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## A Nuclear Magnetic Resonance Study of Substituted-Pyridine Complexes of Iron(II), Cobalt(II), and Nickel(II)

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Nmr studies of paramagnetic octahedral complexes of the types  $M(4\text{-Etpy})_4X_2$ , where  $M = \text{Fe, Co, and Ni}$  and  $X = \text{Cl, Br, I, NCO, NCS, and N}_3$ , and  $M(4\text{-}n\text{-Prpy})_4X_2$ , where  $M = \text{Fe, Co, and Ni}$  and  $X = \text{Cl, Br, I, and NCS}$ , are reported. In all of the complexes the methyl resonances of the coordinated 4-ethylpyridine and the 2-methylene and methyl resonances of the coordinated 4-propylpyridine ligands are dominated almost exclusively by dipolar effects and confirm a magnetic anisotropy inversion effect in the series of cobalt complexes. Further, a similar magnetic anisotropy inversion effect is observed in the ferrous complexes. In all cases where dipolar effects of a certain sign are apparent on the ligand resonances, dipolar shifts of *opposite* sign are observed on the chloroform solvent proton resonance. In addition to these dipolar solvent shifts in systems displaying substantial magnetic anisotropy, it is found that when ligand exchange is slow enough to allow observation of separate resonances for the free and coordinated ligand, the free ligand resonances are shifted significantly from their normal diamagnetic position.

### Introduction

Many studies of the nmr of paramagnetic metal-pyridine and -substituted-pyridine complexes have been reported.<sup>1-5</sup> Most studies have concentrated on the contact shifts observed in these systems. However, a recent study of complexes of the type  $M(\text{py})_4X_2$  where  $M = \text{Co and Ni}$  and  $X = \text{halide or pseudohalide}$ <sup>6</sup> was directed at determining the effect that substituents on the metal have on dipolar effects on the coordinated pyridine ligands. An apparent inversion of the dipolar effect and, hence, magnetic anisotropy, was observed in the series of cobalt(II) complexes. Insofar as this interpretation was based primarily upon separation of the contact and dipolar effects at the 4 position of the coordinated ligand, some doubt remained about the concept of an inversion of magnetic anisotropy. The previous difficulties have led us to seek systems free from ambiguities of interpretation. Accordingly, we have synthesized metal complexes of 4-ethylpyridine and 4-propylpyridine since contact shifts in pyridine complexes are dominated by  $\sigma$  delocalization<sup>7</sup> and, hence, one expects very small contact effects at the methyl position of coordinated 4-ethyl- and 4-propylpyridine.

We have also included in this study the corresponding iron(II) complexes since octahedral iron(II) like cobalt(II) has a T ground state and considerable magnetic anisotropy is to be expected. Further, Mossbauer studies of complexes of the type  $\text{Fe}(\text{py})_4X_2$  have led to a suggestion<sup>8</sup> of variations in the ground state with change in the anion X.

### Experimental Section

The nmr spectra of the complexes were obtained with a Varian A-56/60 spectrometer equipped with a variable-temperature probe. The complexes were examined as 0.1 M solutions in deuteriochloroform containing 1%  $\text{CHCl}_3$  and TMS as an internal reference. Known amounts of excess ligand were always added to ensure that the

equilibria between octahedral and tetrahedral complexes commonly found<sup>9</sup> in these systems were forced to the octahedral side. Degassed solvent was used for the ferrous complexes. Electronic spectra were obtained with a Cary 14 spectrophotometer. X-Ray powder patterns were obtained with a General Electric XRD-5 diffractometer using  $\text{Cu K}\alpha$  radiation.

**Preparation of Complexes.** The nickel and cobalt complexes of the type  $M(\text{ligand})_4X_2$  (ligand = 4-ethylpyridine and 4-*n*-propylpyridine) were prepared by the well-documented procedures for the analogous pyridine and 4-methylpyridine complexes.<sup>10,11</sup> The ferrous complexes were prepared as described for the analogous pyridine and methylpyridine complexes.<sup>12,13</sup> However, only 4:1 complexes were isolated with ethyl- and propylpyridine, unlike the pyridine and picoline systems where 6:1 complexes are obtained under some conditions.

### Results and Discussion

**Structure of the Complexes.** The complexes  $M(\text{py})_4X_2$  where  $X = \text{Cl, Br, and NCS}$  are known to adopt a trans octahedral structure in the solid state<sup>14-16</sup> and their electronic spectra in the solid state have been recorded.<sup>9,17</sup> We therefore examined the electronic spectra of the complexes in solution under conditions similar to those used for the nmr experiments. The results for the 4-*n*-propylpyridine complexes are given in Table I. The 4-ethylpyridine complexes give almost identical spectra. Comparison of the spectra with the solid-state spectra of the corresponding pyridine complexes leaves little doubt that the substituted pyridine complexes have a trans octahedral structure in solutions containing excess ligand. In the solid state all nine of the compounds of the type  $M(4\text{-Etpy})_4X_2$  where  $X = \text{Cl, Br, and I}$  are isomorphous.<sup>18</sup>

**Nmr Data.** The results for the 4-ethylpyridine complexes are presented in Table II. No attempt has been made to

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Table I. Electronic Spectra of 4-*n*-Propylpyridine Complexes of Nickel(II), Cobalt(II), and Iron(II)

Complex	Absorption max, cm <sup>-1</sup> ( $\epsilon_{\text{molar}}$ )
NiL <sub>4</sub> Cl <sub>2</sub> <sup>a</sup>	8300 (6), 10,800 (3), 15,900 (10)
NiL <sub>4</sub> Br <sub>2</sub> <sup>a</sup>	7600 (7), 11,400 (4), 15,900 (11.5)
NiL <sub>4</sub> I <sub>2</sub> <sup>a</sup>	7100 (10), 11,200 sh, 12,500 (4), 15,900 (15)
NiL <sub>4</sub> (NCS) <sub>2</sub> <sup>b</sup>	10,500 (11.5), ~13,000 sh, 17,200 (11)
CoL <sub>4</sub> Cl <sub>2</sub> <sup>c,d</sup>	7100 (1), 8800 (2.5)
CoL <sub>4</sub> Br <sub>2</sub> <sup>c,d</sup>	~6000 (21), <sup>e</sup> 8800 (2.5)
CoL <sub>4</sub> I <sub>2</sub> <sup>c,d</sup>	~5500 (4), 8800 (8)
CoL <sub>4</sub> (NCS) <sub>2</sub> <sup>c</sup>	9500 (7.5)
FeL <sub>4</sub> Cl <sub>2</sub> <sup>a,d</sup>	~8700 sh, 10,600 (3.5)
FeL <sub>4</sub> Br <sub>2</sub> <sup>a,d,f</sup>	6700 (1.5), 10,900 (3.5)
FeL <sub>4</sub> I <sub>2</sub> <sup>a,d</sup>	~5500 <sup>e</sup> (1.5), 11,400 (3.5)
FeL <sub>4</sub> (NCS) <sub>2</sub> <sup>a</sup>	11,400 (6)

<sup>a</sup> 0.1 M in CHCl<sub>3</sub>; also 0.4 M in 4-*n*-propylpyridine. <sup>b</sup> 0.05 M in CHCl<sub>3</sub>. <sup>c</sup> 0.1 M in CHCl<sub>3</sub>; also 3 M in 4-*n*-propylpyridine. <sup>d</sup> Recorded at 0°. <sup>e</sup> Some interference from vibrational overtones. <sup>f</sup> In spectra recorded at room temperature, without excess ligand, a band was observed at ~6000 cm<sup>-1</sup> (~50) which is probably due to formation of a tetrahedral species FeL<sub>2</sub>Br<sub>2</sub>: D. Forster and D. M. L. Goodgame, *J. Chem. Soc.*, 454 (1965).

extrapolate all of the results to a common temperature because of the markedly non-Curie behavior of the cobalt and iron shifts.

Little or no magnetic anisotropy is anticipated for octahedral nickel(II) complexes and thus the shifts in the nickel complexes which show only a small dependence on the halide or pseudohalide coordinated can be attributed almost entirely to contact effects. Because these contact effects in pyridine-type complexes are dictated primarily by effects due to  $\sigma$  delocalization,<sup>2</sup> they attenuate rapidly and thus there are only very small shifts at the terminal methyl positions. By contrast, octahedral cobalt(II) and iron(II) complexes are known from esr studies to exhibit considerable magnetic anisotropy<sup>19,20</sup> and thus substantial dipolar shifts can be anticipated in both cases and the methyl shifts observed for both the cobalt and iron complexes can probably be attributed primarily to dipolar effects. These methyl shifts are observed not only to vary in magnitude with variation in the anion coordinated to the metal but also, more significantly, to vary in sign. In the case of the cobalt complexes the variation in sign is precisely the same as tentatively proposed for the analogous pyridine and picoline complexes.<sup>7</sup> There is also an inversion in the sign of the dipolar shift at the methyl position in the series of iron(II) complexes. However, the inversion is in the opposite sense to that displayed by the cobalt complexes; *i.e.*, for cobalt(II), the chloride, isothiocyanate, isocyanate, and azide have  $\chi_{\parallel} > \chi_{\perp}$  and the bromide and iodide have  $\chi_{\parallel} < \chi_{\perp}$  and for iron(II), the chloride and isothiocyanate have  $\chi_{\parallel} < \chi_{\perp}$  and the bromide and iodide have  $\chi_{\parallel} > \chi_{\perp}$ .

The solvent shifts in these systems confirm the concept of an inversion of magnetic anisotropy in both the cobalt and iron series. The nickel systems give rise to small chloroform solvent shifts (see Table II) which are similar in magnitude to those observed for chloroform solutions containing [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PCoL<sub>3</sub>]<sup>-</sup> and [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PNiL<sub>3</sub>]<sup>-</sup> ions<sup>21</sup> where the shifts were attributed to a contact shift *via* a hydrogen bond between the CHCl<sub>3</sub> and the halide on the metal. If similar weak hydrogen bonding occurs in the systems under examination in this work, then the chloroform molecules can be expected to spend more time close to the metal in the cone of magnetic anisotropy of oppo-

Table II. Magnetic Resonance Data for the 4-Ethylpyridine Complexes of Nickel(II), Cobalt(II), and Iron(II)<sup>a</sup>

Complex	Temp, °C	$\Delta\nu(\beta\text{-H})$	$\Delta\nu(\text{CH}_2)$	$\Delta\nu(\text{CH}_3)$	Solvent shift (CHCl <sub>3</sub> )
NiL <sub>4</sub> Cl <sub>2</sub>	+37	-1900	+435	-30	
	-56		+640 <sup>b</sup>	-40 <sup>b</sup>	+14
NiL <sub>4</sub> Br <sub>2</sub>	+37	-1825	+450	-30	+15
	-56		+635 <sup>b</sup>	-40	+14
NiL <sub>4</sub> I <sub>2</sub>	+37	-1850			
	-56		+640 <sup>b</sup>	-45	+14
Ligand <sup>c</sup>	-56	0	0	0	
	NiL <sub>4</sub> (NCS) <sub>2</sub>	+55		+420	0
NiL <sub>4</sub> (NCO) <sub>2</sub>	-56		+700 <sup>b</sup>	0 <sup>b</sup>	+10
	+55		+444	-9	
NiL <sub>4</sub> (N <sub>3</sub> ) <sub>2</sub>	+55	-1550			
	+12		+493		0
CoL <sub>4</sub> Cl <sub>2</sub>	-58		+700 <sup>b</sup>	-18 <sup>b</sup>	0
	-3	-1900			
CoL <sub>4</sub> Br <sub>2</sub>	-27		+578	+151	-35
	-56			+168 <sup>b</sup>	-48
CoL <sub>4</sub> I <sub>2</sub>	+3	-2600			+67
	-27		+60	-152	+86
CoL <sub>4</sub> (NCS) <sub>2</sub>	-56		~+12 <sup>d</sup>	~-200 <sup>d</sup>	
	-2	-2500			
CoL <sub>4</sub> (NCO) <sub>2</sub>	-27		-294	-345	+112
	-36				+145
CoL <sub>4</sub> (N <sub>3</sub> ) <sub>2</sub>	+37	-1775	+585	+195	-33
	-56			+263 <sup>b</sup>	-58
Ligand <sup>c</sup>	-56	-25	-26	-21	
	+37	-1100			-72
FeL <sub>4</sub> Cl <sub>2</sub>	-22		+1130	+500	-130
	-3	-1260	+1030	+417	-100
FeL <sub>4</sub> Br <sub>2</sub>	-58				-160
	-14	-2615			
FeL <sub>4</sub> (NCS) <sub>2</sub>	-29		+204	-135	+66
	-62		+180 <sup>b</sup>	-221 <sup>b</sup>	+110
Ligand <sup>c</sup>	-62	+17	+15	+9	
	+37	-2000			
FeL <sub>4</sub> I <sub>2</sub>	-33		-15	+48	0
	-45		-10	+63	-5
FeL <sub>4</sub> (NCO) <sub>2</sub>	-62		0 <sup>b</sup>	+114 <sup>b</sup>	-10
	0	-2000	-20	+181	-39
FeL <sub>4</sub> (N <sub>3</sub> ) <sub>2</sub>	-29		+25	+226 br	-63
	-54		+210 <sup>b</sup>	+410 <sup>b</sup>	-98
Ligand <sup>c</sup>	-58	-32	-32	-28	
	+23	-2350			
FeL <sub>4</sub> (NCS) <sub>2</sub>	-33		+142	-106	+17
	-57		+122 <sup>b</sup>	-134 <sup>b</sup>	+21
Ligand <sup>c</sup>	-57	+4	+5	+5	

<sup>a</sup> Shifts from diamagnetic ligand positions in cps at 60 Mcps, calculated from average positions in solutions containing rapidly exchanging excess ligand unless otherwise noted. The complexes were examined as 0.10 M solutions in CDCl<sub>3</sub> containing (a) a 16 molar excess of ligand and (b) a 2 molar excess of ligand. <sup>b</sup> Directly observed coordinated ligand. <sup>c</sup> "Frozen-out" uncoordinated ligand position in the presence of the metal complex. <sup>d</sup> Directly observed coordinated ligand but exchange broadening still marked.

site sign to that which the substituted-pyridine ligands reside in. Hence, if a dipolar shift of a certain sign is observed on the methyl resonance of the coordinated 4-ethylpyridine, then the solvent resonance should be shifted in the opposite direction. This is observed in all cases, leading to spectacularly large solvent shifts in some instances.

In many of the systems it is possible to slow down the rate of ligand exchange by cooling to the point where separate resonances can be observed for both coordinated and uncoordinated ligands. In the presence of the nickel complexes the free ligand resonances are observed at the normal diamagnetic positions, as expected. However, in several of the highly magnetically anisotropic cobalt and iron systems the free ligand resonances are appreciably shifted from their diamagnetic positions. Further, these shifts are always in the same direction as the dipolar sol-

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Table III. Magnetic Resonance Data for the 4-*n*-Propylpyridine Complexes of Nickel(II), Cobalt(II), and Iron(II)<sup>a</sup>

Complex	Temp. °C	$\Delta\nu(\beta\text{-H})$	$\Delta\nu(\text{CH}_2^1)^b$	$\Delta\nu(\text{CH}_2^2)^b$	$\Delta\nu(\text{CH}_3)$	$\Delta\nu(\text{CHCl}_3)$
NiL <sub>4</sub> Cl <sub>2</sub>	+38	-1950	+410	-45	-21	
	-58		+572 <sup>c</sup>	-60	-30 <sup>c</sup>	+16
Ligand <sup>d</sup>	-58	0	0	0	0	
NiL <sub>4</sub> Br <sub>2</sub>	+38	-1950	+418	-51	-22	+12
	-58		+570 <sup>c</sup>	-78 <sup>c</sup>	-30 <sup>c</sup>	+15
Ligand <sup>d</sup>	-58		0		0	
NiL <sub>4</sub> I <sub>2</sub>	+38	-1950	+411	-52	-24	+15
NiL <sub>4</sub> (NCS) <sub>2</sub>	+68	-1825				
	+38		+454		-6	-2
	-58		-645 <sup>c</sup>	0 <sup>c</sup>	0 <sup>c</sup>	
Ligand <sup>d</sup>	-58	0	0	0	0	
CoL <sub>4</sub> Cl <sub>2</sub>	-2	-2150				
	-23		+506	+168	+106	
	-30		+526		+110	-48
	-58				+126 <sup>c</sup>	-60
CoL <sub>4</sub> Br <sub>2</sub>	-2	-2700				
	-30		+45	-166	-110	+68
	-58		-50 <sup>c</sup>	-260 <sup>c</sup>	-154 <sup>c</sup>	+84
CoL <sub>4</sub> I <sub>2</sub>	-2	-2665				
	-30		-336	-424	-258	+104
	-58		<sup>e</sup>	<sup>e</sup>	<sup>e</sup>	+145
	-58		-510 <sup>f</sup>	-615 <sup>f</sup>	-340 <sup>f</sup>	
CoL <sub>4</sub> (NCS) <sub>2</sub>	+38	-1675	+555	+214	+150	-40
	-51			+257 <sup>c</sup>	+188 <sup>c</sup>	-60
Ligand <sup>d</sup>	-51	-15	-14	-15	-16	
FeL <sub>4</sub> Cl <sub>2</sub>	+34	-2080				
	-12		+186	-123	-72	+47
	-29		+180	-150	-89	+58
	-70		+195 <sup>c</sup>	-255 <sup>c</sup>	-164 <sup>c</sup>	+90
Ligand <sup>d</sup>	-70		+12		+10	
FeL <sub>4</sub> Br <sub>2</sub>	+13	-2300				
	-3		-12	+38	+24	
	-40		+30	+75	+42	
	-70		<i>g</i>	<i>g</i>	+106 <sup>c</sup>	-20
FeL <sub>4</sub> I <sub>2</sub>	+13	-1960				
	-3			+215	+150	
	-22		+73	+260	+186	-64
	-70		+380 (?) <sup>c</sup>	Probably off scale	+367 <sup>c</sup>	-130
Ligand <sup>d</sup>	-70	-40	-35		-30	
FeL <sub>4</sub> (NCS) <sub>2</sub>	+37	-2450				
	-3		+138	-90	-51	+18
	-22		+32	-108	-63	+14
	-70		<i>g</i>	-160 <sup>c</sup>	-94 <sup>c</sup>	+23
Ligand <sup>d</sup>	-70	0			0	

<sup>a</sup> Shifts from diamagnetic ligand positions in cps at 60 Mcps, calculated from average positions in solutions containing rapidly exchanging excess ligand unless otherwise noted. The complexes were examined as 0.10 *M* solutions in CDCl<sub>3</sub> containing (a) a 16 molar excess of ligand and (b) a 2 molar excess of ligand. <sup>b</sup> The numbering scheme is py-CH<sub>2</sub><sup>1</sup>-CH<sub>2</sub><sup>2</sup>-CH<sub>3</sub>. <sup>c</sup> Directly observed coordinated ligand. <sup>d</sup> "Frozen-out" uncoordinated ligand position in the presence of the metal complex. <sup>e</sup> Not observed; severe exchange broadening. <sup>f</sup> Solution of complex without excess ligand; the color indicates that the octahedral complex is the predominant species. <sup>g</sup> Obscured by uncoordinated ligand resonances.

vent shifts in the same system. The reason for these free ligand shifts may be simply that the flat pyridine molecules can approach closer to the metal along the *Z* axis of the molecule than the spherical tetramethylsilane internal reference. Whatever the origin of these shifts they clearly add a heretofore unsuspected difficulty to the interpretation of shift data in rapidly exchanging magnetically anisotropic systems. If it is not possible to slow down the exchange sufficiently to observe a separate resonance for the free ligand in such systems, then calculations of the coordinated ligand resonance positions from an average shift must be interpreted with caution if relatively small shifts are involved.

The nmr results for the 4-*n*-propylpyridine complexes are presented in Table III. The interpretation is very similar to that given above for the 4-ethylpyridine complexes. As expected the methyl protons of the *n*-propyl group are not substantially shifted from their diamagnetic position in the nickel complexes. However, both the methyl resonance and the 2-methylene resonance are markedly shifted in

most of the iron and cobalt complexes, due to dipolar effects with the shift at the methylene position always being greater than that at the methyl position. The same trends are observed with respect to variations in magnetic anisotropy as found for the 4-ethylpyridine complexes and the solvent shift confirms the sign of the dipolar shift in all cases.

The  $\alpha$ -,  $\beta$ -, and 1-methylene positions of the 4-ethyl- and 4-*n*-propylpyridine ligands coordinated have substantial contributions from contact effects. It is at first sight surprising that the  $\beta$ -proton resonance in say the cobalt(II) complexes is not more affected by dipolar effects since they are obviously much closer to the metal than the terminal methyl protons which are substantially shifted. Now in the solid state the four pyridine ligands adopt a "propeller-type" configuration,<sup>16</sup> and if the same structure is adopted in solution, one expects the  $\alpha$  and  $\beta$  protons to be situated substantially out of the plane of the four nitrogens and hence the term  $(3 \cos^2 \theta - 1)/r^3$  in the expression for the dipolar shift becomes small.

The shifts at the 1-methylene position of the coordinated ligands are a combination of contact and dipolar effects of similar magnitude in many of the cobalt and iron complexes. The temperature dependence of the dipolar effect in these systems is apparently much greater than that of the contact effect and this leads to unusual temperature dependencies when the effects are opposed. For example in  $\text{Co}(4\text{-Etpy})_4\text{Br}_2$ ,  $\text{Fe}(4\text{-Etpy})_4\text{Cl}_2$ , and  $\text{Fe}(4\text{-Etpy})_4\text{Br}_2$  the shifts at the 1-methylene position decrease with decreasing temperature and in  $\text{Co}(4\text{-}n\text{-Prpy})_4\text{Br}_2$  the shift at the 1-methylene position changes sign with a change in temperature.<sup>22</sup>

The inversion in the sign of magnetic anisotropy in the iron(II) complexes could be significant with respect to a recent study<sup>23</sup> of the Mossbauer spectra of octahedral iron(II)-pyridine complexes. Merrithew, *et al.*, inter-

(22) While this overlap of contact and dipolar effects makes definitive interpretation difficult, it is likely that there is an inversion in the sign of the contact effect at the 1-methylene position in the series of iron(II) complexes in addition to the sign inversion in the dipolar effect. In the majority of pyridine and 4-picoline complexes studied the contact effect gives rise to downfield 4-proton shift and an upfield 4-CH<sub>3</sub> shift (see ref 7 and 9 and references therein). However, tetrahedral cobalt(II) complexes manifest contact shifts in the opposite direction at the 4 position: B. B. Wayland and R. S. Drago, *J. Amer. Chem. Soc.*, **88**, 4597 (1966); G. N. La Mar, *Inorg. Chem.*, **6**, 1939 (1967). Thus, there is some precedence for a variability in sign of the contact effect at the 4 position of pyridine and substituted-pyridine complexes. However, this appears to be the first time such a variation has been found in a closely related series and suggests radical differences in the ground states of the iron(II) complexes.

(23) P. B. Merrithew, P. G. Rasmussen, and D. H. Vincent, *Inorg. Chem.*, **10**, 1401 (1971).

preted their data on  $\text{Fe}(\text{py})_4\text{Cl}_2$  and  $\text{Fe}(\text{py})_4\text{I}_2$  to indicate that the iodide adopted a trans structure whereas the chloride was cis. Elsewhere we have shown<sup>24</sup> that the chloride is in fact also trans. Since in this work we have shown that the chloride and iodide complexes display magnetic anisotropy of opposite sign without a geometric change, it appears likely that a major ground-state change is responsible for both phenomena.

### Conclusions

Dipolar effects are manifested in the nmr spectra of solutions of the iron(II)- and cobalt(II)-substituted-pyridine complexes in the resonances of the coordinated ligand, solvent, and free ligand. The magnetic anisotropy responsible for the dipolar effects in the iron and cobalt series  $\text{ML}_4\text{X}_2$  varies in sign with changes of the anion X.

**Registry No.** Table I  $\text{NiL}_4\text{Cl}_2$ , 36503-14-7;  $\text{NiL}_4\text{Br}_2$ , 36503-15-8;  $\text{NiL}_4\text{I}_2$ , 36503-16-9;  $\text{NiL}_4(\text{NCS})_2$ , 36503-17-0;  $\text{CoL}_4\text{Cl}_2$ , 36537-22-1;  $\text{CoL}_4\text{Br}_2$ , 36503-18-1;  $\text{CoL}_4\text{I}_2$ , 36502-94-0;  $\text{CoL}_4(\text{NCS})_2$ , 36502-95-1;  $\text{FeL}_4\text{Cl}_2$ , 36502-96-2;  $\text{FeL}_4\text{Br}_2$ , 36502-97-3;  $\text{FeL}_4\text{I}_2$ , 36502-98-4;  $\text{FeL}_4(\text{NCS})_2$ , 36502-99-5. Table II  $\text{NiL}_4\text{Cl}_2$ , 36503-00-1;  $\text{NiL}_4\text{Br}_2$ , 36503-01-2;  $\text{NiL}_4\text{I}_2$ , 36503-02-3;  $\text{NiL}_4(\text{NCS})_2$ , 36503-03-4;  $\text{NiL}_4(\text{NCO})_2$ , 36503-04-5;  $\text{NiL}_4(\text{N}_3)_2$ , 36503-05-6;  $\text{CoL}_4\text{Cl}_2$ , 36503-06-7;  $\text{CoL}_4\text{Br}_2$ , 36503-07-8;  $\text{CoL}_4\text{I}_2$ , 36503-08-9;  $\text{CoL}_4(\text{NCS})_2$ , 36537-21-0;  $\text{CoL}_4(\text{NCO})_2$ , 36503-09-0;  $\text{CoL}_4(\text{N}_3)_2$ , 36503-10-3;  $\text{FeL}_4\text{Cl}_2$ , 36503-11-4;  $\text{FeL}_4\text{Br}_2$ , 36503-12-5;  $\text{FeL}_4\text{I}_2$ , 36563-76-5;  $\text{FeL}_4(\text{NCS})_2$ , 36503-13-6.

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## Synthesis, Characterization and Some Reactions of (Dimethyl sulfoxide)pentaamminecobalt(III) Salts

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$[\text{Co}(\text{NH}_3)_5\text{DMSO}](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$  is prepared by reaction of  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$  with DMSO. The chloride and nitrate of the complex cation are obtained by anionic interchange followed by freeze-drying. Characterization and purity checks are accomplished by analysis, visible spectra, repeated crystallization, ionic interchange behavior, conductivity, tga, and infrared spectra. The use of  $[\text{Co}(\text{NH}_3)_5\text{DMSO}]^{3+}$  as the starting ion for syntheses through substitution reactions in the solid phase or in solution using the DMSO lability is considered. As examples we present the thermal substitution reaction of the DMSO by  $\text{Cl}^-$ , an attempt with  $[\text{Co}(\text{CN})_6]^{3-}$ , and, for the processes in solution, the substitution by  $\text{H}_2\text{O}$ ,  $\text{Cl}^-$ , and pyridine. The new method presented for the preparation of  $[\text{Co}(\text{NH}_3)_5\text{py}]^{3+}$  derivatives shows advantages over those previously known.

### Introduction

Several cobalt complexes containing DMSO ligand have been described.<sup>2-6</sup> For this central atom the coordination

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of the ligand is established through the oxygen atom<sup>7</sup> and considering the steric and polarity characteristics of the DMSO molecule the low strength of Co(III)-DMSO bonds can be inferred. If DMSO is present as a substituting ligand in a Co(III) complex containing other stable bonds, *e.g.*, Co(III)-N, it will be expected that the DMSO functions as a good leaving group. This character has been implicitly recognized by Hurst and Taube<sup>8</sup> when, by comparing the spectra of  $[\text{Co}(\text{NH}_3)_5\text{solv}]^{3+}$  obtained with solutions of (methyl

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