5:1 for photolysis of *cis*-$Ru(en)_2Cl_2^+$. These predictions are very well confirmed by the experimental results, summarized in eq 1.

It should be noted that our predictions are largely independent of the specific parameter values, the only critical factor being the ratio of LF strength vs. interelectronic repulsion. If the LF strength decreases, a quartet ground state would tend to be favored in the TBP structure, inducing increased stereoretention in the photosubstitution process.

In conclusion, the present LF model points to important differences in the electronic structure of excited states in d^5 and d^6 systems; application of one and the same photostereochemical model appears inappropriate. A different role of the electronic selection rules and the nonexistence of a thexi state in the RuN_4Cl^{2+} fragment are suggested as new characteristic features of Ru(III) photochemistry. A critical evaluation of these proposals in future experimental work is most desirable.

Acknowledgment. The authors are indebted to the Belgian Government (Programmatie van het Wetenschapsbeleid).

Registry No. *cis*-$Ru(en)_2Cl_2^+$, 38687-00-2; *trans*-$Ru(en)_2Cl_2^+$, 45839-20-1; Ru, 7440-18-8.

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(27) The three TBP distortions resulting in a SPY can be characterized by the one equatorial ligand that becomes apical. See also: Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions", 2nd ed.; Wiley: New York, 1967; p 250.

Contribution from the Department of Chemistry,
University of Pittsburgh, Pittsburgh, Pennsylvania 15260

The pK_a of Pyraziniumpentacyanoruthenate(II), $(CN)_5Ru(pzH)^{2-}$

CRAIG R. JOHNSON and REX E. SHEPHERD*

Received August 5, 1982

The synthesis and characterization of $(CN)_5Ru(pz)^{3-}$ (pz = pyrazine) and its N-methylated derivative, $(CN)_5Ru(pzCH_3)^{2-}$, are described. The proton NMR spectra of pz or $pzCH_3^+$ coordinated to $(NH_3)_5Ru^{2+}$, $(CN)_5Ru^{3-}$, $(CN)_5Fe^{3-}$, and $(CN)_5Co^{2-}$ are discussed. The effective pK_a's of $(CN)_5Ru(pzH)^{2-}$ and $(CN)_5Fe(pzH)^{2-}$ have been measured by spectrophotometric titration as 0.4 ± 0.1 and 0.065 ± 0.06 in contrast with 2.85 ± 0.1 for $(NH_3)_5Ru(pzH)^{3+}$. The influence of CN^- on π back-bonding as compared to that of NH_3 is discussed for complexes of the Fe(II), Ru(II), and Os(II) triad.

The parallels between the spectral properties and chemical reactivities of $(CN)_5FeL^{3-}$ and $(NH_3)_5RuL^{2+}$ complexes (L = aromatic nitrogen heterocycle) have been well documented.[1-3] It has become clear that π back-bonding from the metal to the ligand (L) is important for these low-spin d^6 complexes. The determination of the pK_a of the coordinated pyrazinium ion (pzH^+) has been used to evaluate the back-bonding capability of the metal centers in such complexes. The complexes of pyrazine with $(CN)_5Fe^{3-}$,[1] $(NH_3)_5Ru^{2+}$,[4] and $(NH_3)_5Os^{2+}$[5] have been examined in this regard. Direct comparison of results within the group is hindered by the requirement for a very strong-field ligand (CN^-) to maintain low-spin Fe(II). In order to explore more fully the effect of CN^- on the back-bonding capability of the metal toward the sixth ligand (L), we have prepared a series of $(CN)_5RuL^{3-}$ complexes (L = pyridine, pyrazine (pz), imidazole, pyrazole, and their derivatives).[6] The results of a study of $(CN)_5Ru(pz)^{3-}$ are reported here.

The pyrazine ligand has been important in the development of the chemistry of the $(NH_3)_5RuL^{2+}$ series. The classic experiment of Ford, Rudd, Gaunder, and Taube[4] in determining the pK_a of $(NH_3)_5Ru(pzH)^{3+}$ and the subsequent syntheses of the Creutz–Taube ions,[7] $[(NH_3)_5Ru(pz)Ru(NH_3)_5]^{4+,5+,6+}$, are illustrative of this point. In this paper we report the pK_a's for $(CN)_5Ru(pzH)^{2-}$ and $(CN)_5Fe(pzH)^{2-}$. The results reveal a dramatic influence of CN^- vs. NH_3 in competition with pyrazine for back-donation from Ru(II). A rich chemistry analogous to that found for the $(NH_3)_5RuL^{2+}$ series is suggested for the $(CN)_5RuL^{3-}$ complexes.

Experimental Section

Materials. Aldrich Gold Label pyrazine was used in the syntheses of the complexes. Potassium hexacyanoruthenate(II) trihydrate was used as received from Alfa. *N*-methylpyrazinium iodide was prepared by a literature method.[8] Other chemicals were reagent grade.

Preparation of the Pyrazine Complexes. The preparations of $Na_3[(CN)_5Fepz]\cdot 4H_2O$,[1] $Na_2[(CN)_5Fepz]\cdot xH_2O$,[9] $K_2[(CN)_5Co(pz)]$,[8] and $[(NH_3)_5Ru(pz)](ClO_4)_2$[10] were carried out according to literature procedures with only minor modifications. All complexes were dried and stored under vacuum.

$K_3(CN)_5Ru(pz)\cdot xH_2O$. In a typical preparation, 0.0468 g (0.1 mmol) of $K_4[Ru(CN)_6]\cdot 3H_2O$ was dissolved in 10 mL of water. Pyrazine, 0.08 g (1 mmol), was added. While the mixture was stirred, 10 mL of Br_2 water (0.01 M Br_2, 0.1 M KBr) was added slowly. The reaction of Br_2 with $Ru(CN)_6^{4-}$ is rapid and produces the pale yellow color of $(CN)_5RuOH_2^{3-}$ (λ_{max} = 310 nm). One hour was allowed for the reaction with pyrazine to become complete. As $(CN)_5Ru(pz)^{3-}$ is produced, the yellow color of the solution intensifies. The reaction was checked for completion spectrophotometrically. Upon completion, the solution was chilled in an ice/water bath and the product was precipitated by the addition of cold acetone or a 50/50/ (v/v) mixture

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(1) Toma, H. E.; Malin, J. M. *Inorg. Chem.* **1973**, *12*, 1039–1045.
(2) Taube, H. *Pure Appl. Chem.* **1979**, *51*, 901–912.
(3) (a) Toma, H. E.; Malin, J. M. *Inorg. Chem.* **1973**, *12*, 2080–2083. (b) Allen, R. J.; Ford, P. C. *Ibid.* **1972**, *11*, 679–685. (c) Shepherd, R. E.; Taube, H. *Ibid.* **1973**, *12*, 1392–1401.
(4) Ford, P.; Rudd, D. P.; Gaunder, R.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1187–1194.
(5) Sen, J.; Taube, H. *Acta Chem. Scand., Ser. A* **1979**, *A33*, 125–135.
(6) Other aspects of this work will be reported in future publications. A preliminary report was presented at the 183rd National Meeting of the American Chemical Society, Las Vegas, NV, April 1982.
(7) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1969**, *91*, 3988–3989.
(8) Figard, J. E.; Paukstelis, J. V.; Byrne, E. F.; Petersen, J. D. *J. Am. Chem. Soc.* **1977**, *99*, 8417–8425.
(9) Felix, F.; Ludi, A. *Inorg. Chem.* **1978**, *17*, 1782–1790. The Fe(III) monomer was synthesized by a procedure similar to that described for the dimer, $Na_4[(CN)_5Fe(pz)Fe(CN)_5]$, in this paper. Cl_2, rather than bromine, was used as the oxidant. Excess pz was employed.
(10) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1973**, *95*, 1086–1094.

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of ethanol and diethyl ether. The precipitation is difficult to induce and must be forced with many volumes of the solvent. The yellow precipitate was collected on a glass frit and washed several times with diethyl ether. The product was dried by vacuum desiccation and stored under vacuum. The $K_3[(CN)_5Ru(pz)]\cdot xH_2O$ used for the IR measurements and some of the titration experiments was obtained from a second precipitation, by dissolving the salt in a minimum amount of water and reprecipitating as above. This procedure resulted in a considerable loss of product and no detectable increase in purity.

In some preparations, 0.01 M Br_2 in methanol was used in place of the Br_2 water. In these cases, precipitation of the product was found to be very difficult to induce. The presence of KBr in the Br_2 water is useful, not only in solubilizing the Br_2 but also in precipitating the $K_3[(CN)_5Ru(pz)]\cdot xH_2O$. KBr was not present in the Br_2/CH_3OH solution.

The product was identified as $K_3[(CN)_5Ru(pz)]\cdot xH_2O$ by UV-visible, IR, and NMR spectroscopy (vide infra). Elemental analysis was not performed because problems with the analyses of CN^- complexes have been noted elsewhere.[11] The number of waters of hydration seems to vary with the method and conditions of the preparation. Heating to drive off the water was avoided due to fear of decomposition at elevated temperatures. A crystalline product could not be obtained.

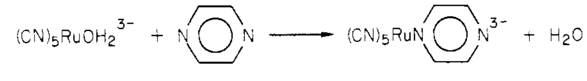
Spectra. IR spectra were taken in KBr pellets on a Beckman Acculab-4 instrument. Since perchlorate salts are potentially explosive, the following procedure was used to avoid grinding and pressing $[(NH_3)_5Ru(pz)](ClO_4)_2$. The Br^- salt was formed by dissolving $[(NH_3)_5Ru(pz)](ClO_4)_2$ in a small amount of a saturated solution of KBr. $KClO_4$ was removed by filtration. The solution was taken to dryness by rotary evaporation followed by vacuum desiccation. The $[(NH_3)_5Ru(pz)]Br_2/KBr$ mixture was then pressed into a pellet for the IR spectrum. NMR spectra were obtained on either a Varian EM-360 or EM-390 instrument at ambient probe temperatures. Chemical shifts were referenced to 3-(trimethylsilyl)propionate (TMPA) as an internal standard. All NMR spectra were of solutions of the complexes in D_2O. UV-visible spectra were recorded with a Varian-Cary 118C spectrophotometer.

Determination of pK_a. The pK_a's of the complexes were determined by spectrophotometric titration. Solutions containing identical aliquots of the complex and varying concentrations of HCl or $HClO_4$ were prepared. The UV-visible spectrum of each solution was obtained quickly after adding the acid and diluting to volume, with allowance for only a brief period for equilibration to room temperature (23 °C). A repeat spectrum was taken for solutions at high acid concentration to insure that the complex was sufficiently stable under these conditions for obtaining reliable absorbance data. The acid dissociation constant was determined for the absorbance vs. $[H^+]$ data by several graphical and numerical methods as described in the Results section. After 1 day at higher acidities changes in the spectra are observed.

Results

The synthesis of $(CN)_5RuL^{3-}$ complexes has eluded previous attempts.[12,13] In contrast to the large volume of work on cyanide complexes of Fe(II) and Fe(III), much less is known about cyanide complexes of Ru(II) and Ru(III).[12] The synthetic route to $(CN)_5Ru(pz)^{3-}$ is shown by eq 1 and 2. Reaction 1 has been reported previously[14] but appears not to have been utilized in the synthesis of complexes of the type reported here. $(CN)_5RuOH^{3-}$ provides a more labile coordination site on the Ru(II) and allows for incorporation of the nitrogen heterocycle as in eq 2.

$$Ru(CN)_6^{4-} + Br_2 \xrightarrow{H_2O} (CN)_5RuOH_2^{3-} + BrCN + Br^- \quad (1)$$



(2)

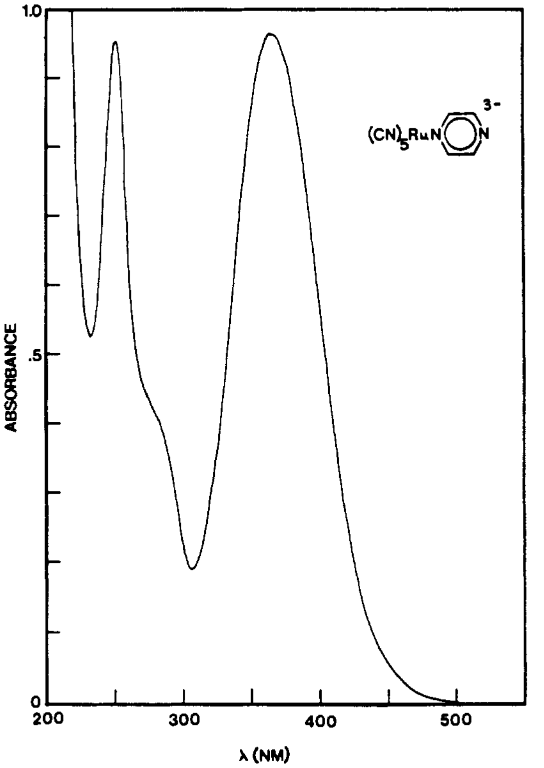


Figure 1. UV-visible absorption spectrum of $(CN)_5Ru(pz)^{3-}$.

It is of interest to note that the reaction of $Fe(CN)_6^{4-}$ with Br_2 results in primarily the oxidation of the Fe(II) center.[15] A greater π interaction between Ru(II) and CN^- than between Fe(II) and CN^- is proposed to account for the preferential atom-transfer path and the resulting aquation in the $Ru(CN)_6^{4-}$ case. The reaction of Br_2 with $Ru(CN)_6^{4-}$ is rapid and produces the yellow color of $(CN)_5RuOH_2^{3-}$ ($\lambda_{max} = 310$ nm). The subsequent reaction with pyrazine causes the pale yellow solution to become much darker yellow as a more intense band grows in at 368 nm. The spectrum of $(CN)_5Ru(pz)^{3-}$ is shown in Figure 1. In analogy to the case for $(CN)_5Fe(pz)^{3-}$ and $(NH_3)_5Ru(pz)^{2+}$, the absorption at 368 nm is assigned to a metal-to-ligand charge-transfer (MLCT) transition. An additional band at 252 nm is assigned as an intraligand ($\pi^* \leftarrow \pi$) transition centered on the coordinated pyrazine. An unresolved shoulder is evident at ~282 nm. This feature may be due to a ligand field (d ← d) transition. A corresponding band is not observed for $(CN)_5Fe(pz)^{3-}$ or $(NH_3)_5Ru(pz)^{2+}$. Approximate molar absorptivities were determined as $\epsilon_{368} = 4.2 \times 10^3\ M^{-1}\ cm^{-1}$ and $\epsilon_{252} = 4.1 \times 10^3\ M^{-1}\ cm^{-1}$.

When strong acid is added to a solution of $(CN)_5Ru(pz)^{3-}$, changes in the electronic spectrum occur as shown in Figure 2B. This series of spectra may be compared to the less complicated absorbance changes that occur upon the acidification of a $(NH_3)_5Ru(pz)^{2+}$ solution (Figure 2A). When $(NH_3)_5Ru(pz)^{2+}$ is titrated with acid, the coordinated pyrazine is protonated (eq 3). The intraligand transition shifts from 250 to 266 nm with an isosbestic point at 262 nm. The MLCT band shifts from 472 to 529 nm with an isosbestic point at 487 nm. The lower energy of this transition upon protonation is consistent with the MLCT nature of the absorption. The isosbestic points verify the presence of only two species in equilibrium.

$$(NH_3)_5Ru(pz)^{2+} + H_3O^+ \rightarrow (NH_3)_5Ru(pzH)^{3+} + H_2O \quad (3)$$

---

[11] Wohlers, H. D.; Van Tassel, K. D.; Bowerman, B. A.; Petersen, J. D. *Inorg. Chem.* **1980**, *19*, 2837–2838.

[12] Sharpe, A. G. "The Chemistry of Cyano Complexes of the Transition Metals"; Academic Press: New York, 1976; Chapter VII.

[13] Vogler, A., personal communication, Universitat Regensburg, FRG, 1982.

[14] Legros, J. *C.R. Hebd. Seances Acad. Sci.* **1959**, *248*, 1339–1342.

[15] Briggs, S. H. C. *J. Chem. Soc.* **1920**, 1026–1034.

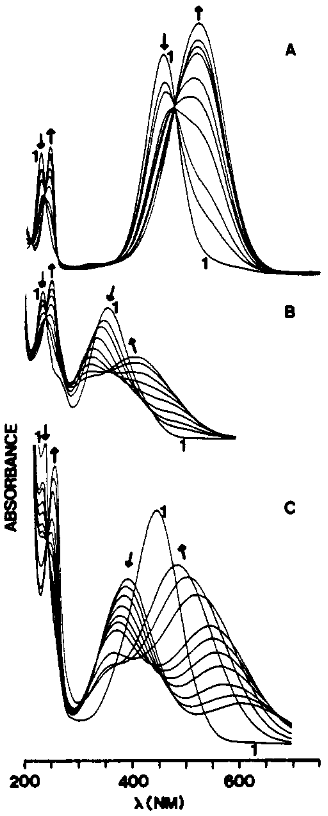


Figure 2. Spectrophotometric titrations of pyrazine complexes: (A) $(NH_3)_5Ru(pz)^{2+}$, $[H^+]$ (10^{-3} M) = 0.0, 0.218, 0.545, 1.09, 2.18, 5.45, 7.63, 10.9, 54.5, 218; (B) $(CN)_5Ru(pz)^{3-}$, $[H^+]$ (M) = 0.0, 0.05, 0.10, 0.25, 0.50, 0.75, 1.00, 1.25, 1.50; (C) $(CN)_5Fe(pz)^{3-}$, $[H^+]$ (M) = 0.0, 0.05, 0.10, 0.20, 0.40, 0.60, 0.90, 1.20, 2.40, 3.60, 4.80. $[H^+]$ is the total concentration of acid added. The spectrum at $[H^+]$ = 0.0 is marked by "1". The arrows indicate the direction of absorbance changes as acid is added.

In contrast, titration of $(CN)_5Ru(pz)^{3-}$ does not produce an isosbestic point in the visible region. Addition of acid to a $(CN)_5Ru(pz)^{3-}$ solution causes the MLCT band at 368 nm to shift toward higher energy. Another hand appears on the low-energy side (~490 nm) of the original MLCT band. This new band also shifts back to higher energy as more acid is added. Unlike $(NH_3)_5Ru(pz)^{2+}$, $(CN)_5Ru(pz)^{3-}$ offers two potential sites for protonation–pyrazine or cyanide. The absorbance changes are consistent with the equilibria shown in eq 4. The position of the MLCT transition is indicated next

$$\begin{tikzcd}
\text{(CN)}_5\text{Ru(pz)}^{3-}\ (368\ \text{nm}) + \text{H}^+ \arrow[r, shift left, "(4a)"] \arrow[d, shift left] & \text{(CN)}_5\text{Ru(pzH)}^{2-}\ ({\sim}490\ \text{nm}) \arrow[l, shift left] \arrow[d, shift left] \\
\text{HCN(CN)}_4\text{Ru(pz)}^{2-}\ ({\sim}330\ \text{nm}) + \text{H}^+ \arrow[u, shift left, "+\text{H}^+"] \arrow[r, shift left, "(4b)"] & \text{HCN(CN)}_4\text{Ru(pz)H}^{+}\ ({\sim}390\ \text{nm}) \arrow[l, shift left] \arrow[u, shift left, "+\text{H}^+"] \arrow[d, "+\text{H}^+"] \\
& \text{further protonation}
\end{tikzcd} \tag{4}$$

to each of the species in eq 4. Protonation of cyanide is known to shift the MLCT to higher energy.[1] The equilibria in eq 4 overlap, and the four species shown are all present during the course of the titration. This explains the lack of an isosbestic point in the visible region. The absorbance data can still be analyzed by the usual methods, however, because an isosbestic point (258 nm) is observed in the ultraviolet region where the coordinated pyrazine absorbs. The energy of the intraligand absorption is not sensitive to protonation on cyanide and changes only when the coordinated pyrazine is protonated.

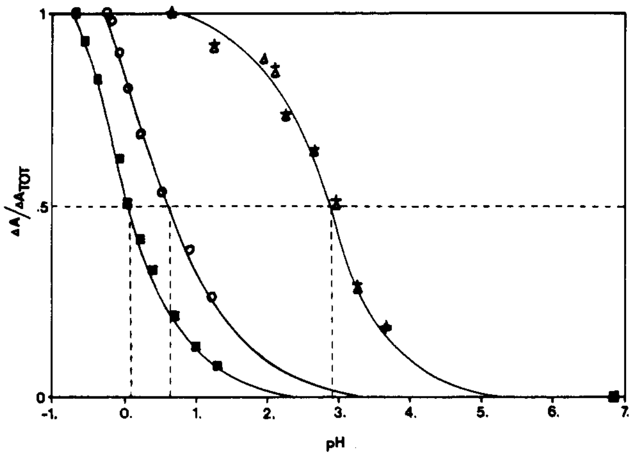


Figure 3. Determination of the pK_a's of pyrazine complexes by a graphical method: (■) $(CN)_5Fe(pz)^{3-}$, 268 nm; (○) $(CN)_5Ru(pz)^{3-}$, 268 nm; (△) $(NH_3)_5Ru(pz)^{2+}$, 268 nm; (+) $(NH_3)_5Ru(pz)^{2+}$, 529 nm.

The titration of $(CN)_5Fe(pz)^{3-}$ is shown in Figure 2C. The behavior is very similar to that for $(CN)_5Ru(pz)^{3-}$. With the appropriate substitution of Fe for Ru, the equilibria of eq 4 apply for $(CN)_5Fe(pz)^{3-}$. Toma and Malin have previously studied the pK_a for protonation of $(CN)_5Fe(pz)^{3-}$ at a cyanide position and found a value of 1.88.[1] In the present work, a much higher acid range was studied. Indeed, eq 4 may need to be altered to show the protonation of pyrazine in competition with the protonation of *two* cyanide positions. As with $(CN)_5Ru(pz)^{3-}$, an isosbestic point is observed in the region of the intraligand absorption, making a pK_a determination possible.

Figure 3 shows the results of a graphical determination of the pK_a's of $(NH_3)_5Ru(pz)^{2+}$, $(CN)_5Ru(pz)^{3-}$, and $(CN)_5Fe(pz)^{3-}$ (protonation on pyrazine). The absorbance changes (ΔA) are normalized by dividing by the total absorbance changes (ΔA_{tot}). This permits presentation of all of the data on one plot. The pK_a is taken as the pH at which $\Delta A/\Delta A_{tot} = 0.5$. For $(NH_3)_5Ru(pz)^{2+}$ the data were treated at 529 nm in addition to 268 nm. The results from treatment of the MLCT region or the intraligand region of the spectrum are essentially identical.

A different treatment of the data is shown in Figure 4. The pK_a is determined from the plot of $[M]/\Delta A$ vs. $1/[H^+]$ as the ratio of slope to intercept according to eq 5,[16] where [M] is

$$\frac{[M]}{\Delta A} = \frac{K}{\Delta\epsilon[H^+]} + \frac{1}{\Delta\epsilon} \tag{5}$$

the total concentration of the protonated and unprotonated forms, ΔA is the difference between the initial absorbance and the absorbance after acid is added, and $\Delta\epsilon$ is the difference between molar absorptivities for the unprotonated and protonated forms. The slopes and intercepts are determined by least-squares analysis. The results of this method are in good agreement with those obtained by the graphical method. The values are reported in Table I, along with the standard deviations of the fits.

The pK_a's reported in this paper should be considered as approximate. The complex nature of the competitive equilibria

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(16) Johnson, C. R.; Shepherd, R. E.; Marr, B.; O'Donnell, S.; Dressick, W. *J. Am. Chem. Soc.* **1980**, *102*, 6277–6235. The form of the equation used in this paper differs from that used presently because the direction of the titration differs. The form of the equation depends on whether the titration starts with the unprotonated form, which is then titrated with acid, or with the protonated form, which is titrated with base. The derivation is essentially the same for either case.

Table I. Spectral and pK_a Data for Pyrazine Complexes

complex (A = NH_3)	MLCT abs, nm (10^{-3} cm^{-1})		$10^{-3}\Delta E$, cm^{-1} [a]	ground state		excited state		ref
	unprotonated	protonated		pK_a(gs)	ΔpK_a[b]	pK_a*	ΔpK_a*[c]	
cis-$A_4ClOs(pz)^+$	465 (21.5)	430 (23.3)	−1.8	7.6 ± 0.3	7.0	3.8	−3.8	17
$A_5Os(pz)^{2+}$	460 (21.7)	428 (23.4)	−1.7	7.4 ± 0.5	6.8	3.8	−3.6	5
$A_5Ru(pz)^{2+}$	472 (21.4)	529 (18.9)	2.3	2.5 ± 0.1	1.9	7.3	4.8	4
				2.85 ± 0.1				this work
$(CN)_5Ru(pz)^{3-}$	368 (27.2)	~490 (20.4)	6.8	0.4 ± 0.1	−0.2	14.7	14.3	this work
cis-$A_4(N_2)Os(pz)^{2+}$	463 (21.6)	640 (15.6)	6.0	0.31	−0.3	12.9	12.6	17
$(CN)_5Fe(pz)^{3-}$	455 (22.0)	~625 (16.0)	6.0	0.065 ± 0.06	−0.54	12.7	12.6	this work
$A_5Ru(pz)^{3+}$	*d*	*d*		−1.0	−1.6	13.0	14.0	2, 4

[a] ΔE is the energy difference between MLCT absorptions of base and acid forms of the complex. ΔE is positive if the energy of the MLCT transition shifts to lower energy upon protonation. [b] ΔpK_a is the difference between the pK_a's of the complexed and free pz. The pK_a of pyrazine is 0.6. [c] ΔpK_a* is the difference between the pK_a's of the ground and excited states of the complex. ΔpK_a* is calculated by eq 6. ΔpK_a* is positive if the pK_a of the excited state is higher than that of the ground state. [d] Not reported.[2]

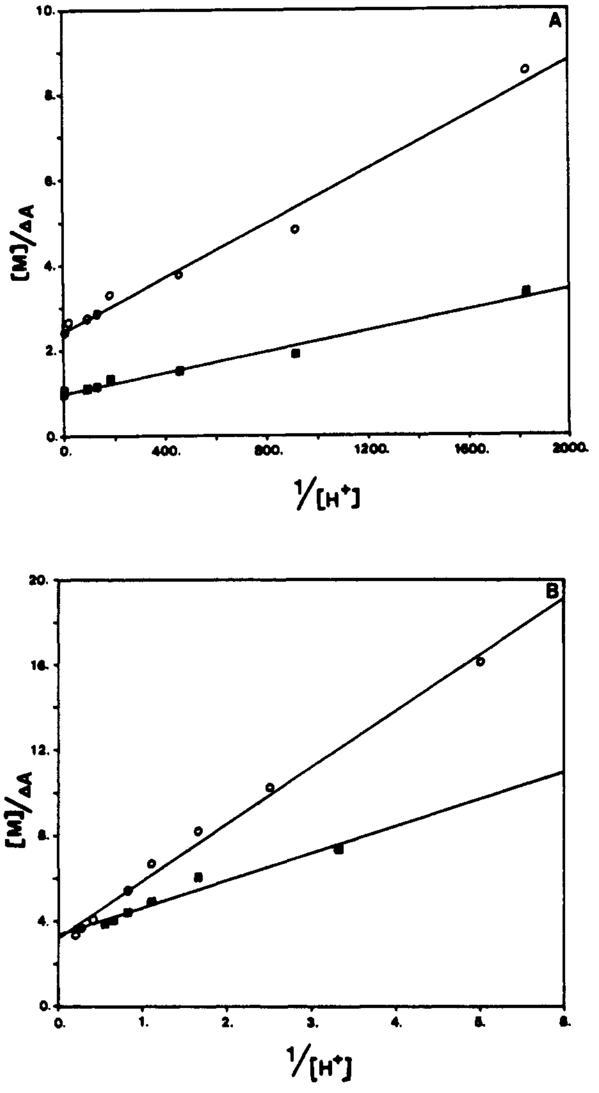

Figure 4. Determination of the pK_a's of pyrazine complexes by linear least-squares analysis: (A) $(NH_3)_5Ru(pz)^{2+}$ at (○) 268 and (■) 529 nm; (B) (○) $(CN)_5Fe(pz)^{3-}$ at 268 nm and (■) $(CN)_5Ru(pz)^{3-}$ at 268 nm.

Table II. NMR Data for Pyrazine Complexes

complex (A = NH_3)	chem shift, ppm[a]		ref
	near H	remote H	
pz	8.69		
$(CN)_5Co(pz)^{2-}$	8.99	8.72	this work
$(CN)_5Ru(pz)^{3-}$	8.72	8.45	this work
$(CN)_5Fe(pz)^{3-}$	9.09	8.24	24, this work
$A_5Ru(pz)^{2+}$	8.72	8.06	23, this work

[a] Vs. internal TMPA.

involved precludes accurate individual determinations of the pK_a's for the several species present. There are additional experimental difficulties that hinder an accurate determination. $(CN)_5Fe(pz)^{3-}$ and $(CN)_5Ru(pz)^{3-}$ are not stable to aquation for long periods at the high acid concentrations needed for complete protonation of the pz. The spectra must be obtained as quickly as possible. Ionic strength (~1 M) was not rigorously maintained due to the high acid concentrations needed. [H^+] was taken as the concentration of acid added since a pH electrode cannot be used at high [H^+]. The titration of $(NH_3)_5Ru(pz)^{2+}$ was carried out the same way as the others, with the satisfying result that the pK_a obtained is in reasonable agreement with that reported previously.[4]

Further changes in the absorbance at 268 nm occur for $(CN)_5Fe(pz)^{3-}$ and $(CN)_5Ru(pz)^{3-}$ at [H^+] higher than that needed for complete protonation of pz. This shows up in Figure 3 as a steepness in the high-acidity end of the titration curves for $(CN)_5Fe(pz)^{3-}$ and $(CN)_5Ru(pz)^{3-}$. Note that the titration curve for $(NH_3)_5Ru(pz)^{2+}$ has a shape more typical of results for such a titration. The limitations of the approach are shown if the data are treated in a slightly different manner. A plot of absorbance vs. $\Delta A/[H^+]$ should give a slope equal to K_a.[17] This treatment works well for $(NH_3)_5Ru(pz)^{2+}$, but the plots show marked curvature for $(CN)_5Fe(pz)^{3-}$ and $(CN)_5Ru(pz)^{3-}$. This type of plot weights the higher acidity data more heavily than that in Figure 4, which weights the low-acidity end very heavily.

Despite these difficulties, the data are useful in making qualitative comparisons with the other data available on pzH^+ complexes. A valuable assessment of the effect of cyanide on the pK_a's is possible because the effect is clearly a large one. Considering the limitations described above, the pK_a's of $(CN)_5Fe(pzH)^{2-}$ and $(CN)_5Ru(pzH)^{2-}$ evaluated in this paper must be taken as composite pK_a's and the equilibria may include several CN^- protonated species.

An independent estimation of the back-bonding capability of the metal in these complexes may be obtained from an evaluation of their NMR spectra. The chemical shifts of several pz complexes are shown in Table II. The spectra are reproduced in Figure 5. Upon coordination of pyrazine to a metal center, the single resonance of the free ligand is split into two. The upfield resonance is due to the protons further from the metal (remote), and the downfield resonance is due to the protons adjacent to the metal (near). Each of these resonances is split in an A_2X_2 pattern. There is a 3.0-Hz coupling between near and remote protons on the same side of the pyrazine ring. There is a 1.5-Hz coupling of near and remote protons across the ring. The magnitude of the coupling

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(17) Magnuson, R. H.; Taube, H. *J. Am. Chem. Soc.* **1975**, *97*, 5129–5136.

Table III. NMR Data for *N*-Methylpyrazinium Complexes

complex (A = NH_3)	chem shift, ppm[a] near H	chem shift, ppm[a] remote H	chem shift, ppm[a] CH_3	ref
$pzCH_3^+$	9.45, 9.01		4.53	this work
$(CN)_5Ru(pzCH_3)^{2-}$	9.50	9.07	4.43	this work
$(CN)_5Fe(pzCH_3)^{2-}$	9.70	8.20	4.15	24
$A_5Ru(pzCH_3)^{3+}$	9.20	8.00	3.20	24
$A_4(N_2)Os(pzCH_3)^{3+}$	*b*	*b*	3.68	17

[a] Vs. internal TMPA. [b] Not reported in ref 17.

does not depend upon the metal center within the certainty of the measurements. The chemical shift is sensitive to the identity of the metal and the remaining ligands. The position of the resonances for the remote H shows the most variation from complex to complex.

NMR data for several *N*-methylpyrazinium ($pzCH_3^+$) complexes, including $(CN)_5Ru(pzCH_3)^{2-}$, are presented in Table III. The position of the methyl resonance of complexes of this ligand is also sensitive to back-bonding from the metal. The methyl group is more shielded as electron density is trnasferred to the ligand π^* orbital by overlap with the filled metal t_{2g} orbitals.

Table IV is a tabulation of IR data for the pz complexes. The important absorptions due to CN^- or pz are listed. It is expected that an increase in electron density in the π^* orbital of pz from metal back-bonding would shift the ring vibrations to lower energy. The pz absorptions vary little from complex to complex, however.

Discussion

pK_a Values. The increase in the pK_a of pzH^+ upon coordination to $(NH_3)_5Ru^{2+}$ has been interpreted to indicate a substantial ground-state interaction between a low-lying π^* orbital of the ligand and the metal t_{2g} orbitals.[4] The increase in the pK_a of the ligand from the free-pz value of 0.6 is consistent with an increase in electron density on the pz ring caused by overlap with the filled metal orbital. The extent of this overlap will be determined by how close the pz π^* orbital and the available metal orbital of proper symmetry are in energy and by the radial extension of this metal orbital. These in turn depend upon the identity of the metal ion and the remaining ligand environment. In a general sense, the better the overlap between the metal and pz orbitals, the higher the pK_a of the coordinated pzH^+. On this basis, within the group Fe(II), Ru(II), and Os(II), the highest pK_a for coordinated pzH^+ is expected for the Os(II) complex because the 5d orbitals are higher in energy than the 4d or 3d orbitals and therefore closer in energy to that of the ligand antibonding orbital. In addition, as anticipated for increasing *n* values, evidence suggests that the radial extension of the orbitals on Ru(II) and Os(II) is greater than for Fe(II).[2] It is also expected that replacement of NH_3 with CN^- in the set of "spectator ligands" will cause the basicity of the coordinated pzH^+ to decrease as CN^- competes effectively for π-electron density (CN^- being a good π acceptor). Examination of the pK_a's in Table I shows that these expectations, in general, hold true. $(NH_3)_5Os(pzH)^{3+}$ has a higher pK_a than $(NH_3)_5Ru(pzH)^{3+}$. $(NH_3)_5Ru(pzH)^{3+}$ has a higher pK_a than $(CN)_5Ru(pzH)^{2-}$. Although comparison is less certain, the results suggest that the pK_a of $(CN)_5Ru(pzH)^{2-}$ is a little higher than that of $(CN)_5Fe(pzH)^{2-}$. This is consistent with the expected order of back-bonding capability, Os(II) > Ru(II) > Fe(II). An interesting effect is seen in the Os(II) series. Substitution of a π donor (Cl^-) for one NH_3 increases the basicity of the complex, and substitution of a π acceptor (N_2) for one NH_3 decreases the basicity sharply.[17] The pK_a of $(NH_3)_5Ru(pzH)^{4+}$ is the lowest reported. Ru(III) has little ability to back-bond to pz, and the observed pK_a is substantially lower than that of the free ligand because of σ polarization from the positive metal center. The pK_a's of $(CN)_5Ru(pzH)^{2-}$ and $(CN)_5Fe(pzH)^{2-}$ are also *less* than that of the free ligand. For these complexes the π back-bonding competes with, but does not overcome, the effect of σ polarization. Although slight, the π back-bonding in $(CN)_5FeL^{3-}$ complexes is important as illustrated by kinetic[3a] and Mössbauer studies.[18]

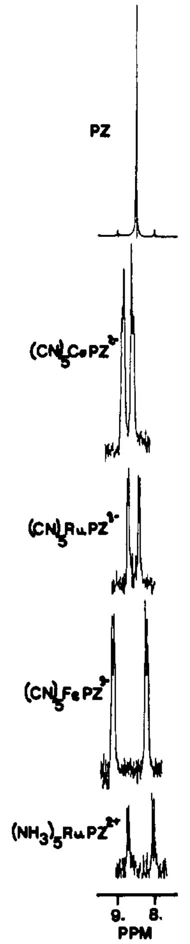

Figure 5. Proton NMR spectra of pyrazine and pyrazine complexes. The chemical shift is in ppm from TMPA.

Table IV. IR Data for Pyrazine and Several Complexes (cm^{-1})[b]

	CN^- region				pz region[a] ν_{8a}	ν_{19b}	ν_{15}	ν_{18a}	ν_{12}	ν_{11}
pz (in C_6H_6)						1414 s	1152 w	1070 w	1019	795
$Na_3[(CN)_5Fe^{II}pz]$	2098 w	2065 s	2045 s	2020 w	1600 m	1422 s	1156 w	1122 w	1057 w	806 w
$K_3[(CN)_5Ru^{II}pz]$	2099 w	2062 s	2043 s	2030 w	1599 m	1413 s	1154 s	1118 m	1056 w	802 s
$[(NH_3)_5Ru(pz)]Br_2$					1595 m	1432 w		1129		830 w
$Na_2[(CN)_5Fe^{III}pz]$		2125 s	2030 w		1599 w	1413 s	1151 s	1119 s	1057 s	802 s
$K_2[(CN)_5Co^{III}pz]$	2208 w	2141 s			1602 m	1420 s	1159 s	1127 s	1062 s	813 s

[a] The fundamentals are assigned as in: Lord, R. C.; Marston, A. L.; Miller, F. A. *Spectrochim. Acta* 1957, *9*, 113–125. [b] Abbreviations: s, strong; m, medium; w, weak.

The discussion of orbital overlap in these complexes can be extended by considering the pK_a of the charge-transfer excited state, pK_a*. The pK_a* can be calculated for each complex by eq 6,[4,19] where pK_a(gs) is the ground-state pK_a, ν_1 is the frequency in wavenumbers of the MLCT absorption of the unprotonated form, and ν_2 is the frequency of the MLCT absorption of the protonated form. The pK_a* values for the complexes under consideration are shown in Table I. If the charge-transfer transitions involve transfer of electron density from a metal orbital to a ligand orbital, the pK_a should increase in the excited state. The difference between the pK_a's of the ground and excited state, ΔpK_a*, should be the largest for a charge-transfer transition from a pure metal orbital to a pure ligand orbital. This would correspond to a transfer of a full unit of electron density upon excitation. As the metal and ligand orbitals overlap and mix from back-bonding in the ground state (i.e., electron density is transferred to the ligand), the amount of electron density transferred upon going to the excited state should decrease proportionally. With a two-orbital model using molecular orbitals formed by overlap of the ligand π^* orbital with the metal orbital of proper symmetry, the percent of ligand and percent of metal orbital character in the ground and excited states must be complementary. For example, if the ground state is 10% ligand and 90% metal, the excited state must be 90% ligand and 10% metal. The result of MLCT excitation in such a case would be to transfer 0.8 electron to the ligand.

$$\mathrm{p}K_a^* = \mathrm{p}K_a(\mathrm{gs}) + \frac{2.86(\nu_1 - \nu_2)}{2.3RT} = \left(\frac{\nu_1 - \nu_2}{476.5}\right)_{298\mathrm{K}} + \mathrm{p}K_a(\mathrm{gs}) \quad (6)$$

The amount of back-bonding (i.e., percent ligand character) in the ground state should be reflected in the basicity of the coordinated pyrazine. As the percent of ligand character increases, the amount of electron density back-donated to the pyrazine increases. This also results in an increase in the electron density of the lone pair of electrons on the remote nitrogen of the pyrazine. A relative estimate of this lone-pair electron density is obtained by a comparison of the pK_a values of the coordinated pyrazinium ion for the series of complexes studied. The magnitude of the pK_a will be influenced by the electronic properties of both the protonated and deprotonated forms of the complex. Protonation of the coordinated pyrazine results in an increase in the amount of back-bonding to the ligand.[17] Thus, back-bonding is more important in the pyrazinium complex than in the pyrazine complex. But the relative order of the amount of back-bonding throughout the series of complexes with $(CN)_5Fe^{3-}$, $(CN)_5Ru^{3-}$, $(NH_3)_5Ru^{2+}$, or $(NH_3)_5Os^{2+}$ will be the same whether the ligand under consideration is pyrazine or pyrazinium ion and will follow the order of the pK_a for each member of the series. The relative basicity of the complex, as measured by the pK_a, is indicative of the relative ability of the metal center to donate electron density to the ligand. The metal center acts as an electron-donating substituent. Protonation at the remote nitrogen is not expected to have any special effect other than to increase the ligand's π-acceptor ability. The pK_a may be used to define a range of metal back-bonding capability for either the pyrazine or the pyrazinium series of complexes if the limiting values can be established. These considerations make it possible to calculate an estimate of the percent of ligand character in the ground- and excited-state molecular orbitals. Of the complexes studied, $(NH_3)_5Ru(pz)^{3+}$ and $(CN)_5Ru(pz)^{3-}$ have the largest values of ΔpK_a*. This is consistent with very little mixing of metal and ligand orbitals. The following assumptions are made. The pK_a of the Ru(III) complex $(NH_3)Ru(pzH)^{4+}$ (−1.0) represents a value expected for no back-bonding and only σ inductive effects. The pK_a* of $(CN)_5Ru(pzH)^{2-}$ (14.7) represents a value expected for complete back-bonding (i.e., transfer of 1e to pz) plus σ inductive effects since this complex has the greatest value of ΔpK_a*. If the σ induction of the metal is considered approximately equal in all complexes, the limiting range of −1.0 to +14.7 pK units is defined. A pK_a of −1.0 represents a value expected for occupation of an orbital with 100% metal character. A pK_a of 14.7 represents a value expected for occupation of an orbital with 100% ligand character. The midrange value, 6.85, would represent an orbital of 50% ligand and 50% metal character. At this pK_a the ground- and excited-state pK_a's would be the same.

Table V. Estimated Ligand Contribution to Ground- and Excited-State Orbitals[a]

complex ($A = NH_3$)	% ligand character		total % accounted for
	ground state	excited state	
cis-$A_4ClOs(pz)^+$	55	31	86
$A_5Os(pz)^{2+}$	54	31	85
$A_5Ru(pz)^{2+}$	22	52	74
$(CN)_5Ru(pz)^{3-}$	9	100[b]	109
cis-$A_4(N_2)Os(pz)^{2+}$	8	89	97
$(CN)_5Fe(pz)^{3-}$	7	87	94
$A_5Ru(pz)^{3+}$	0[b]	89	89

[a] As calculated by eq 7, 7*. [b] Values established by the selection of the pK_a limits.

The percent ligand character for the ground-state and excited-state orbitals is calculated from the pK_a(gs) and pK_a* values, respectively, eq 7 and 7*. Our results by this method are given in Table V. Despite the assumptions used to arrive at the values in Table V, some consistency of results is noted. The distribution of ligand orbital character between the ground and excited states, as calculated by pK_a(gs) and pK_a*, accounts fairly well for the total. The total ligand character found for $(NH_3)_5Os(pz)^{2+}$, $(NH_3)_5Ru(pz)^{2+}$, and *cis*-$(NH_3)_4ClOs(pz)^+$ is less than that for the other complexes. The σ-polarizing ability of the metal centers in these three complexes is probably less than that for the others. The assumed constant inductive effect must be close to that for a Ru(III) center since Ru(III)-like complexes, $(NH_3)_5Ru(pz)^{3+}$ and $(CN)_5Ru(pz)^{3-}$, were used to establish the pK_a range. The metal center in cyanide complexes with a formal +2 oxidation state is very similar to that in a 3+ ion due to extensive back-bonding.[20] For $(NH_3)_5Os(pz)^{2+}$, $(NH_3)_5Ru(pz)^{2+}$, and *cis*-$(NH_3)_4ClOs(pz)^+$ back-bonding to NH_3 or Cl^- is not possible and the inductive effects of the metal centers toward pz would be more characteristic of that for a 2+ ion. It is therefore understandable that these complexes may give the poorest results when the pK_a range is used as established.

$$\text{percent ligand character} = \frac{\mathrm{p}K_a + 1.0}{15.7} \times 100\% \qquad (7, 7^*)$$

The 22% ligand character calculated for the ground state of $(NH_3)_5Ru(pz)^{2+}$ agrees with Taube's estimate of 20% electron transfer to the pz.[21] For $(NH_3)_5Os(pz)^{2+}$ and *cis*-$(NH_3)_4ClOs(pz)^+$ the estimated values for the ground state are greater than 50%; i.e., the ground state has more ligand character than metal character. The charge-transfer transition observed for these Os(II) complexes is best described as being

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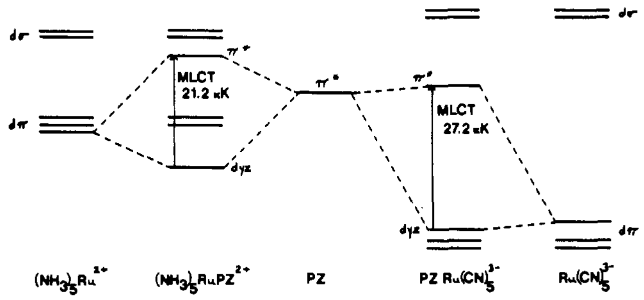

Figure 6. Qualitative molecular orbital diagram comparing the pentaammine- and pentacyanoruthenium pyrazine complexes.

ligand to metal. This is consistent with the increase in energy of the charge-transfer transition upon protonation of the complex. Protonation of the coordinated pz makes transfer of electron density to the metal more difficult. As a consequence of removing electron density from the ligand, the charge-transfer excited state has a pK_a less than that of the ground state. These observations suggest that the dπ orbitals of Os(II) have very nearly the same energy as the π^* orbital on pz.

When the complex contains cyanide, the amount of electron density transferred to pz is small (<10%). This is expected in view of cyanide's ability to compete with pz for π-electron density. A comparison of the effect of CN^- vs. NH_3 as the "spectator ligand" can be made by a simple molecular orbital diagram (Figure 6). The orbitals of the complex are shown as constructed from the five-coordinate fragment plus pyrazine. Ammonia does not stabilize the dπ orbitals on the metal. The dπ orbitals remain high in energy and can interact strongly with the pz π^* orbital. Cyanide lowers the dπ orbitals significantly through back-bonding. This makes back-bonding to the pz less favorable because the energy difference between the pz π^* orbital and the metal orbital of proper symmetry is large.

NMR Spectra. The NMR data of these and similar complexes have been discussed by other workers,[22-25] and we will not go into detail here. A number of mechanisms to account for the chemical shifts observed have been discussed, including contributions from temperature-independent paramagnetism and magnetic anisotropy of the CN^- groups or of the metal-ligand bond. Foust and Ford have discussed these mechanisms[25] and concluded that they are generally not very important influences on the chemical shift. It is useful to interpret the chemical shifts as a combination of σ induction toward the metal center and π back-bonding from the metal causing changes in the electronic distribution on the ligand. Inductive polarization decreases rapidly as the distance from the metal ion increases. The inductive effects will influence the near H of pz most strongly. Back-bonding will effect the electron density over the entire ring but will be most evident at the remote H, where the opposing σ effect is very weak. As a result, the chemical shift of the near H reflects a deshielding due to a strong withdrawal of electron density toward the metal ion only partly offset by back-donation, and the chemical shifts of the remote H reflect a shielding due to an increase in electron density through back-bonding from the metal.

No significant π back-bonding to pz is expected in $(CN)_5Co(pz)^{2-}$. The NMR data for this complex show a deshielding of both the near and remote protons, consistent with a σ-induction-only mechanism. The remote H, being farther from the metal center, is barely influenced. The other complexes in Table II show shielding of the remote H relative to the free ligand, indicating the influence of back-donation. The largest shielding is observed for $(NH_3)_5Ru(pz)^{2+}$, consistent with the largest amount of π delocalization of the complexes in the table.

A comparison of the NMR data for the remote H's of $(CN)_5Ru(pz)^{3-}$ and $(CN)_5Fe(pz)^{3-}$ suggests that back-bonding to the pz is more extensive for the Fe(II) complex. This conclusion does not agree with that made on the basis of the pK_a's of the two complexes. A possible explanation can be suggested if the conclusion that Fe(II) is more strongly back-bonding is accepted. The large deshielding of the near H in $(CN)_5Fe(pz)^{3-}$ suggests that the Fe(II) in this complex is strongly σ polarizing. It is possible that this σ polarization can be felt at the remote N (where protonation takes place) by direct overlap of σ orbitals on the two nitrogens. This overlap would allow direct withdrawal of electron density from the remote N, resulting in a decrease in basicity of the coordinated pz. Therefore the comparison of the basicities of $(CN)_5Fe(pz)^{3-}$ and $(CN)_5Ru(pz)^{3-}$ would not give a valid approximation of the relative amount of π back-bonding because the σ-polarization abilities of the two metal centers are quite different. More work is needed concerning this issue.

The NMR data for the CH_3 group of the *N*-methylpyrazinium complexes also reflect this order in back-bonding capability. The CH_3 group is more shielded in $(CN)_5Fe(pzCH_3)^{2-}$ than in $(CN)_5Ru(pzCH_3)^{2-}$. The overall order of π back-bonding capability is the same for the pz or $pzCH_3^+$ data.

Conclusion

The determination of the pK_a's for $(CN)_5Fe(pzH)^{3-}$ and $(CN)_5Ru(pzH)^{3-}$ provides for a useful extension of the data previously available on other complexes. These complexes provide cases where the electron delocalization onto pz is relatively small. Comparison with the pentaammine complexes, where delocalization is more extensive, allows for an evaluation of the extent of electron delocalization in these complexes.

Acknowledgment. The authors gratefully acknowledge the National Science Foundation, Grant No. CHE 802183, for support of this work.

Registry No. $K_3(CN)_5Ru(pz)$, 84711-74-0; $K_4[Ru(CN)_6]$, 15002-31-0; $[A_5Ru(pz)]Br_2$, 84711-75-1; $A_5Ru(Hpz)^{3+}$, 19441-21-5; $(CN)_5Ru(Hpz)^{2-}$, 84711-76-2; $Na_3[(CN)_5Fe(pz)]$, 37475-70-0; $(CN)_5Fe(Hpz)^{3-}$, 84711-77-3; $K_2[(CN)_5Co(pz)]$, 74312-85-9; $(CN)_5Ru(pzCH_3)^{2-}$, 84711-78-4; $Na_2[(CN)_5Fe(pz)]$, 84711-79-5; *cis*-$A_4ClOs(pz)^+$, 84711-80-8; $A_5Os(pz)^{2+}$, 70252-44-7; *cis*-$A_4(N_2)Os(pz)^{2+}$, 84711-81-9; $A_5Ru(pz)^{3+}$, 38139-16-1.

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