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### Influence of Closed-Shell Cations on the LMCT Transition of Pentacyanoferrate(III) Complexes

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The pentacyanoferrate(III) complexes of imidazoles, pyrazoles, and aminopyridines exhibit ligand-to-metal charge-transfer (LMCT) transitions in the visible region of the absorption spectrum.<sup>1-3</sup> We have shown that these  $(\text{CN})_5\text{Fe}^{\text{III}}\text{L}^{2-}$  complexes exhibit a positive solvatochromism that linearly correlates with the Kosower ( $Z$ ) and Reichardt-Dimroth ( $E_T$ ) solvent polarity scales, as well as the Gutmann acceptor number ( $AN$ ) of the solvent.<sup>4</sup> Current studies in our lab have shown that polarizing, hard cations including  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Al}^{3+}$ , and  $\text{Sc}^{3+}$  can produce similar shifts in the LMCT bands through ion pairing.<sup>19</sup> Bathochromic shifts are produced by the presence of these cations, introduced as electrolyte chloride salts. By contrast, quaternary ammonium salts produce a hypsochromic shift. The site of the aqua-metal cation interaction may be conceivably at either the lone pairs of the coordinated  $\text{CN}^-$  ligands or the non-coordinated lone pair of the  $\pi$ -donor ligand, which allows for the LMCT transition.<sup>1</sup> If the cation were to ion pair in the vicinity of the organic  $\pi$ -donor, a hypsochromic shift is anticipated. The presence of the cation near the  $\pi$ -donor's lone pair should stabilize the ground state more than the excited LMCT state. A reverse effect is anticipated for anions on a cationic species. Sutton and Taube have observed that the cationic complex (4-amino-pyridine)pentaammineruthenium(III) exhibits hypsochromic shifts dependent on the nature of electrolyte anions.<sup>5</sup> A 30-nm hypsochromic shift was observed for this  $\text{Ru}(\text{III})$  cation's LMCT band in the presence of 5 M KF. The order of increased shift was found to be  $\text{F}^- > \text{Cl}^- > \text{PF}_6^- \sim \text{ClO}_4^-$ . Sutton and Taube concluded that the anion of the  $[(\text{NH}_3)_5\text{Ru}^{\text{III}}\text{L}^{3+}, \text{X}^-]$  ion pair stabilized the partial positive charge of the amine ring nitrogen upon delocalization of the amino lone pair into the aromatic ring.<sup>5</sup> The site of the cation interaction in  $[\text{M}^{\text{II}}, (\text{CN})_5\text{Fe}^{\text{III}}\text{L}^{2-}]$  ion pairs is more logically at the lone pairs of the coordinated  $\text{CN}^-$  ligands in keeping with several observations: (1) the LMCT shifts are bathochromic and dependent on the charge of cation,  $\text{M}^{\text{II}}$ , in the ion pair; (2) the Mössbauer spectrum of a given  $(\text{CN})_5\text{Fe}^{\text{III}}\text{L}^{2-}$  complex, including  $\text{Fe}(\text{CN})_6^{3-}$ , is cation-dependent;<sup>6</sup> (3) cations such as  $\text{Mg}(\text{II})$  are observed to be coordinated at  $\text{CN}^-$  and bridging  $(\text{CN})_5\text{Fe}^{\text{III}}\text{L}^{2-}$  units as for example, in the recent structure of  $[\text{Mg}(\text{Meim})_2(\text{H}_2\text{O})_2][(\text{CN})_5\text{Fe}(\text{Meim})]$  (Meim = 1-methylimidazole);<sup>7</sup> (4) large cations accelerate the rate of electron-transfer self-exchange for the  $\text{Fe}(\text{CN})_6^{4-/3-}$  pair ( $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$ ;  $\text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$ ), presumably via cation-bridged ion pairs.<sup>8,9</sup> The bathochromic shifts produced on

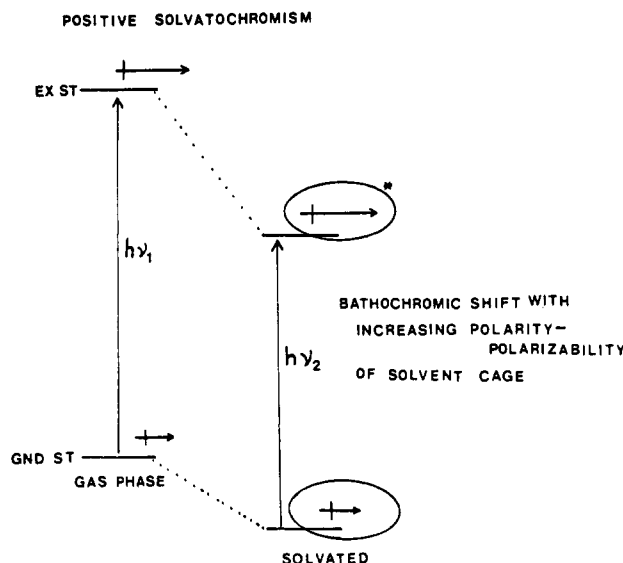


Figure 1. Influence of a solvation cage on a transition having an increased dipole moment.

Table I. Influence of Cations on LMCT Spectra of  $(\text{CN})_5\text{Fe}(\text{dmapy})^{2-}$  and Hydration Energies of the Cations

	$\lambda$ shift, nm/mol	$\lambda$ shift rel to $\text{Li}^+$ , nm/mol	$-\Delta H_{\text{hyd}}^a$ , kcal/mol	$\Delta H_{\text{hyd}}$ rel to $\text{Li}^+$ , kcal/mol
$\text{Li}^+$	7.75	1.00	119.3	1.00
$\text{Na}^+$	6.25	0.81	93.2	0.78
$\text{K}^+$	5.00	0.64	73.0	0.61
$\text{Mg}^{2+}$	19.14	2.47	452.0	3.79
$\text{Ca}^{2+}$	18.39	2.37	373.2	3.12
$\text{Sr}^{2+}$	16.08	2.07	337.9	2.83
$\text{Ba}^{2+}$	$\sim 0$	$\sim 0$	304.2	2.55
$\text{Al}^{3+}$	39.62	5.11	1102.6	9.24
$\text{Sc}^{3+}$	31.50	4.06	935.4	7.84

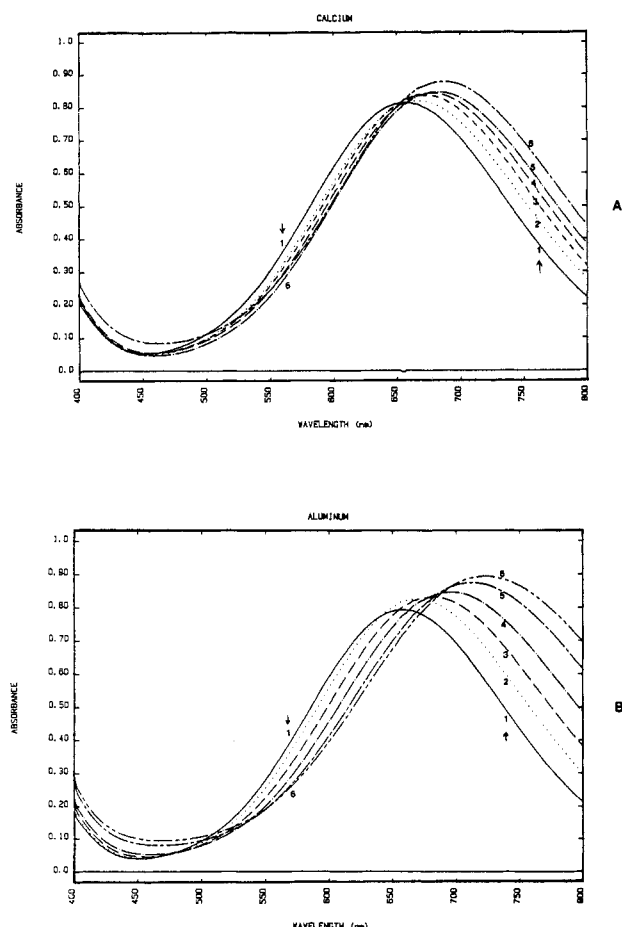
<sup>a</sup> Reference 10.

the LMCT spectra of  $(\text{CN})_5\text{Fe}^{\text{III}}\text{L}^{2-}$  complexes ( $\text{L} = 4$ -(dimethylamino)pyridine, dmapy, and  $\text{L} =$  benzimidazole, bzimH) are the subjects of this report. Greater shifts per mole are observed for the  $[\text{M}^{\text{II}}, (\text{CN})_5\text{Fe}^{\text{III}}\text{L}^{2-}]$  ion pairs than their  $[(\text{NH}_3)_5\text{Ru}^{\text{III}}\text{L}^{3+}, \text{X}^-]$  counterparts when  $\text{M}^{\text{II}}$  is a divalent or trivalent cation, whereas comparable shifts are achieved with monovalent cations vs. the monovalent  $\text{X}^-$  anions.

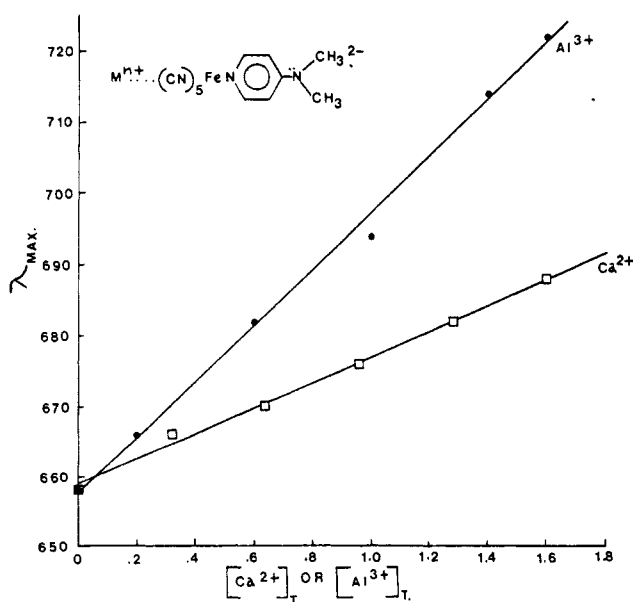
### Results and Discussion

Aqueous solutions of ca.  $5 \times 10^{-4}$  M  $\text{Na}_2[(\text{CN})_5\text{Fe}(\text{dmapy})]$  and  $\text{Na}_2[(\text{CN})_5\text{Fe}(\text{bzimH})]$  exhibit LMCT transitions at 660 and 505 nm, respectively.<sup>1</sup> The LMCT transition in these and related  $\pi$ -donor complexes of  $(\text{CN})_5\text{Fe}^{2-}$  occur with an increase in dipole moment in the excited state.<sup>4</sup> This is established by positive solvatochromism and bathochromic shifts caused by the presence of increasingly polar solvents in the solvent cage. The more polar or ionic cage will stabilize the excited-state species more than the same cage stabilizes the ground-state electronic species (see Figure 1). The presence of increasing amounts of electrolyte salts may serve the same role in aqueous solution that is achieved by changing the acceptor number ( $AN$ ) or solvent polarity ( $E_T$  or  $Z$ ) in nonaqueous solvents.<sup>4</sup> A bathochromic shift, dependent on the concentration of the metallocation species of the electrolyte, is produced by introduction of the electrolyte in  $5 \times 10^{-4}$  M  $(\text{CN})_5\text{Fe}(\text{dmapy})^{2-}$  or  $(\text{CN})_5\text{Fe}(\text{bzimH})^{2-}$  solutions. Representative spectra are presented for the  $(\text{CN})_5\text{Fe}(\text{dmapy})^{2-}$  complex with  $\text{CaCl}_2$  and  $\text{AlCl}_3$  in Figure 2a,b in the range of 0.00–1.60 M added  $\text{CaCl}_2$  or  $\text{AlCl}_3$ . The linear dependence of the shift in the maximum of the LMCT transition is shown in Figure 3 for  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$ . In order to suppress any potential hydrolysis problem causing an equilibrium of  $\text{Al}^{3+}$  and  $\text{AlOH}^{2+}$  species in the  $\text{Al}^{3+}$  data, the influence of  $\text{Al}^{3+}$  was examined in the presence of 0.010 M HCl. In a separate experiment with 0.010 M HCl

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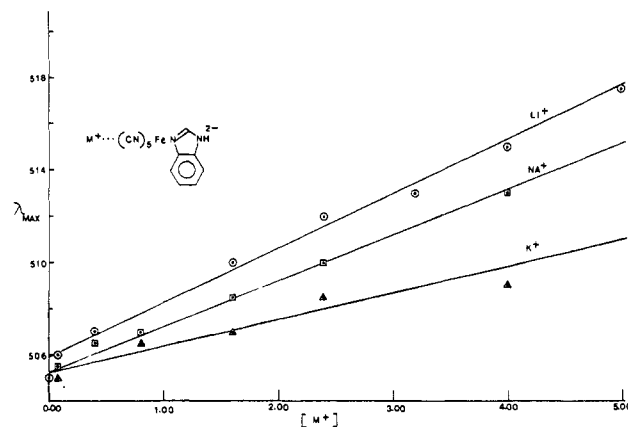


**Figure 2.** (a) Effect of  $\text{CaCl}_2$  on the LMCT transition of  $(\text{CN})_5\text{Fe}(\text{dmapi})^{2-}$  ( $[(\text{CN})_5\text{Fe}(\text{dmapi})^{2-}] = 5.0 \times 10^{-4} \text{ M}$ ,  $[\text{CaCl}_2]_{\text{total}} = 0.00 \text{ M}$  (1), 0.32 M (2), 0.64 M (3), 0.96 M (4), 1.28 M (5), 1.60 M (6)). (b) Effect of  $\text{AlCl}_3$  on the LMCT transition of  $(\text{CN})_5\text{Fe}(\text{dmapi})^{2-}$  ( $[(\text{CN})_5\text{Fe}(\text{dmapi})^{2-}] = 5.0 \times 10^{-4} \text{ M}$ ,  $[\text{H}_3\text{O}^+] = 0.010 \text{ M}$ ,  $[\text{AlCl}_3]_{\text{total}} = 0.00 \text{ M}$  (1), 0.20 M (2), 0.60 M (3), 1.00 M (4), 1.40 M (5), 1.60 M (6)).



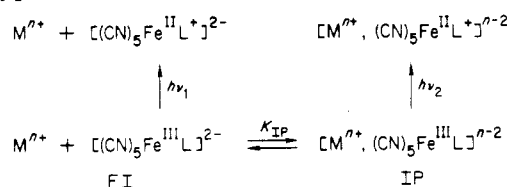
**Figure 3.** Shift in LMCT maximum of  $(\text{CN})_5\text{Fe}(\text{dmapi})^{2-}$  as a function of total  $[\text{Ca}^{2+}]$  and  $[\text{Al}^{3+}]$ .

alone, it was shown that the LMCT maximum remained at 658 nm. An acid-catalyzed loss of dmapi from  $(\text{CN})_5\text{Fe}(\text{dmapi})^{2-}$  was observed with a half-life of about 30 min in 0.010 M HCl. However, the spectral data of this report were obtained with a HP-8450A diode-array spectrophotometer that stores the spectral



**Figure 4.** Shift in LMCT maximum of  $(\text{CN})_5\text{Fe}(\text{bzimH})^{2-}$  as a function of total  $[\text{Li}^+]$ ,  $[\text{Na}^+]$ , or  $[\text{K}^+]$  ( $[(\text{CN})_5\text{Fe}(\text{bzimH})^{2-}] = 5.0 \times 10^{-4} \text{ M}$ ,  $[\text{bzimH}] = 5.0 \times 10^{-3} \text{ M}$ ).

#### Scheme I



data with vidicon scanning within 1.0 s. Therefore, spectra could be obtained by immediately adjusting with HCl to 0.010 M for solutions already adjusted to the needed total  $[\text{Al}^{3+}]$ . By this procedure the spectra are obtained so rapidly that virtually no change due to dmapi dissociation would occur. The related influence of  $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{K}^+$  as LiCl, NaCl, and KCl electrolytes with  $(\text{CN})_5\text{Fe}(\text{bzimH})^{2-}$  is shown in Figure 4. Wavelength has been plotted vs.  $[\text{M}^{n+}]$  as the shifts are small and would be visually minimized had frequency vs.  $[\text{M}^{n+}]$  been selected. The shift of wavelength (nm/mol) for the various ions is given in Table I.

In the limit that the bandwidths and extinction coefficients for the free ion,  $(\text{CN})_5\text{Fe}^{\text{III}}\text{L}^{2-}$ , and the ion pair,  $[\text{M}^{n+}, (\text{CN})_5\text{Fe}^{\text{III}}\text{L}^{2-}]$  are the same, the position of  $\lambda_{\text{max}}$  for the observed LMCT band will follow the fraction of species present as the ion pair. The equilibrium composite will undergo their visible absorptions as shown in Scheme I. When the percentage of the ion pair form is small, the shift per mole of  $\text{M}^{n+}$  should be proportional to the relative values of  $K_{\text{IP}}$  (see below). If we assume that  $K_{\text{IP}}$  follows the normal outer-sphere association constants based on electrostatic attraction, we would predict an approximate sensitivity factor of monovalent:divalent:trivalent ions of 1:5:12 on the basis of typical values of  $K_{\text{OS}}$  constants for (+1,-2), (+2,-2), (+3,-2) ion pairs.<sup>11</sup> If we compare the sensitivity of the shift in wavelength per mole of  $\text{M}^{n+}$  for the series  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Al}^{3+}$ , we find the relative raw data order 1:3.0:6.3, which is in reasonable agreement with a crude, electrostatic model. It is well-known from the ultrasonic studies of Eigen and others<sup>11c</sup> that electrolyte salts exist in equilibria of solvent-separated ion pairs, anion-desolvated ion pairs, contact ion pairs, and the free aquated  $\text{M}(\text{H}_2\text{O})_6^{n+}$  species. The chloride solutions of the salts used in our present study contain only the fully aquated species,  $\text{M}(\text{H}_2\text{O})_6^{n+}$ , and the outer-sphere or solvent-separated ion pairs  $[\text{M}(\text{H}_2\text{O})_6^{n+}, \text{Cl}(\text{H}_2\text{O})_m]^{-}$ .<sup>20</sup> Even for the highly charged  $\text{Al}(\text{H}_2\text{O})_6^{3+}$  case very little inner-sphere

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chloride complex (contact ion pair) exists in these solutions.<sup>20</sup> The concentration of the free aqua ion,  $M(H_2O)_6^{n+}$ , can then be calculated on the basis of  $[Cl^-]_{tot}$  and an estimate of the outer-sphere association constant,  $K_{OS}$ , for  $[M(H_2O)_6^{n+}, Cl(H_2O)_m^-]$ . These  $K_{OS}$  constants may be estimated either from the Fuoss equation or from related ion pair constants from the literature:<sup>11</sup> usually ca.  $0.2 M^{-1}$  for (+1, -1) pairs,  $1.0 M^{-1}$  for (+2, -1) pairs, and  $5 M^{-1}$  for (+3, -1) pairs under ionic strengths of  $0.10$ – $2.0 M$ . In the present study there is no good way to vary the total concentration of a species such as  $Al(H_2O)_6^{3+}$  while a total ionic strength of an "inert" electrolyte is maintained such as by adding LiCl because the  $Li^+$  is also active in shifting the LMCT position and the total chloride will vary with the changing ratio of  $Al(H_2O)_6^{3+} : Li(H_2O)_6^{+}$ . Therefore, the best approach is to obtain what effective value of  $K_{OS}$  is found to bring the data into the theoretical 1:5:12 ratio and then to check whether these values of  $K_{OS}$  are realistic estimates by comparison with known constants for species of the same charge type. The relative order improves to 1:5:12 if allowance is made for competitive outer-sphere ion pair formation of  $[Mg(H_2O)_6^{2+}, Cl^-]$  and  $[Al(H_2O)_6^{3+}, Cl^-]$  using ion pair formation constants of  $0.58$  and  $1.41 M^{-1}$ . The competitive electrolyte equilibrium depletes the available pool of  $Mn(H_2O)_6^{2+}$  and  $Al(H_2O)_6^{3+}$  for ion pair formation with  $(CN)_5FeL^{2-}$ , as in Scheme I. We can estimate the upper boundary for the values of  $K_{IP}$  for the various ion pairs with  $(CN)_5FeL^{2-}$  by taking note of the fact that no deviation from a linear shift in  $\lambda_{max}$  occurs through the electrolyte concentration range of our study:  $5.0 M$  salt with MCl electrolytes or  $1.6 M$  salt with either  $MCl_2$  or  $MCl_3$  electrolytes. Because the peak separation of the  $(CN)_5FeL^{2-}$  and  $[M^{n+}, (CN)_5FeL^{2-}]$  species is much less than the bandwidth, one can assume that the peak maximum will occur at the weighted average position of the contributing peaks for the free  $(CN)_5FeL^{2-}$  ion and the ion pair  $[M^{n+}, (CN)_5FeL^{2-}]$ . It can be shown that  $\lambda_{mixture} = \lambda_{FI} + K_{IP}[M^{n+}]\Delta\lambda(100\% IP)/(1 + K_{IP}[M^{n+}])$ . Significant deviation from a linear response to  $[M^{n+}]$  on the maximum position of  $\lambda_{mixture}$  should occur when  $1 + K_{IP}[M^{n+}] \sim 1.5$ . Therefore, the estimate that  $K_{IP}[M^{n+}] \sim 0.5$  sets limits on the maximum value for  $K_{IP}$  for the  $[Mn^{2+}, (CN)_5FeL^{2-}]$  ion pair.  $K_{IP}$  values must be  $\leq 0.10 M^{-1}$  for  $[M^{+}, (CN)_5FeL^{2-}]$  ion pairs and  $\leq 0.31 M^{-1}$  for either  $[M^{2+}, (CN)_5FeL^{2-}]$  or  $[M^{3+}, (CN)_5FeL^{2-}]$  ion pairs. These estimates as upper limits to  $K_{IP}$  are quite reasonable in that typical outer-sphere ion pair constants of (+1, -2) charge types fall in the range of  $0.2$ – $2 M^{-1}$ , (+2, -2) pairs vary from  $0.3$  to  $14 M^{-1}$ , and (+3, -2) pairs have values from  $3$  to  $16 M^{-1}$  in ionic media below  $\mu = 1.0$ . The constants decrease with increasing ionic strength. Thus, the estimate limits are still reasonable.

In Table I entries are made for the hydration energies of the cations<sup>10</sup> as well as the same values normalized to  $Li^+$ . It can be seen that a good correspondence exists between the relative hydration energies and the shift per mole normalized to  $Li^+$  for the series  $Li^+$ ,  $Na^+$ ,  $K^+$ . The slopes of Figure 4 relative to  $[Li^+]$  for  $(CN)_5Fe(bzimH)^{2-}$  are  $1.00:0.84:0.48$  for  $Li^+:Na^+:K^+$ , again showing the same trend as  $(CN)_5Fe(dmapy)^{2-}$  with these cations. No correction for competitive ion pairing with  $Cl^-$  is necessary to bring the monovalent ion shifts per mole into agreement with the relative hydration energies of  $Li^+$ ,  $Na^+$ , and  $K^+$  to normalized  $Li^+$ . If we assume that the relative shift per mole of  $Mg^{2+}$ ,  $Ca^{2+}$ , and  $Sr^{2+}$  should also follow the relative hydration energies of these ions (an assumption that is not far from correct for the raw data of Table I), the shifts per mole of these ions can be brought into agreement with the relative hydration energies when competitive ion pair constants,  $K_{IP}'$ , of  $0.58 M^{-1}$  ( $Mg^{2+}$ ),  $0.28 M^{-1}$  ( $Ca^{2+}$ ), and  $0.45 M^{-1}$  ( $Sr^{2+}$ ) are applied to reduce the available pool of these divalent ions. The required value of  $K_{IP}' = 0.58 M^{-1}$  for  $Mg^{2+}$  is slightly higher than a reported value of  $0.10 M^{-1}$  for  $Mg^{2+}$  with  $Cl^-$ , but the values for  $Ca^{2+}$  and  $Sr^{2+}$  are in good agreement with the extrapolated values of  $0.3$  ( $Ca^{2+}$ ) and  $0.5$  ( $Sr^{2+}$ ) on the basis of literature values of  $0.10 M^{-1}$  for  $Mg^{2+}$  and  $0.6 M^{-1}$  for  $Ba^{2+}$ .<sup>20</sup> The ion pairs  $[Mg(H_2O)_6^{2+}, Cl^-]$ ,  $[Ca(H_2O)_6^{2+}, Cl^-]$ , and  $[Sr(H_2O)_6^{2+}, Cl^-]$  are assumed to behave as monovalent ions of the same quantum shell in forming their own ion pairs with

$(CN)_5FeL^{2-}$ , contributing a lesser shift. Ion pairs of monovalent anions with  $Ni^{2+}$  are assigned values near  $0.2 M^{-1}$  for  $NCS^-$  and  $HC_2O_4^{12}$  while that of  $[V(H_2O)_6^{2+}, NCS^-]$  has the value of  $0.23 M^{-1}$ .<sup>13</sup> Therefore, one can see that the  $K_{IP}'$  values are again in reasonable agreement with literature values of outer-sphere ion pairs of like charge type. The trivalent ions  $Al^{3+}$  and  $Sc^{3+}$  should also enter into competitive ion pair formation with  $Cl^-$  with  $K_{IP}'$  values of  $1.41 M^{-1}$  and  $1.82 M^{-1}$  for  $Al^{3+}$  and  $Sc^{3+}$ , respectively, in order to obtain correspondence between the observed relative shifts (mm/mol) and the relative hydration energies. The typical values for  $K_{IP}'$  for (+3, -1) ion pairs range from  $3 M^{-1}$   $[(NH_3)_5CoOH_2^{3+}, H_2PO_4^-]$ <sup>14</sup> to  $13 M^{-1}$   $[Cr(H_2O)_6^{3+}, Cl^-]$ .<sup>15</sup> Obviously, the assumption of a single equilibrium to form *only*  $[Al(H_2O)_6^{3+}, Cl^-]$  and  $[Sc(H_2O)_6^{3+}, Cl^-]$  species at high molarities is a source of error in making the calculations that give  $K_{IP}'$  values of  $1.4$  and  $1.8 M^{-1}$  for  $Al^{3+}$  and  $Sc^{3+}$ . The largest error is found for  $Sc^{3+}$ , for which an inner-sphere complex with  $K_f = 12 M^{-1}$  has been reported at much lower ionic strengths. It is also necessary to point out the data must be obtained under conditions of changing activity coefficients due to widely varying molarities of electrolyte salts; therefore, the values given for  $K_{IP}$  and  $K_{IP}'$  are approximate.

When  $[(CH_3)_4N]Cl$  or  $[(C_2H_5)_4N]Cl$  was used as the electrolyte salt, the position of the peak maximum for  $(CN)_5Fe(dmapy)^{2-}$  shifted to higher energy (hypsochromic shift). Nearly saturated solutions of  $(CH_3)_4N^+$  as its chloride salt shifted the LMCT band to  $630 nm$  while  $(C_2H_5)_4N^+$ , near saturation, gave a value of  $622 nm$ . Clearly, the mode of action for the  $R_4N^+$  cations is different from that of the  $M(H_2O)_6^{n+}$  ions ( $M^+ = Li^+$ ,  $Na^+$ ,  $K^+$ ). The presence of cationic charge with  $R_4N^+$  derivatives suggests a destabilizing influence overall, presumably via less favorable excited-state energy relative to the influence of  $R_4N^+$  on the ground state. These results would seem to be important in discerning the role of  $M(H_2O)_6^{n+}$  ions on the LMCT position. The labile ions have the potential to interact directly via the lone pairs on the coordinated  $CN^-$  ligands by displacement of a solvent molecule.  $R_4N^+$  cannot do this. Therefore, formation of a  $\sigma$ -donation complex from the coordinated  $CN^-$  ligand and an empty orbital on the  $M(H_2O)_6^{n+}$  fragment would seem to best explain the difference in the action of  $M(H_2O)_6^{n+}$  vs.  $R_4N^+$ .  $R_4N^+$  cations would probably prefer to form its ion pair with the  $R_4N^+$  group nearest the more hydrophobic region of the dmapy ring of  $(CN)_5Fe(dmapy)^{2-}$ . This location for the ion pairs with  $R_4N^+$  would cause a hypsochromic shift, as mentioned in the introduction. A modified quaternary ammonium cation was prepared by the  $CH_3I$  alkylation of triethanolamine. The resultant  $CH_3N(CH_2CH_2OH)_3^+I^-$  salt was added to a solution of  $(CN)_5Fe(dmapy)^{2-}$  with no shift in  $\lambda_{max}$  from  $660 nm$  at concentrations up to  $1.00 M$  in  $CH_3N(CH_2CH_2OH)_3^+$ .<sup>21</sup> Small changes in the  $CN^-$  to  $Fe(III)$  LMCT region are observed with

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- (16) Reference 10a, p 163.
- (17) Mayer, U.; Gutmann, V.; Gerger, W. *Monatsh. Chem.* **1975**, *106*, 1235–1257.
- (18) (a) Sanderson, R. T. *Inorganic Chemistry*; Reinhold: New York, 1967; p 136. (b) Effective radii are  $0.68 \text{ \AA}$  ( $Al^{3+}$ ) and  $0.89 \text{ \AA}$  ( $Sc^{3+}$ ); Huheey, J. E. *Inorganic Chemistry: Principles of Structure and Reactivity*, 2nd ed.; Harper and Row: New York, 1978; pp 71–74.
- (19) Given in part at the Ninth IUPAC Conference on Nonaqueous Solvents, Pittsburgh, PA, Aug 1984.
- (20) Inner-sphere association constants ( $M^{-1}$ ) at  $25^\circ C$  are  $0$  ( $Li^+$ ),  $0.01$  ( $Na^+$ ),  $0.20$  ( $K^+$ ),  $0.28$  ( $Rb^+$ ),  $0.10$ , ( $Mg^{2+}$ ),  $0.6$  ( $Ba^{2+}$ ),  $1.02$  ( $Ga^{3+}$ ),  $0$  ( $Al^{3+}$ ), and  $12.0$  ( $Sc^{3+}$ ); Sillen and Martell, Eds. *Stability Constants*; The Chemical Society: London, 1964. Smith and Martell. *Critical Stability Constants*; The Chemical Society: London, 1980. Extrapolated values are then  $\sim 0.3$  ( $Ca^{2+}$ ) and  $\sim 0.5$  ( $Sr^{2+}$ ).
- (21) The rates of spontaneous aquation of the  $(CN)_5FeL^{2-}$  complexes were shown to be sufficiently slow that spectral measurements by the diode-array spectrophotometer were essentially constant for 5 min. The spontaneous rate of dissociation of the iodide salt is about twice the rate as with chloride present, but this is still negligible relative to the time required to obtain the necessary comparison data.

the addition of all types of electrolyte salts. This effect may be reconciled with solvent-separated ion pairs for some ions and contact pairs for others. We assume that the  $\text{CH}_3\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3^+$  cations prefer the same hydrophilic solvation region as the  $\text{M}(\text{H}_2\text{O})_6^{n+}$  ions that cause a bathochromic shift in the LMCT band. Those ions in the hydrophilic region near the  $\text{CN}^-$  ligands, which are sufficiently polarizing of the lone pair of a coordinated  $\text{CN}^-$  ligand to form a good bond, may make a contact ion pair,  $[(\text{H}_2\text{O})_5\text{MNCFe}(\text{CN})_4\text{L}]^{n-2}$ . As the polarizing power ( $Z/r$ ) decreases, one anticipates that at some point the sixth hydration energy is substantially more exothermic than bonding to the  $\text{CN}^-$  ligand. Only a solvent-separated ion pair  $[\text{M}(\text{H}_2\text{O})_6(\text{CN})_5\text{FeL}]^{n-2}$  should be produced. This is apparently the observed result in the case of  $\text{Ba}^{2+}$ .

A nearly constant spectral maximum of 666 nm from 0.10 to 0.64 M  $\text{BaCl}_2$  is observed. Above 0.64 M the salt  $\text{Ba}[(\text{CN})_5\text{Fe}(\text{dmapy})]$  precipitates, precluding use of higher molar values of  $\text{Ba}^{2+}$ . Very slight systematic increases on the long-wavelength side of the LMCT transition of  $(\text{CN})_5\text{Fe}(\text{dmapy})^{2-}$  do appear on the spectra with increasing  $[\text{Ba}^{2+}]$ , indicative of electrostatic interaction between  $\text{Ba}^{2+}$  and  $(\text{CN})_5\text{Fe}(\text{dmapy})^{2-}$ . These results suggest that if the  $\text{Fe}^{\text{III}}-\text{C}\equiv\text{N}\cdots\text{M}^{n+}$  distance becomes very large (cationic radius of  $\text{Ba}^{2+} = 1.98 \text{ \AA}$  vs.  $1.12 \text{ \AA}$  for  $\text{Sr}^{2+}$ )<sup>18</sup> there is insufficient exothermicity to formality of the contact ion pair. Outer-sphere association constants also decrease with the increasing distance of separation for like charge-type pairs.  $K_{\text{IP}}$  for  $\text{Ba}^{2+}$  should be smaller than those for the other ions of Table I. Therefore, a smaller fraction of  $(\text{CN})_5\text{FeL}^{2-}$  will be converted to the ion pair. The net result is that ions of quantum level  $n = 6$  are no longer efficient in producing a substantial stabilization of the excited state; the energy separation of the ground and excited states remains reasonably constant over a wide concentration range, even in the presence of solvent-separated ion pairs with  $\text{Ba}(\text{H}_2\text{O})_6^{2+}$  or  $\text{CH}_3\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3^+$ .

Within the inherent limitations imposed by changing activities with changing total electrolyte salt concentration, we believe that the correlation between the shifts per mole relative to  $\text{Li}^+$  for the LMCT bands and the hydration energies (also normalized to  $\text{Li}^+$ ) of the smaller ions is quite excellent. The hydration energy of an ion follows the relationship  $\Delta H_{\text{hyd}} = -167Z^2/r_{\text{eff}}$ ; therefore, it is a function of its charge to effective radius,  $Z/r$ .<sup>16</sup> By virtue of higher charge and smaller radius, one anticipates  $\text{Li}^+$  to be the most efficient in producing a shift in the LMCT spectra for monovalent ions,  $\text{Mg}^{2+}$  for divalent ions, and  $\text{Al}^{3+}$ , ionic radius  $0.51 \text{ \AA}$ , to be greater than  $\text{Sc}^{3+}$ , ionic radius  $0.81 \text{ \AA}$ .<sup>18</sup> Experimentally, the smallest ion of each charge type does produce the greatest shift per mole of the LMCT transition while the sensitivity to charge,  $Z$ , shows  $+3 > +2 > +1$  on the shift. However, the result with  $\text{Ba}(\text{H}_2\text{O})_6^{2+}$  shows that a knowledge of the last hydration energy of each ion is required for a detailed understanding.

The experiments of Sutton and Taube on the influence of  $\text{X}^-$  anions on the spectrum of  $(\text{NH}_3)_5\text{Ru}^{\text{III}}(4\text{-NH}_2\text{py})^{3+}$  were not carried out as a function of concentration; the shift produced by 5 M salts on the LMCT band of this complex were reported together with those of 3.0 M  $\text{Na}_2\text{SO}_4$  and 3.4 M  $\text{CF}_3\text{SO}_3\text{H}$ . The smallest ion,  $\text{F}^-$ , produced the largest shift of 30 nm at 5.0 M. If linearity in concentration is assumed, this gives a 6 nm/mol of  $\text{F}^-$  to be compared with 7.75 nm/mol of  $\text{Li}^+$  for the related  $[\text{Li}^+(\text{CN})_5\text{Fe}(\text{dmapy})^{2-}]$  ion pair. Therefore, the net effect of the ion pair on the LMCT transition is quite similar for monovalent counterions in each case. However, about 9 times the influence of monovalent  $\text{Li}^+$  is achieved by its replacement with  $\text{Al}^{3+}$  after correction for the competitive equilibrium forming  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}, \text{Cl}^-$ .

## Experimental Section

**Electrolyte Salts.** The electrolyte salts used in this study were obtained from several commercial sources: (Aldrich)  $\text{LiCl}$ ; (Alfa)  $\text{ScCl}_3 \cdot 6\text{H}_2\text{O}$ ; (Baker)  $\text{KCl}$ ,  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ; (Fisher)  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ; (Malinkrodt)  $\text{NaCl}$ ,  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ ; (MCB)  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . These analytical grade reagents were used without further purification.  $\text{CH}_3\text{N}(\text{C}_2\text{H}_4\text{O})_3\text{I}$  was prepared by alkylation of triethanolamine. A 0.10-mol sample

of triethanolamine (Fisher) was reacted with 0.13 mol of  $\text{CH}_3\text{I}$  (Aldrich) in ethanol (200 mL) at reflux for 1 h. The salt is filtered off after cooling and recrystallized from ethanol.

**$\text{Na}_2[\text{Fe}(\text{CN})_5\text{L}]$  Complexes.** The ligands benzimidazole and 4-(dimethylamino)pyridine were obtained from Eastman and Aldrich, respectively. These ligands were used without further purification. Preparation of the complexes has been reported previously.<sup>1,2</sup>

**Spectra.** The ultraviolet-visible spectra were recorded with a Varian-Cary 118C spectrophotometer in the case of the  $\text{Fe}(\text{CN})_5(\text{bzimH})^{2-}$  complex and with a Hewlett-Packard 8450A spectrophotometer for the  $\text{Fe}(\text{CN})_5(\text{dmapy})^{2-}$  complex.<sup>21</sup> The  $\lambda_{\text{max}}$  values of spectra taken on the HP-8450A were determined by the instrument's PEAK-FIND function. All spectra were obtained at room temperature in quartz or glass cells.

The solutions on which the spectra were recorded were prepared by dissolving a freshly weighed sample of  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{L}]$  in a 10.0-mL volumetric flask with water. Aliquots of this solution were then added to other 10.0-mL volumetric flasks containing the proper amounts of the predissolved electrolyte salt for final dilution. Spectra were taken as soon as possible after preparation of the solutions in order to minimize the effects of ligand dissociation. For the  $(\text{CN})_5\text{Fe}(\text{bzimH})^{2-}$  series an excess of bzimH at  $5.0 \times 10^{-3} \text{ M}$  (10-fold excess) was added to suppress the problem of ligand dissociation. In the case of  $\text{Al}^{3+}$  all samples were prepared with 0.01 M  $\text{HCl}$  to suppress hydrolysis of the  $\text{Al}^{3+}$ . The aliquot of  $\text{Fe}(\text{CN})_5(\text{dmapy})^{2-}$  solution was added to each acidified sample immediately before recording its spectrum.

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**Registry No.**  $(\text{CN})_5\text{Fe}(\text{dmapy})^{2-}$ , 91209-30-2;  $(\text{CN})_5\text{Fe}(\text{bzimH})^{2-}$ , 91209-20-0;  $\text{Li}^+$ , 17341-24-1;  $\text{Na}^+$ , 17341-25-2;  $\text{K}^+$ , 24203-36-9;  $\text{Mg}^{2+}$ , 22537-22-0;  $\text{Ca}^{2+}$ , 14127-61-8;  $\text{Sr}^{2+}$ , 22537-39-9;  $\text{Ba}^{2+}$ , 22541-12-4;  $\text{Al}^{3+}$ , 22537-23-1;  $\text{Sc}^{3+}$ , 22537-29-7; tetramethylammonium cation, 51-92-3; tetraethylammonium cation, 66-40-0.

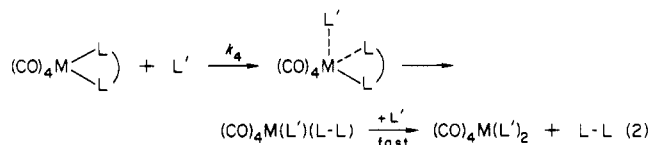
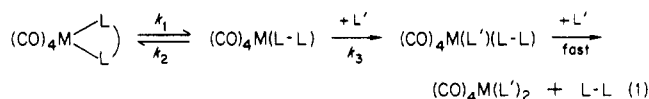
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## Volumes of Activation and Mechanistic Assignment for Chelate Ring Replacement at Tetracarbonylchromium(0) Centers

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Mechanistic studies at chelate ring replacement reactions of tetracarbonylmetal(0) centers, in general, have revealed two possible pathways.<sup>2</sup> The first involves unimolecular ring opening (eq 1), and the second, concerted ring opening under the influence of the incoming nucleophile  $\text{L}'$  (eq 2).



Various systems involving replacement of a chelate ring coordinated through sulfur have been interpreted in terms of these

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(2) Halverson, D. E.; Reisner, G. M.; Dobson, G. R.; Bernal, I.; Mulcahy, T. L. *Inorg. Chem.* 1982, 21, 4285 and references cited therein.