

Stereochemical Trends for Complexes of Cobalt(II) Halides and Thiocyanate with A Series of Mono-, Di- and Tri-methyl-pyridines

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The electronic and vibrational spectra of the cobalt(II) complexes of methyl-substituted pyridines have been systematically investigated in an effort to establish a general relationship between the electronic-steric requirements of the ligands and the stoichiometry, stereochemistry, and stability of the complexes. Some sixty complexes were examined, in which the anions were chloride, bromide, iodide and thiocyanate. The ligands included all possible isomers of the mono- and di-methyl-pyridines, as well as two of the isomeric tri-methyl-pyridines. In the course of this study some twenty new complexes were obtained and characterized, and of special interest among these was an unusual series of square pyramidal cationic species.

Introduction

We recently reported [1] the preparation and study of a new series of nickel(II) complexes with doubly hindered, 2,6-dimethyl-substituted-pyridine ligands (L). These complexes, of the general formula $[\text{NiX}_2\text{L}_2]$ (X = halide or thiocyanate) had a *trans*-square planar geometry and exhibited a unique inertness toward chemical reagents, including strong mineral acids. Consideration of the relevant electronic and steric factors for these Ni(II) species led us to conclude that their lack of reactivity was caused by a complete 'blocking' of the reactive sites, both of the Ni(II) and of the N-donor atoms, by the two α -substituents of each pyridine ring. Scale molecular models further suggested that whereas a *trans*-square planar $[\text{MX}_2\text{L}_2]$ species may indeed be stabilized by steric hindrance, a tetrahedral species of this stoichiometry probably would not be stabilized since the anion-anion edge of the tetrahedron would still offer ample room for attack by an incoming substituent. The scale models also indicated that a $[\text{CoX}_2\text{L}_2]$ tetrahedral species would involve considerable steric repulsion between the two α -CH₃ groups of each pyridine ligand and the neighboring halides or thiocyanates. Steric hindrance, however, often appears to be more forbidding in a scale model than it is in reality, as pointed

out by the existence of fairly stable tetrahedral $[\text{MX}_2\text{L}_2]$ complexes of the bulky tertiary amine quinuclidine [2]. Thus the question remained, whether doubly hindered pyridine ligands might form tetrahedral $[\text{MX}_2\text{L}_2]$ complexes with transition metal ions and, if so, whether such tetrahedral complexes would exhibit a chemical inertness comparable to that of the square planar Ni(II) species.

The information available in the literature on the metal complexes of 2,6-disubstituted pyridines is significantly scarce. In addition to the 2:1 *trans*-planar $[\text{MX}_2\text{L}_2]$ complexes of nickel(II) [1, 3–6], copper(II) [7–14], and palladium(II) [15–17], only a few compounds containing a single ligand per metal ion have been characterized [18–26]. Two widely quoted papers by Allan *et al.* [27, 28], however, described the facile isolation of some stable 2:1 and even 4:1 complexes of 2,6-disubstituted pyridines with several Co(II) and Zn(II) halides. When compared with the abundant information available for the cobalt-halide complexes of mono-hindered pyridines [29–41], Allan's reports raised some intriguing questions. Was it possible for 2,6-disubstituted pyridines to exhibit a steric hindrance comparable to, or even lower than, that of their monosubstituted analogs for which no 4:1 complexes had ever been reported? Or had the latter complexes somehow been overlooked? Alternatively, was it possible that the strong steric hindrance of the doubly-hindered ligands had induced the Co(II) and Zn(II) ions to assume a square-planar geometry? This would be most unusual, since metal ions with d^7 and d^{10} electronic configurations are known to favor tetrahedral or octahedral coordination and to assume a square planar geometry only under the stringent requirements of a rigid polydentate ligand.

In any event, the situation clearly deserved additional investigation. We therefore undertook a systematic study of the complexes formed by Co(II) halides and thiocyanate with all the isomers of the mono- and di-methyl-pyridines (2-Mepy, 3-Mepy, 4-Mepy, 2,3-diMepy, 2,4-diMepy, 2,5-diMepy, 2,6-diMepy, 3,4-diMepy, and 3,5-diMepy) and also with two isomeric tri-methyl-pyridines (2,3,6-triMepy and 2,4,6-triMepy) which are available as high purity samples.

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We chose to focus our efforts on Co(II) because its $d-d$ electronic spectra offer a sensitive, reliable, yet easily accessible structural probe.

Experimental

Starting Materials

The pyridine derivatives (Aldrich Chemical Co.) were dried over solid KOH or BaO , distilled under reduced pressure, and stored over Linde 4A molecular sieves. The purity of each sample was checked by gas chromatography under conditions that would ensure separation of any isomers; also, the infrared spectra of the compounds agreed with those previously reported [42]. Analytical grade, anhydrous cobalt(II) chloride, bromide, and thiocyanate were further dried in an oven at 120°C and stored over phosphorus(V) oxide. Anhydrous cobalt(II) iodide was stored in a sealed vial; prior to use it was finely ground and washed with anhydrous dichloromethane to remove any iodine formed by air-oxidation. All solvents were reagent or spectroscopic grade, and anhydrous.

General Procedures

Analyses: Cobalt was determined by EDTA titration; halides and thiocyanate by the Volhard method; carbon, hydrogen, and nitrogen by micro-analysis (Atlantic Microlab, Atlanta, GA). Complexes previously reported in the literature were checked by cobalt analysis and gave the expected values unless stated otherwise. Complexes reported for the first time in this work were all analyzed for cobalt and anion; selected compounds were also analyzed for carbon, hydrogen and nitrogen. All gave correct analyses for the formulas given in Tables I and II.

Infrared spectra, in the range of $4000-175\text{ cm}^{-1}$, were recorded with a Perkin-Elmer Model 580 Spectrophotometer, equipped with a dry nitrogen purge. Samples were examined as mulls in Nujol and hexachlorobutadiene, between cesium iodine and polyethylene plates. Magnetic moments were measured with a Gouy balance for the powdered solids at room temperature. Electronic ($d-d$) spectra were recorded with a Cary Model 17 Spectrophotometer. Solid samples were examined by diffuse reflectance ($310-1800\text{ nm}$ range) and solutions were examined by absorption using air-tight cells. Moisture-sensitive samples were prepared in a dry box.

Preparation of the Complexes

$[\text{CoX}_2\text{L}_2]$ species ($X = \text{NCS}, \text{Cl}, \text{Br}, \text{I}$) where L is a mono-hindered ligand

These complexes were prepared by the following general method: A saturated, filtered solution of the

cobalt salt in anhydrous ethanol containing 5% of triethylorthoformate was heated to boiling and added dropwise to a hot, stirred ethanol solution of the ligand. (The cobalt-to-ligand mol ratio was approximately 1:5). The reaction mixture was greatly heated for a few minutes and allowed to cool undisturbed to room temperature. Many of the complexes crystallized out almost immediately; others required several hours. If precipitation did not occur spontaneously, it was induced by addition of diethyl ether or hexane, followed by cooling to 0°C and scratching. (This procedure was generally required for the thiocyanate complexes of the mono-hindered lutidines, which are quite soluble). The crystalline products were filtered, washed first with triethylorthoformate and then with ether, and dried *in vacuum*. They were stored in tightly closed containers over Drierite.

$[\text{CoX}_2\text{L}_2]$ species ($X = \text{NCS}, \text{Cl}, \text{Br}, \text{I}$) in which L is a non-hindered ligand

These complexes were prepared similarly to those of the hindered ligands, except that the cobalt-to-ligand mol ratio was kept below 1:2 and the hot ligand solution was slowly added to the hot, stirred cobalt(II) solution. An exception is the $\{\text{Co}(\text{NCS})_2(3,5\text{-diMepy})_2\}_n$ complex, which was prepared by heating the corresponding $[\text{Co}(\text{NCS})_2(3,5\text{-diMepy})_4]$ species to 130°C under constant pumping for 24 hours. (It should be mentioned that this compound cannot be obtained by the general solution method used for all other CoX_2L_2 complexes).

CoX_2L_4 species ($X = \text{NCS}, \text{Cl}, \text{Br}, \text{I}$) in which L is a non-hindered ligand

These complexes were prepared as follows: a hot solution of the cobalt salt in ethanol-triethylorthoformate (5%) was added dropwise to the hot pure ligand (cobalt-to-ligand mol ratio, approximately 1:50). The products which crystallized either immediately or upon cooling, were separated by centrifugation and washed twice with hexane containing approximately 5% of the ligand. The excess solvent was removed by storing the products in a vacuum desiccator containing an open bottle of the appropriate ligand. All the CoX_2L_4 complexes showed a tendency to lose two of the coordinated ligands forming the corresponding $[\text{CoX}_2\text{L}_2]$ species. The CoX_2L_4 complexes were therefore stored in sealed vials; if discoloration occurred (traces of the deeply colored $[\text{CoX}_2\text{L}_2]$ impurities could easily be detected under a microscope), the original compound was restored by treatment with hexane containing 10% ligand. The tendency of the $[\text{CoX}_2\text{L}_4]$ species to dissociate with loss of ligand was found to increase markedly from the thiocyanato- to the iodo-complexes. Indeed it was quite difficult to obtain the latter free of traces of the tetrahedral $[\text{CoI}_2\text{L}_2]$ species.

$[\text{CoL}_4\text{X}]\text{ClO}_4$ species, ($X = \text{Cl, Br, I; L} = 3,4\text{-lutidine}$)

These complexes were obtained as described for the CoX_2L_4 species, except that an excess of lithium perchlorate was added to the solution of cobalt halide prior to reaction with the 3,4-lutidine ligand.

Attempts to prepare CoX_2L_2 and CoX_2L_4 complexes with doubly hindered ligands

Attempts to prepare these complexes by reaction of the cobalt salt with the ligand, by the procedure described for the $[\text{CoX}_2\text{L}_2]$ complexes of the mono-hindered pyridines, consistently failed to yield the desired products. The reaction, which was also attempted in various other solvents (methanol, propanol, tetrahydrofuran, acetone, dichloromethane, chloroform, monochloro- and dichloro-benzene) produced only a variety of insoluble light-green substances whose infrared spectra showed the presence of both hydroxo-species and protonated ligands. Crystalline products containing $[\text{CoX}_4]^{2-}$ ions, $[\text{CoLX}_3]^-$ ions, and the quaternized (cationic) substituted pyridines were occasionally isolated in minor yields. (These species were identified by their characteristic d-d electronic and/or infrared spectra).

To minimize hydrolysis, the following procedure was also attempted: Finely powdered anhydrous cobalt halide, CoX_2 ($X = \text{Cl, Br}$), previously heated in an oven at 120°C for 24 hours, was introduced into a vacuum-line and heated again under vacuum for 24 hours at 120°C . An excess of 2,6-dimethyl-pyridine, previously refluxed over barium oxide and distilled in a carefully dried vacuum system, was then distilled under vacuum into the flask containing the dried Co(II) salt. After the mixture was stirred for several hours, a bright-blue solution and a seemingly homogeneous bright-blue solid were obtained. Spectral analysis of the blue solution revealed only the presence of the $[\text{CoLX}_3]^-$ chromophore identical to the $[\text{CoX}_3\text{N}]$ chromophore discussed by Garrett *et al.* [43]. The blue solid, after being dried under vacuum, gave analyses corresponding to $(\text{LH}^+)[\text{CoX}_3\text{L}]^-$, and its infrared and electronic (reflectance) spectra confirmed this formulation.

Preparation of $(\text{LH}^+)_2[\text{CoI}_4\text{L}]$ where $L = 2,6\text{-diMepy}$

When a hot ethanol solution of CoI_2 was added to hot 2,6-diMepy, a small amount of brownish-green gelatinous precipitate formed immediately. This was separated by centrifugation (its infrared spectrum showed protonated ligands and hydroxo-species) and the resulting dark green solution was allowed to cool slowly. Within a few hours, dark blue crystals with diamond-shaped faces formed on the walls of the flask, while the supernatant solution remained dark green. The dark blue crystals were stable in the presence of an excess of ligand; when exposed to moist

air or dried *in vacuo*, however, they crumbled and turned green. The resulting green product had d-d electronic and infrared spectra identical to those of $(\text{LH}^+)_2[\text{CoI}_4]$. The electronic spectrum of the dark-blue crystals, slightly moist with pure 2,6-diMepy, is shown in Table III and Fig. 2.

The blue crystals were also obtained by dissolving the grass-green $(\text{LH}^+)_2[\text{CoI}_4]$ in hot 2,6-diMepy, and allowing the saturated solution to cool slowly. In turn, the intermediate complex $(\text{LH}^+)_2[\text{CoI}_4]$ was prepared as follows: an ice-cold solution of 2,6-diMepy in acetone was treated with a small excess of concentrated hydroiodic acid and then diluted with hexane; the yellowish solid thus formed was recrystallized from ethanol-hexane. The resulting white crystals of $(\text{LH}^+)\text{I}^-$ were treated with a saturated solution of CoI_2 in ethanol, and the tetraiodocobaltate of the protonated 2,6-dimethylpyridine crystallized out as grass-green needles.

Results and Discussion

The present investigation reports the formula, geometry, and spectral properties of the complexes formed by anhydrous CoX_2 salts ($X = \text{NCS, Cl, Br, I}$) with a series of eleven methyl-substituted pyridine ligands, offering a variety of steric requirements coupled with a gradual variation in basicity. The complexes thus formed are sufficiently numerous to allow the identification of the general relationship existing between these features of the ligands and the coordination pattern of the central Co(II) ion, as illustrated by the results summarized in Tables I-V. (In Table I, complexes reported for the first time in this work are indicated by an asterisk.) From these results the following general trends emerge quite clearly:

Complexes of Unhindered Ligands

The CoX_2 salts listed above, when treated with an unhindered substitute pyridine in a 1:2 mol ratio, readily form crystalline complexes of the general stoichiometry CoX_2L_2 . All but two of these complexes have a pseudotetrahedral (C_{2v}) geometry: the two exceptions, $\text{Co}(\text{NCS})_2(4\text{-Mepy})_2$ and $\text{Co}(\text{NCS})_2(3,5\text{-diMepy})_2$, are octahedral and polymeric with NCS-bridges, similar to the lavender isomer of the pyridine complex, $\{\text{Co}(\text{NCS})_2\text{py}_2\}_n$. When the CoX_2 salts are treated with a large excess of an unhindered substituted pyridine, the reaction proceeds further and crystalline 1:4 complexes of empirical formula CoX_2L_4 are obtained. Under no conditions did we observe complexes containing more than four ligands per Co(II) ion. Indeed, the majority of the 4:1 complexes are themselves stable only in the presence of an excess of free ligand. When washed (*e.g.*, with ethanol), dissolved in a solvent (*e.g.*, dichloromethane), or dried *under vacuum*, the crystalline CoX_2L_4 com-

TABLE I. Formulas, Colors and Geometries of Crystalline Complexes of Co(II) Thiocyanate and Halides with Mono- Di-Methyl-Substituted Pyridines.
(Some relevant references are given. Asterisk indicates this work).

Pyridine Ligand, L	2-Mepy	3-Mepy	4-Mepy	2,3-diMepy	2,4-diMepy	2,5-diMepy	3,4-diMepy	3,5-diMepy
Anionic Ligand, X								
NCS ⁻	[CoX ₂ L ₂] [29, 31, 36] Deep blue <i>Tetr.</i>	[CoX ₂ L ₂] [36] Deep blue <i>Tetr.</i>	{CoX ₂ L ₂ } _n [31, 36] Lilac <i>Oct.</i>	[CoX ₂ L ₂] (*) Deep blue <i>Tetr.</i>	[CoX ₂ L ₂] (*) Deep blue <i>Tetr.</i>	[CoX ₂ L ₂] (*) Deep blue <i>Tetr.</i>	[CoX ₂ L ₂] [32] Deep blue <i>Tetr.</i>	{CoX ₂ L ₂ } _n [32] Lilac <i>Oct.</i>
		[CoX ₂ L ₄] [32] Peach pink <i>Oct.</i>	[CoX ₂ L ₄] [31] Peach pink <i>Oct.</i>				[CoX ₂ L ₄] [32] Peach pink <i>Oct.</i>	[CoX ₂ L ₄] [32] Peach pink <i>Oct.</i>
Cl ⁻	[CoX ₂ L ₂] [29, 31, 36] Deep blue <i>Tetr.</i>	[CoX ₂ L ₂] [27, 36] Deep blue <i>Tetr.</i>	[CoX ₂ L ₂] [31, 27, 36] Deep blue <i>Tetr.</i>	[CoX ₂ L ₂] [41] Deep blue <i>Tetr.</i>	[CoX ₂ L ₂] [41] Deep blue <i>Tetr.</i>	[CoX ₂ L ₂] (*) Deep blue <i>Tetr.</i>	[CoX ₂ L ₂] [32, 41] Deep blue <i>Tetr.</i>	[CoX ₂ L ₂] [32, 41] Deep blue <i>Tetr.</i>
		[CoX ₂ L ₄] [27, 32] Pink <i>Oct.</i>	[CoX ₂ L ₄] [27, 36] Pink <i>Oct.</i>				[CoX ₂ L ₄] [32] Pink <i>Oct.</i>	[CoX ₂ L ₄] [32, 41] Pink <i>Oct.</i>
Br ⁻	[CoX ₂ L ₂] [29, 31, 36] Deep blue <i>Tetr.</i>	[CoX ₂ L ₂] [27, 36] Deep blue <i>Tetr.</i>	[CoX ₂ L ₂] [27, 31, 36] Deep blue <i>Tetr.</i>	[CoX ₂ L ₂] (*) Deep blue <i>Tetr.</i>	[CoX ₂ L ₂] (*) Deep blue <i>Tetr.</i>	[CoX ₂ L ₂] (*) Deep blue <i>Tetr.</i>	[CoX ₂ L ₂] (*) Deep blue <i>Tetr.</i>	[CoX ₂ L ₂] (*) Deep blue <i>Tetr.</i>
		[CoX ₂ L ₄] [27, 32] Pink <i>Oct.</i>	[CoX ₂ L ₄] [31, 27] Pink <i>Oct.</i>					[CoX ₂ L ₄] (*) Pink <i>Oct.</i>
I ⁻	[CoX ₂ L ₂] [29, 31, 36] Blue-green <i>Tetr.</i>	[CoX ₂ L ₂] [27, 36] Blue-green <i>Tetr.</i>	[CoX ₂ L ₂] [31, 36] Blue-green <i>Tetr.</i>	[CoX ₂ L ₂] (*) Blue-green <i>Tetr.</i>	[CoX ₂ L ₂] (*) Blue-green <i>Tetr.</i>	[CoX ₂ L ₂] (*) Blue-green <i>Tetr.</i>	[CoX ₂ L ₂] (*) Blue <i>Tetr.</i>	[CoX ₂ L ₂] (*) Blue-green <i>Tetr.</i>
		[CoX ₂ L ₄] [32] Straw <i>Oct.</i>	[CoX ₂ L ₄] [31] Straw <i>Oct.</i>					[CoX ₂ L ₄] (*) Straw <i>Oct.</i>
							[CoXL ₄]X(*) Blue-black <i>Sq. Pyr.</i>	
								[CoXL ₄]X(*) Black-green <i>Sq. Pyr.</i>

TABLE II. Electronic Absorptions^a of Six-Coordinate Cobalt(II) Thiocyanate and Halide Complexes with Substituted Pyridines.

Complex	Octahedral Species ^b					Tetragonal Species ^c							
	X = NCS			X = Cl		X = Br			X = I				
	⁴ T ₁ (F) →			⁴ T _{1g} (F) →		⁴ E 1(F) →			⁴ E 1(F) →				
	⁴ T _{2g} (F) ⁴ T _{1g} (P) [C. T.]			⁴ T _{2g} (F) ⁴ T _{1g} (P)		⁴ E 1(P) ⁴ E 2(F) ⁴ B ₂ (F)			⁴ E 1(P) ⁴ E 2(F) ⁴ B ₂ (F) [C. T.]				
[CoX ₂ (3-Mepy) ₄]	1118	505	341	1217	518	1659	1158	529					
[CoX ₂ (4-Mepy) ₄]	1059	500	335	1217	523	1635	1176	547	1729	1194	558	394,312	
[CoX ₂ (3,4-diMepy) ₄]	1153	505	329	1223	523		d				d		
[CoX ₂ (3,5-diMepy) ₄]	1188	535	335	1188	518	1664	1147	541	1688	1200	588	412,347	
{CoX ₂ (4-Mepy) ₂ } _n	1164	535	352		e		e				e		
{CoX ₂ (3,5-diMepy) ₂ }	1041	494	335		e		e				e		

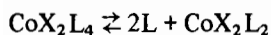
^aFrom diffuse reflectance spectra; wavelengths of absorption maxima are reported in nm; [C. T.] indicates charge transfer absorption. ^bAssignments for regular O_h symmetry. ^cAssignments for D_{4h} symmetry [44]. ^dFive-coordinate species, see Table III. ^eFour-coordinate, pseudo-tetrahedral species, see Table IV.

TABLE III. Electronic (d-d) Absorptions^a of Five-Coordinate, Square Pyramidal Co(II)-Halide Complexes Containing Substituted Pyridines.

Complex	⁴ B ₂	⁴ E(F)	⁴ B ₁	⁴ E(P)	⁴ A ₂ (P) ← ⁴ A ₂ (F)
[CoCl(3,4-diMepy) ₄](ClO ₄)	1476	1156	754	570	446
[CoBr(3,4-diMepy) ₄]Br	1700	1250	741	576	458
[CoI(3,4-diMepy) ₄]I	—	1342	747	588	422
[CoI ₄ (2,6-diMepy)] ^{=b}	—	1470	776	652	470

^aFrom diffuse reflectance spectra; wavelengths of absorption maxima are reported in nm. Assignments made according to Ciampolini [45]. ^bIsolated as the salt of the 2,6-dimethylpyridinium(+1) cation.

plexes tend to dissociate according to the schematic equilibrium equation:



The tendency of the CoX₂L₄ species to undergo this dissociation reaction increases markedly in the order NCS < Cl < Br < I [29, 31].

From the viewpoint of their structure, the CoX₂L₄ complexes fall into two categories: (a) The derivatives of 3-Mepy, 4-Mepy, and 3,5-diMepy, as well as the chloro- and thiocyanato-derivatives of 3,4-diMepy, have light pink colors and electronic spectra characteristic of Co(II) in an essentially octahedral environment. In the spectra of these complexes (Table II), the lower energy absorption ⁴T_{1g} → ⁴T_{2g}(F) shows a splitting which becomes more marked in passing from the stronger NCS⁻ to the weaker I⁻ ligand, indicating a tetragonally distorted (D_{4h}) environment. Indeed, the spectra of these CoX₂L₄ complexes can be fitted quite satisfactorily to the König-Kremer energy level diagrams for d⁷ ions in tetragonal fields, for a dt value of 500 cm⁻¹ and K = 5 [44]. Accordingly, all these complexes may be formulated as non-ionic, *trans*-octahedral species [CoX₂L₄]. (b) The bromo- and iodo-derivatives of 3,4-diMepy have electronic spectra

(Table III) which agree quite well with Ciampolini's energy level diagram for a d⁷ ion in square pyramidal fields [45]. These five-coordinate complexes, therefore, may be formulated as ionic species, [CoX(3,4-diMepy)₄]X, involving both coordinated and free halide ligands. In agreement with this formulation, it was possible to prepare crystalline complexes of the type [CoX(3,4-diMepy)₄]ClO₄ (X = Cl, Br, I), in which one, and only one, of the two original halides is replaced by a non-coordinated perchlorate ion. It is noteworthy that, in the presence of ClO₄⁻ ions, a blue-black five-coordinated [CoCl(3,4-diMepy)₄]ClO₄ could be obtained, although the original pink dichloro-complex, [CoCl₂(3,4-diMepy)₄], is itself six-coordinate. The octahedral dithiocyanato-complex, however, does not change to a five-coordinate ionic species under similar conditions, nor does any of the *trans*-octahedral complexes of the other unhindered pyridines.

Complexes of Mono-Hindered Ligands

This group of complexes displays a strict uniformity of formula and geometry. Regardless of the ligand or anion present, and of the cobalt-to-ligand ratio used, the complexes obtained are pseudotetrahedral (C_{2v}), non-ionic species of the general type [CoX₂L₂]. No

TABLE IV. Electronic (d-d) Absorptions^a of Four-Coordinate [CoX₂L₂] Complexes with Substituted Pyridines.

Anion, X Ligand, L	Tetrahedral Species		Distorted Tetrahedral (C _{2v}) Species ^c				
	X = NCS		X = Cl		X = Br		
	⁴ T ₁ (F)	⁴ T ₁ (P) [C. T.]	⁴ T ₁ (F) ⁴ B ₁ , ⁴ A ₂	⁴ T ₁ (P) ⁴ B ₂	⁴ T ₁ (F) ⁴ B ₁ , ⁴ A ₂	⁴ T ₁ (P) ⁴ B ₂	⁴ T ₁ (P) ← ⁴ A ₂ (F) [C. T.]
2-Mepy	1780(sh), 1211	588	1629 1370	1129 623	1647 1423	1176 635	1776 1423 1176 653 388
3-Mepy	1218	594	1623 1400	1023 623	1635 1442	1071 623	1729 1505 1123 652 371
4-Mepy		d	1618 1394	1047 618	1618 1423	1106 623	1770 1547 1141 647 365
2,3-diMepy	1700(sh), 1200	588	1594 1341	1153 611	1624 1406	1176 623	1611 1441 1223 641 388, 335
2,4-diMepy	1760(sh), 1200	588	1552 1376	1129 611	1623 1458	1205 623	1729 1500 1223 647 382, 329
2,5-diMepy	1223	594	1564 1364	1212 618	1664 1412	1123 647	1659 1452 1223 652 411, 329
3,4-diMepy	1176	582	1623 1429	1058 623	1647 1447	1064 623	1753 1523 1123 652 376
3,5-diMepy		d	1594 1441	1076 611	1652 1424	1076 629	1753 1547 1123 652 358

^aFrom diffuse reflectance spectra; wavelengths of absorption maxima are reported in nm. ^bAssignments for regular T_d symmetry. ^cAssignments for the lower energy absorption (⁴T₁(F) state) follow reference 36. ^dNCS-bridged, polymeric, octahedral species, see Table II.

TABLE V. Electronic (d-d) absorption^a of Four-coordinate [CoLX₃] Complexes of Doubly Hindered Substituted Pyridines.

Anion, X Ligand, L	Tetrahedral Species ^b		Distorted Tetrahedral (C _{3v}) Species ^c				
	X = NCS		X = Cl		X = I		
	⁴ T ₁ (F)	⁴ T ₁ (P)	⁴ T ₁ (F) ⁴ A ₂ , ⁴ E	⁴ T ₁ (P)	⁴ T ₁ (F) ⁴ A ₂ , ⁴ E	⁴ T ₁ (P)	⁴ T ₁ (P) ← ⁴ A ₂ (F)
2,6-diMepy	1180	600	1980 1450	630	~2200 1600	655	1450 700
2,3,6-triMepy	1180	600	1960 1450	640	~2200 1570	670	1460 715
2,4,6-triMepy	1160	600	2000 1425	625	~2200 1470	650	1435 705

^aDichloromethane solutions containing a large excess of free ligand; wavelengths of absorption maxima are reported in nm. ^bAssignments for regular T_d symmetry. ^cAssignments for the lower energy absorption in the distorted (C_{3v}) species follow reference 43.

complex with more than two L ligands per cobalt(II) ion was ever isolated or observed to exist in solution.

The electronic spectra of the $[\text{CoX}_2\text{L}_2]$ complexes of the various mono-hindered pyridines (Table IV) are virtually identical to one another when the anionic ligand X is the same. These spectra are also quite similar to those of the corresponding $[\text{CoX}_2\text{L}_2]$ complexes of unhindered pyridines, except for the fact that the splitting of the lower energy absorption (${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$) is far more pronounced for the complexes of the mono-hindered ligands. This effect, first reported by Lever [36] thus appears to be quite general since it is observed for all the complexes listed in Table IV, regardless of the ligand and anion involved.

Complexes of Doubly Hindered Pyridines

Our consistent failure to obtain complexes of the type $[\text{CoX}_2\text{L}_2]$ when L is a doubly hindered pyridine agrees with an earlier report by Machin and Sullivan [41], and indicates that such complexes have no tendency to form under ordinary reaction conditions, either in the solid state or in solution. Instead, a variety of hydrolysis products is usually obtained, the most common of which appear to be the crystalline halocobaltates of the protonated pyridines, $[\text{LH}^+]_2[\text{CoX}_4]$ and $(\text{LH}^+)[\text{CoX}_3\text{L}]$. (The anionic species present in the latter compounds have spectra (Table V) indicative of the same trigonally distorted tetrahedral geometry reported for the known triphenylphosphine analogs, $[\text{CoX}_3\text{L}]^-$ [46]. From the reaction of CoI_2 with 2,6-dimethylpyridine, a unique five-coordinate adduct of the $[\text{CoI}_4]^{2-}$ ion can be isolated as the beautifully crystalline, dark blue salt $(\text{LH}^+)_2[\text{CoI}_4\text{L}]$ (L = 2,6-diMepy). This adduct, which is also formed by the direct addition of 2,6-diMepy to $(\text{LH}^+)[\text{CoI}_4]$, is however stable only in the crystalline state and in the presence of 'free' ligand. The electronic d-d spectrum of this $(\text{LH}^+)_2[\text{CoI}_4\text{L}]$ complex (Table III) closely resembles in pattern the spectra of the square pyramidal $[\text{CoL}_4\text{X}]$ species previously discussed, except that all absorptions occur at a much lower energy. It is interesting to note that in the two square pyramidal iodo-complexes, $[\text{CoIL}_4]\text{X}$ and $(\text{LH}^+)_2[\text{CoI}_4\text{L}]$, the charge transfer absorptions are shifted toward the ultraviolet so that the compounds display their 'true d-d color'. A similar situation is observed for the dark blue trigonal bipyramidal $[\text{CoI}_3(\text{OH})_2]^{3-}$ species, recently reported by us [4]. In contrast, the charge-transfer bands of the tetrahedral iodocomplexes of cobalt(II) (e.g. $[\text{CoI}_4]^{2-}$, $[\text{CoI}_3\text{L}]^-$, and $[\text{CoI}_2\text{L}_2]$) although occurring in the ultraviolet, have strong tails in the visible region which partly or completely mask the color due to the d-d transitions.

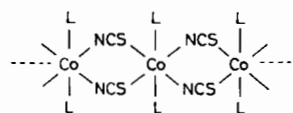
Trends in the Infrared Spectra of the Complexes

For the pseudotetrahedral (C_{2v}) complexes, $[\text{CoX}_2\text{L}_2]$, two infrared active metal-anion stretching

vibrations are expected in the far infrared region and two are indeed observed (Table VI). Their frequency values, as well as their frequency separation, decrease gradually from X = NCS to X = I (e.g., for $[\text{Co}(\text{NCS})_2(2\text{-Mepy})_2]$, $\nu(\text{Co-NCS}) = 322$ and 286 cm^{-1} ; $\Delta\nu = 36 \text{ cm}^{-1}$; for $[\text{CoI}_2(2\text{-Mepy})_2]$, $\nu(\text{Co-I}) = 228$ and 210 cm^{-1} ; $\Delta\nu = 18 \text{ cm}^{-1}$). Of the two expected cobalt-N-pyridine stretching vibrations, however, only one is observed. This absorption occurs near 250 cm^{-1} for all halide complexes, and at about 265 cm^{-1} for the thiocyanato complexes. In this latter species, coupling of the $\nu(\text{Co-N-pyridine})$ to the higher energy $\nu(\text{Co-NCS})$ most likely accounts for the observed frequency increase.

For the five-coordinate and *trans*-octahedral complexes, a single cobalt-halogen and cobalt-nitrogen stretching mode is expected, and one only is observed. The absorptions appear at progressively lower frequencies; for example, the $\nu(\text{Co-X})$ and $\nu(\text{Co-N})$ vibrations of the octahedral species occur some 50 cm^{-1} below those of their tetrahedral counterparts.

For the two NCS-bridged octahedral complexes, $\{\text{Co}(\text{NCS})_2(4\text{-Mepy})_2\}_n$ and $\{\text{Co}(\text{NCS})_2(3,5\text{-diMepy})_2\}_n$, the absorptions in the $\nu(\text{CN})$ region are quite distinctive, consisting of a very strong, sharply split band with peaks at approximately 2120 and 2100 cm^{-1} (Table VII). This pattern is generally taken to be indicative of a *cis*-configuration for the NCS group [48]. In the $\{\text{Co}(\text{NCS})_2\text{L}_2\}_n$ species this indicates a bridging situation in which each metal ion center is surrounded by two *cis*-N and two *cis*-S atoms:



Conclusions

This work defines the previously confused situation in regard to the complexes formed by Co(II) halides and thiocyanate with unhindered, mono-hindered, and di-hindered methyl-substituted pyridines. The following aspects are especially important:

(1) The limiting stoichiometry of the complexes is dictated by the steric requirements of the substituted-pyridine, the maximum number of coordinated ligands being *four* for the unhindered pyridines, *two* for the mono-hindered pyridines, and *one* for the doubly hindered ones. Accordingly, the previously reported 4:1 and 2:1 complexes of Co(II) halides with 2,6-disubstituted pyridine [27, 28] must be considered as erroneously formulated. Furthermore, it seems evident that the steric hindrance arises chiefly from ligand-anion repulsion and increases markedly from the thiocyanato- to the iodo-complexes.

TABLE VI. Metal-Ligand Vibrations (cm^{-1}) for Complexes of Cobalt(II) Thiocyanate and Halides with Mono- and Di-Substituted Pyridines^a

Ligand	X = NCS		X = Cl		X = Br		X = I	
	$\nu(\text{Co}-\text{X})$	$\nu(\text{Co}-\text{N})$	$\nu(\text{Co}-\text{X})$	$\nu(\text{Co}-\text{N})$	$\nu(\text{Co}-\text{X})$	$\nu(\text{Co}-\text{N})$	$\nu(\text{Co}-\text{X})$	$\nu(\text{Co}-\text{N})$
<i>Four-coordinate, tetrahedral $[\text{CoX}_2\text{L}_2]$ complexes</i>								
2-Mepy	322 286	248	336 308	242	264 241	241	228 210	245
3-Mepy	326 280	260	342 304	242	274 245	245	230	240
4-Mepy			341 305	235	277 245	245	246 228	
2,3-diMepy	330 290	245	338 300	240	262 235	235	220	245
2,4-diMepy	320 290sh	260-250	330 300	232	275 238	238	220 215	235sh
2,5-diMepy	330 290	230	334 302	225	256 242	225	220 215	220
3,4-diMepy	338 280	260	346 307	230	272 245	230	240 220	230
3,5-diMepy			345 308	230	278 240	230	226 205	235
<i>Five-coordinate, square pyramidal $[\text{CoXL}_4]X'$ complexes $X' = X \text{ or } \text{ClO}_4^-$</i>								
3,4-diMepy			268	220	220 ^e	220 ^e	195	220
<i>Six-coordinate, trans-octahedral $[\text{CoX}_2\text{L}_4]$ complexes</i>								
3-Mepy	265	215	222	205	193 ^b	210 ^c		d
4-Mepy	255	205	215sh	208 ^c	190 ^b	210 ^c	182	205
3,4-diMepy	268	222	220 ^b	210 ^c				
3,5-diMepy	255	215	212 ^e	212 ^e	190	205	185	205
<i>Six-coordinate, octahedral, NCS-bridged polymeric $\{\text{Co}(\text{NCS})_2\text{L}_2\}_n$ complexes</i>								
4-Mepy	275	205						
3,5-diMepy	280-270	212						

^aAll complexes were examined as thick Nujol mulls between polyethylene plates, using a dry-nitrogen purge. Co-NCS and Co-halogen absorptions appeared as strong bands; Co-N modes varied in intensity from strong to medium. ^bOnly partly resolved from Co-N absorption. ^cOnly partly resolved from strong Co-X absorption. ^dCompound decomposed on mulling. ^eOnly one strong, broad absorption was observed.

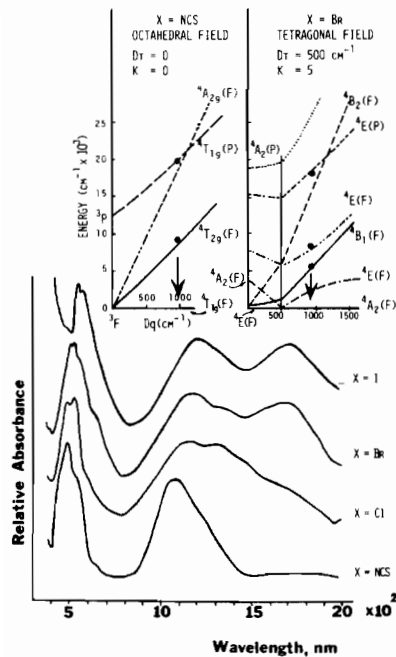


Fig. 1. Electronic d-d absorption spectra (reflectance) of the crystalline six-coordinate $[\text{CoX}_2\text{L}_4]$ complexes ($L = 3,5\text{-diMepy}$). The energy diagrams are adapted from König and Kremer [44] by omission of the doublet states. Black circles indicate the positions of the absorption bands.

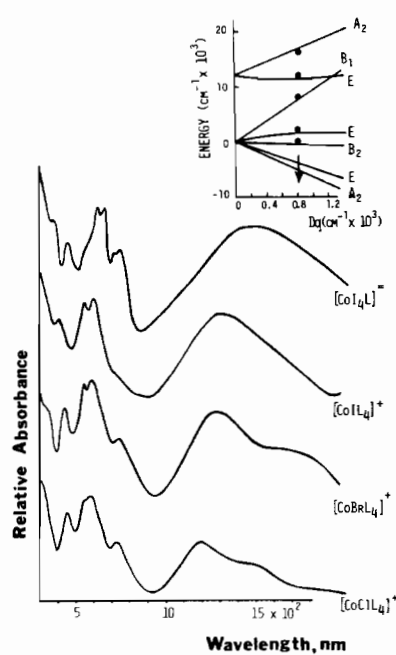


Fig. 2. Electronic d-d absorption spectra (reflectance) of the crystalline five-coordinate complexes $[\text{CoXL}_4]X$ ($L = 3,4\text{-diMepy}$) and $(\text{LH})_2[\text{CoL}_4]$ ($L = 2,6\text{-diMepy}$). The energy diagram is that of Ciampolini [45]. Black circles indicate the positions of the absorption bands.

TABLE VII. Typical Isothiocyanate Vibrations (cm^{-1}) for Cobalt(II) Complexes^a of Mono- and Di-Substituted Pyridines.

Type of Complex	Structure	Ligand	$\nu(\text{C}\equiv\text{N})^b$	$\nu(\text{C}-\text{S})^c$	$\delta(\text{Co}-\text{NCS})^d$
[Co(NCS) ₂ L ₂]	Four-coordinate, tetrahedral	2-Mepy	2080–2060	846	484
		3-Mepy	2080–2066	850–832	480
		2,3-diMepy	2064–2058	828–820	494–480
		2,4-diMepy	2065–2058	843	483
		2,5-diMepy	2065–2050	845	482
		3,4-diMepy	2080	828	479
{Co(NCS) ₂ L ₂ } _n	Six-coordinate, NCS-bridged, octahedral	4-Mepy	2115–2100	792–785	472
		3,5-Mepy	2118–2098	770–754	425–465
[Co(NCS) ₂ L ₄]	Six-coordinate, octahedral	3-Mepy	2050	810	490
		4-Mepy	2055	815–8 ^e	488
		3,4-Mepy	2065	820–810 ^e	485
		3,5-Mepy	2080	800	476

^aAll complexes were examined as mulls in Nujol and hexachlorobutadiene. ^bVery strong absorption. ^cMedium or strong, very sharp absorption. ^dMedium-intensity, very sharp absorption. ^eOverlapping with ligand absorption.

(2) Within each class of complexes, [CoX₂L₄] or [CoX₂L₂], the geometry of the Co(II) ion results from a fine balance of several factors, among which the crystal field stabilization energy and the ionic lattice energy play a predominant role. For example, the spontaneous change from octahedral [CoCl₂L₄] to square pyramidal [CoClL₄]ClO₄ upon addition of ClO₄⁻ ions indicates that the slight increase in lattice energy provided by the larger ClO₄⁻ ion is sufficient to offset the decrease in crystal field stabilization energy due to the lower coordination number. In this context, it is also significant that the ease of formation of the five-coordinate [CoXL₄]X species increases as the ligand field strength of the anionic ligand X decreases. It should be noted that these facile stereochemical rearrangements do not involve changes in spin multiplicity, as indicated both by the magnetic moments and by the electronic spectra of the complexes.

(3) The vibrational energies of the metal–nitrogen (pyridine) and metal–anion bonds decrease gradually with increasing coordination number of the central Co(II) ion: $\nu(\text{M}-\text{X})_{\text{tetrahedral}} > \nu(\text{M}-\text{X})_{\text{five-coordinate}} > \nu(\text{M}-\text{X})_{\text{octahedral}}$.

This frequency trend appears to be quite general not only for Co(II) but for all divalent metal ions, and may therefore serve as a convenient diagnostic tool for these species, for example the complexes of Zn(II), in which the metal itself does not exhibit characteristic d–d absorptions.

(4) The effect of the electronic structure of the central Co(II) is evident from a comparison with the corresponding complexes of Ni(II). For the Ni(II) halides and thiocyanate, the coordination limit is four ligands for the unhindered pyridines (octahedral [NiX₂L₄]), three or two ligands for the mono-hindered pyridines (high-spin trigonal bipyramidal

[Ni(NCS)₂L₃]) or (tetrahedral [NiL₂X₂]), and two ligands for the doubly hindered pyridines (square [NiX₂L₂]). Obviously, the greater stability of a square planar d⁸ system such as Ni(II) compared to a square planar d⁷ such as Co(II), is responsible for the observed differences. Furthermore, the CoX₂ salts do not form either isolable or detectable [CoX₂L₂] species with doubly hindered pyridines, whereas the corresponding NiX₂ salts yield the surprisingly 'stable' *trans*-[NiX₂L₂] complexes. This confirms our earlier suggestion that the lack of reactivity of the Ni(II) species does not arise from electronic effects but rather represents an extreme case of protective steric hindrance by the methyl-substituents of the pyridine ligands.

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