similar (Table II). That a variation in the nature of X-*o*-phen affects the rate of M–P$(OC_6H_5)_3$ and M–CO bond breaking in the same way suggests either that these bonds are affected in much the same way by a change in X-*o*-phen or that the rates are largely determined by the extent of stabilization of the transition state by X-*o*-phen and the nature of the M–L bond is of relatively little importance. Although there is no direct evidence for it, it seems improbable that the M–P$(OC_6H_5)_3$ and M–CO bonds would be weakened to the same extent by an increase in the basicity of X-*o*-phen. If the M–P$(OC_6H_5)_3$ bond has greater σ- and less π-bond character than does the M–CO bond, the more strongly electron-donating *o*-phenanthrolines should weaken the M–P$(OC_6H_5)_3$ bond more than the M–CO bond. On the contrary, the rates of both types of complexes depend on X-*o*-phen in much the same way. It appears that the *o*-phenanthroline strongly influences the relative rate of M–L dissociation whether L is P$(OC_6H_5)_3$ or CO. This influence might be attributed to the ability of X-*o*-phen to stabilize the transition state. The faster rates of L dissociation in complexes containing the more basic X-*o*-phen groups suggests that stabilization of the transition state is greater in these cases. This stabilization may result from the greater capacity of the basic X-*o*-phen groups to provide electron density to the metal during the process of L dissociation. If the magnitude of these stabilizations is large compared to changes in the M–L bond strength, the rates of reaction will be dominated by the nature of the *o*-phenanthroline. Hence, a very large transition-state stabilization by X-*o*-phen not only accounts for the similar effects of X-*o*-phen on the rates of reaction of $M(CO)_3[P(OC_6H_5)_3]$(X-*o*-phen) and $M(CO)_4$(X-*o*-phen) but also accounts for the unusually fast rates of CO dissociation from $M(CO)_4$(X-*o*-phen) as compared to $M(CO)_6$.[1,6]

Finally it should be noted that the reactions of $M(CO)_3[P(OC_6H_5)_3]$(X-*o*-phen) proceed almost exclusively by an SN1 mechanism, whereas an SN2 mechanism carries an appreciable fraction of the reaction of $M(CO)_4$(X-*o*-phen). The diminished role of P(n-$C_4H_9)_3$ attack in the present reactions may be attributed to the steric hindrance of the P$(OC_6H_5)_3$ group in the complex. Taken together with the faster rate of P$(OC_6H_5)_3$ dissociation, the rate of P(n-$C_4H_9)_3$ attack thus becomes very small compared to the rate of P$(OC_6H_5)_3$ dissociation. Only for the complexes $Mo(CO)_3[P(OC_6H_5)_3]$(5-NO_2-*o*-phen) and $Mo(CO)_3[P(OC_6H_5)_3]$(*o*-phen) were k_2 terms established in the rate law. As noted earlier[2] for the $Mo(CO)_4$(X-*o*-phen) complexes, nucleophilic attack occurs more rapidly on the complex bearing the less basic 5-NO_2-*o*-phen ligand than on that containing *o*-phen. It should be emphasized that the k_2 values in the present study are small, and their absence in the $W(CO)_3[P(OC_6H_5)_3]$(X-*o*-phen) reactions could be caused by a small change in the activation parameters of the SN1 or SN2 paths.

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(6) R. J. Angelici, *Organometal. Chem. Rev.*, **3**, 173 (1968).

CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY,
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS 61801

An Outer-Sphere Charge-Transfer Transition in Tris(ethylenediamine)ruthenium(III) Iodide

BY SR. HELEN ELSBERND[1] AND JAMES K. BEATTIE

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Charge-transfer bands in the electronic spectra of coordination compounds are of two types. The more common is due to the transfer of an electron from a ligand to the central metal atom, or *vice versa*. The other involves groups outside the inner coordination sphere of the metal. Few examples of the latter have been reported. The intense ultraviolet bands that appear in the solution spectra of hexaamminecobalt(III)[2-4] and hexaamminechromium(III)[4] complex ions upon addition of halide, thiocyanate, and other anions have been attributed to charge transfer from the anion to the complex cation. Similar outer-sphere charge-transfer transitions have been suggested to account for the spectra observed for a series of salts of $Cr(bipy)_2Cl_2^+$ and $Cr(phen)_2Cl_2^+$ with various anions.[5]

We wish to report that both the salt and the ion pair of iodide with $Ru(en)_3^{3+}$ are striking examples of this outer-sphere charge-transfer phenomenon. The charge-transfer transition is of sufficiently low energy that the absorption occurs as a well-defined band in the visible region of the spectrum. This results in a highly unusual situation with the charge-transfer transition of considerably lower energy than the first d–d transition of the complex.

Experimental Section

Materials.—$[Ru(en)_3]I_3$ was prepared and recrystallized by the method of Meyer.[6] In this procedure $[Ru(en)_3]ZnCl_4$ was oxidized with iodine and dark purple crystals were obtained by the addition of a sodium iodide solution. *Anal.* Calcd for $C_6H_{24}N_6I_3Ru$: C, 10.89; H, 3.65; N, 12.69; I, 57.50. Found: C, 10.94; H, 3.66; N, 12.36; I, 56.42.

The formulation of the product as $[Ru(en)_3]I_3$ was further checked by an ion-exchange technique. Under oxygen-free conditions a solution of known concentration was added to a Dowex 50W-X8 cation-exchange column in the hydrogen form. The eluent was titrated with sodium hydroxide and the charge per ruthenium atom was determined to be +3. All of the iodine present was found to be ionic iodide by titrating the acidified eluent solution with silver nitrate.

Crystals of $[Rh(en)_3]I_3$ doped with $[Ru(en)_3]I_3$ were obtained

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[1] National Institutes of Health Predoctoral Fellow, 1967–1968.

[2] M. Linhard, *Z. Elektrochem.*, **50**, 224 (1944).

[3] H.-H. Schmidtke, *Z. Physik. Chem.* (Frankfurt), **38**, 170 (1963).

[4] H. Yoneda, *Bull. Chem. Soc. Japan*, **28**, 125 (1955).

[5] W. A. Baker, Jr., and M. G. Phillips, *Inorg. Chem.*, **4**, 915 (1965).

[6] T. J. Meyer, Ph.D. Thesis, Stanford University, 1967.

by evaporating an aqueous solution of 359 mg of $[Rh(en)_3]I_3$ and 5.7 mg of $[Ru(en)_3]I_3$ in a vacuum desiccator with concentrated sulfuric acid as the desiccant and a partial nitrogen atmosphere. The crystals obtained were dark purple.

Since aqueous solutions of $Ru(en)_3^{3+}$ are air sensitive, all recrystallizations and preparations of solutions were done under nitrogen in deoxygenated 0.01 M trifluoroacetic acid. Air oxidation of the product results in a strong absorption at 22,300 cm^{-1}.

Spectra.—All spectra in the visible and ultraviolet regions were obtained with a Cary Model 14 recording spectrophotometer. The transmission spectrum of solid $[Ru(en)_3]I_3$ was taken as a Kel-F mull at room temperature and at liquid nitrogen temperature. The visible spectrum of the doped crystal of $[Ru(en)_3]I_3$ in $[Rh(en)_3]I_3$ was recorded using a single crystal at room temperature.

Solution spectra of $[Ru(en)_3]I_3$ with added sodium iodide were obtained using 1-cm cells which were temperature controlled at 25° by circulating thermostated water. The concentration of $[Ru(en)_3]I_3$ was varied over the range $(3.0–0.75) \times 10^{-3}$ M and sodium iodide was 1.5–0.1 M. The ionic medium was maintained at 4.0 M with sodium perchlorate. Solution spectra of $[Ru(en)_3]I_3$ with added sodium bromide were recorded under the same conditions.

Results and Discussion

Solid $[Ru(en)_3]I_3$ is a dark purple, almost black, crystalline material. The color is anomalous among the iodide salts of tris-ethylenediamine complexes of the heavier transition elements: $[Rh(en)_3]I_3$ is white, $[Ir(en)_3]I_3$ is tan, and $[Os(en)_3]I_3$ is yellow. However, the dilute solution spectrum of $[Ru(en)_3]I_3$ displays *no* absorption in the visible region. The lowest energy band, presumably that of a d–d transition, occurs in the ultraviolet region with a maximum at 32,300 cm^{-1} (ϵ 360 ± 25).[6] In addition, the iodide ion absorbs at 44,200 cm^{-1}. For comparison, the solution spectrum of $[Rh(en)_3]I_3$ contains maxima at 33,100 cm^{-1} (ϵ 238) and 27,500 cm^{-1} (ϵ 8).[3]

The absorption spectrum of solid $[Ru(en)_3]I_3$ was obtained as a Kel-F mull and is given in Figure 1. The broad shoulder in the visible region sharpened somewhat when the mull was cooled to 78°K. In order to avoid the light scattering inherent in the mull spectrum, a transmission spectrum of a single crystal of $[Rh(en)_3]I_3$ doped with $[Ru(en)_3]I_3$ was obtained. As shown in Figure 1, the very intense absorption band is centered at 20,700 cm^{-1}. Our plans to obtain polarized crystal spectra were abandoned after a preliminary X-ray investigation indicated that the crystal structure of $[Rh(en)_3]I_3$ is complex and contains eight formula units in the unit cell.[7]

Solutions of $[Ru(en)_3]I_3$ develop a yellow-orange color upon addition of concentrated sodium iodide solution. Spectra of such solutions, shown in Figure 2, contain a definite band in the visible region in addition to the absorption in the ultraviolet region due to $Ru(en)_3^{3+}$. The band maxima at 22,200 and 31,700 cm^{-1} shift slightly with changes in iodide ion concentration. The apparent molar absorptivity at 22,200 cm^{-1}, defined as $\epsilon_{app} = A/[Ru(III)]$, is linearly dependent on the iodide ion concentration over a large range from 0.1 to 1.5 M and at several different concentrations of

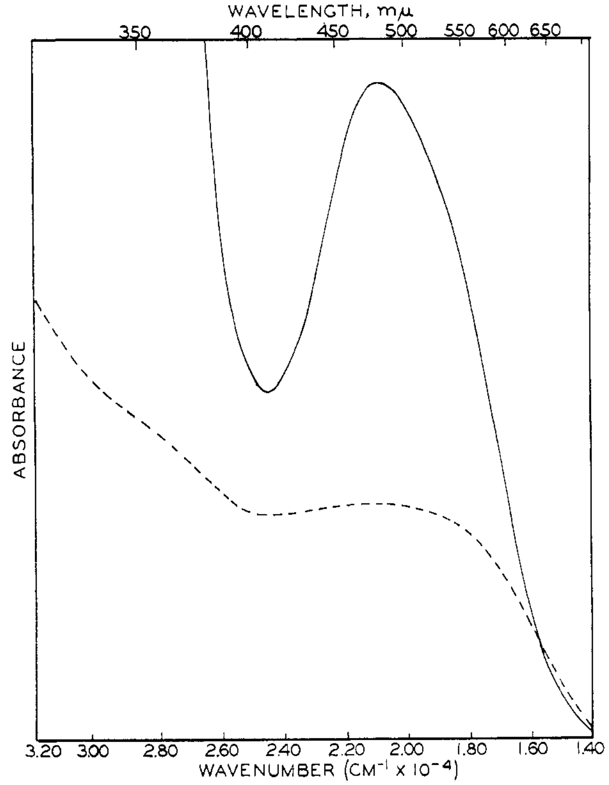

Figure 1.—Absorption spectra of $[Ru(en)_3]I_3$: ———, diluted in $[Rh(en)_3]I_3$ crystal; – – – –, as Kel-F mull.

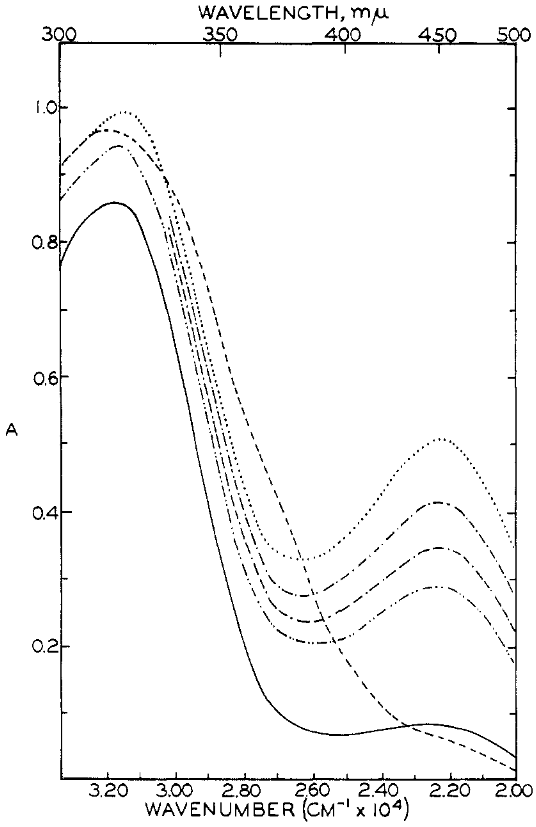

Figure 2.—Absorption spectra of 2.09×10^{-3} M $[Ru(en)_3]I_3$ with various concentrations of added halide salts at 25°, I = 4.0 M: ———, no added halide; – – – –, 0.90 M NaBr; · · · ·, 0.86 M NaI; – · – ·, 0.65 M NaI; – – · – – ·, 0.52 M NaI; – · · – · ·, 0.41 M NaI.

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(7) F. Ross and G. Stucky, private communication, University of Illinois, 1968.

Ru(III) from 0.75×10^{-3} to 3.0×10^{-3} *M*. Air oxidation of $Ru(en)_3^{3+}$ results in very strong absorption at 22,300 cm^{-1} and may account for the small absorption observed at that frequency in the spectra given in Figure 2 when no sodium iodide was added. Even with several recrystallizations of the compound and careful preparations of solutions to exclude air, some residual absorption due to this decomposition product was present.

Attempts to determine the ion-pair association constant, K, for the outer-sphere association

$$Ru(en)_3^{3+} + I^- \rightleftarrows Ru(en)_3^{3+} \cdot I^-$$

and the true molar absorptivity, ϵ, for the outer-sphere complex $Ru(en)_3^{3+} \cdot I^-$ by analyzing spectroscopic data according to the method of Ramette[8] were unsuccessful because experimental errors make the Benesi–Hildebrand equation and related theory for charge-transfer complexes unusable in practice if there is only a very weak interaction, *i.e.*, if $K < 0.2$.[9] By plotting ϵ_{app} *vs.* $[I^-]$, the product $K\epsilon$ was determined to be 212 from the slope of the graph. From spectrophotometric data, it appears that $K < 0.05$ and the molar absorptivity for the charge-transfer transition is of the order 10^3–10^4. While this value for the molar absorptivity is of the magnitude of inner-sphere charge-transfer transitions in coordination compounds, the constant for the outer-sphere association is somewhat less than those reported for comparable outer-sphere complexes.[10] The low value may be due in part to the swamping ionic medium used, but other possibilities, including the formation of higher complexes, cannot be excluded.

The strong absorption observed in the visible region in each of these three different types of spectra—a mull of the solid, a diluted single crystal, and aqueous solution—strongly suggests a transition due to charge-transfer from an outer-sphere iodide ion to the ruthenium metal of the complex cation. In the solid state, the iodide is the anion of the lattice, whereas, in solution, addition of iodide ion results in ion-pair formation and the charge transfer occurs within the associated ion pair. The difference in energy of the transition in the solid and in solution undoubtedly is due to differences in environment.

Further evidence for an outer-sphere charge-transfer transition are the observations that $[Ru(en)_3]Br_3$ is yellow and that addition of sodium bromide to dilute solutions of $[Ru(en)_3]I_3$ results in development of a broad shoulder on the ultraviolet absorption band which extends into the visible region, as shown in Figure 2. The absorbance at 27,000 cm^{-1} depends on the bromide ion concentration. The energy of the charge-transfer band thus varies with the anion in the expected order,[5] *i.e.*, I < Br.

The remarkably low energy of the charge-transfer band is almost certainly due to the spin-paired d^5 electron configuration of the metal. Schmidtke has observed[3] that the charge-transfer transition observed in $[Co(en)_3]I_3 \cdot H_2O$ in the region of 34,000 cm^{-1} is absent in $[Rh(en)_3]I_3 \cdot H_2O$ at least up to 44,000 cm^{-1} where the iodide ion absorbs. He attributed this difference to the larger separation between the t_{2g} and e_g orbitals (in O_h symmetry) for the second-row transition element. In the Rh complex, the e_g acceptor orbital is of such high energy that no charge-transfer absorption is observed in the visible or ultraviolet, while in the Ru complex the hole in the t_{2g} subshell provides an acceptor of sufficiently low energy that the charge-transfer transition is observed in the visible region.

This low-energy outer-sphere charge-transfer phenomenon may be important in the mechanism for electron-transfer reactions in solution, and the solid compounds may prove to be interesting photoconductors.

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(8) R. W. Ramette, *J. Chem. Educ.*, **44**, 647 (1967).

(9) P. R. Hammond, *J. Chem. Soc.*, 479 (1964).

(10) See, for example, F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1967, p 37.