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Pyrazole/Imidazole and Pyrazolato/Imidazolato Complexes of Pentacyanoferrate(II/III) and Pentaammineruthenium(II/III). LMCT Transitions of Low-Spin d^5 Complexes

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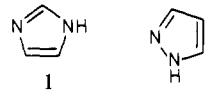
Ligand-to-metal charge-transfer bands are observed for the low-spin d^5 complexes $(CN)_5FeL^{2-}$ and $(NH_3)_5RuL^{3+}$ with coordination of L = imidzole, pyrazole, or numerous derivatives of these parent five-membered rings (methylated imidazoles and pyrazoles, benzimidazoles, hypoxanthine, caffeine, histidines). The LMCT spectral bands appear in the visible and UV regions. The origin of the transitions may be assigned on the basis of HOMO's of imidazole and pyrazole. Deprotonation of the pyrrole NH produces the respective imidazolate or pyrazolate complex, with the LMCT spectra shifted to lower energy for aqueous solution spectra. Data and assignments based on HOMO's of ligands are made for 33 imidazoles and 6 pyrazoles. The pK_a's of pyrazole complexes at 25.0 °C, μ = 0.10 ($NaClO_4$), have been determined by spectrophotometric titration unless otherwise specified (complex, pK_a): $(NH_3)_5RuL^{3+}$, 5.98; $(NH_3)_5CoL^{3+}$, 6.07 (glass electrode, μ = 1.0); $(CN)_5FeL^{2-}$, ~11; $(CN)_5CoL^{2-}$, 10.9 (^1H NMR titration, μ = 1.0). Other coordinated ligand pK_a's were determined at 25 °C as follows: $(NH_3)_5Co(imidazole)^{3+}$, 9.99 ($\mu$ = 1.0); $(CN)_5Co(ImH)^{2-}$, 11.4; $(NH_3)_5Co(3\text{-}MePyzH)^{3+}$, 6.7 (glass electrode); $(NH_3)_5Ru(3,5\text{-}Me_2PyH)^{3+}$, 7.21; $(NH_3)_5Ru(1,2,4\text{-triazole})^{3+}$, 4.3. When imidazole and pyrazole are coordinated to $(NH_3)_5Ru^{3+}$, the acidity of the pyrrole NH increases 5.3 orders of magnitude for imidazole and 8.2 orders of magnitude for pyrazole, indicative of the influence of distance between the central Ru(III) ion and the site of deprotonation. The influence of σ withdrawal by varying the coordinated metal center and the influence of π donation by imidazolate or pyrazolate is discussed. The ^1H NMR spectra for complexes of DL^+, $(NH_3)_5CoL^{3+}$, $(CN)_5CoL^{2-}$, $(NH_3)_5RuL^{2+}$, and $(CN)_5FeL^{3-}$ (L = 3-methylpyrazole) are discussed. The influence of coordination of the following metal centers of 1-methylimidazole on the ^1H NMR spectrum of the respective complexes is reported: D^+, $(NH_3)_5Co^{3+}$, CH_3Hg^+, $(CN)_5Co^{2-}$, $(NH_3)_5Ru^{2+}$, $(CN)_5Fe^{3-}$. σ withdrawal overshadows other factors such as TIP in these complexes, and all resonances are shifted downfield for coordinated pyrazole, 3-methylpyrazole, and 1-methylimidazole except for $(NH_3)_5Ru^{2+}$ and $(CN)_5Fe^{3-}$ centers where π back-bonding reverses the shift of remote sites (H(5) or CH_3 of 1-methylimidazole and H(4) and H(5) of pyrazole).

Introduction

The imidazole side chain of the amino acid histidine is known to form part of the coordination environment of a large number of metalloenzymes.[1] The incorporation of imidazole in the metal sites of numerous proteins suggests that this ligand has properties particularly suited to its biological role. The imidazole (ImH (**1**)) and imidazolate (Im^-) complexes of



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pentacyanoferrate(II/III)[2] and pentaammineruthenium(II/III)[3] have been studied in order to evaluate the σ-donor and π-acceptor abilities of the ligands. The evidence, particularly the observation of ligand-to-metal charge-transfer (LMCT) transitions, suggests that imidazole can act as a π donor in the complexes of low-spin Fe(III) and Ru(III).[2-4] More recently, the LMCT absorptions of Cu(II)-imidazole and Cu(II)-imidazolate chromophores have been studied by Schugar et al. in order to obtain information useful for evaluating the electronic spectra of Cu(II) proteins.[5-7] Complexes of pyrazole (PyzH (**2**)) were found to be very helpful in evaluating the LMCT transitions.[6] Pyrazole has an electronic structure very similar to that of imidazole and is expected to have comparable ligand properties, but modified due to the adjacent location of the pyrrole and pyridine-like nitrogens.

We have extended the study of $(CN)_5FeL^{2-,3-}$ and $(NH_3)_5RuL^{2+,3+}$ complexes to include L = pyrazole or a pyrazole derivative. The pK_a's of several pyrazole complexes are reported, and comparisons are made with the imidazole complexes.

Experimental Section

Materials. The organic ligands were generally used as obtained from one of several suppliers: Aldrich, Eastman, Chemalog, Sigma, Fisher. Imidazole was recrystallized from benzene. 4,5-Dimethylimidazole was prepared previously.[2]

Several metal compounds were used as precursors for the complexes studied. These compounds were $Ru(NH_3)_6Cl_3$, $K_4Ru(CN)_6 \cdot 3H_2O$, $K_3Co(CN)_6$, and CH_3HgCl (Alfa Products), $CoCl_2 \cdot 6H_2O$ (Baker), and $Na_2Fe(CH)_5(NO) \cdot 2H_2O$ (Mallinckrodt).

Preparations. The metal complexes or their salts were prepared by published methods or minor variants thereof: $Fe(CN)_5L^{3-}$,[2,4,8,9] $Fe(CN)_5L^{2-}$,[4,9] $Ru(NH_3)_5L^{2+}$,[10] $Ru(CN)_5L^{3-}$,[11] $Co(NH_3)_5L^{3+}$,[12,13] $Co(CN)_5L^{2-}$,[13] $CH_3Hg(1\text{-MeIm})$.[14] Complexes of the $(CN)_5FeL^{3-}$ series and $CH_3Hg(1\text{-MeIm})$ used in NMR studies were prepared in D_2O by using a 1:1 ligand to metal binding complex ratio.

Spectra. The ^1H NMR spectra were obtained with a Varian EM-360 spectrometer operating at a frequency of 60 MHz with an ambient probe temperature. D_2O (J. T. Baker or Stohler Isotope Chemicals) was used as the solvent with 3-(trimethylsilyl)propionic acid (TMPA, Aldrich Gold Label) as the internal standard for the metal complexes. $CDCl_3$ (Merck) was used with tetramethylsilane (MCB) for some ligands, but most ligands were also dissolved in D_2O. All chemical shifts are reported in δ units.

The ultraviolet-visible spectra were recorded with a Varian-Cary 118C spectrophotometer. Standard quartz cells or the flow cell assembly, which has been described previously,[4] were used. Temperature control utilized the thermostatable cell block and a Forma temperature bath.

Determination of pK_a. The pK_a's of the complexes were determined by spectrophotometric titration. For the complexes stable throughout the pH range studied, this was achieved by using the flow cell con-

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Table I. LMCT Energies of Pyrazole Complexes[a]

ligand (L)	abs, $cm^{-1} \times 10^3$ (λ, nm)	
	$(CN)_5Fe^{III}L$	$(NH_3)_5Ru^{III}L$
pyrazole	22.2 (450), 28.7 (349)	25.5 (392), 38.6 (259), 46.0 (21.7)
pyrazolate	18.3 (545) br	23.3 (429), 39.1 (256)
1,2,4-triazole	24.4 (410), 28.0 (357)	30.9 (324)
3,5-dimethylpyrazole	24.0 (416)	
3,5-dimethylpyrazolate	20.4 (490), 29.4 (340)	23.8 (420), 36.8 (272), 45.2 (22.1)
indazole	16.7 (~600) br, 21.5 (465), 28.2 (355)	17.7 (565), 25.6 (390)
4-methylpyrazole	20.9 (478)	24.0 (417)
4-methylpyrazolate	16.5 (607)	22.3 (448)
3-methylpyrazole	20.7 (484)	23.5 (425)
3-methylpyrazolate	16.6 (604)	21.7 (460)

[a] br = broad.

nected to the titration vessel. For the complexes that were not stable in the deprotonated form, identical aliquots were prepared at varying pH and data obtained immediately at rapid scan speeds.

$Co(CN)_5(PyzH)^{2-}$ was titrated and followed by ^1H NMR. The change in chemical shift of the pyrazole-ring protons upon deprotonation yields the value of the pK_a from a normal titration curve analysis.

Results and Discussion

Ligand-to-Metal Charge-Transfer Absorptions. The LMCT energies of the $(CN)_5FeL^{2-}$ and $(NH_3)_5RuL^{3+}$ complexes (L = pyrazole or derivative) are shown in Table I. The spectra of the pentacyanoferrate(III) complexes of imidazole, imidazolate, pyrazole, and pyrazolate are compared in Figure 1. The pyrazole complex has an absorption band (450 nm) that is identified as a charge transfer from pyrazole to Fe(III) analogous to the previously studied imidazole complex.[2] This absorption moves to lower energy upon deprotonation of the coordinated pyrazole by the addition of aqueous NaOH. The lower energy absorption of the pyrazolate complex compared to the pyrazole complex is consistent with the LMCT assignment. A similar spectral behavior is observed for $(NH_3)_5Ru(PyzH)^{3+}$.

The charge-transfer energies for the Ru(III) complexes are always higher than for the corresponding Fe(III) complex (ca. $(3-4) \times 10^3$ cm^{-1}). This observation is also consistent with the transition being from ligand to metal. The 3d orbitals of the Fe(III) complexes are lower in energy and closer to the filled π orbitals of the ligand than the 4d orbitals of the Ru(III) complexes.

The LMCT transitions for a number of imidazole complexes are shown in Table II. Many of these are reported here for the first time. Also included are the complexes of 4-aminopyridine and 4-(dimethylamino)pyridine. These pyridines, bearing electron-releasing substituents, also display LMCT transitions. Sutton and Taube have previously assigned the observed transition for the $(NH_3)_5Ru^{3+}$ complex of 4-aminopyridine as an LMCT transition.[34] The same assignment (LMCT) has been made for the $(CN)_5Fe(4\text{-aminopyridine})^{2-}$ complex by Hrepic and Malin.[38]

The origin of the bands in the visible and near-UV regions of the spectra of $(CN)_5FeL^{2-}$ and $(NH_3)_5RuL^{3+}$ complexes of imidazoles, pyrazoles, and aminopyridines is further supported by the fact that $(NH_3)_5CoL^{3+}$ and $(CN)_5CoL^{2-}$ analogues do not exhibit transitions other than ligand field in origin. This is shown in Table III where spectral data for various Co(III) complexes of imidazoles, benzimidazoles, and pyrazoles are shown to have the longest wavelength maximum in the vicinity of $(NH_3)_5CoL^{3+}$ or $(CN)_5CoL^{2-}$ with L = NH_3, H_2O, or pyridine. Therefore, when the t_{2g} orbital set is filled by the low-spin d^6 configuration, no $d\pi$ orbital exists for an

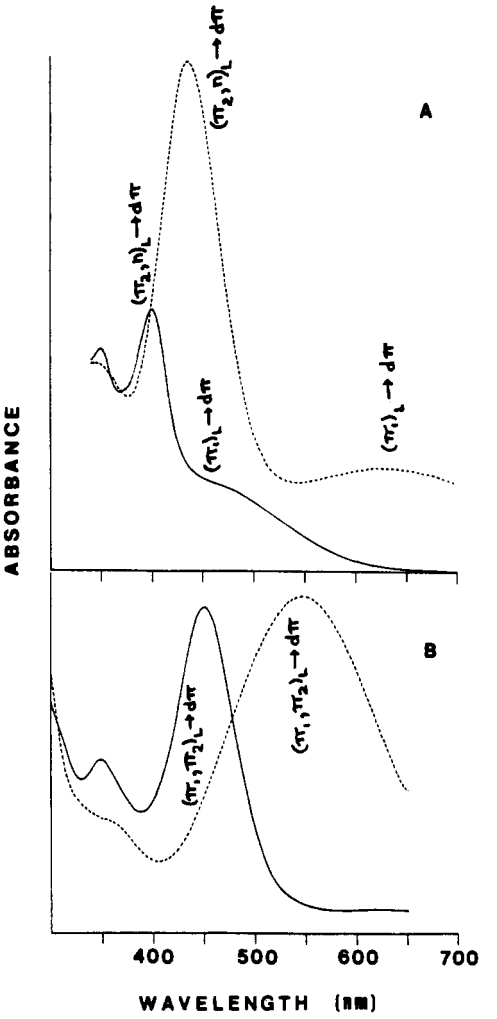

Figure 1. Visible electronic spectra of $(CN)_5FeL^{2-}$ complexes. A: solid line, L = imidazole; dashed line, L = imidazolate. B: solid line, L = pyrazole; dashed line, L = pyrazolate.

appropriate low-energy transition of the type $\pi(L) \rightarrow d\pi$ (LMCT), even for the imidazoles and pyrazoles. Similarly if the ligand does not possess a lone electron pair that may interact with the half-empty $d\pi$ orbital of the low-spin d^5 configuration, the LMCT band is also absent. Ligands of this class include pyridine, methylpyridines, pyridines with withdrawing functional groups (e.g. $-CN$, $-C(O)NH_2$), and pyrazines. This is shown by Table IV for the $(CN)_5FeL^{2-}$ series. No transition red-shifted above the lowest energy transition of $(CN)_5FeNH_3^{2-}$ or $(CN)_5FeOH_2^{2-}$ is detected for the pyridines and pyrazines. The band listed as ligand field (LF) for these complexes may include a component of a $CN^- \rightarrow$ Fe(III) LMCT as shown by the relatively high ϵ in this region, coincident with the d–d band in the ammine and aquo complex.[40,41] It is important to point out that the existence of LMCT assignments for the pyrazoles, imidazoles, and aminopyridines in Tables I and II is based on the presence of an intense transition at even longer wavelengths for each of these ligand classes in a spectral region where no d–d excitation exists for the $Ru(NH_3)_6^{3+}$ or $(CN)_5FeNH_3^{2-}$ parent compounds.

The electronic structures of imidazole and pyrazole have been calculated by several theoretical approaches.[7,15,16] Studies have also been conducted by photoelectron spectroscopy (PES).[17] The results of these studies indicate that

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Table II. LMCT Spectra of Imidazole Complexes [Abs max, $cm^{-1} \times 10^3$ (λ, nm)][a]

ligand	$(CN)_5Fe^{III}$			$(NH_3)_5Ru^{III}$		
	$d\pi \leftarrow (\pi_1)_L$	$d\pi \leftarrow (\pi_2,n)_L$	$d\pi \leftarrow \sigma_{CN}$	$d\pi \leftarrow (\pi_1)_L$	$d\pi \leftarrow (\pi_2,n)_L$	
			Imidazoles			
imidazole	~21.1 (~475) [376][b]	24.8 (403) [1180]	28.1 (356) [981]	23.5 (425)	33.7 (297)	39.2 (255)
1-methylimidazole	~21.1 (475) [461]	24.4 (409) [1820]	28.7 (348) [1370]	24.4 (101)	32.1 (312)	
2-methylimidazole	19.8 (505) [355]	24.8 (404) [1530]	27.9 (358) [1050]	21.5 (465)	32.9 (304)	37.0 (270)
4(5)-methylimidazole	19.0 (525) [400]	24.9 (401) [1330]	28.6 (350) [1050]	21.3 (470)	33.0 (303)	
1,2-dimethylimidazole	20.0 (500) vbr	24.6 (407)	28.6 (350)			
2,4-dimethylimidazole	17.7 (565)	24.8 (403)	28.1 (356)			
4,5-dimethylimidazole	16.8 (595)	24.8 (403)	27.9 (358)	19.2 (520)	32.1 (312)	
imidazolate	16.0 (625)	22.8 (438)		18.2 (550)	27.8 (360)	40.8 (245) sh
2-methylimidazolate		22.5 (448)		16.1 (620) 16.4 (610)	27.2 (367)	39.2 (255) sh
4-methylimidazolate	12.5 (800) br	22.5 (444)		16.7 (600)	27.0 (370)	
4,5-dimethylimidazolate				13.3 (~750)	25.5 (392)	
1-vinylimidazole		23.3 (430)	28.4 (352)			
1-benzylimidazole	21.1 (~475)	24.4 (409)	29.0 (345)			
4-phenylimidazole	16.8 (595)	24.9 (402)	28.4 (352)			
4-imidazoleacetate	18.2 (550)	25.0 (400)	28.3 (353)			
4-imidazoleacrylate	17.6 (567)	24.9 (402)	28.6 (350)			
1,2,4,5-tetramethylimidazole	19.8 (505)	25.1 (398)	28.6 (350)			
urocanic acid	17.6 (567)	24.9 (402)	28.6 (350)			
l-β-imidazolelactic acid	19.4 (515)	24.8 (403)	28.3 (353)			
			Benzimidazoles			
benzimidazole	19.8 (505) [1650]	26.2 (382) [700]	28.4 (352) [950]	22.6 (443)		
2-methylbenzimidazole	19.4 (515)	24.4 (410)	27.9 (358)			
2-phenylbenzimidazole	21.5 (~465) sh	25.4 (394)				
1-methyl-2-phenylbenzimidazole	22.2 (~450) sh	25.1 (398)				
1-ethyl-2-methylbenzimidazole	20.0 (500)	25.5 (392)	28.0 (357)			
5,6-dimethylbenzimidazole	19.0 (527)	26.0 (385)	28.0 (357)			
benzimidazolate	15.4 (650)	26.7 (~375) sh		19.8 (505)		
5.6-dimethylbenzimidazolate	15.6 (640)	26.7 (~375) sh				
			Others			
cyanomethylimidazole	21.7 (460)	24.9 (401)	28.0 (357)			
thiazole		24.3 (411)	28.0 (357)			
4-aminopyridine	17.9 (560) [2750, 3110]	31.3 (320) [2910]		20.0 (501) 19.8 (505) [11 200]	31.3 (320) 31.2 (321) [4790]	38.5 (260) 39.5 (253) [3240]
4-(dimethylamino)pyridine	15.2 (660)	29.2 (342)	37.3 (268)	17.2 (583)	29.7 (337)	36.0 (278)
2-aminopyridine	15.9 (627)	22.0 (455)		19.7 (507)		
3-aminopyridine	14.4 (695)					
cyano	23.8 (420) [1100]	31.2 (321) sh [1210]	33.2 (301) [1549]			
hypoxanthine	20.0 (500) br	23.3 (429)		21.7 (461) [491]	33.3 (300) [1330]	
9-*H*-hypoxanthine	vbr	21.4 (467)		18.9 (529) [859]	28.0 (357) [2020]	
caffeine	18.9 (530)	25.6 (390)	27.9 (359)			
histamine	20.5 (487)	25.0 (400)	28.2 (354)			
histidine	20.7 (484)	24.9 (401)	28.4 (352)	22.2 (450) [290]	33.0 (303) [2100]	
N-*tert*-butoxycarbonyl-*l*-histidine	19.4 (515)	24.8 (403)	28.2 (354)			
1-methylhistidine	20.5 (488)	24.6 (407)	30.0 (345) sh			
histidinate	12.5 (800) br	22.5 (445)		16.7 (600)	27.4 (365)	

[a] sh = shoulder; br = broad; vbr = very broad. [b] Numbers in brackets are molar extinction coefficients in M^{-1} cm^{-1}.

imidazole and pyrazole have three filled molecular orbitals of relatively high energy. These three orbitals are well separated from other lower energy orbitals. Two of these orbitals have π symmetry and are designated π_1 and π_2. The other high-energy orbital (n) consists of the lone pair on the pyridine-like nitrogen. The HOMO, π_1, is based primarily on the carbons of the ring, and π_2 is based primarily on the nitrogens. For imidazole, π_2 and n are very close in energy. With pyrazole, the distinction between π_1 and π_2 in terms of the carbon and nitrogen contributions is less and their energy difference is smaller.

The observed LMCT transitions can now be discussed in terms of what is known about the imidazole and pyrazole orbitals. For the imidazole complexes, the lowest energy absorption can be assigned to a transition from π_1 to the metal orbitals of π symmetry (πd). Due to the nature of π_1, the πd $\leftarrow (\pi_1)_L$ transition is expected to be sensitive to substitution at carbon positions of the imidazole ring. The sensitivity of this lowest energy transition to ring carbon substitution is clearly seen by comparing the values for imidazole, 2-methylimidazole, and 4-methylimidazole, for example. This transition seems most sensitive to substitution at the 4(5)-

Table III. UV-Visible Absorption Maxima of Pentaamminecobalt(III) and Pentacyanocobaltate(III) Complexes

complex	abs max, $cm^{-1} \times 10^3$ (λ, nm)		ref
$Co(NH_3)_6^{3+}$	21.2 (472)	29.8 (336)	35
$(NH_3)_5Co(ImH)^{3+}$	21.2 (471)	30.1 (332)	*a*
	21.1 (472)	30.0 (334)	36
$(NH_3)_5Co(Im)^{2+}$	21.0 (477)	29.4 (340)	*a*
	20.9 (478)	29.2 (344)	36
$(NH_3)_5Co(1\text{-MeIm})^{3+}$	21.2 (471)	30.8 (325) sh[b]	*a*
$(NH_3)_5Co(2\text{-MeImH})^{3+}$	21.0 (476)	30.7 (326)	*a*
$(NH_3)_5Co(2\text{-MeIm})^{2+}$	20.8 (480)	29.9 (335)	*a*
$(NH_3)_5Co(1,2\text{-Me}_2Im)^{3+}$	21.0 (476)	30.3 (330)	*a*
$(NH_3)_5CoOH_2^{3+}$	20.4 (490)	29.1 (344)	35
$(NH_3)_5Co(py)^{3+}$	21.2 (473)	29.6 (338)	35
$(NH_3)_5Co(PyzH)^{3+}$	20.9 (478)	29.4 (340)	*a*
$(NH_3)_5Co(Pyz)^{2+}$	20.7 (483)	29.0 (345) sh	*a*
$Co(CN)_6^{3-}$	32.1 (312)	38.5 (260)	37, 13
$(CN)_5Co(ImH)^{2-}$	28.8 (347)	37.7 (265) sh	*a*
$(CN)_5Co(Im)^{3-}$	28.8 (347)		*a*
$(CN)_5Co(1\text{-MeIm})^{2-}$	29.0 (345)		*a*
$(CN)_5Co(2\text{-MeImH})^{2-}$	28.7 (349)	37.7 (265) sh	*a*
$(CN)_5Co(1,2\text{-Me}_2Im)^{2-}$	28.6 (350)	37.7 (265) sh	*a*
$(CN)_5Co(BnzImH)^{2-}$	28.6 (350)	36.1 (277)	*a*
		37.2 (269)	
		37.5 (267)	
		38.2 (262)	
		41.7 (240)	
$(CN)_5Co(BnzIm)^{3-}$	28.2 (354)	36.2 (276)	*a*
		37.0 (270)	
		38.0 (263) sh	
		39.7 (252) sh	
$(CN)_5CoOH_2^{2-}$	26.3 (380)	32.3 (310) sh	37, 13
$(CN)_5Co(py)^{2-}$	28.3 (353)	37.9 (264) sh	37, 13
		38.8 (258) sh	
$(CN)_5Co(pz)^{2-}$	28.6 (350)	37.2 (269)	*a*

[a] This work. [b] sh = shoulder.

position of the ring. Methyl substitution lowers the LMCT energy, consistent with the methyl group being electron releasing. The HOMO is raised in energy. The next higher energy transition in the spectra of the imidazole complexes is not sensitive to substitution at the carbon positions. This absorption occurs at 402 ± 2 nm for the $(NH_3)_5Ru^{3+}$ series for nearly every imidazole ligand except for the 1-substituted imidazoles. Substitution at the N(1) position, with methyl for example, causes the energy of this LMCT transition to decrease, while the energy of the $d\pi \leftarrow (\pi_1)_L$ transition changes very little. This second LMCT transition is assigned as $\pi d \leftarrow (\pi_2,n)_L$. The sensitivity of this transition to substitution at nitrogen is consistent with the π_2 orbital being nitrogen based. Whether the $d\pi \leftarrow (n)_L$ component of the transition makes an important contribution to the observed absorption band cannot be ascertained. The π_2 and n orbitals should be close in energy, although their energies will change upon coordination of the imidazole to the metal center. Interaction

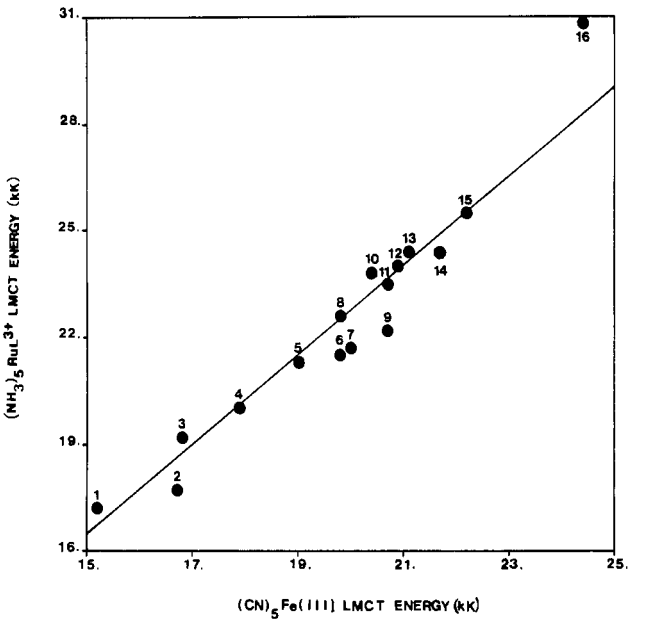

Figure 2. Correlation between the energies of the LMCT transitions of $(NH_3)_5RuL^{3+}$ complexes and $(CN)_5FeL^{2-}$ complexes (L): (1) 4-(dimethylamino)pyridine; (2) indazole; (3) 4,5-dimethylimidazole; (4) 4-aminopyridine; (5) 4-methylimidazole; (6) 2-methylimidazole; (7) hypoxanthine; (8) benzimidazole; (9) histidine; (10) 3,5-dimethylpyrazole; (11) 3-methylpyrazole; (12) 4-methylpyrazole; (13) 1-methylimidazole; (14) imidazole; (15) pyrazole; (16) triazole.

with the metal center is expected to lower the energies of both orbitals, but the n orbital should be lowered more because the interaction of the lone pair with the metal is expected to be greater than the π interaction. The relative magnitudes of these effects are difficult to determine.

Further evidence for the assignments of these transitions is obtained from a comparison of their intensities. The molar absorptivity of the $d\pi \leftarrow (\pi_1)_L$ transition in the $(CN)_5Fe^{2-}$ complexes is $<500\ M^{-1}\ cm^{-1}$ while that of the $d\pi \leftarrow (\pi_2,n)_L$ transition is $>1000\ M^{-1}\ cm^{-1}$. Arguments based on orbital overlap are consistent with the observed intensities. The carbon-based orbital, π_1, will overlap poorly with the metal orbital. The nitrogen-based orbital, π_2, will overlap the $d\pi$ orbitals more efficiently. The transition intensities reflect this difference in the extent of orbital overlap. The integrated intensities of the absorptions were not determined, however, owing to difficulties in resolving the overlapping bands.

In contrast to the imidazole complexes, $(CN)_5Fe(BnzImH)^{2-}$ has a single broad LMCT absorption in the visible region. This seems to indicate that the π_1 and π_2 orbitals of the benzimidazole are close in energy and that the charge transfers from each of these orbitals overlap. Presumably the

Table IV. Spectral Data for $(CN)_5Fe^{III}L$ Complexes Not Displaying LMCT Transitions[a]

	abs, $cm^{-1} \times 10^3$ (λ, nm)				
	LF	(CN) → Fe			
4-methylpyridine	23.9 (418) [1380][b]	27.5 (363) [1100]	34.5 (290) flat	39.5 (253) m	
pyridine	24.2 (414) [1096]	27.2 (368) [794]	35.7 (~280) sh	40.0 (250) m	
isonicotinamide	23.9 (418) [1000]	27.5 (364) [891]	37.7 (265)		
pyrazine	24.0 (416)	30.3 (330) sh	32.8 (305) sh	37.7 (265) m	39.1 (256) m
N-methylpyrazinium	23.7 (422) [2820]				
pyridazine	24.3 (412)	30.8 (~325) sh	33.9 (295)	35.7 (280)	43.5 (230) sh
	24.2 (414) [1700]	27.5 (363) [1400]	35.7 (280)	39.2 (255) m	
2-methylpyrazine	24.0 (416)	31.3 (~320) sh	37.0 (270)		
4-cyanopyridine	24.0 (417)	28.0 (357)	32.3 (310) sh	36.4 (275)	
	24.0 (417)	27.9 (359)	35.7 (280)	38.5 (260)	
ammonia	25.3 (395)				
water	25.4 (394) [743]	29.4 (340) [748]			

[a] This work and ref 38 and 39. [b] Numbers in brackets are molar extinction coefficients in $M^{-1}\ cm^{-1}$.

π_1 orbital of the imidazole ring is brought to an energy close to that of π_2 by a resonance interaction with the benzene ring. The LMCT absorption in the benzimidazole complex shows a sensitivity to substitution at the 1- or 2-positions similar to that seen for the imidazole complexes. Substitution on the benzene ring also changes the energy of the charge transfer, as for example in the 5,6-dimethylbenzimidazole complex.

The pyrazole complexes also show only a single broad LMCT band in the visible region. This is consistent with π_1 and π_2 being close in energy for the pyrazoles, and the transition is assigned as $\pi d \leftarrow (\pi_1,\pi_2)_L$. As with the imidazoles, methyl substitution on the ring produces a red-shift in the LMCT absorption. A single LMCT transition is observed for the complexes of 4-aminopyridine and 4-(dimethylamino)-pyridine. The spectra of $(CN)_5Fe(BnzImH)^{2-}$, $(CN)_5Fe(4\text{-aminopyridine})^{2-}$, and $(CN)_5Fe(4\text{-(dimethylamino)pyridine})^{2-}$ are remarkably similar to the spectra of $(CN)_5Fe(NCS)^{3-}$ and $(CN)_5Fe(N_3)^{3-}$. The complexes of N_3^- and NCS^- also display LMCT absorptions, and their spectra have been discussed in some detail by Gutterman and Gray.[18] The positions of the LMCT absorptions observed for all of these complexes are dependent upon the ionic strength of the solution, the identity of the cation, and the solvent.[19,42] This is a common behavior for charge-transfer transitions.[20]

Additional evidence for the assignment of these charge-transfer transitions has been obtained by resonance Raman spectroscopy.[21] Excitation within the LMCT absorptions of these complexes results in enhancement of internal imidazole ring modes in a manner consistent with the assignments discussed above.

The correlation between the energies of the LMCT transitions of the $(CN)_5Fe^{2-}$ and $(NH_3)_5Ru^{3+}$ series has been demonstrated previously.[2] The additional data presented here permit a useful reevaluation of this correlation over a broader range of ligands. The energies of the $\pi d \leftarrow (\pi_1)_L$ transitions for the $(NH_3)_5Ru^{3+}$ and $(CN)_5Fe^{2-}$ series of complexes correlate linearly as shown in Figure 2. The best line through the data was determined by a linear least-squares fit. The slope was found to be 1.4 ± 0.2. That the slope of this line is greater than 1 is significant. We have recently shown that a similar correlation between the energies of MLCT transitions of the d^6 ion series, $(CN)_5Ru^{II}L^{3-}$, $(NH_3)_5Ru^{II}L^{2+}$, $(NH_3)_5Os^{II}L^{2+}$, and $(CN)_5Fe^{II}L^{3-}$ (with L = a π-acceptor N-heterocyclic ligand), results in linear fits with a slope of less than 1.[22] This was taken as evidence for significant mixing of ligand and metal π orbitals for the best π acceptors of the series. In the present case, the interaction under consideration is once again between π-symmetry orbitals, but the ligand orbitals involved in the interaction are filled π orbitals capable of π donation to the metal. Orbital mixing results in a raising of the πd orbitals and a lowering of the $(\pi)_L$ orbitals, i.e. the energy separation between the orbitals is increased. The largest interaction is expected for the best π-donor ligands (lower left of Figure 2). The interaction is expected to be greater for $(CN)_5FeL^{3-}$ than $(NH_3)_5RuL^{3+}$ because the metal and ligand orbitals are closer in energy for the 3d case. This results in the data points in the lower left corner of Figure 2 being shifted to the right from values expected for no orbital mixing and resulting in a slope >1. Attempts to prepare the $(CN)_5Ru^{III}L^{2-}$ series of complexes are underway.[23] Data for another series would be useful in confirming the description of the results given above.

Comparisons of Cu(II)–Imidazole and –Pyrazole Complexes. The data for the LMCT energies for imidazole and pyrazole complexes of $(CN)_5Fe^{2-}$ and $(NH_3)_5Ru^{3+}$ in Tables I and II produce some interesting comparisons with the data of Schugar et al. on $Cu(ImH)_4^{2+}$ and $Cu(PyzH)_4^{2+}$ and the ring-substituted analogues $Cu(4,5\text{-}Me_2ImH)_4^{2+}$ and $Cu(3,5\text{-}Me_2PyzH)_4^{2+}$.[5-7] Schugar has also utilized the molecular orbital treatment of DelBene and Jaffé[15] for imidazole and pyrazole to account for the LMCT spectra of the $N_3Cu^{II}(ImH)^{2+}$ and $N_3Cu^{II}(PyzH)^{2+}$ types of complexes. The LMCT spectra for the Cu(II) complexes involve $n \rightarrow Cu(II)$, $\pi_2 \rightarrow Cu(II)$, and $\pi_1 \rightarrow Cu(II)$ transitions involving the $d_{x^2-y^2}$ acceptor orbital. The energies of these transitions of N_3CuL^{2+} will be higher than LMCT transitions to a πd orbital of $(CN)_5Fe^{2-}$ or $(NH_3)_5Ru^{3+}$ because the πd level is lowered by the large $10Dq$ value required to produce low-spin configuration of Fe(III) and Ru(III) while the e_g^* level ($d_{x^2-y^2}$) is raised. Therefore, πd for the Fe(III) and Ru(III) systems will be closer to π_1 and π_2 of the imidazole or pyrazole ring. The energies for transitions of the N_3CuL^{2+} series are reported in the literature[15-17] as follows ($cm^{-1} \times 10^3$): $N_3Cu^{II}(ImH)^{2+}$, $\pi_1 \rightarrow Cu(II)$ (32.3), $\pi_2 \rightarrow Cu(II)$ (32.3); $N_3Cu^{II}(4,5\text{-}Me_2ImH)^{2+}$, $\pi_1 \rightarrow Cu(II)$ (28.7), $\pi_2 \rightarrow Cu(II)$ (33.1); $N_3Cu^{II}(PyzH)^{2+}$, $\pi_1 \rightarrow Cu(II)$ (33.2), $\pi_2 \rightarrow Cu(II)$ (33.2); $N_3Cu^{II}(3,5\text{-}Me_2PyzH)^{2+}$, $\pi_1 \rightarrow Cu(II)$ (28.3), $\pi_2 \rightarrow Cu(II)$ (32.2).

It may be seen from these values that the $\pi_2 \rightarrow Cu(II)$ energy is relatively independent of ring substituents while $\pi_1 \rightarrow Cu(II)$ changes with ring substitution. The $\pi \rightarrow \pi^*$ intraligand transitions for imidazole is red-shifted only about 1×10^3 cm^{-1} from the free ligand whether Cu(II) or the d^{10} replacement (Zn(II)) is coordinated at N(3) of imidazole;[5] therefore, the absolute energies of π_1, π_2, and n do not change significantly upon changing one metal center of the same charge to another. If one calculates the shift of π_1 and π_2 upon coordination of the R-substituted ligands relative to their unsubstituted parent imidazole or pyrazole, the value of $\Delta\pi_1$ for the Cu(II) complex of 4,5-Me_2ImH is 3.6×10^3 cm^{-1} while, 3,5-Me_2PyzH shifts 4.9×10^3 cm^{-1}. This value is rather invariant to 4,5-substitution on imidazole as related calculations show 3.3 and 3.7×10^3 cm^{-1} shifts if R = C_2H_5 or i-C_3H_7. The π_2 orbital for the imidazole shifts -0.8×10^3 cm^{-1} (to higher energy) for R = CH_3, -0.7×10^3 cm^{-1} for R = C_2H_5, and -0.2×10^3 cm^{-1} for R = i-C_3H_7. The π_2 level for 3,5-Me_2PyzH shifts -1.0×10^3 cm^{-1} relative to pyrazole. (These values are $\Delta\pi_2$.) Therefore, the spacing between π_1 and π_2 levels in N_3CuL^{2+} is found to be 4.4×10^3 cm^{-1} for R = 4,5-Me_2, 4.0×10^3 cm^{-1} for R = 4,5-Et_2, 3.9×10^3 cm^{-1} for R = 4,5-Pr_2 for imidazoles and 3.9×10^3 cm^{-1} for R = 3,5-Me_2PyzH. In and of themselves, the values of the shifts in the N_3CuL^{2+} series are not particularly informative. However, if the values given for the LMCT transitions of $(CN)_5FeL^{2-}$ and $(NH_3)_5RuL^{3+}$ for the pair imidazole/4,5-dimethylimidazole in Table II are used to evaluate shifts, it is observed that $\Delta\pi_1$ is 4.3×10^3 cm^{-1} and $\Delta\pi_2 = 0.0 \times 10^3$ cm^{-1} for $(CN)_5FeL^{2-}$ and $\Delta\pi_1 = 4.3 \times 10^3$ cm^{-1} and $\Delta\pi_2 = -1.6 \times 10^3$ cm^{-1} for $(NH_3)_5RuL^{3+}$ for the imidazole pair of ligands. Thus, the interesting result is found that $\Delta\pi_1$ is positive and about 4×10^3 cm^{-1} for the imidazole pair, following the order $N_3CuL^{2+} < (CN)_5FeL^{2-} \sim (NH_3)_5RuL^{3+}$. That is to say the tripositive metal centers shift π_1 of the substituted rings slightly more than does Cu(II). A logical explanation may be conceived on the basis of better overlap of the $\pi_L \rightarrow \pi$d transition of the $(CN)_5FeL^{2-}$ and

(18) Gutterman, D. F.; Gray, H. B. *Inorg. Chem.* **1972**, *11*, 1727–1733.
(19) Hoq, M. F.; Johnson, C. R.; Shepherd, R. E., work in progress.
(20) Curtis, J. C.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 224–236.
(21) (a) Jones, C. M.; Johnson, C. R.; Asher, S. A.; Shepherd, R. E., to be submitted for publication. (b) See also: Walters, M. A.; Spiro, T. G. *Inorg. Chem.* **1983**, *22*, 4014–4017.
(22) Johnson, C. R.; Shepherd, R. E. *Inorg. Chem.* **1983**, *22*, 2439–2444.
(23) Henderson, W. W., work in progress.

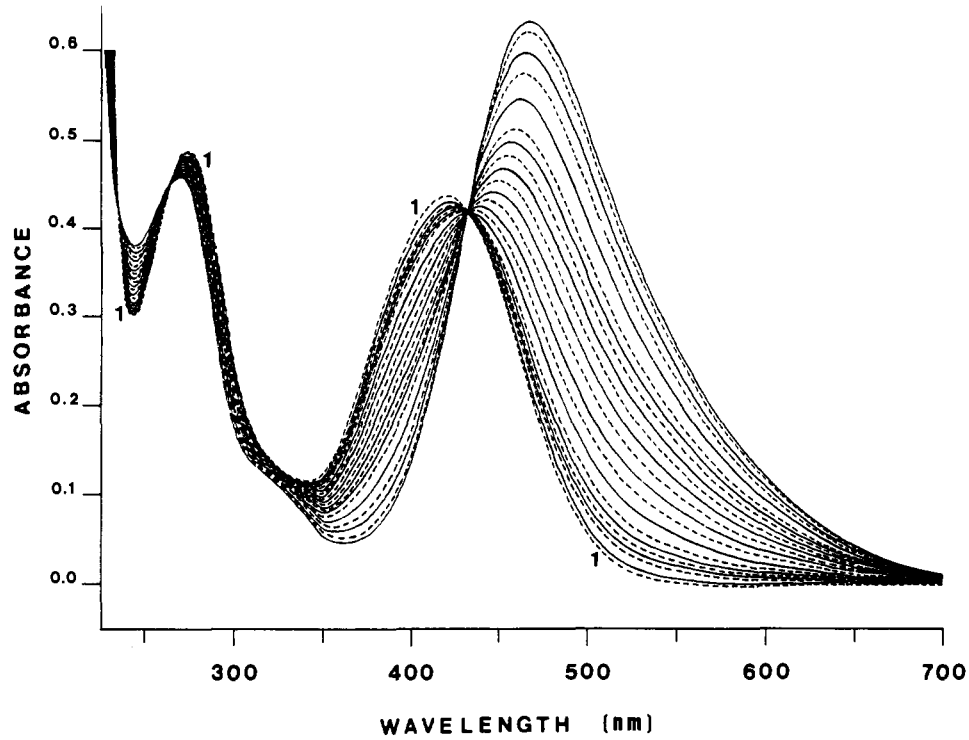

Figure 3. Spectrophotometric titration of $Ru(NH_3)_5(3,5\text{-}Me_2PyzH)^{3+}$ (pH): 4.02, 5.46, 5.91, 6.08, 6.22, 6.33, 6.45, 6.64, 6.79, 6.91, 7.02, 7.13, 7.23, 7.32, 7.42, 7.50, 7.59, 7.80, 8.02, 8.24, 8.60, 9.28. The spectrum at pH 4.02 is marked by 1.

$(NH_3)_5RuL^{2+}$ complexes compared to $\pi_L \rightarrow \sigma d$ for the N_3CuL^{2+} case. The π_2 orbital of the ring is more N-based in character.[15] Therefore, it is logical that shifts of the π_2 level as a function of ring substitution will be less sensitive than for π_1, which involves coefficients of the ring C atoms that are directly attached to substituents and more polarizable than N atoms. Indeed, the values observed for $\Delta\pi_2$ are less than $\Delta\pi_1$ in an absolute sense. Furthermore, the shift of π_2 to higher energy by 0.0×10^3 cm^{-1} for $(CN)_5FeL^{2-}$, 0.8×10^3 cm^{-1} for N_3CuL^{2+}, and 1.6×10^3 cm^{-1} for $(NH_3)_5RuL^{3+}$ follows the intuitive order of true charge on the metal center. The $Fe(CN)_5^{2-}$ moiety has less than the formal 3+ charge on Fe(III) due to the CN^- environment while $(NH_3)_5Ru^{3+}$ and N_3Cu^{2+} will follow the order of their ionic charges since all ligands are neutrals. Finally, the spacing between π_1 and π_2 levels of coordinated 4,5-dimethylimidazole may be noted. Only for R = 4,5-Me_2 or other R groups is π_1 and π_2 separated for the N_3CuL^{2+} complex, while they are more separated for $(CN)_5FeL^{2-}$ and $(NH_3)_5RuL^{3+}$ even for R = H, $\pi_2 - \pi_1$ being 3.7 and 10.2×10^3 cm^{-1} respectively, for L = imidazole. The values for $\pi_2 - \pi_1$ as calculated from the energy differences of LMCT bands is found to be 4.4×10^3 cm^{-1} for N_3CuL^{2+}, 8.0×10^3 cm^{-1} for $(CN)_5FeL^{2-}$, and 12.9×10^3 cm^{-1} for $(NH_3)_5RuL^{3+}$ (L = 4,5-dimethylimidazole). The position of the Fe(III) complex between Cu(II) and Ru(III) may be explained by the advantage of better π overlap and energy match of the 3d (πd) level of low-spin Fe(III) that can shift the $\pi_1 \rightarrow$ Fe(III) transition more effectively than the 3d (σd) level of Cu(II) for more polarizable ligands with R substituents, while combination of orbital symmetry match favoring the $\pi_1 \rightarrow \pi$d transition of Ru(III) is opposed to the influence of raw charge, lowering the energy of π_2 of the ring and increasing the $\pi_2 \rightarrow \pi$d transition. Therefore, the value of $\pi_2 - \pi_1$ will be largest for the R-substituted $Ru(NH_3)_5^{2+}$ complex, but the percentage change is larger for $(CN)_5Fe^{2-}$ compared to the parent imidazole ring.

A reviewer has raised the question as to why the energy of $\pi_1 \rightarrow$ Fe(III) transition decreases from 21.1×10^3 cm^{-1} for imidazole to 20.0×10^3 cm^{-1} for 1,2-dimethylimidazole and 16.8×10^3 cm^{-1} for 4,5-dimethylimidzaole and returns to a higher value of 19.8×10^3 cm^{-1} for 1,2,4,5-tetramethylimidazole. The decreasing energy difference follows the degree of electron-releasing substituents for the first three cases and is logically understood in terms of the previous discussion. The last entry, although it appears anomalous on the basis of electronic effects, may be reconciled if one takes note of the influence of solvatochromism for the $(CN)_5FeL^{2-}$ complexes. This subject is treated for the cases L = imidazole, benzimidazole, 4,5-dimethylbenzimidazole, 2-methylimidazole, and 4-(dimethylamino)pyridine in a separate paper.[42] It is observed in those studies that selective solvation and perturbation of the lone pair region of the imidazole ring will produce hypsochromic shifts of the $\pi_1 \rightarrow$ Fe(III) transition. Thus, the observation is proper as given in Table II.

pK_a Determinations of Coordinated Pyrazoles. One of the effects of coordination of imidazole or pyrazole to a metal ion is that the pyrrole-like nitrogen becomes less basic compared to the free ligand,[1,4,24] A spectrophotometric titration of $(NH_3)_5Ru(3,5\text{-}Me_2PyzH)^{3+}$ is shown in Figure 3. Several isosbestic points are maintained throughout the titration, and the spectral changes are reversible. The methods for the determination of the pK_a from such data have been described previously[4] and are shown in Figure 4. The results are shown in Table V. The small visible spectral changes associated with deprotonation of the coordinated pyrazole of the $(CN)_5Co(PyzH)^{3+}$ complex and its relatively high pK_a made an NMR titration the method of choice for studying this compound. The treatment of these data is shown in Figure 5.

The major effect of the metal center upon the ligand is through σ induction. The positive charge of the metal draws electron density from the ligand, depleting the electron density on the pyrrole nitrogen and lowering the pK_a. Such a σ inductive effect is expected to fall off rapidly with increasing distance of the ionizable proton from the metal ion. On this basis one would predict an order of H_2O > pyrazole > imid-

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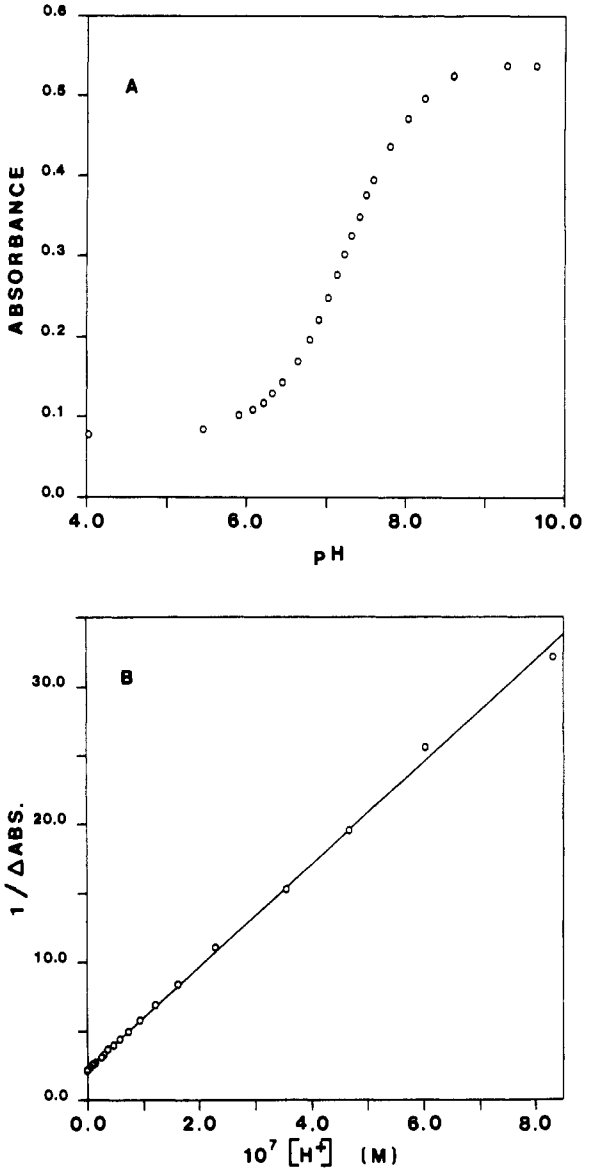


Figure 4. Determination of the pK_a of $(NH_3)_5Ru(3,5\text{-}Me_2PyzH)^{3+}$: (A) spectrophotometric titration at λ = 495 nm; (B) graphical treatment as in ref 4, slope = 3.7×10^7, intercept = 2.29, pK_a = 7.21.

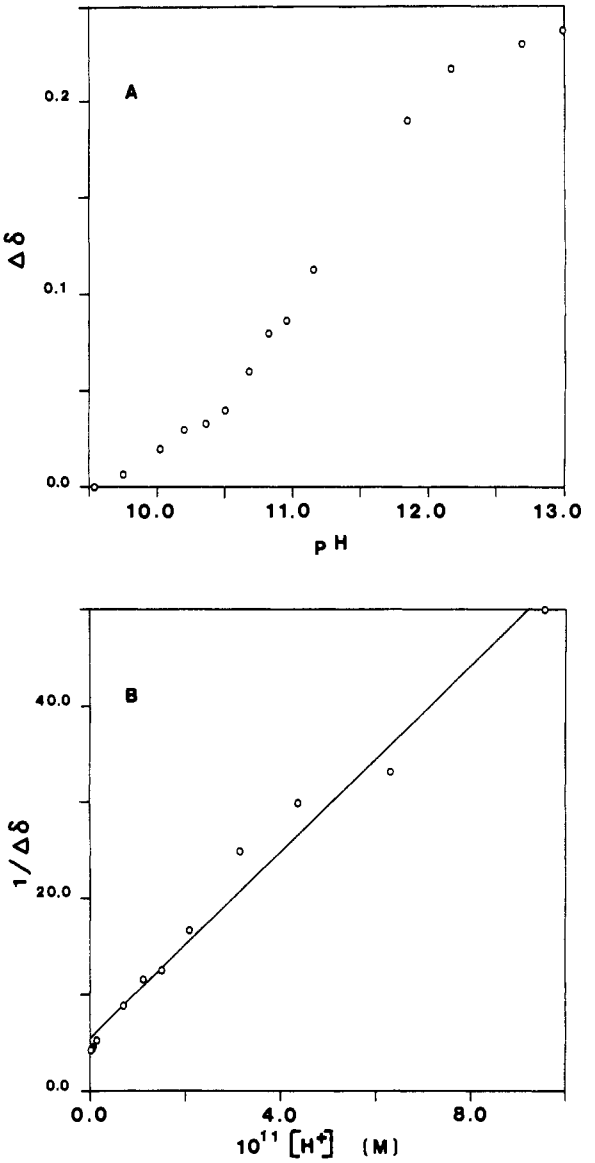


Figure 5. Determination of the pK_a of $(CN)_5Co(PyzH)^{2-}$: (A) $\Delta\delta$ = change in chemical shift of H(4) of the complex; (B) graphical treatment as in ref 4, slope = 4.81×10^{11}, intercept = 5.54, pK_a = 10.9.

Table V. pK_a Values at 25 °C

species	OH_2	PyzH	ImH
free ligand	15.7	14.2[h]	14.2[h]
$(NH_3)_5RuL^{3+}$	4.1[b]	5.98[a]	8.9[c]
$(NH_3)_5CoL^{3+}$	6.4[d]	6.07[a,i]	9.99[a,i]
$(CN)_5FeL^{2-}$	8.4[e]	~11[a]	11.0[f]
$(CN)_5CoL^{2-}$	9.8[g]	10.9[a,i]	~11.4[a,i]
protonated ligand	...	2.5	7.0
$(NH_3)_5Ru(3,5\text{-}Me_2PyzH)^{3+}$		7.21[a]	
$(NH_3)_5Ru(1,2,4\text{-triazole})^{3+}$		~4.3[a]	
$(NH_3)_5Co(3\text{-}MePyzH)^{3+}$		6.7[a]	

[a] This work; μ = 0.10 unless specified. [b] Kuehn, C. G.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98*, 689. Broomhead, J. A.; Basolo, F.; Pearson, R. G. *Inorg. Chem.* **1964**, *3*, 826. [c] Sundberg, R. J.; Bryan, F.; Taylor, I. F.; Taube, H. *J. Am. Chem. Soc.* **1974**, *96*, 381. [d] Harris, S. J.; Tobias, R. S. *Inorg. Chem.* **1968**, *7*, 897. Sillen, L. G.; Martell, A. E. *Spec. Publ.–Chem. Soc.* **1964**, *No. 17*. [e] Espenson, J. H.; Wolenuk, S. G. *Inorg. Chem.* **1972**, *11*, 2034. [f] Reference 4. [g] Haim, A.; Willmarth, W. K. *Inorg. Chem.* **1962**, *1*, 573. [h] Reference 27. [i] μ = 1.00.

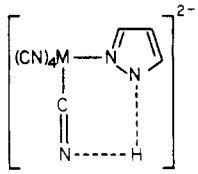
azole for the effect of the metal ion upon the pK_a relative to the free ligand in each case. This trend is seen in Table V. One can conclude that σ donation to pentaammineruthenium(III) and pentaamminecobalt(III) is significant and much greater than donation to pentacyanocobaltate(III) and pentacyanoferrate(III) for the pyrazole complexes. The difference of 5 log units between the values for the two Co(III) complexes indicates the effect of CN^- ions in quenching the positive charge of the metal. Nevertheless, coordination of pyrazole to $Co(CN)_5^{2-}$ and $Fe(CN)_5^{2-}$ still lowers the pK_a by 3 units.

In each case in Table V the trend in increasing enhancement of the ligand acidity follows the order $Co(CN)_5^{2-} \leq Fe(CN)_5^{2-} < Co(NH_3)_5^{3+} < Ru(NH_3)_5^{3+}$.

The trend across a row from one ligand to the next is explained by the distance from the metal center to the ionizable proton. σ-Electron induction falls off rapidly with distance so the effect of σ donation is more pronounced in the aqua complex than in the pyrazole or imidazole complexes. $Ru(NH_3)_5^{3+}$ coordination lowers the pK_a of OH_2 by 11.6 units, pyrazole by 8.2 units, and imidazole by 5.3 units. Similar effects are seen for the other metal ions.

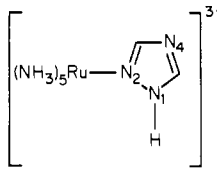
The change in the pK_a's upon coordination of pyrazole or imidazole to $Co(CN)_5^{2-}$ is nearly the same. The pyrazole complexes should have lower pK_a's, but apparently intramolecular hydrogen bonding of the type shown below between

the cyanide ligands and pyrazole increases the stability of the acid form.

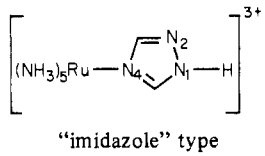


This type of hydrogen bonding has been proposed to account for the high basicity of the bis(pyrazolyl) complex $[Ru(Bipy)_2(Pyz)(PyzH)]^+$.[25]

The pK_a of $Ru(NH_3)_5$(1,2,4-trizole)$^{3+}$ has been determined to be 4.3 (Table V). There are two positions possible for coordination of 1,2,4-triazole to a metal: the 2-position, which is of the "pyrazole" type, and the 4-position, which is of the "imidazole" type.



"pyrazole" type



"imidazole" type

The free ligand 1,2,4-triazole has been reported to have a pK_a equal to 10.26.[26] The effect of aza substitution on pyrrole to give either pyrazole or imidazole is 3.4 pK_a[27] units lower for the pyrrole pK_a, and substitution of a second aza group would be expected to be similar. The difference between the reported values of pyrazole and triazole is 3.9 log units. The change in the acidity of 1,2,4-triazole upon coordination to the $Ru(NH_3)_5^{3+}$ moiety is then $\sim 10^6$. This compares with the 5.3 log unit difference between imidazole and $Ru(NH_3)_5(ImH)^{3+}$ rather than the 8.2 log unit change for pyrazole, suggesting that 1,2,4-triazole is coordinated through N(4).

Also in Table V are the pK_a values for two complexes with methyl-substituted pyrazoles. Methyl is an electron-releasing substituent so one would expect the pK_a of the free ligand to increase with respect to the pK_a of free pyrazole. The complexes $Ru(NH_3)_5(3,5\text{-}Me_2PyzH)^{3+}$ and $Co(NH_3)_5(3\text{-}MePyzH)^{3+}$ do have higher pK_a's than the corresponding pyrazole complexes, but it is unclear as to whether this is a result of the methyl's electronic effect or some steric inhibition, as free-ligand pK_a's are unavailable in the literature. Hoq, Johnson, Paden, and Shepherd[28] have discussed the pK_a values for the 2-methyl- and 4-methyl-substituted imidazoles coordinated to pentaamminecobalt(III) previously. They compared the acidities of the complexes and noted that the basicity increases with proximity to the pyrrole hydrogen. This argues for an electronic explanation, but, again, without accurate free-ligand pK_a's steric effect cannot be properly assessed.

NMR of Coordinated Pyrazoles. Proof of coordination of the pyrazole moiety to the diamagnetic series H^+, $Co(NH_3)_5^{3+}$, $Co(CN)_5^{2-}$, $Ru(NH_3)_5^{2+}$, and $Fe(CN)_5^{3-}$ is readily obtained from the ^1H NMR spectra of the respective complexes. These data are presented in Table VI. The influence of the L_5M group on the ^1H and ^{13}C chemical shifts of imidazoles, pyridines, and pyrazines will be the subject of an extensive, separate paper.[29] However, it is worthwhile to consider the

Table VI. ^1H NMR Data for Pyrazole Complexes

complex[a] (L = PyzH)	chem shift,[b] δ		
	H(3)	H(5)	H(4)
LD^+ [c]	8.27	8.27	6.87
$Co(NH_3)_5L^{3+}$	8.09	7.83	6.68
$Co(CN)_5L^{2-}$ [c]	7.79	7.79	6.46
$Ru(NH_3)_5L^{2+}$	7.90	7.64	6.52
$Fe(CN)_5L^{3-}$	7.60	7.43	6.24
L[c]	7.75	7.75	6.46

complex[a] (L = 3-MePyzH)	chem shift,[b] δ		
	H(5)	H(4)	CH_3(3)
LD^+	8.11	6.63	2.51
$Co(NH_3)_5L^{3+}$	7.61	6.44	2.41
$Fe(CN)_5L^{3-}$	7.56	6.02	2.29
L	7.52	6.11	2.24

[a] Complex is coordinated via N(2). [b] Vs. internal TMPA. [c] H(3) and H(5) are not resolved.

pyrazole series here in that the change in chemical shift, Δδ, for the H(4) ring proton was monitored to determine the pK_a of $(NH_3)_5CoL^{3+}$ (L = pyrazole and 3-methylpyrazole). For comparative purposes, it is worthwhile to compare the pyrazole series to the ^1H data for 1-methylimidazoles. The 1-methylimidazole complexes are reasonably representative cases of the more extensive treatment reserved for imidazoles, pyridines, and pyrazines. Substitution of chemical groups at the carbon positions of imidazole rings introduces some complications that need to be treated in detail.[29] However, the 1-methylimidazole series is close as a model for the pyrazole case as both are five-membered rings of the N_2C_3 type.

The proton NMR spectra of transition-metal complexes with heterocyclic ligands are complex and difficult to interpret. Upon coordination of the ligand to a metal the chemical shifts of the protons on the ligand change, reflecting changes in the electron density in and circulation about the heterocyclic ring. Among the competing effects that have been discussed[2,11,12,30-32] are the temperature-independent paramagnetism of the metal center (TIP), the magnetic anisotropy of the other ligands, changes in the σ-orbital populations in the ring, nuclear quadrupole interactions, and solvent effects. Studies reported thus far suggest that the dominant effect on the chemical shifts will vary depending upon the metal center, the ligand, and the spectator ligands that influence the ligand field strength.

The data from the series of complexes with 1-methylimidazole, pyrazole, and 3-methylpyrazole are best rationalized by considering the σ- and π-charge densities on the ring. Charge densities have been used as the sole justification of the ^1H NMR shifts of (organonitrile)metal complexes $Rh(NH_3)_5(RCN)^{3+}$ and $Ru(NH_3)_5(RCN)^{2+}$,[31] $Fe(CN)_5(ImH)^{3-}$,[2] and pentacyanoruthenate(II) complexes of pyrazine.[11] σ-Charge donation to the metal center removes electron density from the ligand, producing a deshielding effect upon the ring protons. This inductive effect is inversely proportional to distance so that the downfield shift will attenuate at positions remote from the metal. An increase in π density on the ring carbons will cause an upfield shift at the protons attached to those carbons. Therefore, back-bonding from the metal into the ligand π system will cause an upfield change in chemical shift of the ring protons. The π-electron density should be distributed around the ring rather evenly, leading to upfield

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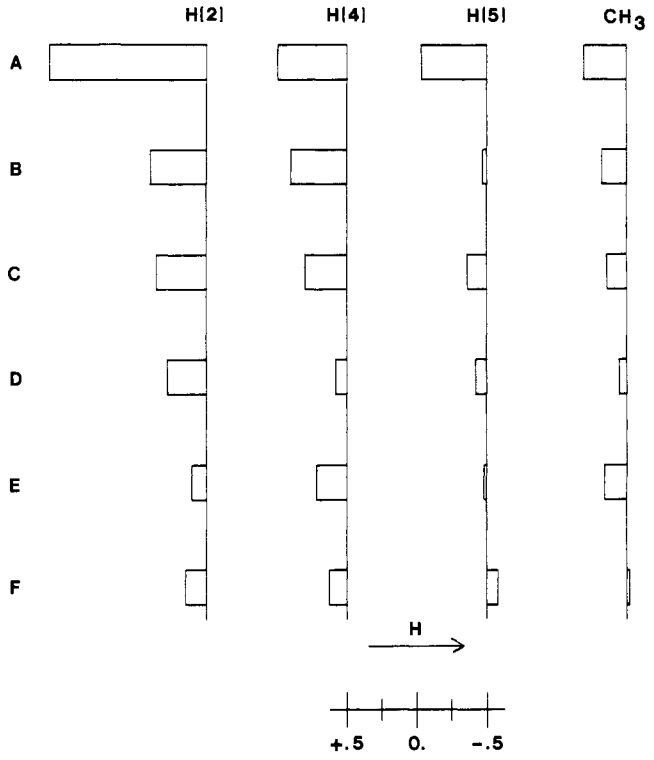

Figure 6. ^{1}H NMR spectral changes of 1-methylimidazole upon complexation (L = 1-methylimidazole): (A) DL^+; (B) $Co(NH_3)_5L^{3+}$; (C) $HgCH_3L^+$; (D) $Co(CN)_5L^{2-}$; (E) $Ru(NH_3)_5L^{2+}$; (F) $Fe(CN)_5L^{3-}$. Shifts are recorded relative to the free ligand with positive shifts downfield, negative shifts upfield (scale is in δ).

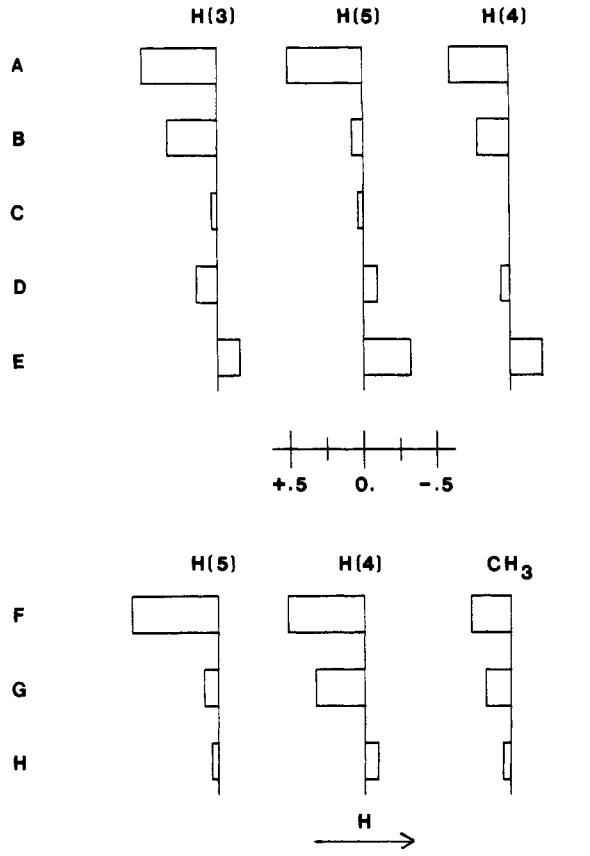

Figure 7. ^{1}H NMR spectral changes of pyrazoles upon complexation: for L = pyrazole, (A) DL^+, (B) $Co(NH_3)_5L^{3+}$, (C) $Co(CN)_5L^{2-}$, (D) $Ru(NH_3)_5L^{2+}$, (E) $Fe(CN)_5L^{3-}$; for L = 3-methylpyrazole, (F) DL^+, (G) $Co(NH_3)_5L^{3+}$, (H) $Fe(CN)_5L^{3-}$.

contributions at all positions. At remote positions, however, the σ effect is small and shielding is expected for metals that have significant π back-bonding to the ligand. The shifts of the adjacent protons reflect the amount of σ donation to the metal but may be influenced more strongly by such effects as temperature-independent paramagnetism and magnetic anisotropy of the ML'_5 moiety.[12,30,32]

All of the chemical shifts for the two protons adjacent to the metal in the 1-methylimidazole complexes are shifted downfield (Figure 6). This indicates significant σ donation for all of these complexes. The chemical shifts of the protons remote from the metal, either H(5) or the CH_3(1) protons, are affected less than the adjacent protons, even to the extent of moving upfield for the $Fe(CN)_5^{3-}$ complex. By considering the position of the H(5) resonance as a measure of π back-bonding in the 1-methylimidazole complexes, the π back-bonding increases in the order $H^+ < HgCH_3^+ < Co(CN)_5^{2-} < Co(NH_3)_5^{3+} < Ru(NH_3)_5^{2+} < Fe(CN)_5^{3-}$.

The adjacent proton in pyrazole (H(3)) is not shifted downfield as much as those adjacent to the metal in the 1-methylimidazole series (Figure 7). This is reasonable since the substituted imidazole is a better σ donor than pyrazole. π back-bonding to the ligand or the TIP influence then becomes important even at adjacent positions, and thus the H(3) resonance in $Fe(CN)_5^{3-}$ is upfield relative to the free ligand. The trend at remote positions is the same (resonances are more shielded by π donation), and if the resonances of the H(5) proton or the H(4) proton are compared, the trend of increasing amounts or π back-bonding of the metal center toward pyrazoles is observed to be $H^+ < Co(NH_3)_5^{3+} < Co(CN)_5^{2-} < Ru(NH_3)_5^{2+} < Fe(CN)_5^{3-}$.

The shift data for the 3-methylpyrazole complexes also follows the order $H^+ < Co(NH_3)_5^{3+} < Fe(CN)_5^{3-}$.

The H(4) resonance of $(CN)_5Co(Pyz)^{3-}$ is downfield of $(CN)_5Co(PyzH)^{2-}$ by δ 0.23. The change in chemical shift in forming the pyrazolate is not as great as the difference produced at H(4) by changes in nature of the L_5M coordinating complex or by H^+, but the downfield shift is in the direction required by greater delocalization in the ring structure of the pyrazolate form.

Conclusion

The behavior of imidazoles and pyrazoles toward low-spin d^5 metal centers is similar. Both exhibit LMCT transitions that may be related to the energies of the HOMO's of the rings with the $Fe(CN)_5L^{2-}$ LMCT at lower energies than $Ru(NH_3)_5L^{3+}$. The influence of coordination of a metal center (L_5M unit = $Ru(NH_3)_5^{2+}$, $Fe(CN)_5^{3-}$, $Co(NH_3)_5^{3+}$, $Co(CN)_5^{2-}$) produces similar effects on the ^{1}H chemical shifts of coordinated imidazoles and pyrazoles, with slightly larger sensitivity for imidazoles; the net effect of coordination of any of these is a complex function of σ withdrawal by the positive metal center, π donation by the L_5M moiety, temperature-independent paramagnetism, and magnetic anisotropy of the other ligands. Deprotonation of the pyrrole hydrogen is enhanced for either coordinated pyrazoles or imidazoles. The pK_a's of coordinated imidazoles and pyrazoles are influenced by 5.3 and 8.2 orders of magnitude, respectively, when these ligands are coordinated to the $(NH_3)_5Ru^{3+}$ center, the moiety that shows the largest enhancement. This is compatible with the view that the anion form (imidazolate and pyrazolate) enters into considerable π donation toward a low-spin d^5 center and that this factor dramatically outweighs the influence of the charge/size ratio of the ions for M(III) = Fe(III), Ru(III), Os(III), Co(III), Rh(III), and Ir(III).[33] For the cases of

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cationic complexes, the closer distance of the pyrrole hydrogen for coordinated pyrazoles vs. imidazoles is manifested in about an additional 3 orders of magnitude decrease in the pK_a of the pyrazole complexes with the same center ($Ru(NH_3)_5^{3+}$ and $Co(NH_3)_5^{3+}$). Imidazoles are stronger σ donors than the pyrazoles; thus, when the 1,2,4-triazole ligand coordinates with $Ru(NH_3)_5^{3+}$, the linkage isomer that is observed in solution is found to be the N(4) or "imidazole-like" coordination as assessed by the net change in the pK_a of $(NH_3)_5Ru$(1,2,4-triazole)$^{3+}$ compared to the free ligand.

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Registry No. $(CN)_5Fe^{III}L$ (L = pyrazole), 91208-81-0; $(CN)_5Fe^{III}$ (L = pyrazolate), 91208-82-1; $(CN)_5Fe^{III}L$ (L = 1,2,4-triazole), 91208-84-3; $(CN)_5Fe^{III}L$ (L = 3,5-dimethylpyrazole), 91208-86-5; $(CN)_5Fe^{III}L$ (L = 3,5-dimethylpyrazolate), 91208-87-6; $(CN)_5Fe^{III}L$ (L = indazole), 91208-89-8; $(CN)_5Fe^{III}L$ (L = 4-methylpyrazole), 91208-91-2; $(CN)_5Fe^{III}L$ (L = 4-methoxypyrazolate), 91208-93-4; $(CN)_5Fe^{III}L$ (L = 3-methylpyrazole), 91208-95-6; $(CN)_5Fe^{III}L$ (L = 3-methylpyrazolate), 91208-97-8; $(CN)_5Fe^{III}L$ (L = imidazole), 61332-60-3; $(CN)_5Fe^{III}L$ (L = 1-methylimidazole), 74353-97-2; $(CN)_5Fe^{III}L$ (L = 2-methylimidazole), 74354-02-2; $(CN)_5Fe^{III}L$ (L = 4(5)-methylimidazole), 91209-00-6; $(CN)_5Fe^{III}L$ (L = 1,2-dimethylimidazole), 91209-02-8; $(CN)_5Fe^{III}L$ (L = 2,4-dimethylimidazole), 91209-03-9; $(CN)_5Fe^{III}L$ (L = 4,5-dimethylimidazole), 91209-04-0; $(CN)_5Fe^{III}L$ (L = imidazolate), 74353-96-1; $(CN)_5Fe^{III}L$ (L = 2-methylimidazolate), 91209-07-3; $(CN)_5Fe^{III}L$ (L = 4-methylimidazolate), 91209-09-5; $(CN)_5Fe^{III}L$ (L = 1-vinylimidazole), 91209-12-0; $(CN)_5Fe^{III}L$ (L = 1-benzylimidazole), 91209-13-1; $(CN)_5Fe^{III}L$ (L = 4-phenylimidazole), 91209-14-2; $(CN)_5Fe^{III}L$ (L = 4-imidazoleacetate), 91209-15-3; $(CN)_5Fe^{III}L$ (L = 4-imidazoleacrylate), 91209-16-4; $(CN)_5Fe^{III}L$ (L = 1,2,4,5-tetramethylimidazole), 91209-17-5; $(CN)_5Fe^{III}L$ (L = urocanic acid), 91209-18-6; $(CN)_5Fe^{III}L$ (L = *l*-β-imidazolelactic acid), 91209-19-7; $(CN)_5Fe^{III}L$ (L = benzimidazole), 91209-20-0; $(CN)_5Fe^{III}L$ (L = 2-methylbenzimidazole), 91209-21-1; $(CN)_5Fe^{III}L$ (L = 2-phenylbenzimidazole), 91209-22-2; $(CN)_5Fe^{III}L$ (L = 1-methyl-2-phenylbenzimidazole), 91209-23-3; $(CN)_5Fe^{III}L$ (L = 1-ethyl-2-methylbenzimidazole), 91209-24-4; $(CN)_5Fe^{III}L$ (L = 5,6-dimethylbenzimidazole), 91209-25-5; $(CN)_5Fe^{III}L$ (L = benzimidazolate), 91209-26-6; $(CN)_5Fe^{III}L$ (L = 5,6-dimethylbenzimidazolate), 91209-28-8; $(CN)_5Fe^{III}L$ (L = thiazole), 91209-29-9; $(CN)_5Fe^{III}L$ (L = 4-aminopyridine), 76231-04-4; $(CN)_5Fe^{III}L$ (L = 4-(dimethylamino)pyridine), 91209-30-2; $(CN)_5Fe^{III}L$ (L = 2-aminopyridine), 91209-32-4; $(CN)_5Fe^{III}L$ (L = 3-aminopyridine), 91209-34-6; $Fe(CN)_6^{3-}$, 13408-62-3; $(CN)_5Fe^{III}L$ (L = hypoxanthine), 91209-35-7; $(CN)_5Fe^{III}L$ (L = 9-*H*-hypoxanthine), 91209-37-9; $(CN)_5Fe^{III}L$ (L = caffeine), 91209-38-0; $(CN)_5Fe^{III}L$ (L = histamine), 91209-39-1; $(CN)_5Fe^{III}L$ (L = histidine), 88181-56-0; $(CN)_5Fe^{III}L$ (L = *N*-*tert*-butoxycarbonyl-*l*-histidine), 91209-40-4; $(CN)_5Fe^{III}L$ (L = 1-methylhistidine), 91209-41-5; $(CN)_5Fe^{III}L$ (L = histidinate), 91209-42-6; $(CN)_5Fe^{III}L$ (L = 4-methylpyridine), 61332-61-4; $(CN)_5Fe^{III}L$ (L = pyridine), 61332-63-6; $(CN)_5Fe^{III}L$ (L = isonicotinamide), 61332-64-7; $(CN)_5Fe^{III}L$ (L = pyrazine), 61332-65-8; $(CN)_5Fe^{III}L$ (L = *N*-methylpyrazinium), 61363-44-8; $(CN)_5Fe^{III}L$ (L = pyridazine), 87350-56-9; $(CN)_5Fe^{III}L$ (L = 2-methylpyrazine), 91209-53-9; $(CN)_5Fe^{III}L$ (L = 4-cyanopyridine), 91209-54-0; $(CN)_5Fe^{III}L$ (L = ammonia), 19413-98-0; $(CN)_5Fe^{III}L$ (L = water), 19413-97-9; $Fe(CN)_5(PyzH)^{3-}$, 74657-56-0; $Ru(NH_3)_5(PyzH)^{2+}$, 91209-57-3; $(NH_3)_5Ru^{III}L$ (L = pyrazole), 80593-48-2; $(NH_3)_5Ru^{III}L$ (L = pyrazolate), 91208-83-2; $(NH_3)_5Ru^{III}L$ (L = 1,2,4-triazole), 91208-85-4; $(NH_3)_5Ru^{III}L$ (L = 3,5-dimethylpyrazolate), 91208-88-7; $(NH_3)_5Ru^{III}L$ (L = indazole), 91208-90-1; $(NH_3)_5Ru^{III}L$ (L = 4-methylpyrazole), 91208-92-3; $(NH_3)_5Ru^{III}L$ (L = 4-methylpyrazolate), 91208-94-5; $(NH_3)_5Ru^{III}L$ (L = 3-methylpyrazole), 91208-96-7; $(NH_3)_5Ru^{III}L$ (L = 3-methylpyrazolate), 91208-98-9; $(NH_3)_5Ru^{III}L$ (L = imidazole), 80593-52-8; $(NH_3)_5Ru^{III}L$ (L = 1-methylimidazole), 81802-55-3; $(NH_3)_5Ru^{III}L$ (L = 2-methylimidazole), 91208-99-0; $(NH_3)_5Ru^{III}L$ (L = 4-methylimidazole), 91209-01-7; $(NH_3)_5Ru^{III}L$ (L = 4,5-dimethylimidazole), 91209-05-1; $(NH_3)_5Ru^{III}L$ (L = imidazolate), 91209-06-2; $(NH_3)_5Ru^{III}L$ (L = 2-methylimidazolate), 91209-08-4; $(NH_3)_5Ru^{III}L$ (L = 4-methylimidazolate), 91209-10-8; $(NH_3)_5Ru^{III}L$ (L = 4,5-dimethylimidazolate), 91209-11-9; $(NH_3)_5Ru^{III}L$ (L = benzimidazole), 81802-40-6; $(NH_3)_5Ru^{III}L$ (L = benzimidazolate), 91209-27-7; $(NH_3)_5Ru^{III}L$ (L = 4-aminopyridine), 78064-35-4; $(NH_3)_5Ru^{III}L$ (L = 4-(dimethylamino)pyridine), 91209-31-3; $(NH_3)_5Ru^{III}L$ (L = 2-aminopyridine), 91209-33-5; $(NH_3)_5Ru^{III}L$ (L = hypoxanthine), 91209-36-8; $(NH_3)_5Ru^{III}L$ (L = 9-*H*-hypoxanthine), 82512-04-7; $(NH_3)_5Ru^{III}L$ (L = histidine), 77760-96-4; $(NH_3)_5Ru^{III}L$ (L = histidinate), 85040-79-5; $(NH_3)_5Ru(3,5\text{-}Me_2PyzH)^{3+}$, 80593-50-6; $Fe(CN)_5(3\text{-}MePyzH)^{3-}$, 74657-57-1; $(NH_3)_5Co(ImH)^{3+}$, 38716-02-8; $(NH_3)_5Co(Im)^{2+}$, 61159-81-7; $(NH_3)_5Co(1\text{-}MeIm)^{3+}$, 91209-43-7; $(NH_3)_5Co(2\text{-}MeImH)^{3+}$, 89955-97-5; $(NH_3)_5Co(2\text{-}MeIm)^{2+}$, 91209-44-8; $(NH_3)_5Co(1,2\text{-}Me_2Im)^{3+}$, 91209-45-9; $(NH_3)_5Co(PyzH)^{3+}$, 38716-02-8; $(NH_3)_5Co(Pyz)^{2+}$, 61159-81-7; $(CN)_5Co(ImH)^{2-}$, 91209-46-0; $(CN)_5Co(Im)^{3-}$, 91209-47-1; $(CN)_5Co(1\text{-}MeIm)^{2-}$, 91209-48-2; $(CN)_5Co(2\text{-}MeImH)^{2-}$, 91209-49-3; $(CN)_5Co(1,2\text{-}Me_2Im)^{2-}$, 91209-50-6; $(CN)_5Co(bnzImH)^{2-}$, 91209-51-7; $(CN)_5Co(bnzIm)^{3-}$, 91209-52-8; $(CN)_5Co(pz)^{2-}$, 64915-93-1; $(CN)_5Co(PyzH)^{2-}$, 91209-55-1; $(NH_3)_5Co(3\text{-}MePyzH)^{3+}$, 91209-56-2; pyrazole, 288-13-1; imidazole, 288-32-4; 3,5-dimethylpyrazole, 67-51-6; 1,2,4-triazole, 288-88-0; 3-methylpyrazole, 1453-58-3.

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