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Coordination Compounds of Nickel(II) with Substituted Pyridines. Square-Planar, Tetrahedral, and Octahedral Compounds of 2,3-, 2,4-, and 2,5-Dimethylpyridine

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The preparation and properties of a new series of coordination compounds of nickel(II) with α -substituted dimethylpyridines (α -lutidines, L) are reported. The compounds are nonelectrolytes of the types $[\text{NiL}_2\text{X}_2]$ ($\text{X} = \text{Cl}^-$, Br^- , I^- , NO_3^- , or NCS^- ; $\text{L} = \alpha$ -lutidine) and $[\text{NiL}_3(\text{NCS})_2]$. Their steric arrangements are discussed on the basis of their magnetic and spectral properties.

Introduction

The coordination compounds of pyridine with transition metal ions are among the most extensively and accurately studied, and it is somewhat surprising, in contrast, that relatively little work of a similar type has been reported for substituted pyridines. Because of the simplicity and rigidity of the pyridine system, and because an appropriate choice of substituents and of their position permits one to vary, simultaneously or independently, both the donor tendency of the N-ring atom and the steric requirements of the molecule, substituted pyridines appear to be especially suited to the investigation of the factors which influence the stereochemistry of metal complexes. Since the problem of the choice of steric configuration in nickel(II) complexes is still largely unsolved, in spite of a wealth of excellent work, we thought it worthwhile to investigate the coordination compounds of nickel(II) with substituted pyridines, starting with the mono- and polysubstituted methylpyridines. The partial results of the work on the α -, β -, and γ -picolines has been published.¹ The present paper reports a similar study on the complexes of the four isomeric α -substituted dimethylpyridines (α -lutidines, designated as L or more specifically as 2,3-L, 2,4-L, 2,5-L, and 2,6-L).

The accurate characterization of the various isomeric lutidines by their physical properties²⁻⁴ is rather recent and little is so far known of their donor properties. However, useful information may be derived by analogy with the behavior of related compounds. It has been found^{5,6} that the electron density on the N-ring atom of heterocyclic bases runs parallel to the base strength for pyridine, α -, β -, and γ -picoline, and for quinoline and isoquinoline. It was also observed⁷

that for pyridine and the picolines the base strength correlates well with the donor properties of the N-ring atom toward a typical acceptor such as BF_3 , except when steric factors become significant. A similar correlation can be expected to hold for the lutidines. In fact it was found by Sacconi, *et al.*,⁸ that the tendency of several pyridine bases, including 2,4-, 2,5-, and 2,6-lutidine, to coordinate along the z -axis of the square-planar complex $\text{Ni}(\text{diacetyl}(\text{bisbenzoyl})\text{hydrazone})$, $[\text{Ni}(\text{DBH})]$, is proportional to their base strength, except for 2,6-L whose methyl groups interfere with the plane of the $[\text{Ni}(\text{DBH})]$ complex. However, 2,6-L forms a relatively stable complex with $[\text{Ni}(\text{DBH})]$, whereas the presence of even one methyl group in the α -position of α -picoline prevents complex formation with BF_3 .⁷ This contradiction cannot be explained simply on the basis of steric requirements, as shown by molecular models; however for metal coordination compounds the influence of π -bonding cannot be neglected.

In general, the base strength of the lutidines increases slightly in the order: $\text{py} < 3,5\text{-L} < 2,5\text{-L} < 2,3\text{-L} < 3,4\text{-L} < 2,6\text{-L} < 2,4\text{-L}$ (the values⁸ of $\text{p}K_a$ being in the same order: 5.30, 6.34, 6.55, 6.56, 6.61, 6.72, 6.80), whereas steric requirements differ largely between the four α -substituted and the two β -substituted lutidines. Therefore we might expect differences of coordinating ability not only between the two classes but also within each class.

Finally, the nickel(II) salts used in this investigation were chosen in order to have a fairly complete series of univalent anions, with donor properties ranging from good (halides) to practically nil (tetrafluoroborate).

Experimental

Starting Materials.—The lutidines (Aldrich Chemical Co.) were distilled under reduced pressure and stored over molecular sieves. Their infrared spectra checked with those reported in the literature.² Anhydrous nickel(II) chloride and bromide (Fielding Chemical Co.) were used without further purification. Anhydrous nickel(II) iodide was purified by extracting first the free iodine with carbon tetrachloride and then dissolving in anhydrous ethanol and filtering off the black residue formed. The resulting ethanol solution was used for the preparation of the

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TABLE I
 ANALYTICAL DATA OF NICKEL(II) COMPLEXES

Compound	Nickel, %		Carbon, %		Hydrogen, %		Halogen, %	
	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
[Ni(2,3-L) ₂ Cl ₂]	16.92	17.07	47.03	48.89	5.20	5.27	20.72	20.64
[Ni(2,4-L) ₂ Cl ₂]			48.41		5.22		21.13	
[Ni(2,5-L) ₂ Cl ₂]			48.16		5.46		20.66	
[Ni(2,3-L) ₂ Br ₂]			38.31	38.85	4.62	4.19	36.55	36.93
[Ni(2,4-L) ₂ Br ₂]			38.70		4.23		36.66	
[Ni(2,5-L) ₂ Br ₂]			39.12		4.31		36.87	
[Ni(2,3-L) ₂ I ₂]	11.22	11.14	32.26	31.91	3.65	3.44		
[Ni(2,4-L) ₂ I ₂]	11.06		32.12		3.75			
[Ni(2,5-L) ₂ I ₂]	11.00		30.97		3.49			
[Ni(2,3-L) ₂ (NCS) ₂]·0.5H ₂ O	11.35	11.61	54.62	54.66	5.42	5.58	22.53 ^a	22.98 ^a
[Ni(2,4-L) ₂ (NCS) ₂]·0.5H ₂ O	11.20		55.01		5.42		22.63 ^a	
[Ni(2,5-L) ₂ (NCS) ₂]·0.5H ₂ O	14.72	14.74	48.56	48.76	4.73	4.80	29.05 ^a	29.17 ^a
[Ni(2,3-L) ₂ (NO ₃) ₂]	14.57	14.78	39.15 ^b	42.36	4.41	4.57		
[Ni(2,4-L) ₂ (NO ₃) ₂]	14.50		41.22 ^b		4.47			
[Ni(2,5-L) ₂ (NO ₃) ₂]	14.60		41.25 ^b		4.48			

^a % SCN⁻. ^b Carbon results are low, probably owing to difficulty in the combustion.

complexes. The ethanol complexes of nickel(II) perchlorate and nitrate were prepared by mixing stoichiometric amounts of anhydrous nickel(II) bromide with silver perchlorate and nitrate, respectively, in ethanol solution. After filtering off the silver bromide and taking the solution to dryness under reduced pressure, the ethanol complexes were obtained as pale green crystals. Nickel(II) thiocyanate hemihydrate was used after crystallization from ethanol.

Preparation of the Complexes of 2,3-, 2,4-, and 2,5-Lutidine.—The complexes prepared, together with their colors, melting or decomposition temperatures, and magnetic moments, are listed in Table I. The complexes of nickel(II) halides and thiocyanate were prepared by addition of excess lutidine to a saturated ethanol solution of the nickel(II) salts. The products separated from the solution as well-formed crystals or microcrystalline powders. These were filtered off, washed with ethyl ether, and dried *in vacuo*. The chloro, bromo, and thiocyanato complexes were also prepared as follows: The finely powdered nickel(II) salt was refluxed for several hours with an excess of lutidine. A solid and a solution were obtained, having the same color. The solid was separated from the hot solution and extracted repeatedly with dichloromethane. The dichloromethane solution, on dilution with ethyl ether, gave the complex as well-formed crystals which were washed and dried as above. A purer crop of crystalline complex was obtained from the hot lutidine solution upon cooling.

The nickel(II) nitrate complexes were prepared by treating a saturated ethanol solution of the nickel(II) nitrate-ethanol complex with an excess of lutidine. The product separated rapidly as well-formed crystals, which were filtered off, washed with ethyl ether, and dried *in vacuo*.

The ethanol complex of nickel(II) perchlorate reacted with lutidine upon warming at about 80° under reduced pressure. The oily product thus obtained was made to crystallize by repeated washing with ethyl ether or cyclohexane and by scraping the walls of the vessel. By this method, 2,4- and 2,5-lutidine gave yellow microcrystalline products, whereas 2,3-lutidine gave pink-lavender well-formed crystals. All these compounds are extremely sensitive to moisture which transforms them into greenish powders; they are also decomposed by most organic solvents. The 2,4- and 2,5-lutidine derivatives are soluble in dichloromethane to give yellow solutions stable in the absence of moist air, but the 2,3-lutidine derivative is completely decomposed even by dichloromethane. Because of their great sensitivity to moisture and solvents, the perchlorate compounds were not obtained pure. Attempts to prepare perchlorate compounds from the acetonitrile-nickel(II) perchlorate complex gave only "mixed ligand" complexes which were not investigated further.

Complexes of 2,6-Lutidine.—The reaction of 2,6-lutidine with nickel(II) salts, carried out as described for the other lutidines,

gave the following incomplete results and was not further investigated at this time. **Chloro complex:** a mixture of a green-yellow and of a deep blue-violet product was obtained. **Bromo complex:** a blue crystalline material was formed which had the correct analysis for NiL₂Br₂, but under the microscope appeared to be a mixture of two substances. **Thiocyanato complex:** obtained as a red crystalline mass, which could not be purified because of its insolubility and did not have a correct analysis. **Nitrate and perchlorate complexes:** no definite products were obtained under the conditions used for the other lutidines. The iodo complex was prepared pure without difficulty and is analogous to the iodo complexes of the 2,3-, 2,4-, and 2,5-lutidines. The chloro, bromo, and thiocyanato complexes are still under investigation.

Analyses.—Carbon and hydrogen were determined by microanalyses (Pascher Mikroanalytisches Laboratorium, Bonn, W. Germany), halogens by the Volhard method, and nickel by titration with EDTA. The analytical data are reported in Table I.

Magnetic susceptibility measurements were made by the Gouy method. The values of the magnetic moment, μ_{eff} , of the solid compounds are listed in Table II. The measurements in solution were only qualitative.

Absorption Measurements.—**Infrared spectra** were taken with a Perkin-Elmer Model 221 recording spectrophotometer equipped with a grating (4000–1400 cm⁻¹) and a sodium chloride prism (1400–650 cm⁻¹). The spectra of the solid complexes were obtained both in KBr disks and in Nujol mulls. The absorption frequencies (cm⁻¹, 700–1700 cm⁻¹ region) of the bromo complexes, arising from the coordinated lutidines, follow.

[Ni(2,3-L)₂Br₂]: 715 vs, 748 s, 790 vs, 850 vw, 975 sh, 990 m, 1008 w (nonresolved), 1020 m, 1073 w, 1135 s, 1180 sh, 1190 s, 1225 m, 1240 sh, 1275 m, 1375 m (nonresolved), 1415 sh, 1420–1465 vs (broad), 1540 w, 1570 sh, 1575 sh, 1592 vs, 1610 sh.

[Ni(2,4-L)₂Br₂]: 720 vw, 750 w, 828 vs, 900 vw, 928 m, 972 vw, 1027 s, 1170 w, 1232 w, 1275 w, 1302 s, 1365 vw, 1390 sh, 1425 s, 1445 m (nonresolved), 1492 s, 1540 sh, 1550 w, 1555 sh, 1618 sh, 1622 vs.

[Ni(2,5-L)₂Br₂]: 722 s, 832 vs, 858 w, 915 sh, 925 vw, 970 vw, 1034 m, 1045 sh, 1070 w, 1142 s, 1220 w, 1243 s, 1285 sh, 1300 s, 1360 sh, 1380 m (broad), 1425 s (nonresolved), 1440 sh, 1453 s, 1490 sh, 1500 vs, 1540 vw, 1555 w, 1570 w, 1605 sh, 1615 m.

The spectra of the other complexes are almost identical in the organic part, but the thiocyanato and nitrate complexes show in addition bands typical of these anions, reported in Table III. The assignments of the anion bands are made according to previously reported investigations.

Visible spectra of the solutions and of the solids in Nujol mulls were taken with a Cary Model 14 recording spectrophotometer and are reported in Tables IV and V and Fig. 1 and 2.

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

Compound	Color	M.p. or dec. temp. ^b	$\mu_{\text{eff.}}$ ^a B.M.
$[\text{Ni}(2,3\text{-L})_2\text{Cl}_2]$	Blue	99° turns pink	3.61
$[\text{Ni}(2,4\text{-L})_2\text{Cl}_2]$	Blue	98° turns white	3.60
$[\text{Ni}(2,5\text{-L})_2\text{Cl}_2]$	Blue-violet	94° turns pink	Diamag.
$[\text{Ni}(2,3\text{-L})_2\text{Br}_2]$	Blue	119° turns gray	3.54
$[\text{Ni}(2,4\text{-L})_2\text{Br}_2]$	Blue	105° dec.	3.53
$[\text{Ni}(2,5\text{-L})_2\text{Br}_2]$	Blue	103° dec.	Diamag.
$[\text{Ni}(2,3\text{-L})_2\text{I}_2]$	Dark green	112° dec.	Diamag.
$[\text{Ni}(2,4\text{-L})_2\text{I}_2]$	Dark green	110° dec.	Diamag.
$[\text{Ni}(2,5\text{-L})_2\text{I}_2]$	Dark green	117° dec.	Diamag.
$[\text{Ni}(2,3\text{-L})_2(\text{SCN})_2] \cdot 0.5\text{H}_2\text{O}$	Yellow-green	105° turns orange	3.32
$[\text{Ni}(2,4\text{-L})_2(\text{SCN})_2] \cdot 0.5\text{H}_2\text{O}$	Green	120° turns yellow	3.34
$[\text{Ni}(2,5\text{-L})_2(\text{SCN})_2] \cdot 0.5\text{H}_2\text{O}$	Red	133° turns yellow	Diamag.
$[\text{Ni}(2,3\text{-L})_2(\text{NO}_3)_2]$	Light green	137° melts	3.17
$[\text{Ni}(2,4\text{-L})_2(\text{NO}_3)_2]$	Light green	146° melts	3.15
$[\text{Ni}(2,5\text{-L})_2(\text{NO}_3)_2]$	Light blue-green	148° melts	3.14

^a At 20°. Diamagnetic corrections were made. ^b Decomposition gives a yellow solid which does not melt.

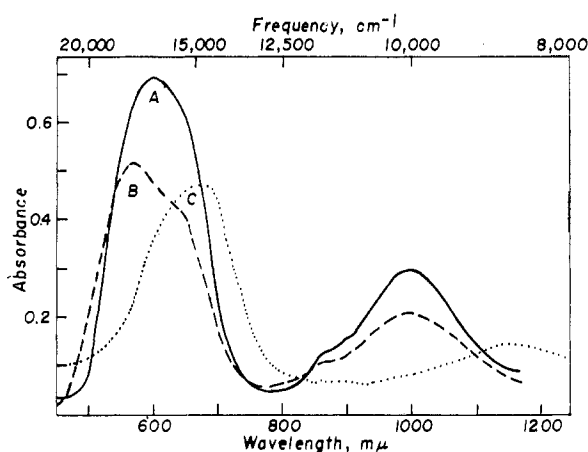


Fig. 1.—Absorption spectra of $[\text{Ni}(2,3\text{-L})_2\text{Br}_2]$: (A) solid in Nujol mull, (B) 0.0039 *M* in CH_2Cl_2 containing excess 2,3-L (1.0 *M*), (C) 0.0026 *M* in CH_2Cl_2 containing excess $[(\text{C}_4\text{H}_9)_4\text{N}]\text{Br}$.

Other Measurements.—Dipole moments and molecular weights could not be measured because most of the complexes studied are not soluble in, are decomposed by, or undergo changes in stereochemistry when treated with solvents suitable for these measurements.

Results

Nickel(II) Chloride and Nickel(II) Bromide Complexes.—The anhydrous NiCl_2 and NiBr_2 form well-crystallized complexes of composition NiL_2X_2 (*L* = lutidine; *X* = Cl, Br), deep blue for 2,3- and 2,4-lutidine and violet for 2,5-lutidine. These complexes are slightly hygroscopic and in water give pale green solutions. They are soluble in most organic solvents capable of coordination, but the electronic spectra of the solutions show that solvation occurs even when the coordinating power of the solvent is not high (as with nitromethane and acetonitrile). In solvents with practically no coordinating power, such as aromatic and saturated hydrocarbons, the complexes are almost insoluble. When treated with dichloromethane, the NiL_2X_2 complexes give a small amount of a yellowish powder, identified as anhydrous NiX_2 , and a deep blue

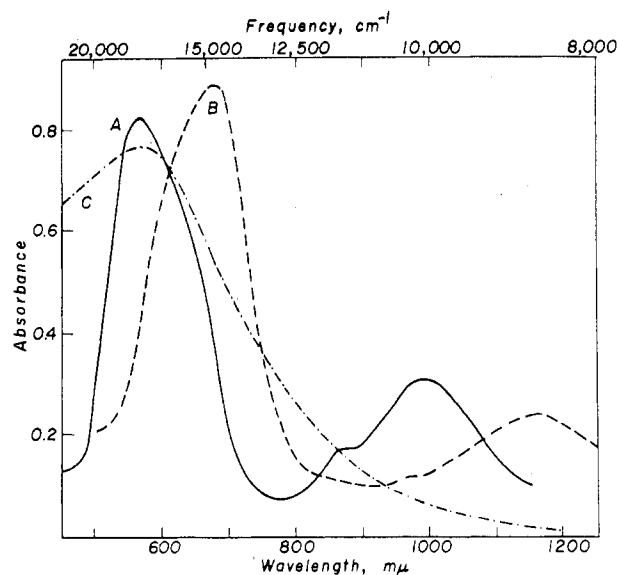


Fig. 2.—Absorption spectra of $[\text{Ni}(2,5\text{-L})_2\text{Br}_2]$: (A) 0.005 *M* in CH_2Cl_2 containing excess 2,5-L (1.0 *M*), (B) 0.0045 *M* in CH_2Cl_2 containing excess $[(\text{C}_4\text{H}_9)_4\text{N}]\text{Br}$, (C) solid in Nujol mull.

solution which on evaporating to dryness separates a solid identical with the starting complex. The filtered deep blue solution has a spectrum similar to that of the corresponding solid compound, though the bands of the latter are much broader, especially in the 500–650 $\text{m}\mu$ region. In other chlorinated solvents, such as 1,2-dichloroethane and chlorobenzene, the complexes NiL_2X_2 behave as in dichloromethane. In dichloromethane containing an excess of free ligand the complexes are completely soluble, and the spectra of the solutions are practically unshifted from the spectra of the corresponding solids and almost identical with those of the solutions in pure dichloromethane. The NiL_2X_2 complexes are also completely soluble in dichloromethane containing excess of halide ion, as tetraphenylarsonium $[(\text{C}_6\text{H}_5)_4\text{As}]^+$ or tetrabutylammonium $[(n\text{-C}_4\text{H}_9)_4\text{N}]^+$ salts, when the halide-to-nickel ratio is in the range of 5 to 10. For a halide-to-nickel ratio of about 8, the spectrum of the solution is similar to that

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

Compound	Medium	Absorption bands ^a
[Ni(2,3-L) ₃ (SCN) ₂].0.5H ₂ O	Solid in KBr and Nujol	2090 sh } CN stretching 2075 vs } 816 m, CS stretching
[Ni(2,4-L) ₃ (SCN) ₂].0.5H ₂ O	Solid in KBr and Nujol	2080 vs, CN stretching 816 s, CS stretching
	Soln. in CH ₂ Cl ₂	2095 vs, CN stretching 855 m, CS stretching
	Soln. in CH ₂ Cl ₂ , containing excess of L ^b	2075 vs, CN stretching
[Ni(2,5-L) ₂ (SCN) ₂].0.5H ₂ O	Solid in KBr and Nujol	2115 vs, CN stretching 859 vs, CS stretching
	Soln. in CH ₂ Cl ₂ , containing excess of L ^b	2080 vs, CN stretching
[Ni(2,3-L) ₂ (NO ₃) ₂]	Solid in KBr and Nujol	1480 vs, ^c NO ₂ asym. stretching 1280-1250 vs, vbr., NO ₂ sym. stretching ... ^d 825 m, nonplanar rocking
[Ni(2,4-L) ₂ (NO ₃) ₂]	Solid in KBr and Nujol	1530-1480 vs, vbr., ^c NO ₂ asym. stretching 1275 vs, vbr., NO ₂ asym. stretching 1015 vs, ^c NO(Ni) stretching 808 vs, nonplanar rocking
[Ni(2,5-L) ₂ (NO ₃) ₂]	Solid in KBr and Nujol	1500-1470 vs, vbr., ^c NO ₂ asym. stretching 1268 vs, NO ₂ sym. stretching 1065 vs, ? 1020 vs, NO(Ni) stretching 808 vs, nonplanar rocking 752 vs, NO ₂ sym. or asym. bending

^a s, strong; m, medium; w, weak; br, broad; v, very. ^b The CS stretching vibration is overlaid by the strong band of the lutidine in this region. ^c Shows ill-defined shoulders and splitting and overlays strong bands of the coordinated lutidine. ^d The NO(Ni) stretching vibration enhances the 1020 cm.⁻¹ band of the coordinated lutidine.

of the solid but shifted to lower wave numbers. The same spectrum, which we attribute to the [NiLX₃]⁻ species, is observed in dichloromethane solutions containing [(*n*-C₄H₉)₄N]₂[NiX₄] and lutidine in the ratio 1:2. However, attempts to isolate the solid salts of the anion [NiLX₃]⁻ were unsuccessful because from its solutions the salts of the [NiX₄]⁻² ion separated. When the halide excess is very large (halide-to-nickel ratio about 20), the spectrum of the tetrahalogen nickelate(II) ion, [NiX₄]⁻², begins to appear. The absorption bands of the NiL₂X₂ compounds, in the solid state, in dichloromethane solution and in dichloromethane solution containing free halide ions, are listed in Table IV. Figures 1 and 2 show the spectra of [Ni(2,3-L)₂Br₂] and [Ni(2,5-L)₂Br₂]. The values of the magnetic moments (Table II) of the solid complexes of 2,3-L and 2,4-L are in the range 3.5-3.6 B.M., whereas the complexes of 2,5-L are diamagnetic in the solid state. However, these 2,5-L complexes become paramagnetic in dichloromethane solution containing either excess lutidine or excess halide.

The above results show that the chloro and bromo complexes of 2,3-L and 2,4-L, and in solution also those of 2,5-L, have a (pseudo) tetrahedral configuration, similar to that observed for other complexes of the type [Ni(ligand)₂X₂].⁹⁻¹⁴ The magnetic moments

of [NiL₂X₂] are intermediate between those⁹ of [Ni{(C₆H₅)₃P}₂X₂], which has a rather distorted tetrahedral structure, and those of [Ni{(C₆H₅)₃PO}₂X₂], to which a practically undistorted tetrahedral configuration has been assigned,¹³ and indicate that the deviation from the true tetrahedral symmetry is rather small. This is in agreement with the lack of splitting in the typical tetrahedral absorption bands.

A comparison of the energies of the absorption bands of the tetrahedral [NiL₂Cl₂] and [NiL₂Br₂] with the nomograph of Liehr and Ballhausen¹⁵ shows a very good agreement, within 5-10%. Thus, in analogy with the assignments made for other nickel(II) complexes of this type,^{16,17} we can assign the bands at 15,000-18,000 cm.⁻¹ to the ³T₁(F) → ³T₁(P) transition (ν₃) and the bands at 8000-10,000 cm.⁻¹ to the ³T₁(F) → ³A₂(F) transition (ν₂). The weak band, or shoulder, at about 11,000 cm.⁻¹ may be assigned to a spin-forbidden transition to an upper state arising from the ¹D state of the free ion. Similar considerations, limited to the spectra in solution, can be made for the complex ions [NiLX₃]⁻ (X = Cl, Br; L = 2,3-, 2,4-, or 2,5-L). For these compounds the agreement with Liehr and Ballhausen's calculated values is not as good as for the complexes [NiL₂X₂], similar to the case of the

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TABLE IV
 ELECTRONIC ABSORPTION SPECTRA OF THE TETRAHEDRAL NICKEL(II) COMPLEXES

Compound	Medium	$\lambda_{\max},^a$ m μ	ν_{\max} , cm. ⁻¹	$\lambda_{\max},^a$ m μ	ν_{\max} , cm. ⁻¹
[Ni(2,3-L) ₂ Cl ₂]	Solid, Nujol mull	~587 ^b	17,035	~977 ^b	10,235
	0.005 <i>M</i> in CH ₂ Cl ₂ contain- ing excess of L ^c	553 (109)	18,083	830 (sh)	12,050
	0.003 <i>M</i> in CH ₂ Cl ₂ contain- ing excess of Cl ^{-d}	~612 (sh)	10,665	987 (48)	10,130
		~575 (sh)	17,390	1110 (34)	9,010
[Ni(2,4-L) ₂ Cl ₂]	Solid, Nujol mull	~583 ^b	17,150	~970 ^b	10,310
	0.004 <i>M</i> in CH ₂ Cl ₂ contain- ing excess of L ^c	550 (122)	18,180	830 (sh)	12,050
	0.005 <i>M</i> in CH ₂ Cl ₂ with excess of Cl ^{-d}	~600 (sh)	16,665	985 (52)	10,150
		~585 (sh)	17,095	~845 (sh)	11,835
[Ni(2,5-L) ₂ Cl ₂]	Solid, Nujol mull	555 ^{b,e}	18,020		
	0.005 <i>M</i> in CH ₂ Cl ₂ contain- ing excess of L ^c	550 (125)	18,180	830 (sh)	12,050
	0.002 <i>M</i> in CH ₂ Cl ₂ contain- ing excess of Cl ^{-d}	~610 (sh)	16,390	980 (59)	10,205
		~575 (sh)	17,390	1125 (43)	8,890
[Ni(2,3-L) ₂ Br ₂]	Solid, Nujol mull	~605 ^b	15,530	~995 ^b	10,050
	0.004 <i>M</i> in CH ₂ Cl ₂ contain- ing excess of L ^c	572 (134)	17,480	865 (sh)	11,560
	0.003 <i>M</i> in CH ₂ Cl ₂ contain- ing excess of Br ^{-d}	~635 (sh)	15,750	1000 (53)	10,000
		~620 (sh)	16,130	1152 (58)	8,680
[Ni(2,4-L) ₂ Br ₂]	Solid, Nujol mull	~601 ^b	16,640	976 ^b	10,245
	0.004 <i>M</i> in CH ₂ Cl ₂ contain- ing excess of L ^c	565 (155)	17,700	863 (sh)	11,590
	0.003 <i>M</i> in CH ₂ Cl ₂ contain- ing excess of Br ^{-d}	~625 (sh)	16,000	997 (25)	10,030
		~625 (sh)	16,000	1165 (49)	8,580
[Ni(2,5-L) ₂ Br ₂]	Solid, Nujol mull	~575 ^{b,e}	17,390		
	0.005 <i>M</i> in CH ₂ Cl ₂ contain- ing excess of L ^c	568 (162)	17,605	865 (sh)	11,560
		~625 (sh)	16,000	990 (60)	10,100
	0.001 <i>M</i> in CH ₂ Cl ₂ contain- ing excess of Br ^{-d}	~625 (sh)	16,000	1153 (53)	8,670
		671 (199)	14,900		

^a Numbers in parentheses represent molar extinction coefficients at band maximum; sh, shoulder. ^b Center of a broad band. ^c The excess of the ligand is in the range of 1 *M* concentration. ^d The halide-to-nickel ratio is in the range of 5 to 10. ^e Diamagnetic solid.

[Ni{(C₆H₅)₃P}X₃]⁻ ions studied by Cotton, *et al.*¹⁸

Solid [Ni(2,5-L)₂Cl₂] and [Ni(2,5-L)₂Br₂], which are diamagnetic, can be assigned an essentially *trans* configuration. Their spectra as Nujol mulls (Table IV, Fig. 2) are similar in the contour and intensity of the bands to those of other square-planar compounds of nickel(II),^{19,20} but the main absorption band is shifted to lower frequencies. Accordingly, the color of the compounds is a deep blue-violet which sharply contrasts with the yellow or orange color of most square-planar nickel(II) compounds. We have been informed²¹ of another deep blue Ni(II) complex having a *trans* square-planar configuration and to our knowledge these are the first reported cases of low spin nickel(II) compounds with a typical high spin (tetrahedral) color.

Nickel(II) Iodide Complexes.—The anhydrous nickel(II) iodide, like the chloride and bromide, forms complexes of composition NiL₂I₂. These are dark green crystalline substances which in the solid state are diamagnetic and can be assigned a (distorted) square-planar configuration. Unfortunately this assignment cannot be substantiated by the absorption spectra of

the solids as Nujol mulls because the very intense charge-transfer bands largely obscure the ligand field absorptions. The behavior of these iodo complexes toward solvents is similar to that of the corresponding chloro and bromo compounds, except that they are less sensitive to moisture. When treated with dichloromethane, the iodo complexes give a yellow-brown solid, identified as NiI₂, and a greenish solution which turns yellow-brown upon dilution. In dichloromethane containing free lutidine they are completely soluble and the solution, greenish or yellow-brown depending on the concentration, appears to be identical with that in pure dichloromethane. It was not possible to obtain reliable values of the magnetism of these solutions because of the low solubility of the compounds. However, the spectra of the solutions, though partially obscured by the charge-transfer bands, are similar¹ to that of [Ni(α -picoline)₂I₂] and indicate a tetrahedral configuration.

Nickel(II) Thiocyanate Complexes.—The 2,3- and 2,4-lutidine give paramagnetic (Table II), yellow-green, crystalline complexes of composition corresponding to NiL₃(NCS)₂·0.5H₂O. When treated with dichloromethane these compounds give a small amount of a yellowish solid (probably nickel thiocyanate) and an orange-red solution from which yellow-green crystals, identical with the starting material, re-form upon evaporation. In the presence of an excess of lutidine, the green crystals dissolve completely to give a yellow-

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TABLE V
 ELECTRONIC ABSORPTION SPECTRA OF THE IODO, ISOTHIOCYANATO, AND NITRATO COMPLEXES

Compound	State	Absorption maxima, cm. ⁻¹	
[Ni(2,3-L) ₂ I ₂]	CH ₂ Cl ₂ soln.	16,260 (0.45) ^a	10,605 (0.045) ^a
		9,880 (0.05) ^a	
[Ni(2,4-L) ₂ I ₂]	CH ₂ Cl ₂ soln.	16,390 (0.16) ^a	10,695 (0.03) ^a
		9,850 (0.035) ^a	
[Ni(2,5-L) ₂ I ₂]	CH ₂ Cl ₂ soln.	16,285 (0.52) ^a	10,640 (0.085) ^a
		9,900 (0.09) ^a	
[Ni(2,3-L) ₃ (SCN) ₂] · 0.5H ₂ O	CH ₂ Cl ₂ soln.	19,230 (0.11) ^a	14,814 (0.6) ^a
[Ni(2,4-L) ₃ (SCN) ₂] · 0.5H ₂ O	CH ₂ Cl ₂ soln.	19,420 (~135) ^a	10,810 (0.04) ^a
	CH ₂ Cl ₂ soln., ex-	14,815 (1.05) ^a	~950 (0.33) ^a
	cess of L		
[Ni(2,5-L) ₂ (SCN) ₂] · 0.5H ₂ O	CH ₂ Cl ₂ soln.	19,230 (0.28) ^a	15,151 (0.18) ^a
[Ni(2,3-L) ₂ (NO ₃) ₂]	CH ₂ Cl ₂ soln.	25,000 (38) ^b	15,750 (19) ^b
		8,890 (8) ^b	
[Ni(2,4-L) ₂ (NO ₃) ₂]	CH ₂ Cl ₂ soln.	25,000 (41) ^b	15,750 (25) ^b
		8,890 (7) ^b	
[Ni(2,5-L) ₂ (NO ₃) ₂]	CH ₂ Cl ₂ soln.	25,000 (47) ^b	15,750 (27) ^b
		8,890 (8) ^b	

^a The numbers in parentheses represent the relative intensity of the bands. ^b The numbers in parentheses represent the molar extinction coefficient.

green solution. The 2,5-lutidine, on the other hand, forms a diamagnetic red crystalline complex of composition NiL₂(NCS)₂ · 0.5H₂O, which gives a rather unstable orange-red solution in pure dichloromethane and a more stable yellow-green solution in dichloromethane containing free lutidine. From this green solution red crystals separate upon concentration.

The orange-red solutions, obtained from either the red or the green crystals, have almost identical electronic absorption spectra with a sharp band at about 19,300 cm.⁻¹. Similarly the yellow-green solutions, obtained from either the green or the red solids in the presence of free lutidine, have nearly identical spectra with absorptions at about 14,800 and 9500 cm.⁻¹.

The infrared absorption frequencies of the thiocyanate group, Table III, also fall into two groups, one for the red (solid and solution) and one for the green (solid and solution) compounds. The frequencies for the red compounds are very close to those reported for the red-orange diamagnetic isothiocyanato complexes Ni(R₃P)₂(NCS)₂,²² whereas the ν(CS) values for the green compounds are lower but still in the range of isothiocyanato complexes. Unfortunately the CS stretching band (in the region 860–780 cm.⁻¹) is observed with difficulty in the red solutions, and in the green solutions it is completely obscured by the strong bands of the free lutidine.

From the above evidence it seems reasonable to assign to the red compound, Ni(2,5-L)₂(NCS)₂ · 0.5H₂O, a square-planar structure with the thiocyanate groups, coordinated through the nitrogen, in *trans* positions. A similar formula and structure may be postulated, by analogy, for the complexes present in the red solutions of the 2,3-L and 2,4-L complexes. The evidence available for the green compounds does not allow one to establish their structure unambiguously. However, on the basis of the information obtained it seems that they may have a dimeric, or polymeric, highly distorted octahedral structure with both bridging and terminal

NCS groups, similar to [Ni(NH₃)₃(NCS)₂].²³ The fact that the infrared spectrum shows only one (rather broad) band in the CN stretching region does not contradict this assumption, because in the case of the weak bridges expected for Ni(II) the CN absorption of the bridging SCN may fall²⁴ in the range 2070–2100 cm.⁻¹ and be unresolved from that of the terminal isothiocyanato groups. Finally, the infrared spectra of these compounds do not show the typical bands of coordinated water,²⁵ and it appears therefore that the 0.5H₂O required by the analysis is lattice water.

Nickel(II) Nitrate Complexes.—These complexes are well-crystallized bright green substances of the formula NiL₂(NO₃)₂. They are fairly stable to moisture and are very soluble in the common organic solvents, except hydrocarbons and ethyl ether. The magnetic moments of the solid compounds (Table II) and the electronic spectra of their dichloromethane solutions (Table V) indicate an essentially octahedral structure. Their infrared spectra show that the nitrate groups are coordinated^{26,27} and have a symmetry consistent with either unidentate or bidentate coordination. The great solubility of these compounds in dichloromethane, a solvent which appears not to coordinate, and the fact that the solutions have the same color as the solids are in favor of a monomeric formula. It seems therefore likely that the complexes NiL₂(NO₃)₂ have a rather distorted octahedral structure, with the nitrate groups acting as bidentate chelating ligands. In agreement with this formulation, the value of Δ, 8890 cm.⁻¹, obtained from their spectra is in good agreement with the value 8760 cm.⁻¹, roughly evaluated by the average environment rule from Δ = 8010 cm.⁻¹ for the octahedral polymeric [Ni(NO₃)₄]⁻²

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and $\Delta = 10,250 \text{ cm.}^{-1}$ for $[\text{Ni}(\text{py})_6]^{+2}$. The small increase in frequency may be ascribed to the chelation effect. Chelation of nitrate groups, suggested for the green paramagnetic complex²⁸ $[\text{Ni}\{(\text{C}_2\text{H}_5)_3\text{P}\}_2(\text{NO}_3)_2]$, has recently been shown by X-ray analysis²⁹ to occur in the complex $[\text{Co}\{(\text{CH}_3)_3\text{PO}\}_2(\text{NO}_3)_2]$.

Conclusions

The present work shows that the number of molecules of α -substituted lutidines which can coordinate to each nickel(II) ion is limited to two, with the exception of the isothiocyanato complexes for which compounds of the type $\text{NiL}_3(\text{NCS})_2$ have also been obtained. Since pyridine and β -substituted lutidines (to be reported) tend to form complexes of the type NiL_4X_2 , the limitation of the stoichiometry of the α -lutidine complexes to NiL_2X_2 may plausibly be ascribed to the steric requirement of the α -lutidines. This also indirectly accounts for the extreme instability of the complexes formed by the nickel(II) salts of noncoordinating anions, as well as for the difficulty in preparing complexes of 2,6-lutidine. Since these latter have not so far been obtained in a sufficiently pure state, we shall limit our considerations here to the complexes of 2,3-, 2,4-, and 2,5-lutidine.

The steric configuration adopted by the NiL_2X_2 complexes appears to be determined by the donor properties of both the anion and the lutidine ligand. Lattice energies also appear to be important, since changes in structure often take place when the solid complexes go into solution. Thus, in solution the chloro, bromo, and iodo complexes are all paramagnetic with a (pseudo) tetrahedral structure, whereas in the solid state the chloro and bromo complexes of 2,3- and 2,4-L are (pseudo) tetrahedral but the cor-

responding complexes of 2,5-L, as well as the three iodo complexes, are diamagnetic and can be assigned a (distorted) square-planar configuration. The change from the low-spin to the high-spin (tetrahedral) state, which accompanies the dissolution of the diamagnetic complexes, is similar to that observed for other complexes of nickel(II).⁹⁻¹²

The difference of structure in the solid state between the chloro and bromo complexes of 2,3- and 2,4-L and those of 2,5-L is rather unexpected, for the ligating abilities of these three lutidines, at least as evaluated from the spectra of their tetrahedral NiL_2Cl_2 and NiL_2Br_2 complexes in solution, do not appear to be appreciably different. However, the slight difference in basicity and probably π -bonding character from 2,3- and 2,4-L to 2,5-L, together with lattice effects, may be responsible for the stabilization of the square-planar configuration of the solid $[\text{Ni}(2,5\text{-L})_2\text{Cl}_2]$ and $[\text{Ni}(2,5\text{-L})_2\text{Br}_2]$. The change from the high-spin state of the chloro and bromo compounds of 2,3- and 2,4-L to the low-spin state of the corresponding solid iodo compounds is similar to that observed for $[\text{Ni}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{X}_2]$ ⁹ and for $[\text{Ni}(\text{quinoline})_2\text{X}_2]$ ³⁰ and may be attributed to an anion effect.

For the isothiocyanato complexes the situation is complicated by the different stoichiometry of the high-spin and low-spin compounds and by the changes in configurations that take place in solution on addition of free lutidine. However, it is observed again that the 2,5-L has a greater tendency to induce spin pairing than the 2,3- and 2,4-L. Finally, since the nitrate group NO_3^- produces a stronger field than the halides Cl^- , Br^- , and I^- , and at the same time is capable of coordinating as a bidentate ligand, the nitrate complexes $[\text{NiL}_2(\text{NO}_3)_2]$ reach octahedral configuration, very likely through chelation of the NO_3^- groups.

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