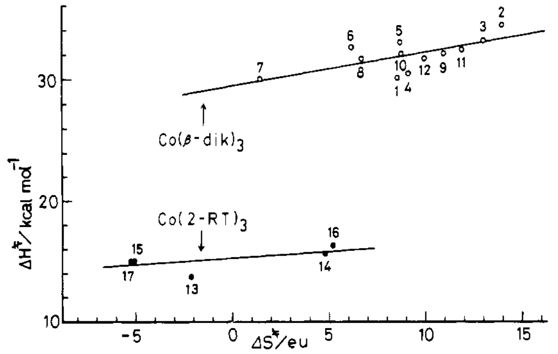

Figure 4. Isokinetic plot for the intramolecular rearrangement of Co(β-dik)$_3$ (○) and Co(2-RT)$_3$ (●) complexes. Numbers and conditions are the same as in Table III.

spectively. An exception occurs for the isomerization of Al(2-C_3H_7T)$_3$. The differences suggest there might be some differences in mechanisms. If the isomerization of Al(2-C_3H_7T)$_3$ occurs by means of the BR mechanism,[3a] the similarity in ΔH^* in the cases of both Al(2-C_3H_7T)$_3$ and $[SiT_3]^+$ suggests that the racemization of $[SiT_3]^+$ also occurs by means of the BR mechanism.

We can compare mechanisms of tropolonato and β-diketonato complexes for only the three cases of Si(IV), Al(III), and Co(III). In the case of Si(IV) complexes, the racemizations of both tris(tropolonato) and tris(β-diketonato) complexes proceed via the BR mechanism as discussed above. For Al(III) complexes, the linearity (isokinetic temperature 500 K) of the isokinetic plot (Figure 3) suggests that the common mechanism of both racemizations is the BR mechanism. In contrast, Co(III) complexes show huge differences between Co(2-RT)$_3$ and Co(β-dik)$_3$. The value of $\Delta H_{\ddagger}$ for Co(2-RT)$_3$ is half that of Co(β-dik)$_3$, and the rate is around 10^{11} times that of the latter. The isokinetic plot (figure 4) places the tropolonato and β-diketonato complexes in different mechanistic groups. The isokinetic temperatures for Co(2-RT)$_3$ and Co(β-dik)$_3$ were 110 and 267 K. This evidence suggests there are different mechanisms in the case of Co(III) complexes. Since it is reasonable for Co(β-dik)$_3$ to racemize via the BR mechanism,[1,2] Co(2-RT)$_3$ may racemize via the non-BR mechanism.

As the variations of the rate constants and activation parameters of Ga(III) and Al(III) complexes are similar, we propose that β-diketonato complexes of both main-group and transition metals and tropolonato complexes of main-group metals racemize via the BR mechanism, intramolecularly, but that the tropolonato complexes of transition metals racemize via the non-BR mechanism, intramolecularly.

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Registry No. $[SiT_3]ClO_4$, 86308-23-8; trichloroacetic acid, 76-03-9.

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University of Pittsburgh, Pittsburgh, Pennsylvania 15260

Metal-to-Ligand Charge-Transfer Spectra of Pentacyanoruthenate(II) Complexes of Aromatic Nitrogen Heterocycles

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The MLCT transitions of $(CN)_5Ru^{3-}$, $(CN)_5Fe^{3-}$, and $(NH_3)_5Ru^{2+}$ complexes of aromatic nitrogen heterocycles (L) correlate linearly with the reduction potentials of these ligands and the Hammett substituent constants, σ_p. The $(CN)_5FeL^{3-}$ complexes are most sensitive to the nature of L. Comparisons are also made to the $W(CO)_5L$ and $(NH_3)_5OsL^{2+}$ complexes where the W(0) complex follows trends established by the parent series but the Os(II) complexes do not. A simple MO description of these complexes is given to account for the trends of the MLCT transitions for metal centers vs. metal centers and for a given metal center with altering the "spectator ligand" set. Back-bonding capabilities of the $(CN)_5Fe^{3-}$, $(CN)_5Ru^{3-}$, and $(CO)_5W$ moieties are found to be about the same (<10% mixing); these may be classed as "hard" centers toward L. The results for the $(NH_3)_5OsL^{2+}$ series show that orbital mixing is sufficient to best describe the observed transitions as ligand-to-metal based, with $(NH_3)_5Os^{2+}$ as a "soft" center toward L. The hardening influence of CN^- toward Fe(II) or Ru(II) is opposite its known softening effect toward Co(III). CN^- operates as a $\sigma - \pi$ donor toward Fe(II) and Ru(II) while only as a σ donor toward Co(III).

Introduction

Extensive studies have been made on $(NH_3)_5RuL^{2+}$ and $(CN)_5FeL^{3-}$ complexes,[1,2] where L represents an aromatic nitrogen heterocycle such as pyridine (py) or pyrazine (pz). These compounds have been well characterized, and their thermal[3] and photochemical[4] reactivities have been investigated. Metal-to-ligand back-bonding has been shown to make an important contribution to the properties of these complexes. The low-spin d^6 configuration of both series of complexes provides filled orbitals of the proper symmetry to interact with relatively low-energy, unoccupied π^* orbitals on the ligand (L). A notable feature of the UV–visible spectra of these complexes is a strong absorption attributable to a metal-to-ligand charge-transfer (MLCT) transition, $\pi^* \leftarrow t_{2g}$.[2,5] The energy of this transition varies with the identity of L in a manner consistent with the ability of the ligand to act as a π acceptor. Studies of complexes where L is a substituted pyridine have shown that electron-releasing substituents increase the energy of the transition while electron-withdrawing substituents decrease the energy.[1a,2b] This is the expected order for a charge

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(1) (a) Ford, P. C. *Coord. Chem. Rev.* **1970**, *5*, 75–99. (b) Taube, H. "Survey of Progress in Chemistry"; Scott, A. F., Ed.; Academic Press: New York, 1973; Vol. 6, Chapter 1.

(2) (a) Toma, H. E.; Malin, J. M. *Inorg. Chem.* **1973**, *12*, 1039–1045. (b) Hrepic, N. V.; Malin, J. M. *Ibid.* **1979**, *18*, 409–413.

(3) (a) Shepherd, R. E.; Taube, H. *Inorg. Chem.* **1973**, *12*, 1392–1401. (b) Toma, H. E.; Malin, J. M. *Ibid.* **1973**, *12*, 2080–2083.

(4) (a) Malouf, G.; Ford, P. C. *J. Am. Chem. Soc.* **1974**, *96*, 601–603; **1977**, *99*, 7213–7221. (b) Figard, J. E.; Peterson, J. D. *Inorg. Chem.* **1978**, *17*, 1059–1063.

(5) Ford, P.; Rudd, De F. P.; Gaunder, R.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1187–1194.

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transfer from metal to ligand.

Toma and Malin have shown that there is a remarkable linear correlation between the energies of the MLCT transitions for the $(NH_3)_5RuL^{2+}$ and $(CN)_5FeL^{3-}$ series over a wide range of different L with varying π-acceptor abilities.[2] The correlation is excellent despite the different set of "spectator" ligands in the two series, NH_3 vs. CN^-. The two series also differ in the radial extension of the orbitals that participate in the back-bonding, 3d(Fe) vs. 4d(Ru). More recently, a limited series of $(NH_3)_5OsL^{2+}$ complexes have been prepared.[6] The trend in the energy of the MLCT transition for this series of complexes is the same as for the $(NH_3)_5RuL^{2+}$ and $(CN)_5FeL^{3-}$ series, but the correlation is not nearly as linear. Data on several $(CO)_5WL$ complexes are also available.[7]

To further investigate the MLCT spectra of low-spin d^6 ions, a new series of $(CN)_5RuL^{3-}$ complexes has been prepared. The $(CN)_5RuL^{3-}$ series can be compared with the $(CN)_5FeL^{3-}$ series to investigate the effect of 3d- vs. 4d-orbital participation in the back-bonding while the set of "spectator" ligands remains constant. Similarly, the $(CN)_5RuL^{3-}$ series can be compared with the $(NH_3)_5RuL^{2+}$ series where the d-orbital level involved is the same but the "spectator" ligands are changed from CN^-, a good π acceptor, to NH_3, which has no π-acceptor capability. The addition of the $(CN)_5RuL^{3-}$ series to the list of d^6 complexes displaying MLCT spectra permits more conclusions to be drawn about the nature of the interaction between the metal d orbitals and the ligand π^* orbitals in this type of complex than had been possible on the basis of only two series, $(CN)_5FeL^{3-}$ and $(NH_3)_5RuL^{2+}$.

Results

The $(CN)_5RuL^{3-}$ complexes exhibit an intense band ($\epsilon \sim 5 \times 10^3$ M^{-1} cm^{-1}) in the visible–near-UV region of the spectrum. The position of this absorption varies with the identity of L. These observations are consistent with the assignment of this transition as a MLCT band. The data for the $(CN)_5RuL^{3-}$ series of complexes are shown in Table I along with data available for other complexes.

It has been shown that CN^- serves as an electron-withdrawing group for $(CN)_5Ru(pz)^{3-}$ (pz = pyrazine).[14] In spite of the advantage of the trianion electrostatically over $(NH_3)_5Ru(pz)^{2+}$ to attract a proton, the pK_a's are found to be 0.4 ± 0.1 for $(CN)_5Ru(pz)H^{2-}$ vs. 2.85 ± 0.10 for $(NH_3)_5Ru(pz)H^{3+}$.[14] The band that has been assigned as the MLCT band for $(CN)_5Ru(pz)^{3-}$ undergoes a shift to lower energy on protonation of the pyrazine, analogous to the behavior of the $(NH_3)_5Ru(pz)^{2+}$ complex.[14,5] Therefore, the bands observed for complexes reported in Table I are likewise assigned as MLCT for the $(CN)_5RuL^{3-}$ series.

Further support for the MLCT assignment comes from comparisons that can be made between the data for the different series. Ford et al. have shown that the energy of the MLCT transition for azine complexes of $(NH_3)_5Ru^{2+}$ correlates with the free-ligand half-wave reduction potential.[5] This type of correlation is expected since the energy of the MLCT transition should show a dependence on the energy of the unoccupied π^* orbital of the free ligand. Figure 1 illustrates the correlation between the MLCT energy and the reduction potential of the ligand. The correlation is excellent for the $(CN)_5Ru^{3-}$, $(CN)_5Fe^{3-}$, and $(NH_3)_5Ru^{2+}$ complexes. The $(NH_3)_5Os^{2+}$ series shows a much poorer correlation. The plot also illustrates that the dependence of the MLCT energy on the energy of the ligand LUMO is not the same for each series, as seen by the difference in the slopes. The energy of the MLCT transition for the $(CN)_5Fe^{3-}$ series is more sensitive to the energy level of the ligand π^* orbital, as measured by the reduction potential of the ligand, than is the MLCT energy for the other series. The energy of the MLCT transition for the $(NH_3)_5Os^{2+}$ series shows less dependence on the ligand reduction potential.

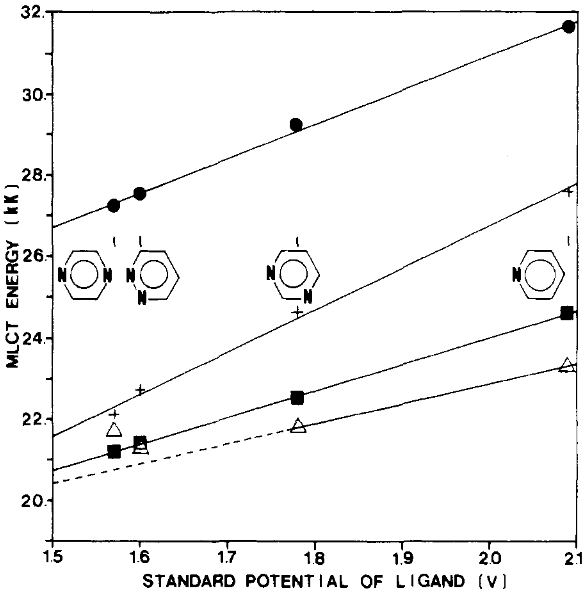

Figure 1. Correlation between the potentials of the ligands and the MLCT energies of their complexes: ●, $(CN)_5RuL^{3-}$; +, $(CN)_5FeL^{3-}$; ■, $(NH_3)_5RuL^{2+}$; △, $(NH_3)_5OsL^{2+}$.

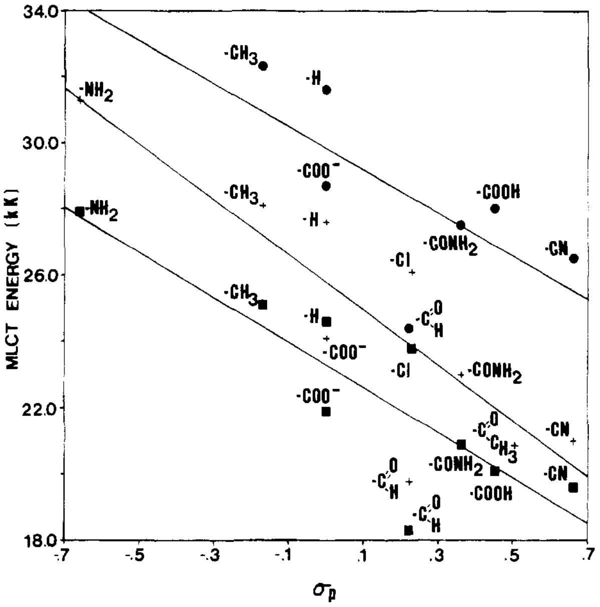

Figure 2. Correlation between the MLCT energies of complexes of para-substituted pyridines and their Hammett substituent constants (σ_p): ●, $(CN)_5RuL^{3-}$; +, $(CN)_5FeL^{3-}$; ■, $(NH_3)_5RuL^{2+}$. Para substituents are shown next to each data point.

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(6) (a) Sen, J.; Taube, H. *Acta Chem. Scand. Ser. A* **1979**, *A33*, 125–135. (b) Magnuson, R. H.; Taube, H. *J. Am. Chem. Soc.* **1975**, *97*, 5129–5136.

(7) (a) Alistair, J. L.; Adamson, A. W. *J. Am. Chem. Soc.* **1982**, *104*, 3804–3812. (b) Wrighton, M. S.; Abrahamson, H. B.; Morse, D. L. *Ibid.* **1976**, *98*, 4105–4109. (c) Pannell, K. H.; Guadalupe, M., de la P. S. G.; Leano, H.; Iglesias, R. *Inorg. Chem.* **1978**, *17*, 1093–1095.

(8) Swain, C. G.; Lupten, E. C., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 4328–4337. Gordon, A. J.; Ford, R. A. "The Chemists Companion"; Wiley: New York, 1972; p 145.

(9) Sutton, J. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 4021–4023.

(10) Shepherd, R. E. Ph.D. Thesis, Stanford University, 1971.

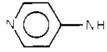
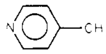
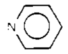
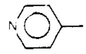
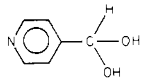
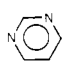
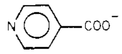
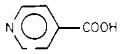
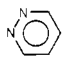
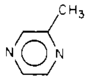
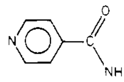
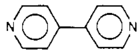
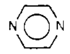
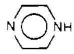
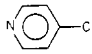
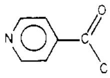
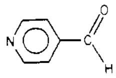
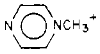
(11) Clark, R. E.; Ford, P. C. *Inorg. Chem.* **1970**, *9*, 495–499.

(12) Toma, M. E.; Malin, J. M. *J. Am. Chem. Soc.* **1975**, *97*, 288–293.

(13) Shepherd, R. E. *J. Am. Chem. Soc.* **1976**, *98*, 3329–3335. See also: Malin, J. M.; Brunschwig, B. S.; Brown, G. M.; Kwan, K.-S. *Inorg. Chem.* **1981**, *20*, 1438–1441.

(14) Johnson, C. R.; Shepherd, R. E. *Inorg. Chem.* **1983**, *22*, 1117.

Table I. MLCT Absorptions of d^6 Complexes (10^3 cm^{-1} (nm))

no.	ligand (L)	$\sigma_p{}^a$	$(NH_3)_5OsL^{2+\,b}$	$(NH_3)_5RuL^{2+}$	$(CN)_5FeL^{3-}$	$(CN)_5RuL^{3-\,j}$	$(CO)_5WL^{n}$
1		−0.660		27.9 (359)^{c}	31.3 (320)^{h}		
2		−0.170		25.1 (398)^{d}	28.1 (356)^{e}	32.3 (310)	28.5 (351)
3		0.0	23.3 (430)	24.6 (407)^{d}	27.6 (362)^{e}	31.6 (316)	28.2 (355)
4		0.227		23.8 (422)^{e}	26.1 (383)^{e}		
5				23.8 (420)^{d}	25.6 (390)^{i}		
6			21.8 (458)	22.5 (445)^{d}	24.6 (407)^{j}	29.2 (342)	
7		0.0		21.9 (457)^{d}	24.1 (415)^{e}	28.7 (348)	
8		0.45		20.1 (497)^{d}		28.0 (357)	
9			21.3 (470)	21.4 (467)^{d}	22.7 (440)^{j}	27.5 (363)	
10				21.4 (467)^{f}	22.3 (449)^{k}	27.6 (362)	
11		0.36	19.7 (508)	20.9 (479)^{d}	23.0 (435)^{e}	27.5 (364)	
12				21.1 (475)^{e}	23.1 (432)^{e}	27.4 (365)	
13			21.7 (460)	21.2 (472)^{d}	22.0 (455)^{e}	27.2 (368)^{l}	
14			23.4 (428)	18.9 (529)^{d}	~16.0 (~625)^{l}	~20.4 (~490)^{l}	
15		0.660		19.6 (510)^{g}	21.0 (476)^{m}	26.5 (377)	22.0 (455)
16		0.502			20.8 (480)^{m}		22.7 (441)
17		0.22		18.3 (545)^{d}	19.8 (505)^{e}	24.4 (410)	21.3 (469)
18				18.4 (542)^{e}	15.1 (655)^{e}	19.1 (524)	

^{a} Hammett substituent constant for para-substituted pyridines.[8] ^{b} Reference 6. ^{c} Reference 9. ^{d} Reference 5. ^{e} Reference 2. ^{f} Reference 10. ^{g} Reference 11. ^{h} Reference 2b. ^{i} Reference 12. ^{j} This work. ^{k} Reference 13. ^{l} Reference 14. ^{m} Reference 4b. ^{n} Reference 7b. The data for the (CO)$_5$WL complexes were obtained in isooctane. References 7a and 7c provide data in other solvents. These data are not included here because the MLCT energy is very solvent dependent. The data for the $(NH_3)_5OsL^{2+}$, $(NH_3)_5RuL^{2+}$, $(CN)_5FeL^{3-}$, and $(CN)_5RuL^{3-}$ complexes were obtained in aqueous solution.

Figure 2 shows the correlation between the MLCT energy and the Hammett substituent constants, σ_p, for complexes with a number of para-substituted pyridines. As previously noted for the $(NH_3)_5RuL^{2+}$ series,[1a,5] there is a general correlation between the energies of this transition and the substituent constant. The linear fit is not good however, with some values, e.g. C(O)H, lying far off the line. Despite the scatter in the data, the trend toward lower charge-transfer energy with more strongly electron-withdrawing substituents is clearly discernible. The energies of the MLCT transitions of the $(CN)_5Fe^{3-}$ series are once again seen to be the most sensitive to the nature of the ligand. The $(NH_3)_5Ru^{2+}$ and $(CN)_5Ru^{3-}$ series show about the same dependence on σ_p.

In Figure 3, the MLCT energies of each series of complexes are plotted against the MLCT energies for the $(CN)_5FeL^{3-}$ series. The data for the positively charged ligands, pyrazinium ion and *N*-methylpyrazinium ion, do not fit well with the other data and are not included in the plot. The data in each series were treated by a linear least-squares program, and the slopes and standard deviations were determined: $(CN)_5RuL^{3-}$, 0.87 ± 0.05; $(CO)_5WL$, 0.87 ± 0.05; $(NH_3)_5RuL^{2+}$, 0.78 ± 0.04; $(NH_3)_5OsL^{2+}$, 0.42 ± 0.23. The data for the $(CN)_5RuL^{3-}$, $(CO)_5WL$, and $(NH_3)_5RuL^{2+}$ series correlate well with the $(CN)_5FeL^{3-}$ data. The $(NH_3)_5OsL^{2+}$ data give a poor fit. The slopes are all less than 1. A slope of less than 1.0 is consistent with the $(CN)_5FeL^{3-}$ series showing the largest changes in energy from ligand to ligand.

Discussion

Ford et al. have presented a molecular-orbital description of $(NH_3)_5Ru(py)^{2+}$.[5] Subsequently, Zwickel and Creutz developed a molecular-orbital treatment of $(NH_3)_5RuL^{2+}$ and *cis*- and *trans*-$(NH_3)_4RuL_2{}^{2+}$ complexes based on symmetry and overlap arguments.[15] The metal-to-ligand charge-transfer

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(15) Zwickel, A. M.; Creutz, C. *Inorg. Chem.* **1971**, *10*, 2395–2399.

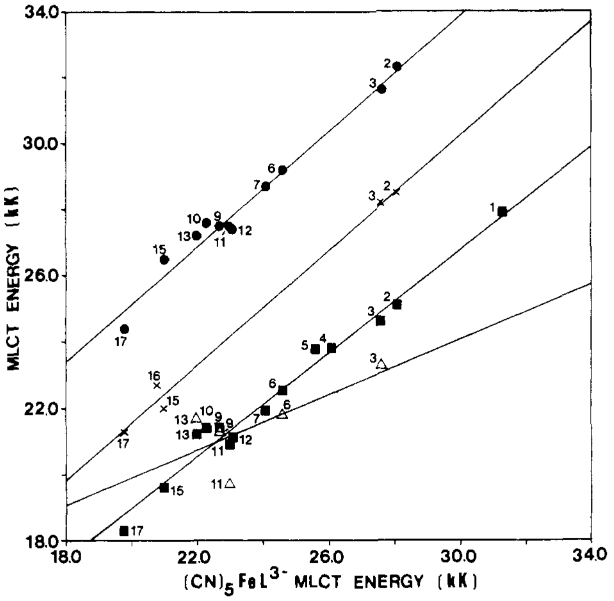

Figure 3. Correlation between the MLCT energies of the complexes and the MLCT energies of the $(CN)_5FeL^{3-}$ complexes: ●, $(CN)_5RuL^{3-}$; ×, $(CO)_5WL$; ■, $(NH_3)_5RuL^{2+}$; △, $(NH_3)_5OsL^{2+}$. Each data point is numbered according to the ligand as identified in Table I.

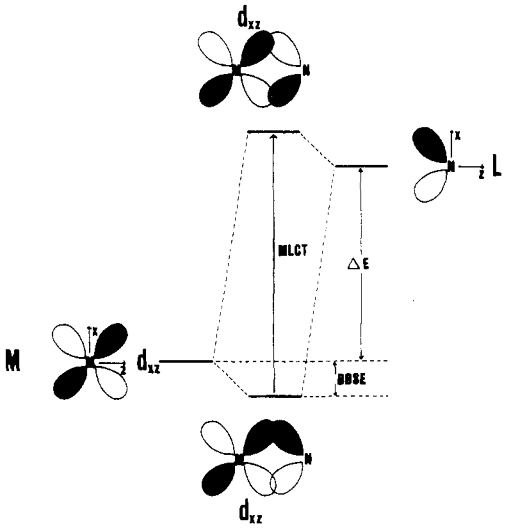

Figure 4. Molecular-orbital description of the back-bonding interaction. M = $(CN)_5Ru^{3-}$, $(CN)_5Fe^{3-}$, $(CO)_5W$, $(NH_3)_5Ru^{2+}$, or $(NH_3)_5Os^{2+}$. L = aromatic nitrogen heterocycle. The metal-to-ligand charge transfer (MLCT) transition and the back-bonding stabilization energy (BBSE) are indicated.

band is described as a transition from a d level to the ligand B_2 antibonding π level. Symmetry orbitals are constructed from the d_{xz} (metal) and $\pi_x{}^*$ (ligand) orbitals, producing a bonding orbital of predominantly metal character and an antibonding orbital of predominantly ligand character (Figure 4). The MLCT transition occurs between these two orbitals.

The back-bonding stabilization energy (BBSE) is the energy difference between the purely metal orbital and the molecular ground state derived from mixing of the metal orbital with the ligand π^* orbital. Qualitatively, two factors will influence the extent of this orbital mixing and the magnitude of the BBSE: (1) the radial extension of the metal d orbital and (2) the energy difference, ΔE, between the metal orbital and the ligand orbital. Greater interaction is expected for orbitals that are close in energy. Metal d orbitals of high energy are favorable for the back-bonding interaction. The ability for metal–ligand orbital interactions is also enhanced if the metal d orbitals extend far into space, enabling effective overlap with the π^* orbital. These considerations lead to the well-known order of back-bonding ability—5d > 4d > 3d. In considering the ability of the metal centers to back-bond to L in the complexes described in this paper, attention must be paid to the remaining ligand environment, the "spectator" ligands. Ammonia will not have much effect on the energy of the t_{2g} orbitals of the metal center and should not alter the ability for back-bonding to π acceptors such as pyrazine in these complexes. Conversely, CN^- and CO will greatly stabilize the t_{2g} orbitals through back-bonding of their own, leaving the capacity to back-bond to a sixth ligand, L, greatly diminished. Figure 5 shows the energy levels of the metal t_{2g} orbitals relative to the pyridine or pyrazine π^* levels. Pyridine is chosen as the best test ligand since its degree of π acidity is the least of those ligands that have been studied in this work and by other groups for complexes of the d^6 type L'_5ML, M = Fe(II), Ru(II), Os(II), W(0). It is found that the $\pi \rightarrow \pi^*$ ligand transition is not changed much from the free-ligand value whether py is coordinated to H^+, $(NH_3)_5Ru^{2+}$, $(NH_3)_5Ru^{3+}$, $(NH_3)_5Os^{2+}$, $(CN)_5Fe^{3-}$, or $(CN)_5Fe^{2-}$.[5,6] (The $W(CO)_5$ case is obscured in the ultraviolet region by transitions of the metal carbonyls.) Therefore, the energies of π orbitals are insensitive to changes in the nature or charge of the attached moiety. Figure 5 should be taken to convey a qualitative ranking of the πd orbital used to generate the molecular orbitals of Figure 4 based on MLCT bands for $Ru(CN)_5py^{3-}$ vs. the other pyridine complexes. The uncertainty in the position of the pyridine π^* orbital of (1–2) × 10^3 cm^{-1} from complex to complex is not a severe limitation for examination of trends. Since pyrazine will interact more strongly upon coordination, raising $d_{xz} + \pi_x{}^*$ and lowering $d_{xz} - \pi_x{}^*$ orbitals, the ordering in the pyrazine complexes should be considered more conservatively. Since back-bonding effects are the smallest for pyridine, the value of the MLCT energy will most closely approximate the value of ΔE (Figure 4) and may be used to order the relative energies of the L'_5M fragments, L′ = NH_3 or CN^-. The expected order of 5d > 4d > 3d is seen for $(NH_3)_5Os^{2+}$ > $(NH_3)_5Ru^{2+}$ > $(CN)_5Fe^{3-}$. The comparison is hindered by the lack of a low-spin $(NH_3)_5Fe^{2+}$ series. Reversal of the order is observed for the CN^- complexes, where

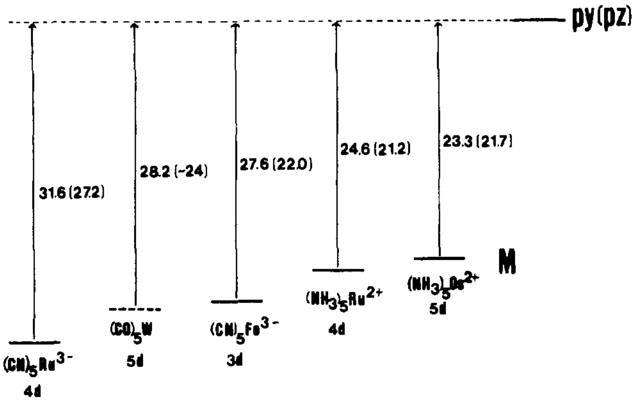

Figure 5. Relative d-orbital energies of the metal complexes based on the energies of the MLCT transitions for the pyridine (py) and pyrazine (pz) complexes in water. The levels are shown for the pyridine complexes. The MLCT energy for the $(CO)_5Wpy$ complex is for an isooctane solution.

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(19) The NMR of these and other complexes will be reported in a future publication.

the 4d level of $(CN)_5Ru^{3-}$ is lower in energy than the 3d level of $(CN)_5Fe^{3-}$. This is consistent with a greater crystal field stabilization energy (CFSE) for the 4d ion, Ru^{2+}. The ordering of the relative energies of L'_5M fragments shown in Figure 5 with py as the π acceptor, albeit a weak one, is the same order as observed by Gray and Beach with CN^- acting as the sixth ligand π acceptor.[20] The MLCT bonds for $Fe(CN)_6^{4-}$, $Ru(CN)_6^{4-}$, and $Os(CN)_6^{4-}$ follow the order of decreasing energy Ru(II) > Os(II) > Fe(II). The MLCT energies are spaced ca. 2.6×10^3 cm^{-1} for $Ru(CN)_6^{4-}$ vs. $Fe(CN)_6^{4-}$ with transitions near 50×10^3 cm^{-1}.[20] From Figure 5 the spacing for $Ru(CN)_5^{3-}$ vs. $Fe(CN)_5^{3-}$ with py as the acceptor is about 4.0×10^3 cm^{-1}, near 30×10^3 cm^{-1} for comparison. Thus, the spacing predicted from Figure 5 appears to be in good agreement with the hexacyanide spectra. The $(CO)_5W$ 5d-orbital level falls between the two CN^- series. CO, a very good π acceptor, should greatly stabilize the W t_{2g} orbitals, but direct comparison with the other series is difficult because of the difference in the formal oxidation state of the central ion, +2 for all others in Figure 5 vs. 0 for W.

The trends in Figures 1–5 can now be examined in light of the considerations outlined above. The $(CN)_5FeL^{3-}$ series relies on a 3d-orbital level for back-bonding. This orbital is at relatively low energy and has the smallest radial extension. On this basis, this series is expected to display little mixing of metal and ligand orbitals. Therefore, the MLCT transition for this series is considered to be from an almost pure metal orbital to an almost pure ligand orbital. As such, the energy of the MLCT transition for this series is the most sensitive to changes in the energy of the π^* orbital as the identity of the ligand is changed. The $(NH_3)_5RuL^{2+}$ and $(NH_3)_5OsL^{2+}$ series show less dependence on the nature of L. Back-bonding is more important in these complexes with 4d- and 5d-orbital participation and NH_3 "spectator" ligands. The effect of this greater back-bonding ability will be most pronounced with the best π-acceptor ligands, to the left of the plot in Figure 3. The larger BBSE for these complexes results in a lowering of the $d_{xz} - \pi_x^*$ molecular orbital and raising of the $d_{xz} + \pi_x^*$ orbital. The energy of the MLCT transition then increases from the value expected for the energy difference on the basis of pure metal and pure ligand orbitals. Thus, the MLCT energies to the left of Figure 3 gradually become larger than would be expected if there was little back-bonding as in the $(CN)_5FeL^{3-}$ series. For weaker π acceptors such as pyridine or 4-methylpyridine, back-bonding is weak for all complexes. The result is a slope less than 1 in Figure 3. As more mixing of orbitals due to back-bonding occurs, the excited state takes on more metal-orbital character and the energy of this orbital depends less on the identity of L. As pointed out above, the $(NH_3)_5RuL^{2+}$ and $(NH_3)_5OsL^{2+}$ MLCT energies show less dependence on L than the $(CN)_5FeL^{3-}$ series. The $(CN)_5RuL^{3-}$ complexes behave more like $(CN)_5FeL^{3-}$ series in terms of sensitivity to the π-acceptor character of L.

Compared to $(CN)_5Fe^{3-}$, the $(CN)_5Ru^{3-}$ and $(CO)_5W$ moieties have a less favorable energy for back-bonding, the t_{2g} orbitals being low in energy, but a more favorable radial extension, the 4d and 5d orbitals being spacially more expansive. The result is that the back-bonding capabilities of $(CN)_5Ru^{3-}$ and $(CO)_5W$ are about the same as that for $(CN)_5Fe^{3-}$, i.e. less than those for $(NH_3)_5Ru^{2+}$ and $(NH_3)_5Os^{2+}$. This fact is supported by the similar pK_a value of $(CN)_5Ru(pz)H^{2-}$ (0.4 ± 0.1) vs. that of $(CN)_5Fe(pz)H^{2-}$ (0.06 ± 0.06); the CN^- stretching frequencies for the parent pyrazine complexes are nearly identical.[14] The amount of back-bonding to pyrazine in $(CN)_5Ru(pz)^{3-}$ and $(CN)_5Fe(pz)^{3-}$ was previously estimated to be about the same (9% vs. 7%, the slight difference being outside the accuracy of the estimates).[14] Back-bonding also contributes little to the stability of the metal–pyrazine bond in $(CO)_5Wpz$.[16] The slopes of the $(CN)_5RuL^{3-}$ and $(CO)_5WL$ series in Figure 3 are a little less than 1 and do suggest better back-bonding capability for $(CN)_5Ru^{3-}$ and $(CO)_5W$ with good π acceptors than for $(CN)_5Fe^{3-}$. Thus $(CN)_5Ru^{3-}$ is softer compared to $(CN)_5Fe^{3-}$.

The poor correlation of the $(NH_3)_5OsL^{2+}$ data with the data for the other series deserves further discussion. It has been noted previously that the ground-state molecular orbital of $(NH_3)_5Os(pz)^{2+}$ contains substantial ligand character compared to metal character.[6,14] As a consequence, the observed charge transfer for this complex is best described as ligand to metal. The unperturbed metal and ligand orbitals are probably at about the same energy in this complex. As a result of the extensive orbital mixing in this complex, the energy of the charge transfer is substantially larger than would be predicted on the basis of the unperturbed orbitals. This results in a noticeable turnup in the MLCT energy for the $(NH_3)_5OsL^{2+}$ series in the plots in Figures 1 and 3 on going toward the better π-acceptor ligands.

Conclusion

The ability of the $(CN)_5Ru^{3-}$, $(CO)_5W$, $(CN)_5Fe^{3-}$, $(NH_3)_5Ru^{2+}$, and $(NH_3)_5Os^{2+}$ moieties to engage in back-bonding with a potential π-accepting sixth ligand can be described in terms of the "softness" of each metal center. The metal centers of $(CN)_5Ru^{3-}$, $(CO)_5W$, and $(CN)_5Fe^{3-}$ *are made to appear* "harder" to the sixth ligand than for the ammine analogues because of the large π-acceptor ability of CN^- and CO. It must be remembered, however, that the relatively small amount of back-bonding to L in these complexes can have an important influence on their reactivities and stabilities.[3] The metal centers in $(NH_3)_5Ru^{2+}$ and $(NH_3)_5Os^{2+}$ retain their "softness" defined relative to "normal" first-row transition-metal 2+ ions and can back-bond effectively to the sixth ligand. Back-bonding is particularly extensive for the $(NH_3)_5OsL^{2+}$ complexes. These results are within expectations based on intuitive chemical sense, but subtle trends in back-bonding capabilities cannot be demonstrated without examining series of ligands with different metal centers and different "spectator" ligands.

An interesting contrast can be made between the results of this study and the classic comparison of the SCN^- complexes of $(NH_3)_5Co^{3+}$ and $(CN)_5Co^{2-}$.[17] The N-bonded isomer is thermodynamically favored with $(NH_3)_5Co^{3+}$, while $(CN)_5Co^{2-}$ favors the S-bonded complex. This observation seems to indicate that CN^- makes the Co^{3+} center "softer". This effect of CN^- vs. NH_3 contradicts the conclusion reached above that CN^- makes the metal center "harder". These opposing effects can be reconciled if the back-bonding capability of Co^{3+} is considered. The high-oxidation state and low d-orbital energy are unfavorable for strong back-donation. Consequently, no low-energy MLCT band is observed for either $(NH_3)_5Co(pz)^{3+}$ or $(CN)_5Co(pz)^{2-}$, for example. The cyano ligand in $(CN)_5Co^{2-}$ acts primarily to donate σ-electron density to the metal center, which is only partly removed by the weak π back-bonding. The result is a net accumulation of negative charge on the metal center, which "softens" it. Cyanide has a somewhat different effect on the Ru^{2+} center in $(CN)_5Ru^{3-}$. Donation of σ-electron density to a 2+ metal center will be less than to a 3+ metal center. Back-donation of electron density to the CN^- will be an additional effect that reduces the t_{2g} electron density and makes the metal center "harder" than if π bonding to CN^- or another spectator ligand is absent.

More data on different $(CO)_5WL$ and $(NH_3)_5OsL^{2+}$ complexes would be useful. Examination of other series, particularly the $(CO)_5MoL$ and $(CN)_5OsL^{3-}$ complexes, may help

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in putting the discussion of bonding in this type of complex on a more quantitative basis.

Experimental Section

UV–visible spectra were recorded with a Varian-Cary 118 C spectrophotometer. The energy of the MLCT transition was determined from the spectrum of a freshly prepared aqueous solution of each complex at room temperature. The pyrimidine and pyridazine complexes of pentacyanoferrate(II) were prepared in solution according to the procedure described by Toma and Malin for other complexes of the series.[2a] The pentacyanoruthenate(II) complexes were prepared by allowing an excess of the ligand, L, to react with a solution of $(CN)_5RuOH_2^{3-}$. Solutions of $(CN)_5RuOH_2^{3-}$ were prepared from the reaction of Br_2 with $Ru(CN)_6^{4-}$.[18] Details of the synthetic procedure are given elsewhere.[14] With the exception of *N*-methylpyrazinium ion, the ligand was added to the solution of $Ru(CN)_6^{4-}$ prior to adding Br_2. In the *N*-methylpyrazinium case, the ligand was added immediately after the Br_2. The solid complexes were isolated by precipitation with cold acetone for L = pyridine, 4-methylpyridine, 4,4′-bipyridine, pyrimidine, pyridazine, pyrazine, 2-methylpyrazine, isonicotinamide, isonicotinic acid, and *N*-methylpyrazinium ion. The spectra of complexes with other ligands were obtained on the reaction mixture or after isolation of the complex on an anion-exchange resin and elution with 4 M $NaClO_4$. The spectra of the redissolved solids were in agreement with spectra of the reaction mixture prior to isolation of the complex. The isolated solids were characterized by NMR.[19] Over the time of 1 day, solutions of the pentacyanoruthenate(II) complexes undergo slow spectral changes, indicating some aquation or decomposition.

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Registry No. $(CN)_5FeL^{3-}$ (L = pyrimidine), 86260-12-0; $(CN)_5FeL^{3-}$ (L = pyridazine), 86260-13-1; $(CN)_5RuL^{3-}$ (L = 4-methylpyridine), 86260-14-2; $(CN)_5RuL^{3-}$ (L = pyridine), 86260-15-3; $(CN)_5RuL^{3-}$ (L = pyrimidine), 86260-16-4; $(CN)_5RuL^{4-}$ (L = isonicotinato), 86260-17-5; $(CN)_5RuL^{3-}$ (L = isonicotinic acid), 86260-18-6; $(CN)_5RuL^{3-}$ (L = pyridazine), 86260-19-7; $(CN)_5RuL^{3-}$ (L = 2-methylpyrazine), 86260-20-0; $(CN)_5RuL^{3-}$ (L = isonicotinamide), 86260-21-1; $(CN)_5RuL^{3-}$ (L = 4,4′-bipyridine), 86260-22-2; $(CN)_5RuL^{3-}$ (L = 4-cyanopyridine), 86260-23-3; $(CN)_5RuL^{3-}$ (L = 4-formylpyridine), 86260-24-4; $(CN)_5RuL^{2-}$ (L = *N*-methylpyrazinium), 84711-78-4.

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Photochemistry of MLCT Excited States. Effect of Nonchromophoric Ligand Variations on Photophysical Properties in the Series *cis*-$Ru(bpy)_2L_2^{2+}$

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The photophysical properties of the low-lying, emissive metal to ligand charge transfer (MLCT) excited states of a series of complexes of the type *cis*-$Ru(bpy)_2L_2^{2+}$ (L = pyridine, pyridazine, $^1/_2$ phenanthroline, $^1/_2$ bipyridine, *N*-methylimidazole, 2-(2-aminoethyl)pyridine) have been investigated. The results lead to a self-consistent picture of the roles of different decay pathways in determining excited-state lifetimes. The lifetime of the MLCT excited state(s) is shown to be dictated by (1) a radiative decay pathway (k_r) that is relatively insensitive to variations in L, (2) a nonradiative transition to the ground state (k_{nr}), the rate constant for which varies as predicted by the energy gap law for radiationless transitions, and (3) the rate of a thermally activated transition between the MLCT state and a low-lying, metal-centered dd excited state. It is the latter transition and the role that the ligands L play in stabilizing the MLCT state relative to the dd state that provide a reasonable explanation for the absence of room-temperature emission and/or the appearance of ligand-loss photochemistry in cases where L is a phosphine, arsine, or CO group.

The low-lying metal to ligand charge transfer (MLCT) excited state(s) of the ion $Ru(bpy)_3^{2+}$ (bpy is 2,2′-bipyridine) has been used in a number of photosensitization schemes.[1] The bases for its popularity include the following: (1) The ion is easily prepared and relatively stable toward photodecomposition. (2) The MLCT excited state(s) is long-lived at room temperature in fluid solution. (3) The excited state luminesces visibly at room temperature in fluid solution, which provides a valuable spectral probe for monitoring photochemical processes. (4) The excited state undergoes facile energy transfer or electron transfer, in the latter case to give stable oxidized, $Ru(bpy)_3^{3+}$, or reduced, $Ru(bpy)_3^{+}$, products.

In order to design new and perhaps more elaborate sensitizers related to $Ru(bpy)_3^{2+}$, it is important to understand the factors that are important in dictating its excited-state properties. In fact, the results of a variety of experimental and theoretical studies have led to an increasingly detailed account of the excited-state structure of $Ru(bpy)_3^{2+}$:

(1) The absorption spectrum is dominated by optical transitions to MLCT states largely singlet in character.[2]

(2) Following optical excitation, rapid ($\tau < 1$ ps), efficient ($\phi \sim 1$) decay occurs to the emitting MLCT state(s), which are largely triplet in character.[3] The effect of spin–orbit coupling is to mix the singlet and triplet states, but the two different types of states retain much of their initial spin character.

(3) The emitting, redox-active state is really a manifold of three closely spaced states largely triplet in character. A fourth slightly higher state may also exist, having a greater degree of singlet character than the lower three.[4,6e]

(4) In the low-lying MLCT states, the excited electron appears to be localized on a single ligand although no doubt transferring between ligands on a relatively short time scale.[5]

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