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Cobalt(II) Complexes of 2,6-Lutidine N-oxide

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Cobalt(II) complexes containing the Lewis base 2,6-lutidine N-oxide (2,6-LuNO) have been synthesized and examined by a number of physical methods. The halide complexes ($[Co(2,6\text{-}LuNO)_2X_2]$; *X = Cl, Br, I) are found to be tetrahedral in the solid state, in nitromethane and dichloromethane solutions, and in the 2,6-LuNO-dichloromethane mixed solvent system. Only the iodide complex reacts in 2,6-LuNO-nitromethane (to produce* $[Co(2,6\text{-}LuNO)_3I]I$*) and in pure 2,6-LuNO (to produce* $[Co(2,6\text{-}LuNO)_5]I_2$*) solutions. The thiocyanate complex,* $[Co(2,6\text{-}LuNO)_2(NCS)_2]$ *— while pseudotetrahedral in dichloromethane and nitromethane solutions—is five-coordinate in the solid state, with one of the thiocyanate groups acting as a bridging ligand. The solid state data for the perchlorate complex,* $Co(2,6\text{-}LuNO)_4(ClO_4)_2$*, do not at present allow for an unequivocal designation of structure. The various possibilities are discussed. Dissolution of the perchlorate compound in nitromethane produces a concentration-dependent mixture of species, while dissolution in dichloromethane yields a four-coordinate cation which interacts with the hydrogen-bonding solvent. Dissolution of the compound in pure 2,6-LuNO or in the 2,6-LuNO-nitromethane solvent system produces* $[Co(2,6\text{-}LuNO)_5]^{2+}$*. A similar result is also obtained in 2,6-LuNO-dichloromethane solutions, although solvent-solute interaction is suspected.*

Introduction

In the past decade the study of transition metal complexes of aromatic amine N-oxides has been both voluminous and diverse.[1,2] It is surprising therefore that a number of questions concerning the structures of some often studied complexes have still not been satisfactorily answered. Thus Byers *et al.*[3] have interpreted their own and earlier[4-6] spectral and magnetic data to imply that manganese, iron, cobalt, and nickel complexes of the form $[M(R\text{-}pyNO)_5](ClO_4)_2$ (R = H or other substituents; pyNO = pyridine N-oxide) are in fact distorted from octahedral symmetry. Reedijk[7] has shown, however, that the existence of bands at 7200 cm^{-1} in cobalt(II) and nickel(II) complexes, thought[3] to be part of the « d-d » transitions in ligand fields of less than O_h symmetry, may be due to the presence of a ligand overtone. Since the observed[3,4] splitting of a « d-d » transition for $[Cr(pyNO)_6](ClO_4)_3$ (also thought[3] to be distorted) occurs at approximately 15,000 cm^{-1}, the above explanation[7] can not be valid for this complex, and thus the problem of the stereochemistry of these complexes must await X-ray studies.

Although most substituted pyridine N-oxides exhibit a coordination number of six towards cobalt(II) and nickel(II),[2-4,8,9] here also there are some unusual results. Thus while 4-ethoxypyridine N-oxide ($4\text{-}OC_2H_5pyNO$) reacts with the metal nitrates to form $[M(4\text{-}OC_2H_5pyNO)_6]^{2+}$ ($M = Co^{II}, Ni^{II}$) complexes,[10] it also reacts with metal perchlorates to form pentacoordinate complexes (equation (1)), which become six-coordinate only in the presence of excess base.[11] Why two different types of complexes should be formed in the presence of non-coordinating anionic ligands is not readily apparent.

$$M^{2+} + 5L \rightarrow [ML_5]^{2+} + \text{excess } L \rightleftarrows [ML_6]^{2+}$$
$$(M = Mn^{II}, Co^{II}, Ni^{II}, Zn^{II}) \qquad (1)$$

In those cases in which the position of substituents on the aromatic ring has been varied, the results are also puzzling. Thus while six-coordinate nickel(II) and cobalt(II) complexes are formed with 2-, 3-, or 4-cyanopyridine N-oxide,[12] the nature of the picoline N-oxide complexes is noticeably affected by the positioning of the methyl group on the ring. Thus the 4- and 3-picoline N-oxides react with Co^{II} to form six-coordinated complexes,[3,4,8,13] while the compound formed with 2-picoline N-oxide has been shown to contain trigonal-bipyramidally coordinated cobalt(II), both in the solid state[14] and in solution[3,13] (the spectral data attributed by Schmauss and Specker[13] to $[Co(2\text{-}RpyNO)_6]^{2+}$ ($R = CH_3, C_2H_5$) are actually due to $[Co(2\text{-}RpyNO)_5]^{2+}$, and for the picoline N-oxide complex agree with those of Byers *et al.*[3]). Nelson and

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Ragsdale[15] have reported, however, that the nickel(II) perchlorate complexes of 2-picoline and 2-ethylpyridine N-oxide contain six-coordinated nickel(II), with the complexes being formulated as $[Ni(2\text{-}CH_3pyNO)_4](ClO_4)_2$ and $[Ni(2\text{-}C_2H_5pyNO)_6](ClO_4)_2$. The ligand bridges, postulated in the 2-picoline complex for the achievement of six-coordination,[15] are easily broken upon dissolution of the complex in a ligand-nitromethane solvent,[13] with the solution species becoming $[Ni(2\text{-}CH_3pyNO)_6]^{2+}$ and exhibiting the same electronic spectral data as was found for the 2-ethylpyridine N-oxide complex in both the solid state and ligand-nitromethane solution.[15]

In an attempt to study the effects of bulky substituents on the coordinating ability of pyridine N-oxides, we have untaken studies utilizing 2,6-lutidine N-oxide (hereafter called 2,6-LuNO). It has already been shown[16] that the presence of two α-methyl groups reduces the enthalpy of interaction of this Lewis base with $VO(acac)_2$ to a value below those measured for the three picoline N-oxides and other less sterically hindered lutidine N-oxides. Thus it was originally anticipated that reaction of 2,6-LuNO with cobalt(II) should produce a four-coordinate, tetrahedral cation, similar to those found for various alkyl- and aryl-substituted phosphine oxides.[17,18] In addition comparisons between the coordinating behavior of 2,6-LuNO and trimethylamine N-oxide (TMNO)—regarding donor strength, complex stereochemistry, and coordination number—were desired. Thus although the two bases are architecturally somewhat similar, the N-O pi-bonding present in the aromatic base should reduce its donor stength toward cobalt(II) to a value below that for TMNO,[19,20] as has previously been noted in reaction with hydrated protons and VO(acac).[16]

Preliminary reports[21-23] concerning cobalt(II) complexes of 2,6-LuNO, confined mainly to the solid state, have stated that complexes of the type $[Co(2,6\text{-}LuNO)_2X_2]$ (X = Cl,[21,22] Br,[21]) are pseudotetrahedral, while those of the types $[Co(2,6\text{-}LuNO)_2Y_2]$ (Y = NCS,[21] NO_3,[21] NO_2,[23]) and $[Co(2,6\text{-}LuNO)Z_2]$ (Z = Br, I)[22] are pseudooctahedral. Acetone solutions of the nitrite compound, however, exhibit electronic spectra indicative of either a distorted tetrahedral or distorted octahedral stereochemistry about the cobalt ion.

Kluiber and Horrocks[24] have isolated the 1:1 adduct of 2,6-LuNO with cobalt(II) acetylacetonate. From a consideration of stoichiometric and electronic spectral data, it is likely that a square pyramidal arrangement of ligands exists about the metal ion. Although the formation of a 2:1 adduct is prevented because of steric interactions between the ligand and the 1:1 adduct, water is readily added to fill the sixth coordination position.

While this study was in progress, reports of the solid and solution behavior of metal perchlorate complexes of 2,6-LuNO have appeared.[13,25,26] Comparisons of pertinent data and analysis of reported results will be presented later.

Experimental Section

Materials. 2,6-Lutidine N-oxide was obtained commercially from Aldrich Chemical Company and was used for synthetic purposes with no prior purification. For spectral work it was vacuum distilled and then stored in the dark over Linde 4-A molecular sieves. Glass wool was added to the distillation flask to reduce bumping. Fisher Certified dichloromethane and Eastman Spectrograde nitromethane were stored over molecular sieves for several days prior to use. Eastman Practical 2,2-dimethoxypropane (DMP), Alfa Inorganics hydrated cobalt(II) bromide and iodide, Alfa Inorganics anhydrous cobalt(II) thiocyanate, and G. F. Smith Hydrated cobalt(II) perchlorate were used as purchased. All other materials were common laboratory reagent ones, used with no further purification.

Synthesis. Dianionbis(2,6-Lutidine N-oxide)cobalt (II). The cobalt salts were dissolved in warm ethanol and gravity filtered into a mixture of ethanol and excess ligand (based on a 2:1 combining ratio of ligand to salt). Precipitation occurred immediately in all cases, yielding blue products for the chloride and bromide, blue-green for the iodide, and violet-purple for the thiocyanate. The mixtures were stirred as they cooled, with anhydrous ether added to complete the reaction. Vacuum filtration was followed by washing with ether and drying under vacuum. None of the complexes is hygroscopic. *Anal.* Calcd for $C_{14}H_{18}CoN_2O_2Cl_2$: C, 44.70; H, 4.82. Found: C, 45.12; H, 5.08. Calcd for $C_{14}H_{18}CoN_2O_2Br_2$: C, 36.10; H, 3.84. Found: C, 36.45; H, 4.01. Calcd for $C_{14}H_{18}CoN_2O_2I_2$: C, 30.05; H, 3.22; Co, 10.55. Found: C, 30.08; H, 3.26; Co, 10.25. Calcd for $C_{16}H_{18}CoN_4O_2S_2$: C, 45.62; H, 4.27. Found: C, 46.02; H, 4.52.

Tetrakis(2,6-Lutidine N-oxide)cobalt(II) perchlorate. Hydrated cobalt(II) perchlorate was dehydrated in a mixture of DMP and 2,6-LuNO for two hours. Addition of ether to the reaction flask produced an initial purple oil, which gradually solidified as a rust-red product. The mixture was stirred in ether for one-half hour, after which the product was vacuum filtered, washed with ether, and dried under vacuum. It does not appear to be appreciably hygroscopic. *Anal.* Calcd for $C_{28}H_{36}CoN_4O_{12}Cl_2$: : C, 44.80; H, 4.80; N, 7.43. Found: C, 45.05; H, 4.93; H, 7.41.

The preparation of $[(n\text{-}C_4H_9)_4N]_2CoI_4$ was adapted from that previously used for the methyltriphenylarsonium salt.[27]

Physical Measurements. The solid state electronic spectra were obtained from Cary 14 and Beckman

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DK-2A spectrophotometers, using the mull method previously described.[20] Solution spectra were obtained only from the Beckman instrument. In those cases involving partial or complete use of 2,6-LuNO as the solvent, the concentration of dry, distilled 2,6-LuNO was the same for both reference and sample solutions. The same procedure was followed for the addition of $(n\text{-}C_4H_9)_4NI$ to a solution of the iodide complex.

The infrared data for the range 4000-650 cm^{-1} were obtained from a Beckman IR-5A infrared spectrophotometer. The samples were ground into a nujol paste, and sodium chloride plates were used. The spectra were calibrated with polystyrene bands.

The magnetic data for the solid complexes were obtained by the Guoy method, using $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ as a standard.[28] The dichloromethane solution magnetic data for $[Co(2,6\text{-}LuNO)_4]^{2+}$ were obtained from a Varian A60-D spectrometer, using the nmr method of Evans as explained in detail previously.[20] Shifts of protons in the inert solvents cyclohexane and hexamethyldisilane between «diamagnetic» and «paramagnetic» environments were obtained 20-45 minutes after preparation of the solutions. The results obtained were independent of solvent. Solution temperatures were determined by measuring the proton nmr spectrum of neat ethylene glycol. The proton isotropic shifts of $Co(2,6\text{-}LuNO)_4(ClO_4)_2$ were obtained on the same instrument, using dichloromethane as a solvent and hexamethyldisilane as an internal standard. The diamagnetic shifts for the 2,6-LuNO protons were obtained from the literature.[24,29]

Conductance values were obtained as before,[19] using a solution of potassium chloride as a calibrant.

Spectrochemical Calculations. The determination of Dq and B′ for 2,6-LuNO in $[Co(2,6\text{-}LuNO)_4]^{2+}$ were performed using the method of Drago.[30] Values of Dq and B′ for 2,6-LuNO in the $[Co(2,6\text{-}LuNO)_2X_2]$ (X = Cl, Br, I, NCS) complexes were obtained through use of the average environment rule.[27] In all cases the centers of the multipeaked transitions were determined by a center-of-gravity technique.

Results

Electronic spectral results for the complexes are listed in Tables I-III and shown in Figures 1-4. Since the halide complexes are not very soluble in dichloromethane and nitromethane solutions (with or without added 2,6-LuNO), studies of their spectral patterns as a function of solute concentration were not attempted. The extremely low solubility of the thiocyanate complex ($<10^{-3}$ molar) precludes the listing of its molar absorptivities, although those for the visible peaks certainly exceed 500.

The iodide complex is the only one of the halide complexes which appears to undergo extensive reactions in solution. The removal of iodide ion from the coordination sphere occurs when excess 2,6-LuNO is added to a blue-green nitromethane solution of the complex. The deep blue solution which is produced has a molar conductance of 99.5, indicating that a 1:1 uni-univalent electrolyte is present.[31] Addition of excess iodide ion to nitromethane solutions of the complex displaces 2,6-LuNO from the coordination sphere, as is apparent from a comparison of the electronic spectral data for the $[Co(2,6\text{-}LuNO)_2\text{-}I_2\text{-}I^-]$ system (Table II, Figure 1) and those of $[CoI_4]^{2-}$.

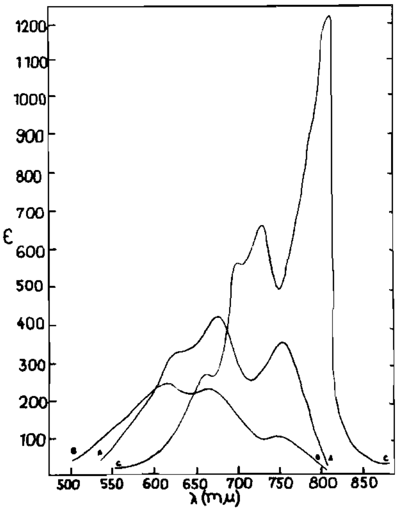

Figure 1. Visible electronic spectra of $[Co(2,6\text{-}LuNO)_2I_2]$ in dichloromethane solution (curve A), in nitromethane solution with added 2,6-LuNO (curve B), and in nitromethane solution with added iodide ion. (curve C).

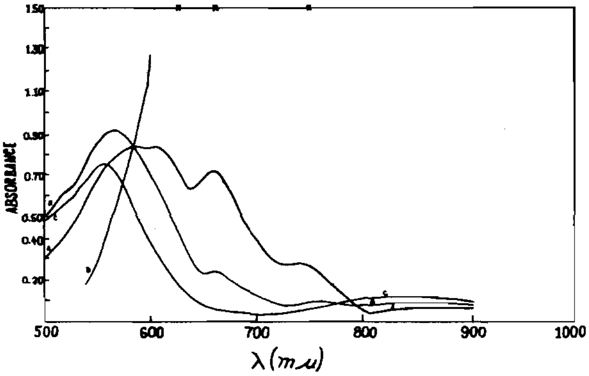

Figure 2. Visible electronic spectra of $[Co(2,6\text{-}LuNO)_2I_2]$ in 2,6-LuNO as a function of solute concentration: 2.74×10^{-2} molar (curve A), 1.12×10^{-2} molar (curve B), and 4.79×10^{-3} molar (curve C). The points designated « x » are those signifying maximum absorption for $[Co(2,6\text{-}LuNO)_2I_2]$ in ligand-free dichloromethane (curve D).

The iodide complex also undergoes a concentration-dependent reaction in pure 2,6-LuNO (Figure 2). When the absorbances for the four solutions shown are normalized to the same metal ion concentration and cell path length, it is found that (a) an isosbestic point exists at 578 mμ and (b) the spectrum of the most dilute solution of complex in 2,6-LuNO (containing the highest free ligand to complex ratio) does not pass through this point. Thus only two stable,

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Table I. Electron Spectra of $[Co(2,6\text{-}LuNO)_2X_2]$ Complexes

X	Solvent	λ(ε)	λ(ε)	λ(ε)	λ(ε)	λ(ε)	λ(ε)
Cl^-	mull [a]	608	640	674	1380	1600	1720
Cl^-	CH_2Cl_2 [a]	596(240)	638(360)	675(385)	1390(65)	1575(sh) [c]	1850(49) [d]
Cl^-	CH_2Cl_2+2,6-LuNO [a]	596(241)	636(366)	675(398)			
Cl^-	CH_3NO_2 [a]	600(260)(sh) [c]	636(357)	670(367)			
Cl^-	CH_3NO_2+2,6-LuNO [a]	600(sh)[c]	636(336)	675(350)			
Cl^-	2,6-LuNO [a]	600(sh) [c]	630(sh)[c]	680(353)			
Br^-	mull [a]	620	655	692	1420	1670	
Br^-	CH_2Cl_2[a]	610(sh) [c]	648(405)	700(375)	1425(90)	1600(sh) [c]	1850(49) [d]
Br^-	CH_2Cl_2+2,6-LuNO [a]	605(sh) [c]	646(401)	697(371)			
Br^-	CH_3NO_2 [a]	600(sh) [c]	645(404)	690(359)			
Br^-	CH_3NO_2+2,6-LuNO [a]	610(sh) [c]	646(352)	693(296)			
Br^-	2,6-LuNO [a]	610(sh) [c]	648(283)	688(230)			
NCS^-	mull [b]	504	560	770	1760		
NCS^-	CH_2Cl_2 [a]	564(sh) [c]	615	646	1225	1505	
NCS^-	CH_3NO_2 [a,e]	582(sh) [c]	615	636			

[a] pseudotetrahedral, four-coordinate. [b] five-coordinate. [c] sh = shoulder. [d] very broad absorption. [e] saturated solution.

Table II. Electronic Spectra of $[Co(2,6\text{-}LuNO)_2I_2]$.

Solvent	λ(ε)	λ(ε)	λ(ε)	λ(ε)	λ(ε)	λ(ε)	λ(ε)
mull [a]	625	680	730		1500	1730	
CH_2Cl_2 [a]	632(328)	670(430)	745(340)		1485(107)	1720(58)	
CH_2Cl_2+2,6-LuNO [a]	626(308)	668(395)	743(300)				
CH_3NO_2 [a]	625(325)	665(450)	738(320)				
CH_3NO_2+2,6-LuNO [a,e]	616(241)	668(236)	750(103)		1340(sh) [d]	1470(72)	
$CH_3NO_2+Bu_4N^+I^-$ [a]	664(281)	697(536)	722(647)	780(1217)	1920(119)		
$[n\text{-}Bu_4N]_2CoI_4$ [a] in CH_2Cl_2	669(253)	697(577)	732(878)	783(1200)			
2,6-LuNO [c] (2.74×10^{-2} molar)	586(151)	610(151)	670(128)	745(53)	870(9.7)	1240(30)	1478(36)
2,6-LuNO [b] (4.74×10^{-3} molar)	525(sh)	562(138)	855(21)	1950(21)			

[a] pseudotetrahedral, four-coordinate. [b] five-coordinate. [c] mixture of species. [d] sh = shoulder. [e] A nitromethane solution of this complex (3.09×10^{-1} molar) with added 2,6-LuNO (178/1 excess) has a molar conductance of 99.5.

Table III. Electronic Spectra of $Co(2,6\text{-}LuNO)_4(ClO_4)_2$.

Solvent	λ(ε)	λ(ε)	λ(ε)	λ(ε)	λ(ε)	λ(ε)
mull [a]	535	1185				
CH_2Cl_2 [b]	~525(sh) [c]	575(99-151) [d]	~950(sh)	1150(18-28) [d]	1735(19)	
CH_3NO_2 [e] (7.75×10^{-2}molar)	~525(sh)	582(150)	870(11)	1180(45)	~1280(sh)	1680(21)
CH_3NO_2 [f] (5.13×10^{-3} molar)	567(124)	835(15)				
CH_3NO_2+2,6-LuNO [f]	~515(sh)	562(149)	853(21)	2015(21)		
2,6-LuNO [e] (5.66×10^{-3} molar)	~520(sh)	569(92)		1100(10)	1900(10)	>2100
2,6-LuNO [f] (4.97×10^{-3} molar)	515(sh)	560(143)	860(15)			
CH_2Cl_2+2,6-LuNO [e] (50/1 molar ratio)	515(sh)	579(114)	862(14)	1155(18)		
CH_2Cl_2+2,6-LuNO [e] (153/1 molar ratio)	~520(sh)	563(83)	870(16)	1120(10)	>2100	
CH_2Cl_2+2,6-LuNO [f] (209/1 molar ratio)	~520(sh)	564(77)	856(16)			

[a] Assignments of transitions given in text. [b] Distorted tetrahedral, four-coordinate. [c] sh = shoulder. [d] The values for the molar absorptivities of these peaks change with solute concentration. See text for discussion. [e] Mixture of four- and five-coordinate species. [f] Five-coordinate.

non-transient species are present in this system, one of them being the unreacted iodide complex (Curve D). Since the spectrum of the solution containing the highest free ligand to complex ratio does not pass the isosbestic point, only the final product must exist in this solution.

The nature of the perchlorate complex in solution is also dependent upon its environment. Thus in dichloromethane solutions (Table III) the molar absorptivities of the transitions centered at 575 mμ and 1135 mμ consistently increase over the concentration range of 3.4×10^{-3} to 9.5×10^{-2} molar, while that of the peak centered at 1735 mμ is essentially unaffected. Thus while the center of gravity of the visible transition remains roughly constant, that for the infrared one shows an increase in energy as the solute concentration increases.

In nitromethane solutions of the perchlorate complex, there is a direct solvent-solute interaction, the extent of which is a funcion of solute concentration (or of the solvent to complex molar ratio). The changes in the spectra (Table III) indicate that while a mixture of species is present in more concentrated solutions, conversion to only one solvated entity is most likely in the more dilute solutions. This type of reaction has been noted elsewhere.[25]

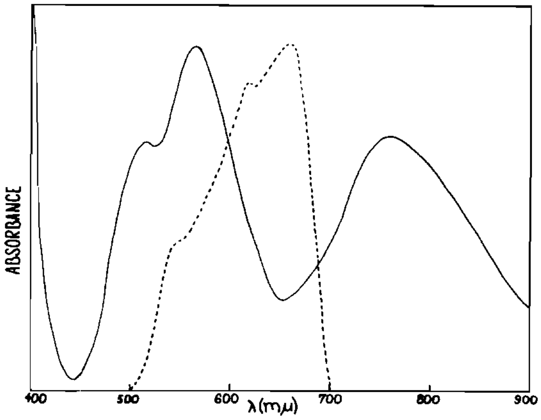

Figure 3. Visible electronic spectra of [$Co(2,6\text{-}LuNO)_2(NCS)_2$] in the solid state (———) and in dichloromethane solution (- - - -). ε values are arbitrary for the solid state data.

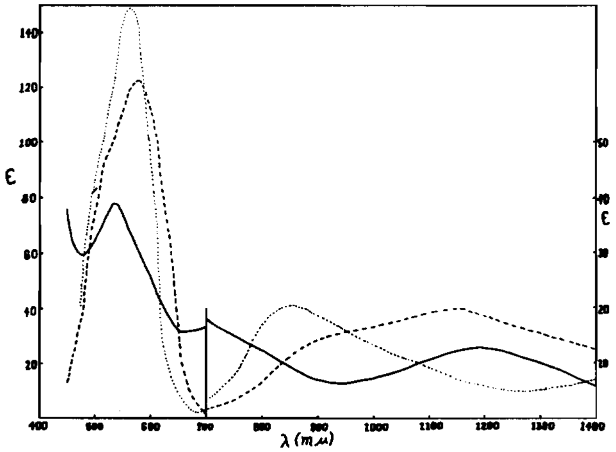

Figure 4. Electronic spectra of [$Co(2,6\text{-}LuNO)_4(ClO_4)_2$] in the solid state (———), in dichloromethane solution (3.36×10^{-2} molar, - - -), and in 2,6-LuNO-nitromethane solution (· · · ·). ε values are arbitrary for the solid state data (the discontinuity at 700 mμ is due to a change in sources).

Addition of excess 2,6-LuNO nitromethane solutions of the complex results in the easy formation of a new species, which in turn undergoes no reaction as the amount of added 2,6-LuNO is increased. Dissolution of the complex in pure 2,6-LuNO, however, results in the formation of at least two separate entities, whose relative amounts depend upon the ligand to complex molar ratio. While the spectrum of a fairly concentrated solution of the complex in 2,6-LuNO (solvent/complex = 155/1) is quite rich in transtions (Table III), that of a more dilute solution (in which the same ratio is 1800/1) is simpler and is identical to that observed in 2,6-LuNO-nitromethane solutions of the complex.

Two separate effects are noted when the complex is dissolved in 2,6-LuNO-dichloromethane solutions. Below a 2,6-LuNO/complex molar ratio of 200/1, changes in positions of maximum absorption and disappearance of some bands in the near infrared region are noted. Above the aforementioned 2,6-LuNO/complex ratio, no marked trends in the values of maximum absorptions or molar absorbtivities are noted, either as the 2,6-LuNO/complex molar ratio increases or as the concentration of the complex itself increases. The nature of the spectrum is essentially the same as those noted when the perchlorate complex is present in 2,6-LuNO-nitromethane solutions or in low concentration in pure 2,6-LuNO, although the molar aborbtivity of the main visible transition is noticeably less than those in the other two systems.

For those cases in which tetrahedral or pseudotetrahedral cobalt(II) is present, the split peaks seen in the regions of 1200-1900 mμ and 550-780 mμ are assigned to the ν_2 and ν_3 transitions, respectively. The special case of $Co(2,6\text{-}LuNO)_4(ClO_4)_2$ in dichloromethane will be discussed later.

Since the difference between the energy level diagrams of trigonal bipyramidal[32] cobalt(II) in D_{3h}[34] and C_{3v}[35] symmetries involve only the labelling and not the number or relative energies of the various states, it makes little difference which particular scheme is used. The transitions seen in the spectra of the five-coordinate species are assigned as follows: ν_1-not seen; ν_2-1760-2100 mμ; ν_3-770-870 mμ; ν_4-560-570 mμ; ν_5-500-525 mμ (this last transition is sometimes seen as a shoulder on the more intense ν_4 peak and in one case is not seen at all).

The infrared data shown in Table IV are generally typical of those reported previously for complexes of α-substituted pyridine N-oxides.[13,21,25,36] Although most of the band assignments are unambiguous, there is a problem in assigning some bands for the thiocyanate complex. The definite appearance of two strong, separate C–N stretching modes (one at 2160 cm^{-1}, indicating a bridging thiocyanate group and another at 2092 cm^{-1}, indicating a nitrogen-bonded thiocyanate group)[37] would seem to indicate that two separate C–S stretching modes should also be seen. Since the band at 783 cm^{-1} is easily assigned to the bridging C–S stretching frequency[37] (that at 797 cm^{-1} is analogous to the C–H deformation vibration found in all other 2,6-LuNO complexes), the corresponding C–S stretching mode for the N-bonded thiocyanate should be found in the 820-840 cm^{-1} region,[33,37,38] which is exactly the region in which the N–O bending mode is expected. Thus the observed band at 821 cm^{-1} may be a composite of the two separate bands or may simply be assigned to the more intense N–O bending mode. Two bands are noted in the N–O

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(32) All five-coordinate complexes are assumed to be approximately tigonal bipyramidal for reasons previously listed in discussing the stereochemistry of the [$Co(TMNO)_2X_2$] (X = Cl, Br, I, NCS) complexes in the solid state.[33]

(33) D.W. Herlocker, *Inorg. Chem.*, *8*, 2037 (1969).

(34) M. Ciampolini, N. Nardi, and G.P. Speroni, *Coord. Chem. Revs.*, *1*, 222 (1966).

(35) M. Ciampolini and I. Bertini, *J. Chem. Soc., Sect. A*, 2241 (1968).

(36) H.N. Ramaswamy and H.B. Jonassen, *J. Inorg. Nucl. Chem.*, *27*, 740 (1965).

(37) J.L. Burmeister, *Coord. Chem. Revs.*, *3*, 225 (1968).

(38) S.M. Nelson and T.M. Shepard *J. Inorg. Nucl. Chem.*, *27*, 2123 (1965).

Table IV. Infrared Spectral Data for Cobalt(II) Complexes.

Compounds	ν_{N-O}(stretch)	ν_{N-O}(bend)	ν_{C-H}(deformation)	Other
2,6 LuNO	1267 cm^{-1}	844 cm^{-1}	762 cm^{-1}	
$Co(2,6\text{-}LuNO)_2Cl_2$	1200	831	799	
$Co(2,6\text{-}LuNO)_2Br_2$	1199	833	799	
$Co(2,6\text{-}LuNO)_2I_2$	1200	829	797	
$Co,2,6\text{-}LuNO)_2(NCS)_2$	1195	821 [a]	797	2092, 2160 cm^{-1}; 783 cm^{-1} [b]
$Co(2,6\text{-}LuNO)_4(ClO_4)_2$	1220 [c], 1196	831	791	1073 - 1101 cm^{-1} [d]

[a] This band may be due to an overlapping of the N-O bending mode and the C-S stretching mode of the nitrogen-bonded thiocyanate. [b] The higher frequency bands are assigned to the C-N stretching frequencies of the coordinated thiocyanates, while the lower frequency band is assigned to the C-S stretching frequency. [c] The band is asymmetrically shaped and is much broader than the band at 1196 cm^{-1}. [d] This broad band is assigned to ν_3 of the perchlorate ion.

Table V. Magnetic Data for Cobalt(II) Complexes.

Compound	$\chi_m \times 10^6$	$\chi_m \times 10^6$	$\chi_m' \times 10^6$	T(°C)	μ(B.M.)
$Co(2,6\text{-}LuNO)_2Cl_2$	24.4	9200	9340	22.0	4.70 ± 0.06 [a,b]
$Co(2,6\text{-}LuNO)_2Br_2$	20.3	9410	9570	30.0	4.81 [a]
$Co(2,6\text{-}LuNO)_2I_2$	17.1	9560	9570	29.0	4.85
$Co(2,6\text{-}LuNO)_2(NCS)_2$	20.0	8420	8580	24.0	4.52 [a]
$Co(2,6\text{-}LuNO)_4(ClO_4)_2$	12.4	9280	9520	22.0	4.75 [c]
$Co(2,6\text{-}LuNO)_4(ClO_4)_2$ [d]	10.6	7950	8190	41.0	4.54

[a] Ramaswamy and Jonassen (ref. 21) report μ = 4.59, 4.61, and 4.75 for the chloride, bromide, and thiocyanate complexes, respectively. [b] Brown *et al.* (ref. 22) report μ = 4.7 for the chloride complex. [c] Karyannis *et al.* (ref. 25) report μ = 4.73 for the perchlorate complex. [d] Dichloromethane solution.

Table VI. Average Environment Calculations.

Compound	$\nu_3(cm^{-1})$	$\nu_2(cm^{-1})$	$\Delta(cm^{-1})$	$B'(cm^{-1})$	Dq(2,6-LuNO) [a]	B'(2,6-LuNO)[a]
$Co(2,6\text{-}LuNO)_2Cl_2$	15,670	5,787	3,353	760	359	800
$Co(2,6\text{-}LuNO)_2Br_2$	15,360	5,540	3,207	752	350	803
$Co(2,6\text{-}LuNO)_2I_2$	14,810	5,510	3,155	724	356	806
$Co(2,6\text{-}LuNO)_2(NCS)_2$	16,670	7,092	4,100	764	355	837
$[Co(2,6\text{-}LuNO)_4]^{2+}$	18,315	6,900	3,960	888	396	888

[a] The Dq and B' values for the anions are taken from ref. 20 and are averages of solution values reported by Cotton *et al.*, *J. Am. Chem. Soc.*, *83*, 4690 (1961).

stretching region for the perchlorate complex, one at approximately the same energy as is found in the other complexes (1196 cm^{-1}) and a weaker, broader one at higher energies (1220 cm^{-1}). While it is tempting to assign the two bands to N-O stretching frequencies of differently bonded ligands, other factors (to be considered in the Discussion) must be considered.

The magnetic data in Table V show some differences between presently and previously[21] reported data. In the cases of the chloride and bromide complexes, it appears that the higher values of the magnetic moments are more consistent with the fairly low values for the average Dq for the complexes (Table VI).[27,39] The magnetic moment reported earlier[21] for the thiocyanate complex refers to a six-coordinate species, whose synthesis (according to earlier[21] instructions) could not be repeated in this work. The presently reported value is consistent with infrared and electronic spectral data (see Discusison section).

The solution magnetic data for the perchlorate complex is identical for samples utilizing either cyclohexane or hexamethyldisilane as the measure of the magnetic susceptibility of the compound. The frequency separations for the « diamagnetic » and « paramagnetic » protons of the inert solvents[20] are different from that observed for the protons in dichloromethane, indicating that dichloromethane-solute interaction is occuring. For this reason the magnetic susceptibilities were calculated on the basis of the frequency shifts of the inert solvent protons.

The spectrochemical calculations shown in Table VI were obtained in order to test the « average environment » rule for 2,6-LuNO in both its pseudotetrahedral dianion complexes and its « tetrahedral » perchlorate complexes. The general consistency of the Dq and B′ values in the first four comples is contrasted with the values obtained for the perchlorate complex. Since the « average environment » rule has been shown to be quite valid for a large number of tetrahedral and pseudotetrahedral cobalt(II) complexes,[20,27] such results indicate that the perchlorate complex is distorted from a tetrahedral arrangement. Since actual magnitudes of Dq and B′ for 2,6-LuNO in the perchlorate complex depend upon its concentration (the molar absorbancies vary as shown in Table III), nothing quantitative should be inferred from the data presented, other than the fact that the Dq and B′ values are different. Utilizing solution values for Dq and μ (the complex concentration for both measurements was about 0.03 molar) a va-

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(39) R.H. Holm and F.A. Cotton, *J. Chem. Phys.*, *32*, 1158 (1960).

lue of -166 cm^{-1} was obtained [40] for λ', the spin-orbit coupling constnat.

The nuclear magnetic resonance spectrum of the complex was obtained in an approximately 0.3 molar dichloromethane solution. Utilizing hexaxmethldisilane as an internal standard, peaks were observed at -696 Hz (downfield, with a relative area of 6), at -1496 Hz (downfield, with a relative area of 2), and $+ 800$ Hz (upfield with a relative area of 1). From a knowledge of the relative areas, the downfield peaks were assigned to the α-methyl and β-protons, while the upfield peak was assigned to the γ-proton. Utilizing the diamagnetic shift values[24,29] of -145 Hz, -430 Hz, and -419 Hz for the α-methyl, β-, and γ-protons respectively, isotropic shifts of -551 Hz, -1066 Hz, and $+ 1219$ Hz were obtained for the three types of protons. Similar patterns have previously been obtained for various pyridine N-oxides bonded to paramagnetic metal ions,[8,24,41] the result being interpreted in terms of a delocalization of metal electron density of α spin (parallel to the external magentic field) onto the ligand primarily thru a pi type of delocalization.

No attempt is made to ascertain the contact and pseudocontact contributions to the observed shifts, since the geometry of the solution species is not accurately known. In addition solvent-solute interaction is noted, since dilution of the sample from 0.3 molar to 0.03 molar results in an upfield shift of approximately 150 Hz for the β-proton resonance. Dilution of the sample from 0.3 to 0.1 molar also results in a downward shift of about 35 Hz for the γ-proton resonance. Thus the reduction in solute concentration increases the solvent to solute ration and the extent of the solvent-solute interaction. In addition the proton resonance of dichloromethane in the complex solution is found at a frequency 7 Hz upfield from that found for the neat solvent. This type of interation has also been noted chloroform solutions of metal ion complexes and has been ascribed to hydrogen bonding with the solute.[24,42]

The ratios of the isotropic shifts for the various protons ($\alpha/\beta = 0.52$, $\gamma/\beta = -1.14$) do not correlate with those for the metal acetylacetonate adducts [M(acac)$_2$·2,6–LuNO][24] (Co–α/β = 3.67, γ/β = -3.65; Ni–α/β = 1.71; γ/β = -2.46). Such a correlation should occur if the method of electron delocalization throughout the ligand is the same in all cases and if no pseudocontact or solvent-solute interactions are important.[24] Although the [Co, Ni(4-CH$_3$C$_5$H$_4$NO)$_6$]$^{2+}$ complexes do indeed have identical ratios for isotropic shifts,[8] the solvent-solute interactions mentioned above, along with pseudocontact shifts due to the presence of dissimilar ligands in the acetylacetonate adduct,[24] have obviously complicated the situation.

Discussion

Halide Complexes. The colors, solid state electronic spectra, and magnetic moments of these compounds are typical of pseudotetrahedral cobalt(II) complexes. Such conclusions have been reached previously,[21,22] although no electronic spectral data were listed for the chloride complex,[21] and those magnetic data listed for the chloride and bromide complexes[21] appear to be too low. Since unsubstituted pyridine N-oxide reacts with cobalt(II) halides[5,43] to produce complexes of the form [Co(pyNO)$_6$][CoX$_4$] (X = Cl, Br),[44] it is obvious that steric effects have reduced the coordination number of the cobalt ion from six to four. It has also been shown, however, that some consideration must be given to electronic effects, since 4-ethoxypyridine N-oxide also forms a pseudotetrahedral complex with cobalt(II) chloride.[11]

Dissolution of the complexes in both dichloromethane and nitromethane produces electronic spectra similar to those for the complexes in the solid state, indicating that the dissolution process has not effected the nature of the ligand field. Dissolution of [Co(TMNO)$_2$X$_2$] (X = Cl, Br, I) complexes in acetonitrile and dichloromethane resulted, however, in very distinct changes in spectral and magnetic behavior,[20] which were shown[33] to be due to a reduction in coordination number from five to four as the compounds dissolved. While [Co(4-OC$_2$H$_5$pyNO)$_2$Cl$_2$] has also been shown to exist in nitromethane solutions as a pseudotetrahedral species,[11] similar CoL$_2$Cl$_2$ (L = 2,4-LuNO, 2,4,6-ColNO; ColNO = collidine N-oxide) complexes purportedly dissolve in nitromethane and N,N-dimethylformamide solutions to produce six-coordinated species.[36] Since the steric conditions present in complexes of 2,6-LuNO are more similar to those of 2,4-LuNO and 2,4,6-ColNO than to those of 4-ethoxypyridine N-oxide, the results reported by Ramaswamy and Jonassen[36] are thus surprising. It appears, however, that the spectra obtained for the two complexes in nitromethane[36] bear a much stronger resemblance to those of five-coordinate species[34,35] than six-coordinate ones. The spectral data for the same two complexes in DMF are difficult to interpret but certainly are not those for cobalt(II) in an octahedral array. These data are also at variance to those reported by the same authors for the [Co(2,6-LuNO)$_2$X$_2$] (X = Cl, Br) complexes dissolved in DMF,[21] in which case the cobalt ion is supposed to retain a coordination number of four. There appears to be no ready explanation why a 2,4,6-ColNO complex in DMF should react with the solvent to produce a six-coordinate metal ion,[36] while the metal ion in the equally crowded 2,6-LuNO complex remains four-coordinated.[21] Close scrutiny of the reported spectral data for [Co(2,6-LuNO)$_2$Br$_2$] in DMF[21] indicates that a mixture of species is definitely present (including a four-coordinate one, which may contain DMF in the first coordination sphere). Thus it is probably best to regard these solution data[21,36] and their previous interpretations as unreliable.

Addition of excess 2,6-LuNO to dichloromethane of all these complexes and to nitromethane solutions of the chloride and bromide complexes (Tables I, II) has no great effect on the electronic spectra of the complexes, although in some cases reductions in molar absorptivities of 10-15% are noted. The results

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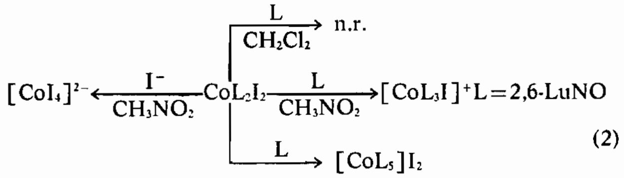
(40) F.A. Cotton and G. Wilkinson, « Advanced Inorganic Chemistry », Interscience, New York. N.Y., 1966, p. 872.
(41) E. E. Zaev and Yu. N. Molin, *J. Strukt. Chem.*, *7*, 639 (1966) *Zh. Strukt Khim.*, *7*, (680) (1966).
(42) M. F. Retting and R. S. Drago, *J. Am. Chem. Soc.*, *88*, 2966(1966).
(43) K. Issleib and A. Kreibich, *Z. anorg. allgem. Chem.*, *313*, 339(1962).
(44) J. A. Betrand and D. L. Plymale, *Inorg. Chem.*, *3*, 775(1964).

indicate, however, that the major species present are still the pseudotetrahedral complexes. Addition of excess 2,6-LuNO to a nitromethane solution of the iodide complex, however, produces a royal blue solution whose conductance value indicates that the complex should be formulated as $[Co(2,6\text{-}LuNO)_nI]I$ ($n = 3, 4,$ or 5). Since the electronic spectrum (Figure 1) of the species is definitely not that of a six-coordinate species, that last choice is rejected. Although the molar absorptivities of the visible transitions are somewhat lower than those normally noted for pseudotetrahedral complexes (especially that for the transition located at 750 mμ), they are much larger than those noted for the five-coordinate complexes observed in this study (Tables II and III). The electronic spectral pattern is also quite similar to those found for pseudotetrahedral $[Co(TMNO)_3X]^+$ ($X = Cl$,[20] Br[45]) and $[Co(HMPA)_3I]^+$ [46] complexes.

The non-reactivity of the chloride and bromide complexes under these conditions can be rationalized on the basis of their greater metal-halogen bond strengths. The non-reactivity of the iodide complex in dichloromethane-2,6-LuNO solutions is due to the low dielectric constant of dichloromethane, which does not easily facilitate a transfer of charge in solution.[47] The large difference in donor strength between 2,6-LuNO and TMNO is apparent, since reactions between $[Co(TMNO)_2X_2]$ ($X = Br, I$) and TMNO in acetonitrile produce $[Co(TMNO)_4]^{2+}$, while $[Co(TMNO)_2Cl_2]$ reacted similarly in acetonitrile to produce $[Co(TMNO)_3Cl]^+$.[20] Another indication for the fairly low donor strength of 2,6-LuNO is its removal from the cordination sphere of $[Co(2,6\text{-}LuNO)_2I_2]$ when excess iodide ion is added in nitromethane, producing $[CoI_4]^{2-}$ (Table II, Figure 1).

The only spectral change noted when $[Co(2,6\text{-}LuNO)_2Cl_2]$ is dissolved in pure 2,6-LuNO is a loss in the fine structure of its visible transition (Table I), indicating that no reaction has occurred. The bromide complex reacts with the solvent, as evidenced by the significant reductions in molar absorptivities. Since the positions of maximum absorption do not change, and since no new absorption peaks are observed, it would appear that the major solution species is still $[Co(2,6\text{-}LuNO)_2Br_2]$.

Dissolution of $[Co(2,6\text{-}LuNO)_2I_2]$ in pure 2,6-LuNO produces an equilibrium mixture of two species (Figure 2), one of them being the unreacted complex. As the molar ratio of solvent to complex increases, the reaction is driven to completion (Curve C), at which point essentially no unreacted complex remains. Since the visible spectrum of the final product is more similar to those of known five-coordinate species[3,11,33-35] than to those of four-coordinate species, the final product most be $[Co(2,6\text{-}LuNO)_{3+x}I_{2-x}]I_x$ ($x = 0, 1,$ or 2). The strong similarities between the electronic spectrum of this species and that of $[Co(2\text{-}CH_3pyNO)_5]^{2+}$ [3,14] is an indication that the species is best formulated as $[Co(2,6\text{-}LuNO)_5]I_2$. Although no previous complexes of this type have been reported, examples of tetrahedral complexes containing ionic iodides ($[Co(TMNO)_4]I_2$[20,45] and $[Co(HMPA)_4]I_2$[46]) have recently been reported. The various reactions of $[Co(2,6\text{-}LuNO)_2I_2]$ are summarized below (2).



(2)

Thiocyanate Complex. Although the halide complexes do not undergo a change in stereochemistry upon dissolution, the violet-purple thiocyanate complex dissolves in both dichloromethane and nitromethane to yield a royal blue solution. While no molar absorptivities could be obtained for the solution species due to its extremely low solubility, the solution electronic spectrum (Figure 3) is typical of pseudotetrahedral cobalt(II) complexes. Since the infrared data reveal the existence of two different C–N stretching vibrations (one assigned to a bridging thiocyanate group and one to an N-bonded thiocyanate group), and only one N–O stretching vibration (at essentially the same energy as found in the halide complexes), the coordination number of the cobalt(II) ion in the solid state must be five. The magnetic moment of 4.52 B.M., while very low for a six-coordinate cobalt (II) complex, is similar to those for a number of five-coordinate cobalt(II) complexes containing bonded thiocyanate.[48-50] In addition the solid state visible electronic spectrum is very similar to that for $[Co(TMNO)_2(NCS)_2]$, which has been shown to be five-coordinate in the solid state.[33] Although both the 2,6-LuNO and TMNO complexes of cobalt(II) thiocyanate are thus five-coordinate in the solid state and pseudotetrahedral in solution,[20] five-coordination is acheived in the former case by bridging TMNO and in the latter by bridging thiocyanate.

An earlier report[21] described $[(Co(2,6\text{-}LuNO)_2(NCS)_2]$ as containing six-coordinate cobalt(II) in the solid state, conclusions which are at variance with ours. Efforts to obtain the « pink » compound from methanolic solutions[21] (as opposed to the ethanolic solution method described in the Experimental Section), yielded only the violet, five-coordinate species previously described. In addition while the reported color, magnetic moment, and infrared spectrum of the « pink » compound are different[21] from those of the violet compound studied herein, the reported electronic spectrum is surprisingly the same as that reported in Table I. One possible explanation is that these two compounds exhibit a rare type of linkage isomerism.[37] Since the violet compound does not show any tendency, even after periods of a year, to change color or any of its physical properties, it may very well be the more stable of the two modifications.

Perchlorate Complex. Although the solid state infrared spectrum (Table IV) of the perchlorate complex would appear to indicate that perchlorate coordination is either weak or non-existent, the magnetic

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(45) D. Herlocker, *J. Inorg. Nucl. Chem.*, 30, 2197(1968).

(46) M. R. Rosenthal and R. S. Drago, *Inorg. Chem.*, 5 1612(1966); HMPA = $[(CH_3)_2N]_3PO$.

(47) R. S. Drago and K. F. Purcell in « Advances in Inorganic Chemistry ». Vol. 6, F. A. Cotton, ed., Interscience Publishers, Inc., New York, N. Y., 1965, pp. 271-322.

(48) M. Ciampolini and N. Nardi, *Inorg. Chem.*, 6, 445(1967).

(49) J. S. Judge and W. A. Baker, *Inorg. Chim. Acta*, 1, 239(1967).

(50) Z. Dori and H. B. Gray, *Inorg. Chem.*, 7, 889(1968).

and electronic spectral data argue against designation of the complex as containing four-coordinate, tetrahedral cobalt(II). Thus its color is much less intense, its electronic transitions are higher in energy, and its magnetic moment is much higher than those of $[Co(TMNO)_4](ClO_4)_2$, which does contain tetrahedrally coordinated cobalt(II).[19,20] These conclusions agree with those of Karayannis *et al.*[25]

If a tetrahedral structure for the complexed metal ion can be eliminated from consideration, there still exist three other possibilities—square planar cobalt (II) with non-coordinated perchlorate ions; six-coordinate, polymeric cobalt(II) with bridging 2,6-LuNO molecules; and six-coordinate, monomeric cobalt(II) with coordinated perchlorate ions. After consideration of X-ray powder pattern, spectral, and magnetic evidence, Karayannis *et al.*[25] have assigned square-planar monomeric structures to the $[M(2,6\text{-}LuNO)_4](ClO_4)_2$ ($M = Fe^{II}$, Co^{II}, Ni^{II}, and Cu^{II}) complexes and a square pyramidal structure to $[Mn(2,6\text{-}LuNO)_4OClO_3]ClO_4$. Only in the case of the cobalt complex is their evidence less than convincing. Thus the argument is made that since the stability of planar systems decreases in the order $Ni^{II} > Co^{II} > Fe^{II}$,[51] the isolation[25] of square-planar complexes of nickel (diamagnetic) and iron (half-quenched spin) implies that the cobalt complex must also be square-planar. Since the above stability scheme[51] was obtained from a situation in which all ligand fields are strong enough to cause spin pairing, it may very well not be valid to assume such an ordering if the ligand field about the cobalt(II) ion is weak, as it is in this compound.

If the above stability scheme is thus considered not relevant in this case, it is necessary to consider whether arrays of ligands found to produce a square-planar stereochemistry about a nickel(II) ion also produce a different molecular arrangement about a cobalt(II) ion. It has recently been found that some tetradentate Schiff bases which form square-planar complexes with nickel(II)[52] form tetrahedral ones with cobalt (II).[53] The same behavior is found with a linear, tetradentate pyrrolic ligand.[54] In cases involving monodentate ligands, it has been shown that while $[Ni(3,4\text{-lutidine})_4](ClO_4)_2$ contains square-planar, four-coordinate nickel(II)[55,56] and $[Ni(3,5\text{-lutidine})_4(ClO_4)_2]$ contains pseudooctahedral, six-coordinate nickel(II)[55,57] the analogous cobalt(II) complexes both contain pseudooctahedral, six-coordinate cobalt.[58] In addition while it has been found that chloroform will partially remove coordinated perchlorate and tetrafluoroborate anions from the coordination sphere of $[Ni(C_5H_5N)_4(anion)_2]$,[59] causing the formation of yellow, square-planar nickel complexes, no such behavior has been noted for the analogous cobalt complexes.[60] Thus the existence of a square-planar array of ligands in a nickel(II) complex need not guarantee the same stereochemical arrangement in the stoichiometrically analogous cobalt(II) compound.

The apparent differences between the electronic spectral data reported earlier[25] and those in Table III (extra transitions are found at 358 mμ (27,930 cm^{-1}), 770 mμ (13,020 cm^{-1}), and 1390 mμ (7200 cm^{-1}) are easily explained. Thus the highest energy peak is undoubtedly a charge-transfer peak,[4,9] while the lowest energy one may be due to a ligand overtone.[7] The remaining extra peak is a shoulder on an intense peak in the visible region and was not seen in this work. The two peaks common to both reports (Figure 4, Table III) are found at energies normally assigned to the ν_1 and ν_3 transitions in octahedrally or pseudooctahedrally coordinated cobalt(II), with the shoulder seen at 770 mμ[25] probably being ν_2.

If the environment can be considered to be epproximately octahedral about the cobalt ion, it is necessary to determine if possible the nature of the six bonding sites. Although the magnetic moment of the complex is similar in magnitude to those for other six-coordinate cobalt(II) complexes containing various pyridine N-oxides,[3,4,61] it offers no clue in this matter. The appearance of two different N–O stretching frequencies in the complex (Table IV) is not in itself evidence for two different types of bonding sites, bridging and terminal. Thus it has been shown[3] that two different N–O stretching frequencies are found in many $[M(4\text{-}RpyNO)_6]^{2+}$ complexes, in which no bridging ligands are expected. In addition infrared spectral data for the truly square planar[62] $[Cu(pyNO)_4]^{2+}$ complex[4,63] contains two separate N–O stretching frequencies, a situation explained[3] by assuming a reduction in the symmetry of the MO_4 moiety to something less than D_{4h}. If bridging 2,6-LuNO molecules are indeed present in this complex, it seems logical that the « extra » stretching mode should have an energy lower than that found in the $[Co(2,6\text{-}LuNO)_2X_2]$ complexes (Table IV) rather than higher.[63] These several considerations would seem to rule against considering the complex as being polymeric because of bridging 2,6-LuNO ligands.

Although infrared data appear to indicate little or no perchlorate-metal interaction in $Co(2,6\text{-}LuNO)_4(ClO_4)_2$, it has recently been found that in some $[ML_4(ClO_4)]^+$ (L = arsine or phosphine oxides) complexes, in which the metal is known by other means to be five coordinate,[64-67] no splitting of the ν_3 perchlorate band at approximately 1100 cm^{-1} is seen. Preparation of analogous complexes[67] containing the slightly stronger bonding[68] perrhenate ion, ReO_4^-, indicates that metal-anion bonding does take place in these cases.[67] Studies are currently under way to prepare $[Co, Ni(2,6\text{-}LuNO)_4(ReO_4)_2]$ in an effort to determine the extent of metal-anion interaction.

Although there should be some splitting of the ν_1 and ν_3 electronic transitions of the perchlorate com-

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(51) J. Chatt and B. J. Shaw., *J. Chem. Soc.*, 285 (1961).
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plex if such a tetragonally distorted ligand field exists, the breadth of the bands (Table III, Figure 4) may prevent the observance of such splittings. Obtaining spectra at lower temperature[3] may reveal these splittings, although any bands which might be found at approximately 1400 mμ might well be due to ligand overtones.[7] Thus at present the solid state data can best be interpreted as being due to a six-coordinate cobalt(II) complex, in which the metal-perchlorate interaction is weak but finite. These conclusions contrast with the results obtained for the $[Co(TMNO)_4]^{2+}$ cation, which has been shown to be tetrahedral in nature in a variety of compounds.[19,20,45]

Schmass and Specker[13] have reported the preparation of $[(Co2,6\text{-}LuNO)_4(H_2O)_2]\ (ClO_4)_2$ and $[Co(2,6\text{-}LuNO)_6](ClO_4)_2 \cdot 2H_2O$. Although very little solid state data were reported, it seems logical that the coordination spheres of both compounds are identical and contain four molecules of 2,6-LuN0 and two of water. The extra molecules of 2,6-LuN0 in the second compound are most pabably contained in the lattice.

That any metal-anion interaction is weak is indicated by the fact that $[Co(2,6\text{-}LuNO)_4(ClO_4)_2]$ dissolves readily in dichloromethane to produce intensely blue-purple solutions, whose electronic spectral patterns (Table III, Figure 4) and magnetic data (Table V) are similar to those of tetrahedral cobalt(II) cations.[17,18,27,45,69] The low molar absorptivities noted for the visible transitions and the large separation of peaks present in the near infrared region (4960 cm^{-1}, as opposed to 1500-2000 cm^{-1} for $[CoX_4]^{2-}$ (X = Cl, Br, I)[27] and 900-1500 cm^{-1} for $[Co(2,6\text{-}LuNO)_2X_2]$ (Tables I and II)) are quite similar to those noted for $[Co(DMA)_4]^{2+}$ (DMA = N,N-dimethylacetamide),[70] which is assumed to contain a distorted tetrahedral cation. In an attempt to determine whether $[Co(2,6\text{-}LuNO)_4]^{2+}$ is likewise distorted, comparisons of Dq and B′ values for 2,6-LuNO in its pseudotetrahedral complexes and its supposedly tetrahedral perchlorate complex were made (Table VI). The results differ from those found earlier[20] in analogous TMNO complexes, in which Dq and B′ were constant, and they indicate that there is indeed some distortion from the expected tetrahedral arrangement, although the difference in the calculated and observed Dq values for 2,6-LuNO is much smaller than that observed for DMA (490 cm^{-1} in $[Co(DMA)_4]^{2+}$[70] vs. 330 ± 15 cm^{-1} in $[Co(DMA)_2X_2]$ (X=Cl, Br, I)[71]). Utilizing solution values of Δ and μ for DMA,[70] a value of-233 cm^{-1} is calculated[40] for λ', in comparison with a value of -166 cm^{-1} obtained for 2,6-LuNO and -178 cmλ' for the free cobalt ion. Thus the degree of distortion for the $[Co(2,6\text{-}LuNO)_4]^{2+}$ complex does not appear to be as large as what is expected for $[Co(DMA)_4]^{2+}$.

While a weak metal-nitrogen interaction (to supplement the strong metal-oxygen interaction) was proposed[70] as the reason for the distortion of the DMA complex, such a situation is not possible here, since only the oxygen in 2,6-LuNO can serve as a bonding site. It is known, however, than M-O-N linkages in pyridine N-oxide complexes are bent both in the solid state[14] and in solution,[8,24,41] due to the presence of a lone pair of electrons on the oxygen. In the present case a strictly tetrahedral ordering of the 2,6-LuNO molecules might cause excessive non-bonded interactions between some of the various methyl groups, an interaction which can be reduced only by flattening the ideally tetrahedral CoO_4 moiety, thereby producing the observed results. In a similar case there is evidence to indicate that bis (3,3′,5,5′-tetramethyldipyrromethene-4,4′-dicarboxylate) cobalt(II)—assumed to contain tetrahedrally coordinated cobalt(II),[72] even though the molar absorptivities in the visible region are lower than normal—may in fact have a primary cooordination sphere of only D_2 symmetry.[73]

The variation of spectral intensities of the perchlorate complex in dichloromethane is not due to the existence of more than one solute, since the positions of maximum absorption are concentration independent. The electronic spectral, nmr, and solution magnetic data all indicate a solvent-solute interaction which is obviously concentration dependent. The interaction is probably a hydrogen-bonding one, involving solvent protons and the pi-electron density of the aromatic rings and/or the oxygen bonding site on the coordinated ligands.

In nitromethane, however, a concentration dependent reaction occurs. The species present when the complex concentration is low is probably $[Co(2,6\text{-}LuNO)_4(CH_3NO_2)]^{2+}$, since its spectrum is similar to that for $[Co(2,6\text{-}LuNO)_5]I_2$. At higher complex concentrations, bands similar to those found for both $[Co(2,6\text{-}LuNO)_4]^{2+}$ and $[Co(2,6\text{-}LuNO)_4(CH_3NO_2)]^{2+}$ are found, indicating the presence of appreciable amounts of both species. These conclusions are in agreement with earlier ones.[25] In addition it has been found[25] that acetone reacts with $[Co(2,6\text{-}LuNO)_4]^{2+}$ to produce $[Co(2,6\text{-}LuNO)_4(C_3H_6O)]^{2+}$.

The addition of 2,6-LuNO to a nitromethane solution of the perchlorate complex produces a violet solution whose electronic spectrum (Figure 4) is the same as that found for $[Co(2,6\text{-}LuNO)_2I_2]$ in 2,6-LuNO (Figure 2) and is analogous to those found by Byers *et al.*[3] for $[Co(2\text{-}CH_3pyNO)_5]^{2+}$ and Karayannis *et al.*[11] for $[Co(4\text{-}OC_2H_5pyNO)_5]^{2+}$. The reductions in transition energies from those in the last two cases are due to metal-ligand bond weakening caused by greater steric interaction among the bulkier 2,6-LuNO ligands. The spectral results are in good agreement with those reported by Karayannis *et al.*[25] for the same system and by Enriquez *et al.*[26] for $[Co(2,6\text{-}LuNO)_4]^{2+}$ dissolved in a $2,6\text{-}LuNO\text{-}CD_3NO_2\text{-}(CD_3)_2CO$ mixed solvent. All data indicate the presence of $[Co(2,6\text{-}LuNO)_5]^{2+}$ under these conditions. While Schmauss and Specker[13] have also oberved the reaction of the perchlorate complex with added 2,6-LuNO in nitromethane, they have assumed the solution species to be $[Co(2,6\text{-}LuNO)_6]^{2+}$, an assumption which is refuted by this and other studies.[3,11,25,26]

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Dissolution of the perchlorate complex in 2,6-LuNO also produces $[Co(2,6\text{-}LuNO)_5]^{2+}$ (Table III), but only in dilute solutions, in which a high solvent to complex ratio exists. In more concentrated solutions a mixture of complexes containing both four- and five-coordinate cobalt(II) is present. The non-reactivity of the five-coordinate complex even in the presence of huge amounts of extra ligand (as opposed to the case of $[Co(4\text{-}OC_2H_5pyNO)_5]^{2+}$ which reacted[11] with excess base to form the six-coordinate species) is assumed to be due to steric problems. The contrasting results observed for $[Co(TMNO)_4]^{2+}$, which was found to be stable in acetonitrile and dichloromethane to which excess TMNO had been added,[20,45] indicate that more room is available about the cobalt (II) ion for 2,6-LuNO, since the methyl groups are somewhat farther from the coordination site than they are in TMNO.

Interpretation of the data obtained when the perchlorate complex reacts with excess 2,6-LuNO in dichloromethane involves consideration of both the positions and intensities of the various absorption peaks. Thus the shift of the most intense visible band and the gradual disappearance of bands in the near infrared region can be attributed to the reaction of the four-coordinate complex with excess base to form $[Co(2,6\text{-}LuNO)_5]^{2+}$, as was discussed earlier the cases of the 2,6-LuNO and 2,6-LuNO-nitromethane solvent systems (Table III). The difference in the ease of conversion of $[Co(2,6\text{-}LuNO)_4]^{2+}$ in the different solvents is due to the difference in dielectric constants for the various solvents.[47] Summarized below are the various solution reactions of $[Co(2,6\text{-}LuNO)_4(ClO_4)_2]$ (3).

$$\begin{tikzcd}
 & {[CoL_4]^{2+}} \arrow[dr, "L"] & \\
{[CoL_4(ClO_4)_2]} \arrow[ur, "CH_2Cl_2"] \arrow[rr, "L"] \arrow[dr, "CH_3NO_2"'] & & {[CoL_5]^{2+}} \quad L=2{,}6LuNO \\
 & {[CoL_4(CH_3NO_2)]^{2+}} \arrow[ur, "L"'] &
\end{tikzcd} \tag{3}$$

Although the positions of the electronic transitions assigned to $[Co(2,6\text{-}LuNO)_5]^{2+}$ are essentially the same in 2,6-LuNO-dichloromethane solutions (in which the excess base/metal complex ratio is $\geqslant 200/1$) as they are in both neat 2,6-LuNO and 2,6-LuNO-nitromethane solutions, the molar absorptivity of the visible ν_4 transition is only about half that found in these other solvents (and for $[Co(2,6\text{-}LuNO)_5]I_2$ in 2,6-LuNO (Table II)). Since dichloromethane reacts with $[Co(2,6\text{-}LuNO)_4]^{2+}$, producing concentration-dependent molar absorptivities (Table III), it is possible that such an interaction is occurring here also, thus causing a smaller than expected absorbance for some transitions in this system. While an increase in cobalt ion concentration to approximately 0.06-0.08 molar might similarly cause an increase in the molar absorptivities of $[Co(2,6\text{-}LuNO)_5]^{2+}$, the concentration of excess 2,6-LuNO in dichloromethane needed for complete transition of $[Co(2,6\text{-}LuNO)_4]_2^{+}$ into $[Co(2,6\text{-}LuNO)_5]^{2+}$ would be approximately 12-14 molar. In such a solution, the solvent properties would be drastically different from those of either pure dichloromethane or of dichloromethane with moderate amounts of added 2,6-LuNO. Thus in this case the behavior of the dichloromethane may prevent the obtaining of spectral data for $[Co(2,6\text{-}LuNO)_5]^{2+}$ completely analogous to those in the other situations discussed.

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