectrum is now almost identical with that of $[\text{Ni}(\text{py})_6](\text{ClO}_4)_2$, as for the 3,4-L complex. The electronic spectra of

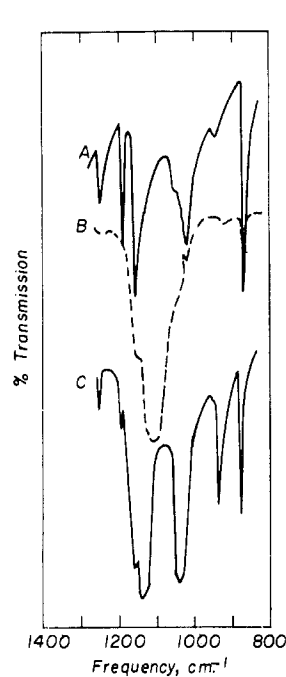


Fig. 4.—Infrared spectra of: A, $[\text{Ni}(3,5\text{-L})_4\text{Br}_2]$ in KBr; B, $[\text{Ni}(3,5\text{-L})_4](\text{ClO}_4)_2$ in CH_2Cl_2 solution; C, $[\text{Ni}(3,5\text{-L})_4](\text{ClO}_4)_2$ in Nujol mull.

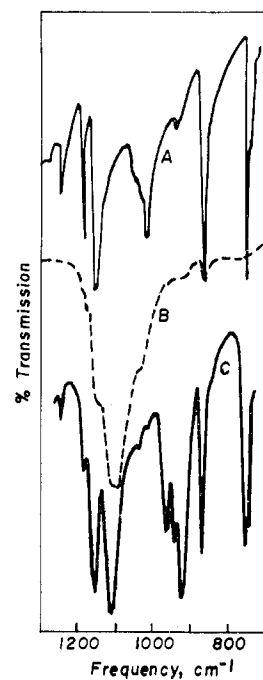


Fig. 5.—Infrared spectra of: A, $[\text{Ni}(3,5\text{-L})_4\text{Br}_2]$ in KBr; B, $[\text{Ni}(3,5\text{-L})_4](\text{BF}_4)_2$ in CH_2Cl_2 solution; C, $\text{Ni}(3,5\text{-L})_4(\text{BF}_4)_2$ in Nujol mull.

$\text{Ni}(3,5\text{-L})_4(\text{ClO}_4)_2$ (solid, solution, and solution with excess lutidine) are listed in Tables IV and V.

Attempts to isolate the blue $[\text{NiL}_6](\text{ClO}_4)_2$ failed because the blue solutions, on evaporation to dryness or precipitation with hydrocarbons or ethyl ether, gave again either the yellow $[\text{Ni}(3,4\text{-L})_4](\text{ClO}_4)_2$ or the blue $[\text{Ni}(3,5\text{-L})_4](\text{ClO}_4)_2$.

The lutidine complexes of nickel(II) tetrafluoroborate resemble closely those of the perchlorate. The 3,4-L complex is a yellow diamagnetic substance of formula $\text{Ni}(3,4\text{-L})_4(\text{BF}_4)_2$, analogous to the corresponding perchlorate both in the solid state and in solution. The 3,5-L complex is a pale blue paramagnetic substance of formula $\text{Ni}(3,5\text{-L})_4(\text{BF}_4)_2$, which in the solid state has a magnetic moment (Table I) corresponding to an essentially octahedral structure. The coordination of the tetrafluoroborate ion is confirmed by the infrared spectrum of the solid complex (Fig. 5). In place of the very strong broad band⁸ corresponding to the ν_3 mode of the BF_4^- ion at about 1100 cm^{-1} , the spectrum shows two very strong bands at $1120\text{--}1110 \text{ cm}^{-1}$ and at 925 cm^{-1} . Also, the strong band of the coordinated 3,5-lutidine at 752 cm^{-1} , which in the other complexes is very sharp and narrow, now appears slightly broader at 758 cm^{-1} , with two well-defined shoulders at 752 and 763 cm^{-1} , respectively. This may be considered an indication that the ν_1 mode of the BF_4^- ion at about 760 cm^{-1} had become infrared active, as observed⁷ in $(\text{CH}_3)_3\text{Sn} \cdot \text{BF}_4$, for which it has been reported that the BF_4^- ion coordinates as a bidentate group. In addition, the spectrum of $[\text{Ni}(3,5\text{-L})_4(\text{BF}_4)_2]$ shows a new band of medium-

weak intensity at 959 cm^{-1} , not well resolved from the strong 925 cm^{-1} absorption. Tentative assignments of the anion bands in the spectrum of $[\text{Ni}(3,5\text{-L})_4(\text{BF}_4)_2]$ can be made by analogy with the spectrum of the perchlorate ion⁶ and are reported in Table III. Like the corresponding perchlorate, the 3,5-L tetrafluoroborate complex dissolves in dichloromethane to give a yellow solution, having an electronic spectrum (Table V) identical with that of the 3,4-L compound and an infrared spectrum that shows the typical absorption of the free BF_4^- ion (Table III). It may be mentioned here that finely powdered $[\text{Ni}(3,5\text{-L})_4(\text{BF}_4)_2]$ reacts to a large extent with KBr, under the conditions used for making the disks for infrared spectra, to give uncoordinated BF_4^- , whereas the analogous perchlorate complex $\text{Ni}(3,5\text{-L})_4(\text{ClO}_4)_2$ remains unaltered. The electronic spectra of $\text{Ni}(3,5\text{-L})_4(\text{BF}_4)_2$ (solid, solution, and solution with excess lutidine) are given in Tables IV and V.

Discussion and Conclusions

The direct reaction of nickel(II) salts with an excess of 3,4- and 3,5-lutidine yields two series of new complex compounds, $\text{Ni}(3,4\text{-L})_4\text{X}_2$ and $\text{Ni}(3,5\text{-L})_4\text{X}_2$ (X = univalent anion), which are similar except for a few significant differences limited to the solid state. Magnetic and spectral properties show in fact that in the solid complexes of 3,5-L the central nickel(II) attains a distorted octahedral structure by coordination of the anions. This not only occurs with the common donor anions such as the halides and NCS^- , but also with NO_3^- , which is usually considered to have poor donor properties, and even with ClO_4^- and BF_4^- , which are typical noncoordinating anions. With 3,4-L, on the other hand, the octahedral arrangement NiL_4X_2 is attained only with $\text{X} = \text{Cl}^-$, Br^- , NCS^- , and NO_3^- , whereas a square-planar structure results when $\text{X} = \text{I}^-$, ClO_4^- , BF_4^- .

Of this series of complexes, the perchlorate and tetrafluoroborate compounds appear to be the most interesting. The compound $[\text{Ni}(3,5\text{-L})_4(\text{ClO}_4)_2]$ is one of the few known metal complexes containing coordinated perchlorate groups,^{6,19,20} and $[\text{Ni}(3,5\text{-L})_4(\text{BF}_4)_2]$ is to our knowledge the first observed example of monodentate coordination of the BF_4^- ion. The only other reported case of coordinated BF_4^- is trimethyltin tetrafluoroborate,⁷ $(\text{CH}_3)_3\text{Sn}\cdot\text{BF}_4$, in which the BF_4^- ion appears to act as a bidentate bridging ligand. The formation of $[\text{Ni}(3,5\text{-L})_4(\text{ClO}_4)_2]$ and $[\text{Ni}(3,5\text{-L})_4(\text{BF}_4)_2]$ is remarkable as it takes place easily in the presence of ethanol, a rather good donor solvent for nickel(II), and in the presence of an excess of the lutidine ligand. However, the existence of these octahedral complexes, $[\text{Ni}(3,5\text{-L})_4(\text{ClO}_4)_2]$ and $[\text{Ni}(3,5\text{-L})_4(\text{BF}_4)_2]$, is limited to the solid state. In dichloromethane solution they dissociate to give

the uncoordinated anions and the diamagnetic square-planar complex cation $[\text{Ni}(3,5\text{-L})_4]^{+2}$ and become similar to the corresponding 3,4-L complexes.

In the spectra of the $[\text{Ni}(3,4\text{-L})_4]\text{X}_2$ salts ($\text{X} = \text{ClO}_4^-$, BF_4^-) a shift to lower frequencies is observed on passing from the solid to the dichloromethane solution and may be attributed²¹ to interactions of the solvent molecules with the nickel(II) ion along the z -axis of the square-planar complex. These interactions are too weak to alter the magnetic state of the nickel(II) ion, but when an excess of the lutidine ligand is added to the solution the axial perturbation becomes much stronger and the complex species changes from the yellow diamagnetic $[\text{NiL}_4]^{+2}$ to the blue paramagnetic $[\text{NiL}_6]^{+2}$. The spectra of $[\text{Ni}(3,4\text{-L})_6]^{+2}$ and $[\text{Ni}(3,5\text{-L})_6]^{+2}$ show that 3,4- and 3,5-lutidine occupy in the spectrochemical series a position very close to that of pyridine, as confirmed by the similarity of the spectra of $[\text{NiL}_4\text{Cl}_2]$ and $[\text{NiL}_4(\text{NCS})_2]$ with those of the corresponding pyridine complexes. In view of this evidence the existence and stability of the $[\text{NiL}_4]^{+2}$ complex ion appears more remarkable. Spin pairing in nickel(II) complexes is usually induced by chelating ligands or by monodentate ligands which produce a strong field. Since the field of the 3,4- and 3,5-lutidine is much weaker than that of the ligands (alkylphosphines, thiocyanate ion) which usually form diamagnetic nickel(II) complexes, the stabilization of the low-spin state in $[\text{NiL}_4]^{+2}$ probably results from a fine balance between the perturbing powers of the lutidines and of the anions, and when in solution also from the influence of the solvent.

It is surprising that in the solid state, while the 3,4-L complexes maintain the square-planar configuration, those of 3,5-L become octahedral through coordination of the ClO_4^- and BF_4^- anions. It seems likely that the slight difference in basicity²² and possible π -bonding character of the two lutidines, as well as lattice energies, are in this case the factors determining the difference in stereochemistry.

Of the other complexes prepared, only the chloro and bromo derivatives require a few additional comments. In the solid state they are similar to the corresponding pyridine complexes but, unlike them, dissociate in dichloromethane solution with loss of some of the coordinated lutidine to give an equilibrium mixture of two new compounds. One is the tetrahedral $[\text{NiL}_2\text{X}_2]$ and the other is an octahedral species, very likely associated through halogen bridges. Similar equilibria are known for cobalt(II) complexes of the type $[\text{Co}(\text{py})_2\text{X}_2]$,²³ for $[\text{Ni}(\text{quinoline})_2\text{Cl}_2]$,²⁴ and also for the some nickel(II) chelates.²⁵ The octahedral complex $[\text{NiL}_4\text{X}_2]$ can be obtained in solution only if a sufficient amount of free lutidine is present.

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In the solid state the complexes $[\text{NiL}_4\text{X}_2]$ lose lutidine on heating. In this way we have obtained in a pure state the compound $[\text{Ni}(3,4\text{-L})_2\text{Br}_2]$, and the preparation of other compounds of this type is in progress. The blue-violet $[\text{Ni}(3,4\text{-L})_2\text{Br}_2]$ closely resembles the corresponding complexes of 2,3- and 2,4-lutidine. Its magnetic moment, as well as its electronic spectrum, is consistent with a pseudo-tetrahedral configuration,

only slightly distorted from the true T_d symmetry. Thus octahedral, tetrahedral, and square-planar configurations can be obtained for the complexes of nickel(II) salts with 3-substituted lutidines, depending on the anion, the lutidine ligand, and the physical state of the complex.

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CONTRIBUTION FROM THE UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN,
AND THE POLYTECHNIC INSTITUTE OF BROOKLYN, BROOKLYN, NEW YORK

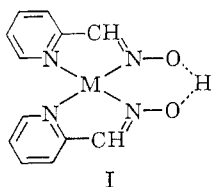
Some Homo- and Heteropolynuclear Chelates

BY CHUI FAN LIU AND C. H. LIU

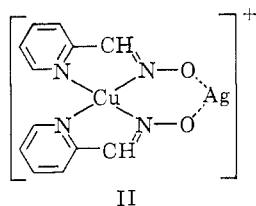
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The complex compounds *cis*-bis(pyridine-2-aldoxime)copper(II), -palladium(II), and -platinum(II) themselves have been successfully used as coordinating agents. They behave as oxygen-donor bidentate ligands in forming metal chelates. Homopolynuclear chelates and heteropolynuclear chelates have been prepared containing one, two, or three of these "metal-complex" chelating agents.

Previous investigations¹⁻³ showed that square-planar complexes of pyridine-2-aldoxime were capable of intramolecular hydrogen bonding in the following type of structure.



It seems reasonable that in this type of structure, the oximate oxygens are so situated that other cations may substitute for the hydrogen ion to form regular metal coordination compounds. Potentiometric measurements have shown the existence of the following Cu(II)-Ag(I) heteropolynuclear chelate.⁴



The present investigation is concerned with the ability of complexes with this type of structure to coordinate with other metal ions to form isolable homo- and heteropolynuclear chelates.

Experimental

Homopolynuclear Chelates. Bis[bis(pyridine-2-aldoxime)copper(II)]copper(II) Perchlorate.—Pyridine-2-aldoxime was obtained from Aldrich Chemical Company, Milwaukee, Wis., and used without further purification. An aqueous solution of 1.70 g. (0.01 mole) of cupric chloride dihydrate in about 50 ml. was treated with 2.44 g. (0.02 mole) of pyridine-2-aldoxime dissolved in the stoichiometric volume of 0.1 *F* sodium hydroxide (1:1 by mole). The dark green solution was filtered, and solid sodium perchlorate was added. A crystalline precipitate formed which was filtered out, washed with distilled water, and air dried. *Anal.* Calcd. for $[\text{Cu}(\text{C}_5\text{H}_5\text{N}_2\text{O})_2]_2\text{Cu}(\text{ClO}_4)_2$: C, 32.97; H, 2.29; N, 12.82. Found: C, 32.64; H, 2.28; N, 12.75. The same compound was obtained when dihydrogen bis(pyridine-2-aldoxime)copper(II) sulfate² was neutralized with sodium hydroxide (1:2 by mole) and sodium perchlorate was added to the resulting solution.

The iodide of this homopolynuclear chelate was prepared in the same manner as the perchlorate. *Anal.* Calcd. for $[\text{Cu}(\text{C}_5\text{H}_5\text{N}_2\text{O})_2]_2\text{CuI}_2$: C, 31.10; H, 2.16; N, 12.10. Found: C, 31.53; H, 2.29; N, 12.49.

Bis[bis(pyridine-2-aldoxime)copper(II)]copper(II) Sulfate.—A solution of 4.57 g. of dihydrogen bis(pyridine-2-aldoxime)copper(II) sulfate trihydrate² in about 50 ml. was neutralized with the stoichiometric amount of 1 *F* sodium hydroxide. The resulting solution was evaporated on a steam bath to a very small volume, and about 100 ml. of methanol was added, followed by the addition of about 200 ml. of dioxane. Upon slow evaporation at room temperature, crystals formed. These were filtered out, washed with dioxane and then ether, and air dried. *Anal.* Calcd. for $[\text{Cu}(\text{C}_5\text{H}_5\text{N}_2\text{O})_2]_2\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$: C, 34.99; H, 3.13; N, 13.62. Found: C, 34.10; H, 3.16; N, 13.98.

Dichloro[bis(pyridine-2-aldoxime)copper(II)]copper(II).—An aqueous solution of 1.70 g. of cupric chloride dihydrate in about 50 ml. was treated with 2.44 g. of pyridine-2-aldoxime dissolved in the stoichiometric volume of 0.1 *F* sodium hydroxide. Upon the addition of excess sodium chloride, a green precipitate formed which was filtered out, washed with distilled water, and air dried. *Anal.* Calcd. for $[\text{Cu}(\text{C}_5\text{H}_5\text{N}_2\text{O})_2]\text{CuCl}_2 \cdot \text{H}_2\text{O}$: C, 31.51;

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