$$k_{\mathrm{obsd}} = \left\{k_1{}^{\mathrm{f}}\frac{k_{\mathrm{am}}}{k_{\mathrm{Cl}}} + k_2{}^{\mathrm{f}}\left([\mathrm{Cl}^-] + \frac{k_{\mathrm{am}}[\mathrm{am}]}{k_{\mathrm{Cl}}}\right)\right\} \left\{\frac{K_{\mathrm{s}} + [\mathrm{Cl}^-]}{[\mathrm{am}]} + \frac{k_2{}^{\mathrm{f}}K_{\mathrm{s}}}{k_1{}^{\mathrm{f}}} + \frac{k_{\mathrm{am}}}{k_{\mathrm{Cl}}}\right\}^{-1}$$

For the processes $\mathrm{Pt(L)Cl_3^-}$ + MeOH = *trans*-$\mathrm{[Pt(L)(MeOH)Cl_2]}$ + $\mathrm{Cl^-}$ (K_{s}) or $\mathrm{Pt(L)Cl_3^-}$ + am = *trans*-$\mathrm{[Pt(L)(am)Cl_2]}$ + $\mathrm{Cl^-}$ (K_{am}) at equilibrium, let $[\mathrm{Pt(L)Cl_3^-}] = c_{\mathrm{a}}$, [*trans*-$\mathrm{Pt(L)(MeOH)Cl_2}$] = c_{b}, and [*trans*-$\mathrm{Pt(L)(am)Cl_2}$] = c_{c} and ϵ_{a}, ϵ_{b}, and ϵ_{c} represent their molar extinctions at the wavelength used in the measurement. Then

$$K_{\mathrm{s}} = \frac{c_{\mathrm{b}}[\mathrm{Cl}^-]}{c_{\mathrm{a}}} \qquad (4)$$

and

$$K_{\mathrm{am}} = \frac{c_{\mathrm{c}}[\mathrm{Cl}^-]}{c_{\mathrm{a}}[\mathrm{am}]} \qquad (5)$$

Let a "pseudo equilibrium quotient" be defined as

$$K' = \frac{c_{\mathrm{c}}[\mathrm{Cl}^-]}{(c_{\mathrm{a}} + c_{\mathrm{b}})[\mathrm{am}]} \qquad (6)$$

In the absence of added amine, the absorbance at equilibrium is

$$A = \epsilon_{\mathrm{a}}c_{\mathrm{a}} + \epsilon_{\mathrm{b}}c_{\mathrm{b}} \qquad (7)$$

(for a 1-cm light path) and

$$c_{\mathrm{a}} + c_{\mathrm{b}} = C_0 \qquad (8)$$

gives the total concentration of Pt(II) species. Eliminating c_{b} from (4) and (8) gives, after rearrangement

$$[\mathrm{Cl}^-]^{-1} = C_0/K_{\mathrm{s}}c_{\mathrm{a}} - 1/K_{\mathrm{s}} \qquad (9)$$

If K_{s} is large enough, the complex will be fully solvolyzed in the absence of added chloride so that

$$A_0 = \epsilon_{\mathrm{b}}C_0 \qquad (10)$$

where A_0 is the absorbance of the solution in the absence of added chloride (and amine). Combining (7), (8), and (10) gives

$$c_{\mathrm{a}} = (A - A_0)/(\epsilon_{\mathrm{a}}) \qquad (11)$$

and combining (9) with (11) gives

$$[\mathrm{Cl}^-]^{-1} = C_0(\epsilon_{\mathrm{a}} - \epsilon_{\mathrm{b}})/K_{\mathrm{s}}(A - A_0) - K_{\mathrm{s}}^{-1} \qquad (12)$$

Thus, plotting $[\mathrm{Cl}^-]^{-1}$ against $(A - A_0)^{-1}$ should give a straight line with intercept K_{s}^{-1}.

If the complex is not fully dissociated in the absence of added chloride, then K_{s} will be small enough for it to be possible to reach a limit at high chloride concentration, where very little of the complex remains in the methanol form. The absorbance will then be independent of $[\mathrm{Cl}^-]$ when the concentration is high enough. If the limiting absorbance is designated as A_∞, then

$$A_\infty = \epsilon_{\mathrm{a}}c_{\mathrm{a}} \qquad (13)$$

Eliminating c_{a} from (4) and (8) gives

$$[\mathrm{Cl}^-] = C_0K_{\mathrm{s}}/c_{\mathrm{b}} - K_{\mathrm{s}} \qquad (14)$$

and replacing c_{b} with use of (7), (8), and (13) gives

$$[\mathrm{Cl}^-] = C_0(\epsilon_{\mathrm{a}} - \epsilon_{\mathrm{b}})K_{\mathrm{s}}/(A_\infty - A) - K_{\mathrm{s}} \qquad (15)$$

so that a plot of $[\mathrm{Cl}^-]$ against $(A_\infty - A)^{-1}$ should be a straight line with intercept $-K_{\mathrm{s}}$.

In the presence of added amine it is necessary to combine the two equilibria. Equation 3 can be rewritten as

$$K' = [C_0 - (c_{\mathrm{a}} + c_{\mathrm{b}})][\mathrm{Cl}^-]/ (c_{\mathrm{a}} + c_{\mathrm{b}})\{[\mathrm{am}]_{\mathrm{T}} - [C_0 - (c_{\mathrm{a}} + c_{\mathrm{b}})]\} \qquad (16)$$

where $[\mathrm{am}]_{\mathrm{T}}$ is the total amount of amine present. If measurements are made at a wavelength where $\epsilon_{\mathrm{a}} = \epsilon_{\mathrm{b}}$ and where the free amine does not absorb significantly

$$A = \epsilon_{\mathrm{a}}(c_{\mathrm{a}} + c_{\mathrm{b}}) + \epsilon_{\mathrm{c}}[C_0 - (c_{\mathrm{a}} + c_{\mathrm{b}})] \qquad (17)$$

Let the absorbance equal A_0 when no amine is present and A_∞ when all the platinum is in the form of the amine complex; then $A_0 = C_0\epsilon_{\mathrm{a}}$ and $A_\infty = C_0\epsilon_{\mathrm{c}}$. Combining these with (16) and (17) gives $K' = (A_0 - A)[\mathrm{Cl}^-]/(A - A_\infty)\{[\mathrm{am}]_{\mathrm{T}} - (A_0 - A)/(\epsilon_{\mathrm{a}} - \epsilon_{\mathrm{c}})$, which on rearrangement gives

$$(A - A_\infty)^{-1} = K'[\mathrm{am}]_{\mathrm{T}}/(A_0 - A)[\mathrm{Cl}^-] - K'/(\epsilon_{\mathrm{a}} - \epsilon_{\mathrm{c}})[\mathrm{Cl}^-] \qquad (18)$$

Combining (4), (5), and (6) gives $K_{\mathrm{am}} = K'(1 + K_{\mathrm{s}}/[\mathrm{Cl}^-])$.

Registry No. $\mathrm{[Pt(PMe_3)Cl_3]^-}$, 44630-63-9; $\mathrm{Et_4N[Pt(PEt_3)Cl_3]}$, 56544-60-6; $\mathrm{Et_4N[Pt(P(}$*n*$\mathrm{-Bu)_3)Cl_3]}$, 84835-91-6; $\mathrm{Et_4N[Pt(PPh_3)Cl_3]}$, 84835-92-7; $\mathrm{Bu_4N[Pt(P(OMe)_3)Cl_3]}$, 62428-87-9; $\mathrm{[Pt(AsEt_3)Cl_3]^-}$, 44968-34-5; *n*-$\mathrm{BuNH_2}$, 109-73-9; pip, 110-89-4; c-$\mathrm{HxNH_2}$, 108-91-8; mor, 110-91-8; 3,5-$\mathrm{Me_2py}$, 591-22-0; 4-Mepy, 108-89-4; py, 110-86-1; 3-Clpy, 626-60-8; 4-CNpy, 100-48-1; 3,5-$\mathrm{Cl_2py}$, 2457-47-8.

Notes

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Mössbauer Spectroscopy of Mixed-Metal Bimetallic Complexes Containing the Pentacyanoferrate(II) Metal Center

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There have been numerous studies on the thermal[1-6] and photochemical[7] reactions of unsaturated, nitrogen heterocyclic ligands (L) bound to the pentacyanoferrate(II) metal center. The near-ultraviolet and visible spectra of these complexes are dominated by an intense metal-to-ligand charge-transfer (MLCT) band assigned as $d_\pi(\mathrm{M}) \rightarrow p_{\pi^*}(\mathrm{L})$ in character.[2] The energy of the MLCT band maxima is very sensitive to substituent changes on L (i.e., the energy of the π^* orbitals of free L), with more electron-withdrawing substituents causing red shifts in the MLCT maximum as well as greater

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Table I. Absorption Spectra, Isomer Shifts, and Quadrupole Splitting Values for Pentacyanoferrate(II) Complexes, $(CN)_5Fe^{II}L$, at 298 and 77 K[a]

L	ν_{max}(MLCT), μm^{-1} [b]	δ, mm/s[c]	QS, mm/s[d]	Γ_1, mm/s[e]	Γ_2, mm/s[e]
		298 K			
NH_3		0.032 (1)	0.713 (2)	0.329 (3)	0.327 (3)
		0.028 (1)[f]	0.694 (2)[f]		
py	2.76	0.005 (2)[f]	0.802 (4)[f]		
NC-py$Rh^{III}(NH_3)_5$	2.50	0.029 (3)	0.843 (7)	0.461 (5)	0.429 (6)
NC-py$Co^{III}(CN)_5$	2.33	0.051 (2)	0.758 (4)	0.349 (3)	0.350 (5)
pz	2.22	0.015 (1)[f]	0.897 (3)[f]		
4,4′-bpy$Co^{III}(CN)_5$	2.20	0.049 (4)	0.777 (7)	0.372 (10)	0.379 (10)
4,4′-bpy$Rh^{III}(NH_3)_5$	2.08	0.024 (2)	0.932 (4)	0.445 (6)	0.423 (6)
pz$Co^{III}(CN)_5$	1.90	0.045 (1)	0.787 (1)	0.354 (2)	0.364 (2)
pz$Rh^{III}(NH_3)_5$	1.75	0.004 (1)	1.027 (2)	0.391 (2)	0.417 (3)
N-Mepz	1.51	0.011 (2)	1.069 (3)	0.448 (3)	0.553 (3)
		77 K			
NH_3		0.101 (1)	0.715 (2)	0.393 (4)	0.391 (4)
NC-py$Rh^{III}(NH_3)_5$	2.50	0.095 (3)	0.831 (6)	0.509 (5)	0.477 (8)
NC-py$Co^{III}(CN)_5$	2.33	0.114 (1)	0.778 (3)	0.362 (3)	0.391 (4)
4,4′-bpy$Co^{III}(CN)_5$	2.20	0.108 (2)	0.770 (4)	0.389 (5)	0.412 (6)
4,4′-bpy$Rh^{III}(NH_3)_5$	2.08	0.083 (2)	0.869 (4)	0.413 (7)	0.400 (7)
pz$Co^{III}(CN)_5$	1.90	0.112 (2)	0.780 (5)	0.357 (6)	0.373 (7)
pz$Rh^{III}(NH_3)_5$	1.75	0.075 (2)	1.007 (3)	0.372 (4)	0.388 (4)
N-Mepz	1.51	0.073 (2)	1.072 (3)	0.487 (3)	0.571 (6)

[a] Powdered samples, under vacuum (see Experimental Section). [b] ν_{max} of the MLCT band ($d_\pi(Fe) \rightarrow \pi^*(L)$). [c] Isomer shift reported vs. α-iron with errors in the least significant digits in parentheses. [d] Quadrupole splitting with errors in the least significant digits in parentheses. [e] Full width at half-maximum in order of increasing velocity of the peak, with errors in the least significant digits in parentheses. [f] Reference 8, same instrument.

ground-state delocalization of electron density into L (π-back-bonding).[2]

Numerous types of instrumental methods have been used, in addition to electronic spectroscopy, to probe the extent of π-back-bonding from Fe(II) into various L ligands. One of the probes used has been ^{57}Fe Mössbauer spectroscopy.[8-10] Mössbauer results have shown that isomer shift values change with the amount of π-back-bonding (π-back-bonding reduces the screening of s-electron density).

Recently, we reported[1] the preparation and thermal stability of a number of mixed-metal, bimetallic complexes containing the pentacyanoferrate(II) or pentaammineruthenium(II) metal centers. Spectroscopically, attaching the second metal center to a remote site of the ligands pyrazine (pz), 4-cyanopyridine (4-CNpy), or 4,4′-bipyridine (4,4′-bpy) gave rise to a red shift of the MLCT band just as would be expected for a Lewis acid substituent. However, the photochemistry of these bimetallic complexes[11,12] does not follow the trends observed for the monometallic systems. The monometallic Fe(II)[7] complexes show photosubstitution reactions with loss of L and have quantum yields that depend on the energy of the MLCT maximum. That is, when the energy of the MLCT maximum is greater than ~2.1 μm^{-1}, photosubstitution quantum yields are large and relatively invariant but drop off dramatically as the MLCT maximum is red shifted from 2.1 μm^{-1}. The interpretation for the Fe(II)[7] and the analogous Ru(II)[13] systems, as well as the similar behavior observed for $(CO)_5WL$ complexes,[14] is that the dropoff point coincides with a crossover of the ligand-substituent-sensitive, but unreactive, MLCT excited state and a ligand-substituent-insensitive, but reactive, ligand field (LF) excited state.

The lack of correlation of the photochemistry of the monometallic Fe(II) and Ru(II) systems with that of their bimetallic counterparts (large photosubstitution quantum yields are observed for complexes with the MLCT maximum >2.1 μm^{-1}) had led to the studies reported in this work. The goal of this work was to use Mössbauer spectroscopy to assess whether d-orbital participation of the remote metal centers bound to pentacyanoferrate was responsible for the anomalous photochemical results observed in the bimetallic systems.

Experimental Section

Materials. Analytical reagent grade compounds were used for all preparations described in this work. Water used for synthesis was distilled and then passed through a demineralizer.

Synthesis. The complexes $[Rh(NH_3)_5L](ClO_4)_3$, $K_2[Co(CN)_5L]$, $[(CN)_5FeLRh(NH_3)_5]$, and $Na_3K_2[(CN)_5FeLCo(CN)_5]$ were prepared as previously reported.[1] The monometallic Fe(II) complexes, $Na_x[Fe(CN)_5L]$, were prepared by the procedure of Toma and Malin[2] and Figard et al.[15]

The purity of all complexes was determined by comparison of the electronic spectra with the previously reported values. Electronic spectra were recorded on a Cary 14 or a Bausch & Lomb Spectronic 2000 spectrophotometer.

Mössbauer Spectroscopy. Mössbauer spectra were obtained on an Austin Science Associates constant-acceleration spectrometer in conjunction with a Canberra Series 30 multichannel analyzer. The New England Nuclear source was 50–45 mCi of ^{57}Co in a rhodium matrix. Doppler velocity calibration was obtained by a nonlinear least-squares routine fitted to the line positions of the National Bureau of Standards iron-foil Mössbauer standard 1541. All isomer shifts are referenced to α-iron. Spectra were fitted with use of a modified version of the National Bureau of Standards program[16] called MONBS4, which fits Lorentzian curves on a parabolic base line to the data.

Powdered material was packed in an aluminum holder that had either Mylar or cellophane windows. The holder was a 28 × 44 mm

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plate, 1.5 mm thick. A 12-mm diameter hole in the center of the plate held the compound. Since spectral line widths are dependent on sample thickness,[17] all Fe complexes and Fe–Co bimetallic complexes had 10 mg of Fe/cm^2, and the heavy-metal Fe–Rh complexes had 5 mg of Fe/cm^2. Spectra were recorded under vacuum at room temperature (298 ± 3 K) and at liquid-nitrogen (77 K) temperature.

Results

The complexes listed in Table I are organized according to descending frequency of the maximum of the Fe(II) → L metal-to-ligand charge-transfer (MLCT) transition. (The ligand abbreviations in Table I and the text correspond to py = pyridine, NC-py or 4-CNpy = 4-cyanopyridine, pz = pyrazine, 4,4′-bpy = 4,4′-bipyridine, and *N*-Mepz = *N*-methylpyrazinium). The MLCT band is the dominant spectral feature in the near-UV–vis spectral region with molar extinction coefficients ranging from 3×10^3 to 10^4 M^{-1} cm^{-1}.[1] The assumption that the MLCT band is localized mainly on the Fe(II) center and the bridging ligand is consistent with assignments made previously by Creutz and Taube[18] for $(NH_3)_5Ru^{II}pzRh^{III}(NH_3)_5{}^{5+}$.

The ^{57}Fe Mössbauer data for monometallic and bimetallic pentacyanoferrate(II) complexes are listed in Table I. Isomer shifts and quadrupole splitting are shonw for both 298 and 77 K spectra. The same qualitative trends are observed for data obtained at the two temperatures with the exception that the spread between the Fe–Rh and Fe–Co bimetallic species is much smaller at 77 K. The trend for the monometallic and Fe–Rh bimetallic complexes is that the isomer shift gets smaller as the maximum of the MLCT band shifts to shorter frequency (longer wavelength). The isomer shifts of the Fe–Co bimetallic complexes are more positive than any of the other complexes and also tend to be insensitive to the nature of the bridging ligand.

The quadrupole splitting (Table I) can be separated as well into a series containing the monometallic and bimetallic Fe–Rh complexes and a series of bimetallic Fe–Co complexes. The former series of complexes shows larger quadrupole splitting values as the MLCT maximum is shifted to lower frequency. The Fe–Co series shows an insensitivity of the quadrupole splitting to the nature of the bridging ligand, and the Δ value is smaller than those for all of the other complexes listed in this work with the exception of $Fe(CN)_5(NH_3)^{3-}$.

Discussion

The data on both the isomer shift value and quadrupole splitting can be separated into two classes of behavior. When L is either the free nitrogen base or the nitrogen base bound to pentaamminerhodium(III), properties consistent with remote metal centers acting as Lewis acids are observed. That is, the substituent group pentaamminerhodium(III) displays only an inductive effect on the π-system of the heterocycle and is not involved in any remote interaction with the π electrons on Fe(II). Although it does not appear that the pentacyanocobaltate(III) bound to the nitrogen base is participating in any remote π interactions either, there is a difference in the behavior of these complexes. Since $Co(CN)_5{}^{2-}$ is the only substituent in this study with a large negative charge, it is not surprising that the center shift values are larger for this series than for the Fe(II)/Rh(III) systems. These results imply that π-back-bonding into the heterocycle is not as great in the case of Fe(II)/Co(III) complexes as it is for the Fe(II)/Rh(III) counterparts. This is further confirmed by the fact that the quadrupole splitting is smaller for the Fe(II)/Co(III) complexes than for the Fe(II)/Rh(III) complexes[8] or that L appears to the Fe(II) center to be more like a CN$^-$ ligand when L contains $Co(CN)_5{}^{2-}$.

In a comparison of the various substituents that may be bound to the remote end of pyrazine in $Fe(CN)_5pz^{3-}$, there are some trends that are observed. If we equate the smaller isomer shift values with increasing σ-donor/π-acceptor ability of L, we see the trend

$$CH_3{}^+ > Rh(NH_3)_5{}^{3+} > \text{free base} > Co(CN)_5{}^{2-}$$

Thus it appears that the negatively charged $Co(CN)_5{}^{2-}$ substituent, even though it lowers the energy of the Fe(II) → L MLCT transition by lowering the energy of the π* orbital vs. that for free base, is not allowing as much π-back-bonding from the Fe(II) to the nitrogen heterocycle π-system in the ground state. Since there is a better energy match for d_π(Fe) and π*(L) when $Co(CN)_5{}^{2-}$ is bound to the free base, reduction of π-back-bonding must come from reduced orbital overlap.

A complementary result is obtained by looking at the differences between various $Rh(NH_3)_5{}^{3+}$ and $Co(CN)_5{}^{2-}$ remote-bound L systems. Any electrostatic repulsions between $Co(CN)_5{}^{2-}$ and $Fe(CN)_5{}^{3-}$ should be reduced as the bridge gets longer (separates metal centers). For the bridging ligands 4-CNpy, 4,4′-bpy, and pz this is observed by comparing the difference in isomer shift and quadrupole splitting between Rh(III)-bound and Co(III)-bound remote centers.

	4-CNpy	4,4′-bpy	pz
Δδ(298 K), mm/s	0.022	0.025	0.041
ΔQS(298 K), mm/s	0.085	0.155	0.240

Finally, it is interesting to note that all $Co(CN)_5{}^{2-}$-containing mixed-metal bimetallic complexes have isomer shift and quadrupole splitting values that are very similar to each other. This is not the case for the $Rh(NH_3)_5{}^{3+}$ bimetallic complexes. The major difference in these systems is the presence of additional ligands capable of π-back-bonding (i.e., CN$^-$) in the Co(III) system, which is not available for Rh(III). Thus it appears that $Co(CN)_5{}^{2-}$ is acting as an electronic shunt. As the bridging ligand is changed, the amount of π-back-bonding from Fe(II) into the bridging ligand is normalized by increasing or decreasing participation of CN$^-$ ligands bound to Co(III) in π-back-bonding and thus adjusting the electron density on Co(III).

The conclusion we have reached from the Mössbauer study on these bimetallic complexes is that, in general, the remote metal center can be treated as an electron-withdrawing substituent on the bridging ligand. There are some subtle differences in the roles of $Rh(NH_3)_5{}^{3+}$ and $Co(CN)_5{}^{2-}$ metal centers in the π-back-bonding ability of L, but these factors do not explain the anomolous photochemical results described in the introduction[12] for the mixed-metal bimetallic complexes.

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Registry No. $Na_3[Fe(CN)_5NH_3]$, 14099-05-9; $Na_3[Fe(CN)_5(py)]$, 56028-27-4; $(CN)_5Fe(NC\text{-}py)Rh(NH_3)_5$, 81230-42-4; $Na_3K_2[(CN)_5Fe(NC\text{-}py)Co(CN)_5]$, 81230-45-7; $Na_3[Fe(CN)_5(pz)]$, 37475-70-0; $Na_3K_2[(CN)_5Fe(4,4'\text{-}bpy)Co(CN)_5]$, 81230-44-6; $(CN)_5Fe(4,4'\text{-}bpy)Rh(NH_3)_5$, 70649-69-3; $Na_3K_2[(CN)_5Fe(pz)Co(CN)_5]$, 81230-43-5; $(CN)_5Fe(pz)Rh(NH_3)_5$, 71050-65-2; $Na_2[Fe(CN)_5(N\text{-}Mepz)]$, 37475-66-4.

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