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## Coordination Chemistry of Imidazole Derivatives. A Search for Carbon-Bound Chelates with First-Row Transition Metal Ions

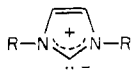
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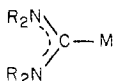
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Structural conclusions about complex ions formed from several imidazole derivatives, from which chelates could result if carbon-metal bonding occurred, have been deduced from NMR data and electronic absorption spectra. None of the ligands examined show evidence of formation of carbon-bound chelates with Co(II) or Cu(II). Less extensive studies with Ni(II) and Fe(II) also gave no evidence of carbon-bound species. Two crystalline substances, dichlorobis[1-(2-pyridylmethyl)benzimidazole]cobalt and dichlorobis[1-(2-pyridylmethyl)-4,5-dimethylimidazole]cobalt were examined by x-ray diffraction. Dichlorobis[1-(2-pyridylmethyl)benzimidazole]cobalt crystallized from acetonitrile as blue crystals in the space group  $P\bar{1}$  with  $Z = 2$ ,  $a = 10.314$  (3) Å,  $b = 11.458$  (2) Å,  $c = 12.442$  (4) Å,  $\alpha = 63.37$  (2)°,  $\beta = 74.58$  (2)°,  $\gamma = 82.17$  (2)°,  $\rho_{\text{calcd}} = 1.45$  g cm<sup>-3</sup>, and  $\rho_{\text{obsd}} = 1.43$  g cm<sup>-3</sup>. Least-squares refinement of 2600 independent reflections with  $F^2 \geq 3\sigma(F^2)$  gave a conventional  $R$  factor of 0.030. Dichlorobis[1-(2-pyridylmethyl)-4,5-dimethylimidazole]cobalt crystallized from Me<sub>2</sub>SO- $d_6$  as blue crystals in the space group  $P2_1/c$  with  $Z = 4$ ,  $a = 8.343$  (2) Å,  $b = 16.982$  (3) Å,  $c = 19.297$  (4) Å,  $\beta = 117.35$  (2)°,  $\rho_{\text{calcd}} = 1.38$  g cm<sup>-3</sup>, and  $\rho_{\text{obsd}} = 1.39$  g cm<sup>-3</sup>. Least-squares refinement of 3121 independent reflections with  $F^2 \geq 3\sigma(F^2)$  gave a conventional  $R$  factor of 0.036. In both cases, the Co<sup>2+</sup> ion was tetrahedrally coordinated by Cl<sup>-</sup> ions and by two organic ligands coordinated via the imidazole nitrogen in agreement with the conclusions drawn from solution data.

The imidazolium ylide has been identified as a ligand which can complex with transition metal ions via the carbon atom C(2). The parent imidazole molecule, R = H, has been shown

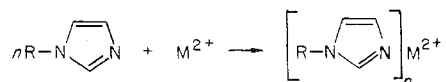


to complex in this manner with Ru(II) and Ru(III).<sup>1</sup> The 1,3-dimethyl derivative (R = CH<sub>3</sub>) gives carbon-bound structures with Fe(0) and Cr(0) in carbonyl species.<sup>2</sup> The 1,3-diphenyl derivative forms a carbon-bound complex with Hg(II).<sup>3</sup> Histidine forms a carbon-bound complex with Ru(II) and Ru(III).<sup>4</sup> This mode of bonding can be viewed as a type of metal-carbene complexation and is therefore related structurally to carbon-bound amidinium species.<sup>5</sup>



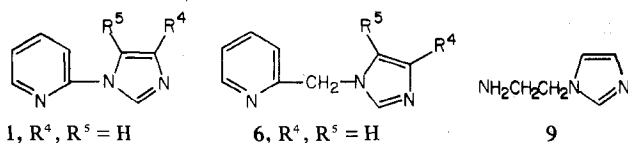
Among the metal ion centers which form stable complexes of this type are Cr, Fe, Mn, Co, and Ni, although the majority of the reported examples involve the heavier transition metals. Some<sup>6</sup> of the iron complexes are in the formal II oxidation state.

In view of the importance of the imidazole ring of histidine as a metal ion binding site in metalloenzymes,<sup>7</sup> it is of interest to know the limiting conditions for formation of carbon-bound complexes of imidazole. It is clear from a variety of synthetic, spectroscopic, and crystallographic studies that the first-row transition metal ions usually form bonds with imidazole and its simple alkyl derivatives via the pyridine nitrogen, the



maximum coordination varying with the identity of the metal ion and the substitution on the imidazole ring.<sup>7</sup> The proposition has occasionally been advanced<sup>8</sup> that the protonated nitrogen is also a metal-binding site but this seems unlikely and has not been demonstrated to occur.<sup>7,9</sup> Shepherd<sup>10</sup> has studied Fe(II) and Fe(III) complexes with simple imidazole derivatives and histidine in mixed complexes with cyanide ion and found no evidence for complexation via C(2).

As a further step toward defining the limits in which carbon complexation of the imidazole ring is feasible, we have studied ligands 1-9 in which a chelation could occur if bond formation occurred at C(2) of the imidazole ring. Complexes of these ligands with Co(II), Cu(II), Ni(II), and Fe(II) were studied

1, R<sup>4</sup>, R<sup>5</sup> = H2, R<sup>4</sup> = CH<sub>3</sub>, R<sup>5</sup> = H3, R<sup>4</sup> = H, R<sup>5</sup> = CH<sub>3</sub>4, R<sup>4</sup>, R<sup>5</sup> = CH<sub>3</sub>5, R<sup>4</sup>, R<sup>5</sup> = benzo6, R<sup>4</sup>, R<sup>5</sup> = H7, R<sup>4</sup>, R<sup>5</sup> = CH<sub>3</sub>8, R<sup>4</sup>, R<sup>5</sup> = benzo

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to determine if the possibility of such chelation would promote carbon complexation.

### Experimental Section

**Ligand Preparation.** Ligands 1-5 were prepared from 2-bromopyridine and the appropriate imidazole following a known procedure.<sup>11</sup> Ligands 6-8 were prepared by alkylation of the sodium salt of the appropriate imidazole with 2-chloromethylpyridine in liquid ammonia. Ligand 9 was prepared by alkylation of imidazole with 2-bromoethylphthalimide followed by cleavage of the phthalimide group with hydrazine. A similar synthesis has been reported.<sup>12</sup> All but 1, 5, and 9 are new compounds and satisfactory elemental analyses were obtained. Full details will be published elsewhere.

**NMR Experiments.** Solutions of pure ligand (1.0 *m*) in Me<sub>2</sub>SO-*d*<sub>6</sub> were prepared. Successive additions of solutions of the salts were made using microliter syringes. The spectra were recorded on a Perkin-Elmer Hitachi R-20 instrument at ambient temperature and are referenced to internal TMS.

**Visible Spectra.** The visible spectra were measured by successive additions of ligand to solutions of the salts in Me<sub>2</sub>SO. The spectra were recorded on a Coleman-Hitachi EPS-3T instrument.

**Characterization of Solid Complexes.** Solid complexes were obtained from warm solutions of metal salts and the organic ligand. In several of the preparations heating was continued for 2-5 h. There is no reason to believe this heating period is necessary for the success of the preparations.

Co(4)<sub>2</sub>Br<sub>2</sub>·1/3H<sub>2</sub>O was obtained by heating 150 mg of hydrated CoBr<sub>2</sub> with 300 mg of 4 in ethanol at 60 °C for 5 h. A blue solid precipitated on cooling. The crystals submitted for analysis were obtained by slow evaporation of a chloroform solution.

Co(4)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> precipitated from a solution of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 4 in ethanol which was stirred at room temperature for 3 h. Recrystallization was accomplished by dissolving the precipitate in chloroform-ethanol and allowing the solution to partially evaporate.

Co(7)<sub>2</sub>Cl<sub>2</sub> was obtained by allowing a Me<sub>2</sub>SO solution of CoCl<sub>2</sub>·6H<sub>2</sub>O and 7 (1:2 molar ratio) to partially evaporate. Several large blue crystals were isolated by filtration and rinsed with ether.

Co(8)<sub>2</sub>Cl<sub>2</sub> was obtained from a warm solution of CoCl<sub>2</sub>·6H<sub>2</sub>O and 2 equiv of 8 in acetonitrile. Crystals deposited on cooling and were recrystallized from acetonitrile.

Cu(1)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> was obtained from an acetonitrile solution of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O and 1 (1:2 molar ratio) kept at 70 °C for 4 h. The acetonitrile was evaporated and the residue crystallized from chloroform-ether.

Cu(5)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> was obtained similarly.

**X-Ray Diffraction. Crystal data for Co(8)<sub>2</sub>Cl<sub>2</sub>:** mol wt 548; space group P1; Z = 2; ρ<sub>calcd</sub> = 1.45, ρ<sub>obsd</sub> = 1.43 g cm<sup>-3</sup>; a = 10.314 (3), b = 11.458 (2), c = 12.442 (4) Å; α = 63.37 (2), β = 74.58 (2), γ = 82.17 (2)°; V = 1267 Å<sup>3</sup>; μ(Mo Kα) 9.5 cm<sup>-1</sup>; F(000) = 562.

**Crystal data for Co(7)<sub>2</sub>Cl<sub>2</sub>:** mol wt 504; space group P2<sub>1</sub>/c; Z = 4; ρ<sub>calcd</sub> = 1.38, ρ<sub>obsd</sub> = 1.39 g cm<sup>-3</sup>; a = 8.343 (2), b = 16.982 (3), c = 19.297 (4) Å; β = 117.35 (2)°; V = 2428.5 Å<sup>3</sup>; μ(Mo Kα) = 9.8 cm<sup>-1</sup>; F(000) = 1044.

Preliminary cell dimensions were obtained using the Enraf-Nonius program SEARCH to locate 15 independent reflections. Refined cell dimensions and their estimated standard deviations were calculated from a least-squares refinement of the preliminary values against the observed values of ±θ for a number of strong general reflections (28 for Co(8)<sub>2</sub>Cl<sub>2</sub> and 28 for Co(7)<sub>2</sub>Cl<sub>2</sub>).

Diffraction data were collected from small crystals mounted on glass fibers with epoxy resin. The diffraction patterns for Co(8)<sub>2</sub>Cl<sub>2</sub> and Co(7)<sub>2</sub>Cl<sub>2</sub> were examined by the ω-scan technique and found to be satisfactory. The diffraction intensities were measured at 293 K on an Enraf-Nonius four-circle CAD-4 diffractometer controlled by

a PDP8/E computer, using Mo Kα radiation from a highly oriented graphite monochromator. The θ-2θ scan technique was used to record the intensities of all reflections for which 1° < 2θ < 48° for Co(8)<sub>2</sub>Cl<sub>2</sub> and 1° < 2θ < 46° for Co(7)<sub>2</sub>Cl<sub>2</sub>. The symmetric scans were centered on the calculated peak positions (λ(Mo Kα) 0.7107 Å). Scan widths (SW) were based on using the formula SW = A + B tan θ where A is estimated from the mosaicity and B tan θ allows for the increase in width of the peak due to separation of Mo Kα<sub>1</sub> and Mo Kα<sub>2</sub>. A = 0.6° and B = 0.2° were used. For each reflection, the calculated scan angle was extended by 25% at either side to estimate the background count. Reflection data were considered significant if intensities registered 10 counts above background during a rapid prescan, while insignificant reflections were automatically rejected by the computer. A total of 3432 independent intensities were recorded for Co(8)<sub>2</sub>Cl<sub>2</sub> of which 2600 had F<sup>2</sup> > 3σ(F<sub>0</sub><sup>2</sup>), where (F<sub>0</sub><sup>2</sup>) was estimated from the counting statistics. A total of 3385 independent reflections were recorded for Co(7)<sub>2</sub>Cl<sub>2</sub> of which 3121 had F<sub>0</sub><sup>2</sup> > 3σ(F<sub>0</sub><sup>2</sup>). These data were used in the final refinement of the structural parameters.

For both crystals the intensities of four standard reflections, monitored at 100 reflection intervals, showed no greater fluctuations than those expected from Poisson statistics during the data collection. The raw intensity data were corrected for Lorentz and polarization effects. Gaussian absorption corrections were applied to the data for Co(8)<sub>2</sub>Cl<sub>2</sub> and spherical absorption correction was used for Co(7)<sub>2</sub>Cl<sub>2</sub>.

**Solution and Refinement of the Structures.** Full-matrix least-squares refinement was based on F, and the function minimized was Σw(|F<sub>o</sub> - |F<sub>c</sub>||<sup>2</sup>). The atomic scattering factors were taken from Cromer and Waber<sup>13</sup> and those for hydrogen from Stewart et al.<sup>14</sup> The effects of anomalous dispersion were included in F<sub>c</sub> using Cromer and Ibers' values<sup>15</sup> for Δf' and Δf''. Agreement factors are defined as R = Σ(|F<sub>o</sub> - |F<sub>c</sub>||) / Σ|F<sub>o</sub>| and R<sub>w</sub> = Σw(|F<sub>o</sub> - |F<sub>c</sub>||) / Σw|F<sub>o</sub>|. To minimize computer time, the initial calculations were carried out on the first 1000 reflections.

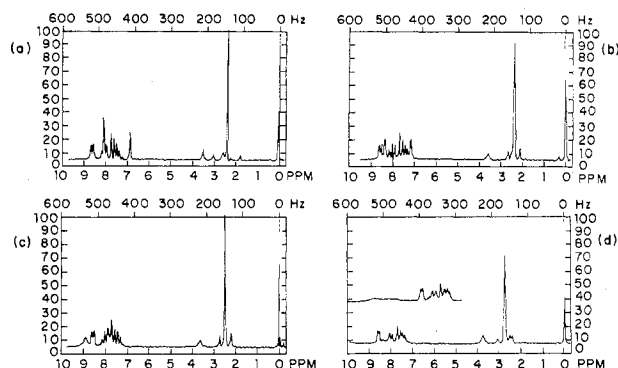
For each crystal, Patterson functions located the metal and the two halogen atoms, and the remaining nonhydrogen atoms were located from Fourier difference maps. For Co(8)<sub>2</sub>Cl<sub>2</sub>, the remaining diffraction data were then added to the calculation, isotropic temperature factors were introduced, and hydrogen atoms were inserted as fixed atoms at their calculated positions with fixed temperature factors β = 5.0, assuming C-H = 1.0 Å. After refinement, the hydrogen atoms were reinserted at their new calculated positions. The model converged with R = 3.0%, R<sub>w</sub> = 3.9% for Co(8)<sub>2</sub>Cl<sub>2</sub>. The diffraction data for Co(7)<sub>2</sub>Cl<sub>2</sub> were treated as for Co(8)<sub>2</sub>Cl<sub>2</sub> and the model converged with R = 3.6%, R<sub>w</sub> = 4.4% after refinement. The error in an observation of unit weight is 1.2 for Co(8)<sub>2</sub>Cl<sub>2</sub> and 1.5 for Co(7)<sub>2</sub>Cl<sub>2</sub>.

A final structure factor calculation with all observed and unobserved reflections included (no refinement) gave R = 3.8% and 4.3% for Co(8)<sub>2</sub>Cl<sub>2</sub> and Co(7)<sub>2</sub>Cl<sub>2</sub>, respectively. A final Fourier difference map was produced in each case and showed no features. A table of the observed structure factors is available as supplementary material.

### Results

The complete series of ligands was studied by NMR using Co<sup>II</sup>Cl<sub>2</sub> and Co<sup>II</sup>(NO<sub>3</sub>)<sub>2</sub> solutions in Me<sub>2</sub>SO-*d*<sub>6</sub>. The results with 1-(2-pyridyl)-5-methylimidazole (3) are typical. The free ligand as a 1.0 *m* solution in Me<sub>2</sub>SO exhibits the expected features but with some overlap of the aromatic multiplets. Successive additions of 0.1 *m* CoCl<sub>2</sub>·6H<sub>2</sub>O in Me<sub>2</sub>SO-*d*<sub>6</sub> were made, to generate ligand:metal ratios in the range of ~1000:1 to ~50:1. The spectra shown in Figure 1 show successive broadening and downfield shift of signals due to the imidazole protons resulting eventually (solution d) in signals attributable exclusively to the pyridine ring protons and two broad signals due to the imidazole ring protons. The residual pyridine signals show only modest broadening. The methyl signal is shifted slightly downfield and is slightly broadened. These solutions were deep blue and no qualitative color change was evident as the metal:ligand ratio was increased.

Use of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in place of the CoCl<sub>2</sub>·6H<sub>2</sub>O solution resulted in similar selective shifting and broadening of the imidazole ring protons. At the highest metal:ligand ratio examined (~1:50) there is only slight broadening of the pyridine proton signals. The carbon-13 NMR spectrum reveals



**Figure 1.** Proton NMR spectra of **3** after successive additions of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ : (a) pure ligand; (b) ligand:metal = 500; (c) ligand:metal = 166; (d) ligand:metal = 41.5.

**Table I.**  $^{13}\text{C}$  Spectral Data for Compound **6**

Carbon	$\delta$	Multiplicity in ORD	Carbon	$\delta$	Multiplicity in ORD
1	137.9	d	6	122.9	d
2	120.0	d	7	137.3	d
3	128.8	d	8	121.5	d
4	51.4	t	9	149.4	d
5	156.8	s			

a similar selective broadening of the signals due to imidazole carbons. The proton-decoupled spectrum of the pure ligand **6** showed nine well-resolved singlets which are assigned as in Table I on the basis of off-resonance decoupling results and chemical shifts. Addition of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  to give a metal:ligand ratio of 1:200 resulted in significant broadening of the  $\text{CH}_2$  signal (51.4 ppm) and of the signal at 128.8 ppm. The signals at 120.0 and 137.9 ppm were broadened to an even greater extent. At a metal:ligand ratio of 1:12, the five pyridine carbon signals remained relatively sharp, a broad peak near 80 ppm may possibly be assigned to C(3), but the C(1), C(2), and C(4) signals were not detectable.

Proton NMR spectra of ligands **1–8** were recorded after successive additions of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . The observed positions of signals assigned to imidazole ring protons and protons on carbons  $\alpha$  to the imidazole ring were plotted against metal ion concentration. Except for compound **7** plots were linear for all protons which were satisfactorily resolved.

**Table II.** Contact Shift Data<sup>a</sup>

	Ligand $\delta$				$\Delta\delta$ ( $\text{CoCl}_2$ )				$\Delta\delta$ ( $\text{Co}(\text{NO}_3)_2$ )			
	H( $\alpha$ )	H(2)	H(4)	H(5)	H( $\alpha$ )	H(2)	H(4)	H(5)	H( $\alpha$ )	H(2)	H(4)	H(5)
<b>1</b>		8.65	7.25	8.03	-85	-100	-105		-110	-135		(-120)
<b>2</b>		8.45	2.23 <sup>b</sup>	7.54	-90	+25 <sup>b</sup>	-60		-55	+25 <sup>b</sup>		<i>c</i>
<b>3</b>		8.05	6.92	2.36 <sup>b</sup>	-110	-160	-15 <sup>b</sup>		-140	-130		-15 <sup>b</sup>
<b>4</b>		7.91	2.13 <sup>b</sup>	2.28 <sup>b</sup>	-95	+25 <sup>b</sup>	-12 <sup>b</sup>		-90	+25 <sup>b</sup>		-12 <sup>b</sup>
<b>5</b>		8.97				-75			-45			
<b>6</b>	5.30	7.87	6.95	7.20	-15	(-100)	<i>c</i>	<i>c</i>	-18	(-150)	<i>c</i>	<i>c</i>
<b>7</b>	5.17	7.55	2.05 <sup>b</sup>	1.97 <sup>b</sup>	<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>
<b>8</b>	5.58	8.35			-35	-240			-20	-300		

<sup>a</sup> Ligand  $\delta$  values are for 1 *m* ligand in  $\text{Me}_2\text{SO}-d_6$  referenced to internal TMS.  $\Delta\delta$  give the slope of plots of  $\delta$  in ppm vs. metal ion concentration in molality. For all entries where slopes are given, plots were linear over the range  $(0-5) \times 10^{-3}$  *m*. Estimated accuracy is  $\pm 10\%$  except for entries in parentheses which are  $\pm 25\%$ . <sup>b</sup> Methyl substituent. <sup>c</sup> Overlap prevents satisfactory shift measurement. <sup>d</sup> Nonlinear relationship between observed shift and metal ion concentration.

The data are given in Table II.

The free ligand signals were readily assigned for the  $\alpha$  and imidazole 2 protons on the basis of chemical shift. The assignment of C(4) and C(5) protons and methyl groups depends upon chemical shifts for compounds **2** and **3**. The structures assigned **2** and **3** are based on **2** being the major product in the synthesis and the fact that it is the less strongly absorbed on alumina of the two isomers, a result which is consistent with the more hindered nature of the imidazole nitrogen in this isomer. The correctness of this structural assignment has been verified by a crystal structure determination on compound **3**.<sup>16</sup>

Ligands **6** and **7** were also examined in solutions containing 1 equiv of trifluoroacetic acid to determine the effect of protonation of the imidazole ring. The imidazole 2 proton of **6** showed broadening and a downfield shift but the magnitude of the shift was about one-third of that observed in the absence of trifluoroacetic acid. Compound **7**, in contrast, showed only general broadening of the spectrum with little shift of the imidazole protons even at a ligand:metal ratio of  $\sim 20$ .

The behavior of ligand **9** was pH dependent. The free base in  $\text{Me}_2\text{SO}-d_6$  showed broadening of both the aromatic and aliphatic proton signals, the  $\text{CH}_2$  group adjacent to the ring being shifted less than the  $\text{CH}_2\text{-NH}_2$  group. In  $\text{D}_2\text{O}$  at pH values where the primary amino group was protonated, the aliphatic protons remained as sharp triplets at  $[\text{Co}(\text{II})] = 6.7 \times 10^{-3}$  *m* while the aromatic protons were broadened and shifted downfield.

Ligands **1–8** showed selective broadening of the imidazole protons in the presence of  $\text{Cu}(\text{NO}_3)_2$  in the concentration range  $2 \times 10^{-4}$  to  $4 \times 10^{-3}$  *m*. Less extensive broadening of the other signals was observed. The chemical shifts caused by the addition of Cu(II) were smaller than in the case of Co(II) and could not be determined with accuracy since the broadened signals overlapped the remaining aromatic protons. Addition of  $\text{Cu}(\text{NO}_3)_2$  to **9** in  $\text{Me}_2\text{SO}-d_6$  also led to broadening of all ligand signals.

Much less extensive surveys of the behavior of these ligands with Fe(II) and Ni(II) were also done. Addition of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  to ligand **6** resulted in a downfield shift and broadening of the signals due to imidazole ring protons. There was also a downfield shift and slight broadening of the methylene signal. The broadening of the pyridine protons was very slight and there was no shift in the position of these signals. Resolution of the pyridine signals was not significantly changed up to a metal:ligand ratio of 1:50. Addition of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  to solutions of ligand **7** resulted in only minor change in the appearance of the NMR spectrum up to a ligand:metal ratio of 250:1. The imidazole ring proton at 7.52 ppm was broadened somewhat more than the other signals but was clearly evident at this ligand:metal ratio. Definite broadening was evident at a 100:1 ratio but even at this ratio the effect on the spectrum of the ligand was not dramatic. At 25:1 all signals had broadened considerably.

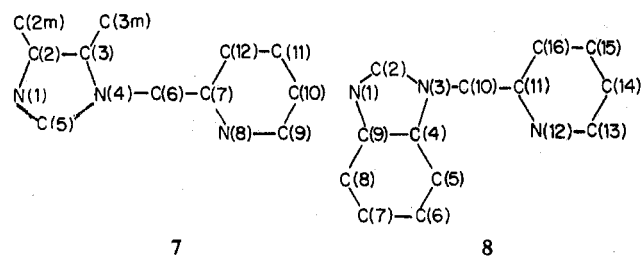


Figure 2. Numbering schemes adopted for ligand molecules in crystal structures.

Solutions of **1** in the presence of  $\text{NiCl}_2 \cdot \text{H}_2\text{O}$  at ligand:metal ratios of 1000:1, 1:500, 1:250, and 1:100 showed extreme broadening of the imidazole signals with little effect on the pyridine signals.

Visible spectra in  $\text{Me}_2\text{SO}$  were recorded for some of the ligands in the range of ligand to metal ratios from 0.5:1 to 50:1. The spectra varied with increasing ligand concentration, indicating the existence of a mixture of species in solution. For **1** and  $\text{CoCl}_2$  the  $\lambda_{\text{max}}$  shifted from 674 to 636 nm on increasing the ligand:metal ratio from 0.5 to 50:1. The extinction coefficients ( $\epsilon$ ) remained roughly constant at  $1.3\text{--}1.4 \times 10^2$ . Similarly with **6** the observed maximum shifted from 680 to 638 nm. In this case an increase in apparent  $\epsilon$  occurred from  $1.2 \times 10^2$  to  $2.0 \times 10^2$  at 25:1 before dropping to  $1.7 \times 10^2$  at 50:1. Solutions of **6** and  $\text{Co}(\text{NO}_3)_2$  showed maximum absorbance at 544 nm in the L:M ratio range 0.5 to 2:1 but then began to shift toward shorter wavelength and maximum absorbance was at 506 nm at L:M = 50:1. The extinction coefficient increased after the 2:1 ratio was reached and was 74 at 50:1. Addition of  $\text{LiCl}$  to a solution containing  $\text{Co}(\text{NO}_3)_2$  and **6** immediately generated the blue color and spectrum characteristic of the  $\text{6-CoCl}_2$  solutions. Solutions of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  to which **7** was added showed a shift of the maximum absorbance from 680 to 620 as L:M increased from 0.5 to 50 and the apparent  $\epsilon$  increased from  $1.4 \times 10^2$  to  $7.0 \times 10^2$  at 25:1 before dropping to  $5.9 \times 10^2$  at 50:1.

In order to have comparable data on imidazole itself similar spectra were recorded in  $\text{Me}_2\text{SO}$ . With  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  the absorption maximum shifted from 668 nm at L:M = 0.5 to 620 nm at L:M = 50. For  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  the maximum was at 548 nm for L:M = 0.5 and at 506 nm for L:M = 50. The extinction coefficients were  $\sim 2 \times 10^2$  for the chloride solutions and  $\sim 40$  for the nitrate solutions.

Solutions of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  to which **6** was added showed an increasing extinction coefficient for a broad absorption near 700 nm in the L:M range 0.5:1 to 5:1. The spectrum remained essentially unchanged as the L:M ratio was increased above 5:1.

Solid complexes were prepared at ligand:metal ratios of 2:1 where the restricted number of imidazole nitrogen donors would be expected to maximize competitive involvement of the pyridine ring nitrogen in complex formation. Several compounds were isolated as crystalline substances and two of these  $\text{Co}(\text{8})_2\text{Cl}_2$  and  $\text{Co}(\text{7})_2\text{Cl}_2$  were subjected to crystallographic analysis. The structures are described with reference to the ligand-numbering schemes given in Figure 2. Tables III and IV contain the bond lengths and angles. The digits in parentheses in the tables are the estimated standard deviations in the least significant figure quoted and were derived from the inverse matrix in the course of the least-squares refinement calculations. Figure 3 gives stereoscopic pair views of the molecular units in  $\text{Co}(\text{8})_2\text{Cl}_2$  and  $\text{Co}(\text{7})_2\text{Cl}_2$ . Final atomic positions and thermal parameters are available as supplementary data.

For the complex  $\text{Co}(\text{8})_2\text{Cl}_2$  the unit cell contains two discrete complex molecules which are well separated from each other

Table III

a. Bond Lengths (Å) for $\text{Co}(\text{8})_2\text{Cl}_2$			
Co-Cl(1)	2.259 (1)	C(14)-C(15)	1.357 (4)
Co-Cl(2)	2.242 (1)	C(15)-C(16)	1.377 (4)
Co-N(1)	2.014 (2)	N(1')-C(2')	1.330 (2)
Co-N(1')	2.031 (2)	N(1')-C(9')	1.400 (2)
N(1)-C(2)	1.327 (2)	N(3')-C(2')	1.340 (2)
N(1)-C(9)	1.409 (2)	N(3')-C(4')	1.391 (3)
N(3)-C(2)	1.342 (2)	N(3')-C(10')	1.460 (2)
N(3)-C(4)	1.394 (3)	N(12')-C(11')	1.337 (3)
N(3)-C(10)	1.466 (3)	N(12')-C(13')	1.341 (3)
N(12)-C(11)	1.329 (3)	C(4')-C(5')	1.389 (5)
N(12)-C(13)	1.341 (3)	C(4')-C(9')	1.399 (3)
C(4)-C(5)	1.386 (5)	C(5')-C(6')	1.383 (5)
C(4)-C(9)	1.398 (3)	C(6')-C(7')	1.390 (6)
C(5)-C(6)	1.382 (5)	C(7')-C(8')	1.381 (5)
C(6)-C(7)	1.390 (6)	C(8')-C(9')	1.397 (5)
C(7)-C(8)	1.376 (5)	C(10')-C(11')	1.507 (3)
C(8)-C(9)	1.390 (5)	C(11')-C(16')	1.377 (3)
C(10)-C(11)	1.506 (3)	C(13')-C(14')	1.363 (4)
C(11)-C(16)	1.373 (3)	C(14')-C(15')	1.378 (4)
C(13)-C(14)	1.365 (4)	C(15)-C(16')	1.370 (4)
b. Bond Lengths (Å) for $\text{Co}(\text{7})_2\text{Cl}_2$			
Co-Cl(1)	2.258 (1)	C(10)-C(11)	1.338 (4)
Co-Cl(2)	2.268 (1)	C(11)-C(12)	1.380 (3)
Co-N(2)	2.015 (2)	N(1')-C(2')	1.391 (2)
Co-N(1')	2.016 (2)	N(1')-C(5')	1.307 (2)
N(1)-C(2)	1.386 (2)	N(4')-C(3')	1.367 (3)
N(1)-C(5)	1.316 (2)	N(4')-C(5')	1.337 (2)
N(4)-C(3)	1.383 (3)	N(4')-C(6')	1.468 (2)
N(4)-C(5)	1.336 (2)	N(8')-C(7')	1.338 (3)
N(4)-C(6)	1.467 (3)	N(8')-C(9')	1.348 (3)
N(8)-C(7)	1.317 (3)	C(2')-C(2m')	1.497 (3)
N(8)-C(9)	1.340 (3)	C(2')-C(3')	1.369 (3)
C(2)-C(2m)	1.524 (3)	C(3')-C(3m')	1.513 (3)
C(2)-C(3)	1.364 (3)	C(6')-C(7')	1.509 (3)
C(3)-C(3m)	1.537 (3)	C(7')-C(12')	1.376 (3)
C(6)-C(7)	1.509 (3)	C(9')-C(10')	1.365 (4)
C(7)-C(12)	1.354 (3)	C(10')-C(11')	1.365 (4)
C(9)-C(10)	1.343 (4)	C(11')-C(12')	1.355 (4)

and with no unusually close contacts between neighboring metal or ligand atoms. The metal atom is in a tetrahedral environment. Comparison of the bond lengths and angles at the metal with  $\text{Co}(\text{imidazole})_2\text{Cl}_2$ <sup>17</sup> is given in Table V. The Co-Cl distances are similar and the Co-N distances are 0.01–0.03 Å longer. As with the imidazole complex the Cl-Co-Cl angle is somewhat larger than the N-Co-N angle, which approximates the tetrahedral value. The pyridine ring nitrogen is not involved with coordination to any metal ion in this structure.

The unit cell of the complex  $\text{Co}(\text{7})_2\text{Cl}_2$  contains four discrete complex molecules which, like those of  $\text{Co}(\text{8})_2\text{Cl}_2$ , are well separated from each other with no unusually close contacts between neighboring metal or ligand atoms. The metal atom is in a tetrahedral environment. A list of metal-ligand bond lengths is included in Table V. The coordination environment at Co is similar to that in  $\text{Co}(\text{8})_2\text{Cl}_2$  but the N-Co-N angle is opened somewhat.

## Discussion

From the point of view of detecting possible chelates involving the pyridine nitrogen and the imidazole-2 carbon, the solution NMR results are unambiguous. The lack of significant isotropic shift or broadening of the resonance signals due to the pyridine ring protons indicates little interaction of the metal ion center with the pyridine nitrogen. The behavior of the C(2) proton of the imidazole ring is normal, giving no evidence that C(2) is deprotonated.

The signs of the isotropic shifts observed with Co(II) for the imidazole ring protons are internally consistent for all of the imidazoles studied, although there is considerable variation in magnitude of the observed shifts. All the shifts are

Table IV

a. Bond Angles (deg) for $\text{Co}(8)_2\text{Cl}_2$			
Cl(1)-Co-Cl(2)	116.6 (1)	C(13)-C(14)-C(15)	118.6 (3)
Cl(1)-Co-N(1)	105.8 (1)	C(14)-C(15)-C(16)	119.7 (3)
Cl(1)-Co-N(1')	105.7 (1)	C(11)-C(16)-C(15)	119.3 (3)
Cl(2)-Co-N(1)	111.9 (1)	Co-N(1')-C(2')	123.5 (1)
Cl(2)-Co-N(1')	109.2 (1)	Co-N(1')-C(9')	130.6 (1)
N(1)-Co-N(1')	107.1 (1)	C(2')-N(1')-C(9')	104.8 (3)
Co-N(1)-C(2)	127.4 (1)	C(2')-N(3')-C(4')	107.1 (2)
Co-N(1)-C(9)	126.8 (1)	C(2')-N(3')-C(10')	126.9 (2)
C(2)-N(1)-C(9)	104.9 (2)	C(4')-N(3')-C(10')	125.9 (2)
C(2)-N(3)-C(4)	107.6 (2)	C(11')-N(12')-C(13')	116.5 (3)
C(2)-N(3)-C(10)	126.5 (3)	N(1')-C(2')-N(3')	113.8 (3)
C(4)-N(3)-C(10)	125.7 (3)	N(3')-C(4')-C(5')	131.7 (3)
C(11)-N(12)-C(13)	117.1 (3)	N(3')-C(4')-C(9')	105.6 (2)
N(1)-C(2)-N(3)	113.0 (2)	C(5')-C(4')-C(9')	122.6 (3)
N(3)-C(4)-C(5)	132.1 (3)	C(4')-C(5')-C(6')	116.6 (3)
N(3)-C(4)-C(9)	105.3 (2)	C(5')-C(6')-C(7')	121.2 (3)
C(5)-C(4)-C(9)	122.6 (3)	C(6')-C(7')-C(8')	122.3 (3)
C(4)-C(5)-C(6)	116.0 (3)	C(7')-C(8')-C(9')	117.2 (3)
C(5)-C(6)-C(7)	123.3 (3)	N(1')-C(9')-C(4')	109.2 (2)
C(6)-C(7)-C(8)	121.3 (3)	N(1')-C(9')-C(8')	130.8 (2)
C(7)-C(8)-C(9)	117.6 (3)	C(4')-C(9')-C(8')	120.0 (3)
N(1)-C(9)-C(4)	109.1 (2)	N(3')-C(10')-C(11')	112.9 (3)
N(1)-C(9)-C(8)	130.6 (2)	C(10')-C(11')-N(12')	115.8 (2)
C(4)-C(9)-C(8)	120.3 (3)	C(10')-C(11')-C(16')	121.0 (3)
N(3)-C(10)-C(11)	111.9 (3)	N(12')-C(11')-C(16')	123.1 (3)
C(10)-C(11)-N(12)	115.9 (2)	N(12')-C(13')-C(14')	124.5 (3)
C(10)-C(11)-C(16)	121.4 (3)	C(13')-C(14')-C(15')	118.8 (3)
N(12)-C(11)-C(16)	122.7 (3)	C(14')-C(15')-C(16')	119.2 (3)
N(12)-C(13)-C(14)	123.7 (3)	C(11')-C(16')-C(15')	118.9 (3)
b. Bond Angles (deg) for $\text{Co}(7)_2\text{Cl}_2$			
Cl(1)-Co-Cl(2)	118.6 (1)	C(9)-C(10)-C(11)	118.5 (3)
Cl(1)-Co-N(1)	103.1 (1)	C(10)-C(11)-C(12)	118.8 (3)
Cl(1)-Co-N(1')	113.2 (1)	C(11)-C(12)-C(7)	119.3 (3)
Cl(2)-Co-N(1)	110.0 (1)	Co-N(1')-C(2')	129.7 (2)
Cl(2)-Co-N(1')	102.1 (1)	Co-N(1')-C(5')	124.3 (2)
N(1)-Co-N(1')	110.0 (1)	C(2')-N(1')-C(5')	105.8 (3)
Co-N(1)-C(2)	128.4 (2)	N(1')-C(2')-C(2m')	121.7 (2)
Co-N(1)-C(5)	124.8 (2)	N(1')-C(2')-C(3')	108.4 (3)
C(2)-N(1)-C(5)	106.3 (2)	C(2m')-C(2')-C(3')	129.9 (2)
N(1)-C(2)-C(2m)	121.1 (3)	C(2')-C(3')-C(3m')	130.7 (3)
N(1)-C(2)-C(3)	108.7 (3)	C(2')-C(3')-N(4')	106.4 (2)
C(2m)-C(2)-C(3)	130.2 (2)	C(3m')-C(3')-N(4')	122.9 (2)
C(2)-C(3)-C(3m)	131.6 (3)	C(3')-N(4')-C(5')	107.3 (3)
C(2)-C(3)-N(4)	106.1 (2)	C(4')-N(4')-C(6')	126.6 (3)
C(3m)-C(3)-N(4)	122.3 (3)	C(5')-N(4')-C(6')	124.9 (2)
C(3)-N(4)-C(5)	107.5 (2)	N(4')-C(5')-N(1')	112.2 (3)
C(3)-N(4)-C(6)	127.0 (2)	N(4')-C(6')-C(7')	111.1 (3)
C(5)-N(4)-C(6)	124.9 (3)	C(6')-C(7')-N(8')	115.2 (3)
N(4)-C(5)-N(1)	111.4 (2)	C(6')-C(7')-C(12')	121.8 (3)
N(4)-C(6)-C(7)	112.0 (2)	N(8')-C(7')-C(12')	122.9 (2)
C(6)-C(7)-N(8)	115.4 (3)	C(7')-N(8')-C(9')	116.5 (2)
C(6)-C(7)-C(12)	122.1 (2)	N(8')-C(9')-C(10')	122.7 (3)
N(8)-C(7)-C(12)	122.5 (3)	C(9')-C(10')-C(11')	120.0 (3)
C(7)-N(8)-C(9)	116.5 (3)	C(10')-C(11')-C(12')	118.2 (3)
N(8)-C(9)-C(10)	124.3 (3)	C(11')-C(12')-C(7')	119.7 (3)

Table V. Comparison of Co Coordination in  $\text{Co}(8)_2\text{Cl}_2$  and  $\text{CoIm}_2\text{Cl}_2$ 

	$\text{Co}(8)_2\text{Cl}_2$	$\text{Co}(7)_2\text{Cl}_2$	$\text{CoIm}_2\text{Cl}_2$ <sup>17</sup>
Co-N, Å	2.014, 2.031	2.015, 2.016	1.989, 1.997
Co-Cl, Å	2.259, 2.242	2.258, 2.268	2.264, 2.237
N-Co-N, deg	107.1	110.0	105.4
Cl-Co-Cl, deg	116.6	118.6	111.2

downfield except for a methyl group at C(4).

In comparison with the pyridine system which has been extensively studied and discussed,<sup>18</sup> there are few comparable data for imidazoles. In agreement with the present results,  $\Delta\delta$  for imidazole itself is downfield for both H(2) and H(4), H(5) in  $\text{CoIm}_6^{2+}$  in methanol under conditions where fast exchange and tautomeric proton shifts average the H(4), H(5) signals.<sup>19</sup> In that solvent and in  $\text{D}_2\text{O}$  and  $\text{Me}_2\text{SO}$  with  $\text{Co}(\text{II})$ , the magnitude of the shift of H(2) is less than the H(4), H(5) average.<sup>20,21</sup>

It is interesting that the anions have a significant role in controlling the structure of the species in the  $\text{Me}_2\text{SO}$  solutions which were studied. The presence of halide ion leads to the blue color characteristic of tetrahedral species. For imidazole, **1**, and **6**,  $\epsilon$  began to drop significantly only above a ligand:metal ratio of >25 indicating that tetrahedral species are dominant at least up to that concentration range. Structural assignments have been made and correlated with electronic absorption data for a number of complexes of imidazole.<sup>22</sup>  $\text{CoIm}_4^{2+}$  apparently adopts tetrahedral geometry in a perchlorate salt. This substance absorbs at 565 nm in acetone ( $\epsilon \sim 5.6 \times 10^2$ ). Octahedral  $\text{Co}(\text{II})$  complexes containing four or six imidazole ligands are reported to have absorbance maxima at 480–520 nm ( $\epsilon \sim 20$ ). A  $\text{CoIm}_2(\text{NO}_3)_2$  species which absorbs at 550 nm ( $\epsilon$  258) was regarded as difficult to classify. The electronic spectrum is intermediate between those of tetrahedral and octahedral species. The  $\text{CoIm}_2\text{X}_2$  species where X = halide are unequivocally tetrahedral<sup>17</sup> and absorb maximally near

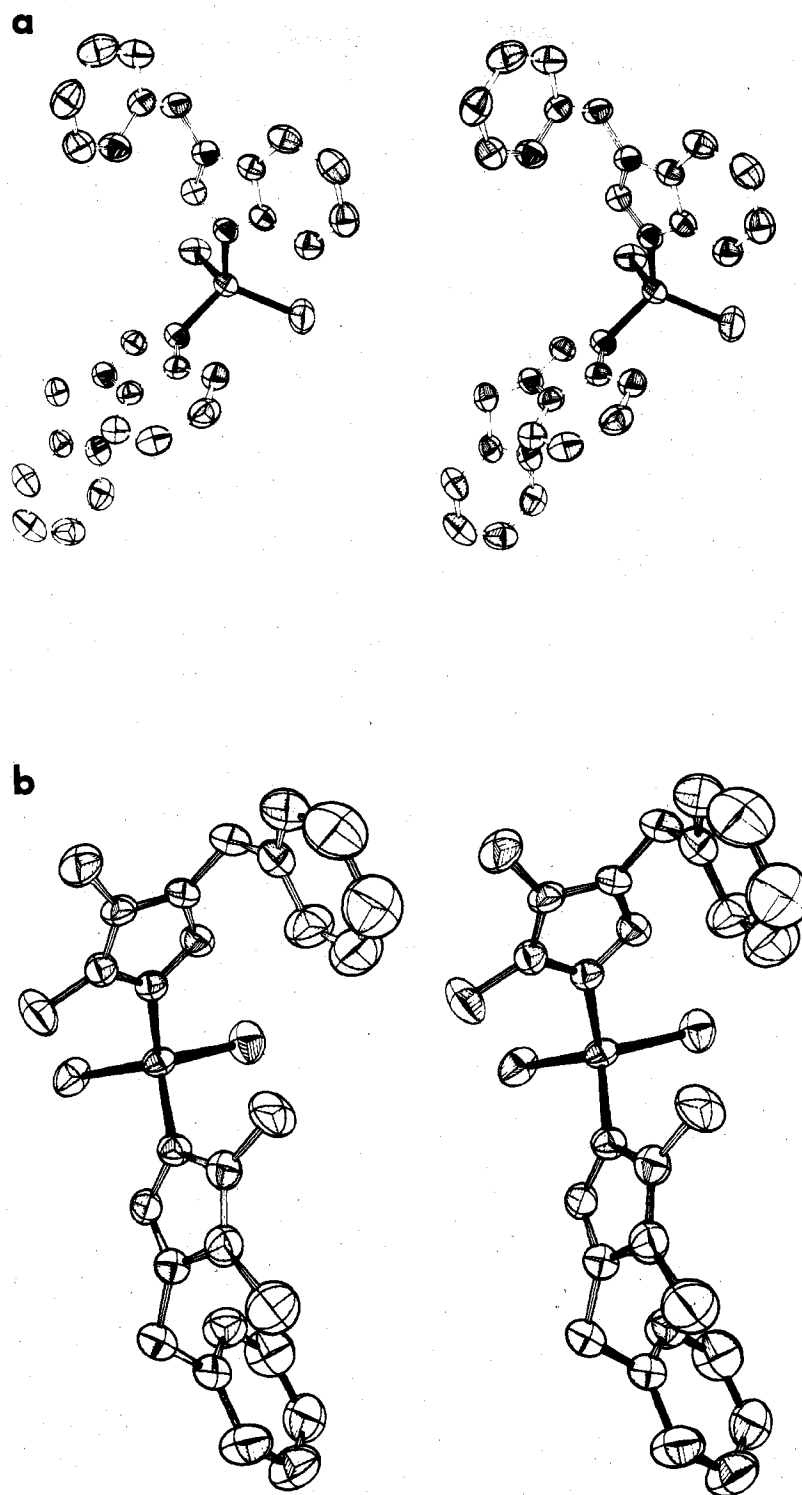


Figure 3. Stereoscopic pair views of (a)  $\text{Co}(\mathbf{8})_2\text{Cl}_2$  and (b)  $\text{Co}(\mathbf{7})_2\text{Cl}_2$ .

615 nm.<sup>23</sup> Evidence that species of tetrahedral geometry with two imidazoles and two halide ions coordinated to cobalt persist at ligand:metal ratios of greater than 2 has been obtained from both preparative and spectroscopic studies.<sup>24</sup> The behavior of the ligands 1–8 toward  $\text{Co}(\text{II})$  in the presence of either halide or nitrate anions therefore seems to parallel that seen for imidazole complexes. Tetrahedral geometry is adopted in the presence of halide in the inner coordination sphere. The spectra indicate that octahedral coordination is present in the nitrate solutions but there is no direct evidence for the number of imidazoles which are coordinated. The fact that chloride

is maintained in the cobalt coordination sphere in preference to the available excess imidazole may be due to a synergistic interaction between the imidazole and the anion.<sup>25</sup> It may also be due to a solvent effect since much greater affinity for  $\text{Co}(\text{II})$  is exhibited by chloride ion in organic solvents than in aqueous solution.<sup>26</sup>

The pyridine nitrogen is a significantly weaker base toward  $\text{Co}(\text{II})$  than imidazole and the imidazole binding sites apparently completely dominate the structural situation.<sup>27</sup> This conclusion is supported by the solid-state structures determined for  $\text{Co}(\mathbf{8})_2\text{Cl}_2$  and  $\text{Co}(\mathbf{7})_2\text{Cl}_2$ . The metal ion is in a tetrahedral

environment and the pyridine nitrogen is not coordinated.

Structural modifications which might reduce the preference for binding at the imidazole nitrogen would include increasing the steric bulk adjacent to the imidazole nitrogens, as in **4** and **7**, or competitive protonation at this site, which is more basic than the pyridine nitrogen. Neither of these structural changes is apparently sufficient to make the pyridine nitrogen the preferred ligand site. The complexes of **4** and **7** are not qualitatively different from those of **1** and **6**. In the studies of solutions of **6** and **7** containing 1 equiv of  $\text{CF}_3\text{CO}_2\text{H}$ , there is evidence for a decreased extent of complexation at the imidazole nitrogen, because the slopes in the plots of chemical shift vs. cobalt concentration are significantly reduced. The signals of the pyridine ring protons still remain essentially unaffected by the presence of  $\text{Co(II)}$ , however. An *N*-ethyl salt of **1** showed similar behavior. The spectrum was unaffected by the addition  $\text{Co(II)}$  indicating that the positively charged ligand with only a pyridine nitrogen as a potential coordination site remains uncomplexed in  $\text{Me}_2\text{SO}$  solution.

Ligand **9** represents a case where the primary amino group would be expected to be similar to the imidazole ring in basicity toward  $\text{Co(II)}$ .<sup>28</sup> This is evidently the case as the  $\text{CH}_2$  group adjacent to the amino substituent shows more broadening than would be anticipated if the imidazole ring was the sole site for complexation. It is not possible, however, to make any conclusion about the relative ratio of ligand molecules complexed at the amino as opposed to the imidazole nitrogen, since we have no data concerning the magnitude<sup>29</sup> of broadening resulting from the alternative modes of ligation. There is no indication of chelation with carbon bonding.

The studies of  $\text{Fe(II)}$  and  $\text{Ni(II)}$  were limited but did not reveal any reason to believe these ions were behaving differently from  $\text{Co(II)}$  or  $\text{Cu(II)}$ .

In conclusion, this study has detected no tendency for carbon complexation via imidazolium ylide species for the first-row transition metal ions. At this point it seems likely that the strong  $\pi$ -donor properties and inertness to substitution which characterize  $\text{Ru(II)}$  may be essential to the stability of such complexes. Assistance of  $\text{Ru(II)}$  in the deprotonation at C(2) which is required to permit ylide formation may also be crucial.

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**Registry No.** **1**, 25700-14-5; **2**, 62154-59-0; **3**, 62154-60-3; **4**, 62154-61-4; **5**, 25660-37-1; **6**, 62154-62-5; **7**, 62154-63-6; **8**, 62154-64-7;  $\text{Co(7)}_2\text{Cl}_2$ , 62154-44-3;  $\text{Co(8)}_2\text{Cl}_2$ , 62154-43-2;  $\text{Co(Cl)}_2$ ,

7646-79-9;  $\text{Co(NO}_3)_2$ , 10141-05-6;  $^{13}\text{C}$ , 14762-74-4.

**Supplementary Material Available:** Tables listing positional and thermal parameters and observed and calculated structure amplitudes and figures showing unit cells (31 pages). Ordering information is given on any current masthead page.

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