

### Optical Outer-sphere Ligand to Metal Charge Transfer in the Ion Pair $[\text{Ru}(\text{NH}_3)_6]^{3+}[\text{Rh}(\text{CN})_6]^{3-}$

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Charge transfer (CT) excited states are of great importance in the photophysics and photochemistry of transition metal complexes [1–3]. These CT states are usually of the inner-sphere type. Optical electron transfer may take place from the ligand to the metal (LMCT) [4], from the metal to the ligand (MLCT) [4], from one metal to another metal (MMCT) [4], or from one ligand to another ligand (LLCT) [5–9]. Optical CT transitions are expected to occur also as outer-sphere processes. Despite the growing interest in intermolecular photoredox reactions [10] not much is known about optical outer-sphere CT. While outer-sphere MMCT has been studied for some time [4, 10–13] MLCT [14] and LLCT [15] of this type were reported only recently. We now wish to present evidence for the occurrence of an optical outer-sphere LMCT transition.

For the present study we selected the ion pair  $[\text{Ru}^{\text{III}}(\text{NH}_3)_6]^{3+}[\text{Rh}(\text{CN})_6]^{3-}$ . The absorption spectrum of aqueous  $[\text{Ru}^{\text{III}}(\text{NH}_3)_6]^{3+}$  [16] is shown in Fig. 1. Upon addition of  $[\text{Rh}(\text{CN})_6]^{3-}$  the extinction increased between 270 and 340 nm (Fig. 1). Since  $[\text{Rh}(\text{CN})_6]^{3-}$  absorbs only below 280 nm [17] this increase must be caused by the interaction in the ion pair. A chemical reaction is unlikely because the complex cation and anion are substitutionally stable. We suggest that this increase of extinction is due to the presence of a new absorption band which is assigned to an outer-sphere CT transition within the ion pair. This new CT band appears well resolved in the difference spectrum which is obtained by subtraction of the spectrum of the components from that of the ion pair (Fig. 1). At concentrations above  $\sim 10^{-3}$  M the new band follows the Lambert–Beer law with  $\epsilon = 29$  at  $\lambda_{\text{max}} = 297$  nm. At lower concentrations the ion pair starts to dissociate. The intensity of this band begins to decrease.

The new absorption of the ion pair  $[\text{Ru}(\text{NH}_3)_6]^{3+}[\text{Rh}(\text{CN})_6]^{3-}$  is assigned to an outer-sphere LMCT transition from the coordinated cyanide of  $[\text{Rh}(\text{CN})_6]^{3-}$  to Ru(III) of  $[\text{Ru}(\text{NH}_3)_6]^{3+}$ . This assignment is based on the following considerations.

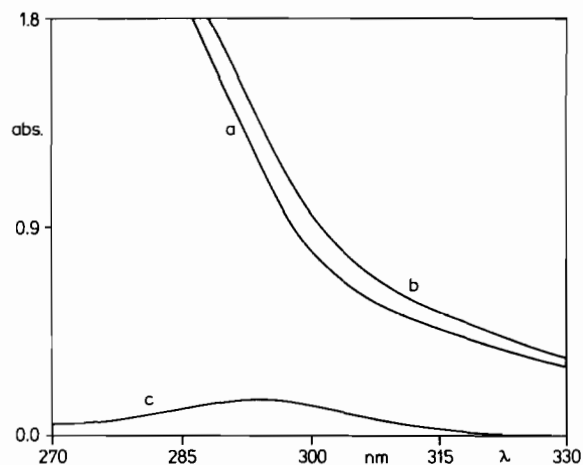


Fig. 1. Electronic absorption spectra of aqueous  $5.1 \times 10^{-3}$  M  $[\text{Ru}(\text{NH}_3)_6](\text{NO}_3)_3$  (a), an aqueous solution containing  $5.1 \times 10^{-3}$  M  $[\text{Ru}(\text{NH}_3)_6](\text{NO}_3)_3$  and  $5.1 \times 10^{-3}$  M  $\text{K}_3[\text{Rh}(\text{CN})_6]$  (b), and the difference spectrum ( $c = b - a$ ); 298 K, 1-cm cell.

Rh(III) is very redox inert and does not participate in low-energy CT transitions [4]. Ion pairs of the type  $[\text{Ru}(\text{NH}_3)_6]^{3+}\text{X}^-$  and  $[\text{Ru}(\text{NH}_3)_5\text{py}]^{3+}\text{X}^-$  ( $\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{I}^-$ ) are well known to display low-energy bands which belong to outer-sphere  $\text{X}^-$  to Ru(III) CT transitions [18, 19]. We measured also the spectrum of the ion pair  $[\text{Ru}^{\text{III}}(\text{NH}_3)_6]^{3+}\text{CN}^-$  which contains the  $\text{CN}^-$  to Ru(III) CT absorption at  $\lambda_{\text{max}} = 406$  nm ( $\epsilon = 174$ ). The blue shift of this CT band which takes place when free cyanide is replaced by coordinated cyanide of  $[\text{Rh}(\text{CN})_6]^{3-}$  may be related to the stabilization of the occupied ligand orbitals which takes place upon coordination. Other observations support also the LMCT assignment of the new absorption band of  $[\text{Ru}(\text{NH}_3)_6]^{3+}[\text{Rh}(\text{CN})_6]^{3-}$ . The long-wavelength absorption of  $[\text{Ru}^{\text{III}}(\text{CN})_6]^{3-}$  at  $\lambda_{\text{max}} = 475$  nm is clearly assigned to an inner-sphere LMCT transition from the coordinated  $\text{CN}^-$  to Ru(III) [20]. It is then interesting to compare the energy of the  $\text{CN}^-$  to Ru(III) LMCT transition of  $[\text{Ru}^{\text{III}}(\text{CN})_6]^{3-}$  (inner-sphere) and the ion pair  $[\text{Ru}(\text{NH}_3)_6]^{3+}[\text{Rh}(\text{CN})_6]^{3-}$  (outer-sphere). The increase of the energy of this transition in the ion pair is certainly due, at least partially, to the difference of the redox potentials. While in the complex  $[\text{Ru}(\text{NH}_3)_6]^{3+}$  Ru(III) is reduced to Ru(II) at  $E_{1/2} = -0.18$  V versus SCE it requires  $E_{1/2} = 0.70$  V in the case of  $[\text{Ru}(\text{CN})_6]^{3-}$  [11]. In addition, a distance effect may be important. A CT transition requires larger energies if the distance between an electron donor and acceptor increases [4, 11]. The distance between  $\text{CN}^-$  and Ru(III) is doubtless larger in the ion pair when compared with  $[\text{Ru}(\text{CN})_6]^{3-}$ .

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