$C_6H_4OMe)_3$ analogue. (4) The phosphine effect on the k_r process is also interesting, because in $[Cu(dmp)\{P(p\text{-}C_6H_4OMe)_3\}_2]^+$ the largest k_r value is one of the important factors leading to the greatest ϕ_{MV^+} value. However, it is still ambiguous what type of factor is important in the k_r process. Previously, McMillin et al. suggested that the k_r step is sensitive to the self-exchange rate.[9a] Unfortunately, the self-exchange reaction rates of Cu(I) complexes examined have not been measured yet, and further discussion is omitted here. We need more detailed and systematic investigations to get a clear explanation about the phosphine ligand effect on the photochemical reactivity of Cu(I) complexes.

In conclusion, the activity of $[Cu(dmp)(PR_3)_2]^+$ in the photoreduction of MV^{2+} has been improved by substituting PPh_3 with $PCyPh_2$ or $P(p\text{-}C_6H_4OMe)_3$, because the lifetime of the excited state is lengthened and/or the oxidative quenching by MV^{2+} becomes faster.

Acknowledgment. The authors gratefully acknowledge the support of the Ministry of Education (Japan) through a Grant-in-Aid for Scientific Research (No. 59540397).

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Photochemistry of the Ion Pairs $Rh(bpy)_3^{3+}M(CN)_6^{4-}$ (bpy = 2,2'-Bipyridyl) with M = Fe, Ru, Os following Outer-Sphere Metal to Ligand Charge-Transfer Excitation

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Received July 17, 1986

Optical metal to ligand charge-transfer (MLCT) transitions play an important role in the photophysics and photochemistry of transition-metal complexes.[1-3] This electronic transition is an intramolecular (inner-sphere) process. It involves the promotion of a d electron of the metal to an empty orbital of a ligand coordinated to this metal. MLCT transitions occur at low energies if the metal is a reducing one and the ligand has available empty low-energy orbitals. Typical examples are the complexes $Ru(bpy)_3^{2+}$[4,5] (bpy = 2,2'-bipyridyl) and $M(CN)_6^{4-}$ (M = Fe, Ru, Os).[6,7] In the latter case MLCT excitation is associated with the generation of solvated electrons.[8-10] We report here on intermolecular (outer-sphere) MLCT transitions and the photochemistry following this type of CT excitation. In this case the optical transition involves the promotion of an electron from the metal of one complex to the ligand of another complex.

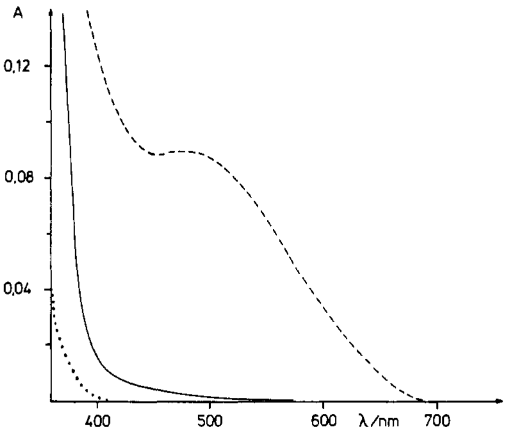

Figure 1. Electronic absorption spectra of aqueous 2.7×10^{-3} M $[Rh(bpy)_3](ClO_4)_3$ (···), 2.7×10^{-3} M $K_4[Fe(CN)_6]$ (—), and a mixture of both solutions (- - -) (298 K, 1-cm cell).

The ion pairs $Rh(bpy)_3^{3+}M(CN)_6^{4-}$ with M = Fe, Ru, Os were selected for this study. The colorless complex $Rh(bpy)_3^{3+}$ shows its longest wavelength absorption at λ_{max} = 320 nm ($\epsilon = 4.25 \times 10^4$).[11,12] This band is assigned to an intraligand $\pi\pi^*$ transition of the bpy ligand. Since Rh(III) is rather redox-inert, CT transitions of $Rh(bpy)_3^{3+}$ do not appear at low energies. The colorless complexes $M(CN)_6^{4-}$ which contain reducing metals do not absorb above 400 (Fe), 300 (Ru), and 300 nm (Os). Ligand field and MLCT bands occur at shorter wavelength.[6,7]

When aqueous $Rh(bpy)_3^{3+}$ and $M(CN)_6^{4-}$ were mixed, the solutions turned immediately reddish for M = Fe (λ_{max} = 480 nm; Figure 1), yellow for Os (λ_{max} = 400 nm), and slightly yellow for Ru (λ_{max} = 379 nm). These colors are due to the appearance of new absorption bands (Figure 1). At fairly high equimolar concentrations ($>10^{-3}$ M) of complex cations and anions these bands follow the Lambert–Beer law with ϵ = 61 (Fe), 110 (Ru), and 155 M^{-1} cm^{-1} (Os). It is assumed that at this concentration ion pairing was complete. The deviation from the Lambert–Beer law at much lower concentrations ($<10^{-4}$ M) was used to estimate the ion-pair association constant ($K = 3800$ M^{-1} of $Rh(bpy)_3^{3+}$-$Fe(CN)_6^{4-}$.

We suggest that these new absorption bands are assigned to outer-sphere MLCT transitions from the reducing metals M(II) of $M(CN)_6^{4-}$ to the empty low-energy π^* orbitals of the bpy ligand of $Rh(bpy)_3^{3+}$. While $M(CN)_6^{4-}$ is oxidized at $E_{1/2}$ = 0.19 (Fe), 0.70 (Ru), and 0.40 V (Os),[13] the complex $Rh(bpy)_3^{3+}$ is reduced at $E_{1/2} = -0.7$ V[14,15] vs. SCE. As expected, the outer-sphere MLCT bands shift to lower energies if the reducing power of $M(CN)_6^{4-}$ increases. However, these shifts do not match the potential differences exactly. The deviations can be caused by different reorganizational energies χ, which are associated with electron transfer. These energies, which are calculated according to the equation $\chi = E_{op} - \Delta E$,[16,17] are χ = 13 650 (Fe), 15 100 (Ru), and 16 130 cm^{-1} (Os).

Upon irradiation of the outer-sphere MLCT band of the ion pair $Rh(bpy)_3^{3+}Fe(CN)_6^{4-}$ (λ_{irr} = 546 nm) the cation $Rh(bpy)_3^{3+}$ underwent a photoaquation to $Rh(bpy)_2(H_2O)_2^{3+}$. At the irradiating wavelength both constituents of the ion pair do not absorb light. The formation of $Rh(bpy)_2(H_2O)_2^{3+}$ (λ_{max} = 318 nm, ϵ = 28 300)[15] led to a decrease of the optical density in the region of the $\pi\pi^*$ intraligand absorption of the coordinated bpy ligand. The release of bpy was detected by its fluorescence at λ_{max} = 325 nm. The quantum yield of photoaquation of $Rh(bpy)_3^{3+}$ was $\Phi = 2.4 \times 10^{-3}$.

We suggest that this photoaquation takes place according to the scheme

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$$\mathrm{Rh^{III}(bpy)_3{}^{3+}Fe^{II}(CN)_6{}^{4-}} \xrightarrow{h\nu} \mathrm{Rh^{III}(bpy)_2(bpy^-)^{2+}Fe^{III}(CN)_6{}^{3-}} \tag{1}$$

$$\mathrm{Rh(bpy)_3{}^{2+}Fe(CN)_6{}^{3-} \rightarrow Rh(bpy)_3{}^{2+} + Fe(CN)_6{}^{3-}} \tag{2}$$

$$\mathrm{Rh(bpy)_3{}^{2+} \rightarrow Rh(bpy)_2{}^{2+} + bpy} \tag{3}$$

$$\mathrm{Rh(bpy)_2{}^{2+} + Fe(CN)_6{}^{3-} + 2H_2O \rightarrow Rh(bpy)_2(H_2O)_2{}^{3+} + Fe(CN)_6{}^{4-}} \tag{4}$$

The ion pair generated by outer-sphere MLCT excitation (eq 1) may diffuse apart (eq 2). Equation 3 describes only the fact that $\mathrm{Rh(bpy)_3{}^{2+}}$ is known to release a bpy ligand.[14,15] The mechanism of this reaction is not quite clear. Various possibilities, including a disproportionation, are feasible.[15] Finally, electron transfer and subsequent formation of $\mathrm{Rh(bpy)_2(H_2O)_2{}^{3+}}$ (eq 4) is the last step of this mechanism. The low quantum yield of the overall reaction is probably determined by the rapid thermal reversal of the optical CT transition. This back electron transfer competes with the diffusion step (eq 2). The ion pairs $\mathrm{Rh(bpy)_3{}^{3+}M(CN)_6{}^{4-}}$ with M = Ru, Os seem to be also light-sensitive upon outer-sphere MLCT excitation. However, in this case the CT bands occur at shorter wavelength and thus are overlapping with intramolecular absorption bands of the complexes. For this reason a selective outer-sphere MLCT excitation could not be achieved.

It should be mentioned here that related optical outer-sphere CT transitions in ion pairs involving electron transfer between two metals (MMCT) are well-known.[18-20] This type of CT excitation may also induce photochemical reactions of transition-metal complexes.[19] In this context it is also of interest that intramolecular MLCT transitions between remote groups were observed recently.[21] But in this case through-bond as well as through-space interactions between the remote redox centers may cause the appearance of the MLCT band.[21]

Experimental Section

Materials. $\mathrm{[Rh(bpy)_3](ClO_4)_3}$[22] and $\mathrm{K_4[Os(CN)_6]}$[23] were prepared by literature procedures. $\mathrm{K_4[Ru(CN)_6]}$ was commercially (Heraeus) available.

Photolysis. The light source was an Osram HBO 100 W/2 lamp. A Schott PIL 546 interference filter was used for the selection of the mercury line at 546 nm. Photolyses were carried out in 1-cm spectrophotometer cells at room temperature. For quantum yield determinations the complex concentrations were such as to have essentially complete light absorption. The total amount of photolysis was limited to less than 5% to avoid light absorption by the photoproducts. Absorbed light intensities were determined by a Polytec pyroelectric radiometer, which was calibrated and equipped with a RKP-345 detector.

Progress of the photolyses was monitored by UV-visible spectrophotometry. The extent of photolysis of $\mathrm{Rh(bpy)_3{}^{3+}}$ in aqueous solution was determined by measuring the decrease of extinction at 320 nm. At this wavelength the extinction coefficients of $\mathrm{Rh(bpy)_3{}^{3+}}$ and the photoproduct $\mathrm{Rh(bpy)_2(H_2O)_2{}^{3+}}$ are $\epsilon = 4.25 \times 10^4$ and $\epsilon = 2.8 \times 10^4$. Free bipyridyl, which was released in the photolysis, has a negligible absorption at 320 nm.

Instrumentation. Electronic absorption spectra were obtained on a Kontron Uvikon 810 spectrophotometer. The emission spectrum of free bipyridyl was recorded on a Hitachi 850 fluorescence spectrophotometer.

Acknowledgment. Financial support for this research by the Volkswagenstiftung and the Fonds der Chemischen Industrie is gratefully acknowledged.

Registry No. $\mathrm{Ru(bpy)_3{}^{3+}}$, 18955-01-6; $\mathrm{Fe(CN)_6{}^{4-}}$, 13408-63-4; $\mathrm{Ru(CN)_6{}^{4+}}$, 21029-33-4; $\mathrm{Os(CN)_6{}^{4-}}$, 19356-45-7; $\mathrm{Ru(bpy)_2(H_2O)_2{}^{3+}}$, 47514-50-1.

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Reexamination of the Crystal Structure of [(4-Methylimidazole)pentaamminecobalt(III)] Trichloride Dihydrate

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Received November 19, 1986

The structure of the title compound has been described by Henderson, Shepherd, and Abola[1] (hereafter HSA). The space group was reported as $Pna2_1$, with a = 7.011 (2), b = 10.373 (3), and c = 21.420 (3) Å. There are a number of difficulties with their report. First, the unit cell dimensions are wrong. The values of a and c must be interchanged to give even approximate agreement with the reported bond distances, and b must be changed to 10.573 Å to give nearly complete agreement (as well as agreement with the reported volume). Second, the reported z coordinates for the heavy atoms except Nh(2), Nh(3), Nh(4), and Nh(5) are all nearly 0 or $^1/_2$; the x and y coordinates of the pairs Nh(2), Nh(5) and Nh(3), Nh(4) are nearly the same, and their z coordinates average to 0. These observations strongly suggest that the molecule lies in a mirror plane. Accordingly, I have performed refinements in space group $Pnma$ (No. 62), after interchanging the reported y and z coordinates and adding $^1/_4$ to the new y coordinates to give the standard setting. The data were the 1257 reflections reported observed by HSA; the weights were computed according to Hughes,[2] with $4F_{\min} = 18.8$. A refinement of the coordinates and anisotropic thermal parameters of the heavy atoms, minimizing $\sum w(F_o{}^2 - F_c{}^2)^2$, with fixed contributions from hydrogen atoms (placed by calculation or from difference maps), converged with an R index of 0.048 ($R = \sum(F_o - |F_c|)/\sum F_o$). There were 104 parameters refined, including a secondary extinction parameter.[3] The results were significantly better than those of HSA, particularly in that the Co-N bond distances, which ranged from 1.930 (16) to 1.992 (10) Å (1.967 (27) Å average) for HSA, now ranged from 1.964 (4) to 1.969 (3) Å (1.966 (3) Å average), and the thermal parameters of the ammine nitrogen atoms were all nearly the same (average of U_{eq} is 0.0352 (4) Å^2, vs. 0.0368 (154) Å^2 for HSA).

The refinement of HSA included some of the hydrogen atoms. The thermal parameters of all the listed hydrogen atoms were refined; the values of U obtained range from 0.000(!)(12) to 1.094 (116) Å^2. The range of numbers is remarkable, and both extreme values have little physical meaning. The range of N-H and C-H distances, where H positional parameters were refined (0.694 (24)-1.095 (48) Å), is also great. The geometry about Nh(5) is far from tetrahedral, with H-N-H angles of 135 (6), 73 (7), and 108 (6)°. A refinement in $Pnma$ including all the hydrogen atoms in one matrix with all the other parameters diverged: the thermal parameters of two of the hydrogen atoms on the solvent water molecules became negative, that of a third exceeded B = 40 Å^2, and the hydrogen atoms bonded to Nh(1) and M(5) shifted to positions up to 3 Å away from the nitrogen atom and the carbon atom. A refinement keeping the coordinates and thermal parameters of the hydrogen atoms on the water molecules and those on Nh(1) and M(5) fixed, but shifting nine hydrogen atoms and their isotropic temperature factors, converged with R = 0.045, marginally better than the refinement of heavy-atom parameters only. The refined hydrogen B values ranged from 2.2 (13) to 8.4 (22) Å^2, and the H-C or H-N distances from 0.79 (5) to 1.17 (8) Å (average 0.90 (12) Å). The refinement of the hydrogen atoms, then, tells us nothing about the hydrogen atom geometry

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