

Photoredox Reaction of $[\text{Hg}(\text{cyclam})]^{2+}[\text{Co}(\text{CO})_4]^-$ Induced by Outer Sphere Charge Transfer Excitation

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The ion pair $[\text{Hg}(\text{cyclam})]^{2+}[\text{Co}(\text{CO})_4]^-$ displays a Co(-I) to Hg(II) metal-to-metal charge transfer (MMCT) band at 288 nm. Upon MMCT excitation the ion pair undergoes a photoconversion to $[\text{HgCo}_2(\text{CO})_8]$.

Photoredox processes induced by metal-to-metal charge transfer (MMCT) excitation have attracted much attention in recent years [1–4]. These processes may be exploited for applications in artificial photosynthesis and photocatalysis [5, 6]. They also facilitate our understanding of optical and thermal electron transfer in general [7, 8]. A point of particular interest is the relationship between inner-sphere (IS) and outer-sphere (OS) CT interaction of closely related donor/acceptor systems such as suitable binuclear complexes (e.g. $[(\text{NH}_3)_5\text{Ru}(\text{II})(\mu\text{-NC})\text{Ru}(\text{II})(\text{CN})_5]^-$ [9]) and the corresponding ion pairs (e.g. $[\text{Ru}(\text{II})(\text{NH}_3)_6]^{3+}[\text{Ru}(\text{II})(\text{CN})_6]^{4-}$ [10, 11]). IS MMCT transitions are not restricted to ligand-bridged complexes. They also occur if a reducing and an oxidizing metal center are connected by a direct, but polar metal–metal bond such as Hg(II)–Co(-I) in $[\text{HgCo}_2(\text{CO})_8]$ [12]. Here, we describe the CT interaction and the resulting photoactivity of the ion pair $[\text{Hg}(\text{cyclam})]^{2+}[\text{Co}(\text{CO})_4]^-$ with cyclam = 1,4,8,11-tetraazacyclotetradecane. This example demonstrates that under suitable conditions the CT interaction which is present in a polar metal–metal bond can still be observed if both metal centers are separated in an ion pair. Our observation does not only represent the first case of an OS CT interaction involving Hg^{2+} as an acceptor, it is also a valuable contribution to the photochemistry of mercury compounds which is receiving considerable interest in recent years [12–16].

Results and Discussion

When solutions of $[\text{Hg}(\text{cyclam})](\text{ClO}_4)_2$ [17] and $\text{Na}[\text{Co}(\text{CO})_4]$ in ethanol were mixed a new absorption ($\lambda_{\text{max}} = 288 \text{ nm}$, $\epsilon = 1600$) appeared (Fig. 1) which is not present in the electronic spectra of the separate components. At concentrations above $\sim 10^{-4} \text{ M}$ this new band obeyed the Lambert-Beer law while it disappeared at lower concentrations due to the dissociation of the ion pair $[\text{Hg}(\text{cyclam})]^{2+}[\text{Co}(\text{CO})_4]^-$.

Light absorption by the 288 nm band of the ion pair was associated with a photolysis which yielded $[\text{HgCo}_2(\text{CO})_8]$. The trinuclear complex was identified by its characteristic absorption at $\lambda_{\text{max}} = 328 \text{ nm}$, $\epsilon = 25,100$ [12] (Fig. 1). At $\lambda_{\text{irr}} = 313 \text{ nm}$ the ion pair photolyzed with a quantum yield of $\phi = 0.005$. The photochemical conversion to $[\text{HgCo}_2(\text{CO})_8]$ could not be driven very far since the trinuclear complex underwent a secondary photolysis according to the equation $[\text{HgCo}_2(\text{CO})_8] \rightarrow \text{Hg} + \text{Co}_2(\text{CO})_8$ with $\phi = 0.45$ at $\lambda_{\text{irr}} = 333 \text{ nm}$ [12].

Ion pairs which consist of the donor anion $[\text{Co}(\text{CO})_4]^-$ and the acceptor cations Ti^+ [18], $[\text{Co}(\text{C}_5\text{H}_5)_2]^+$ [19], and $[\text{Co}(\text{CO})_3(\text{PPh}_3)_2]^+$ [20] have been shown to display OS MMCT bands. Accordingly, we expected to observe an OS CT interaction also with Hg^{2+} as acceptor which provides an empty 6s orbital at relatively low energies. However, Hg^{2+} and $[\text{Co}(\text{CO})_4]^-$ do not associate to an ion pair but react immediately with the formation of $[(\text{OC})_4\text{Co}(-\text{I})-\text{Hg}(\text{II})-\text{Co}(-\text{I})(\text{CO})_4]$ [21, 22]. In this trinuclear complex the acceptor property of Hg(II) is expressed by a polar $\text{Hg}^{\delta+}-\text{Co}^{\delta-}$ bond which is characterized by a Co(-I) to Hg(II) IS MMCT transition at $\lambda_{\text{max}} = 328 \text{ nm}$ [12]. The

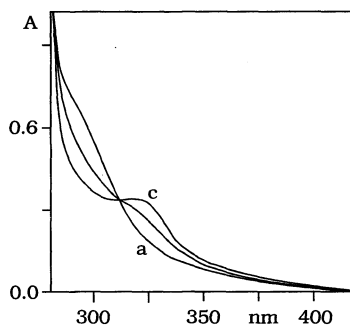


Fig. 1. Spectral changes during the photolysis of a mixture of $5.02 \times 10^{-4} \text{ M}$ $\text{Na}[\text{Co}(\text{CO})_4]$ and $5.02 \times 10^{-4} \text{ M}$ $[\text{Hg}(\text{cyclam})](\text{ClO}_4)_2$ in ethanol under argon at (a) 0, 5, and (c) 25 min irradiation time with $\lambda_{\text{irr}} = 313 \text{ nm}$ and a 1 cm cell.

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strong tendency of Hg(II) to act as an IS acceptor is underscored by further examples such as $[(\text{CN})_5\text{Co}(+\text{I})-\text{Hg}(\text{II})-\text{Co}(+\text{I})(\text{CN})_5]^{6-}$ and $[(\text{NC})_2\text{Hg}(\text{II})(\mu\text{-NC})\text{Fe}(\text{II})(\text{CN})_5]^{4-}$ [13].

However, if Hg^{2+} is incorporated into a macrocyclic ligand such as cyclam an IS interaction is prevented. $[\text{Hg}(\text{cyclam})]^{2+}$ and $[\text{Co}(\text{CO})_4]^-$ associate then to an ion pair which displays a Co(-I) to Hg(II) OS MMCT band at $\lambda_{\text{max}} = 288 \text{ nm}$. It is intriguing that this transition occurs at higher energies than the corresponding IS MMCT transition of $[\text{HgCo}_2(\text{CO})_8]$ ($\lambda_{\text{max}} = 328 \text{ nm}$). A comparison is hampered by the fact that the extent of metal-metal interaction is quite different in both cases. While it is rather weak in the ion pair a strong coupling is provided by the direct metal-metal bond in the trinuclear complex. Nevertheless, the energy difference of the MMCT transitions could also reflect the different distances

between the redox centers Hg(II) and Co(-I) in both cases. According to the Hush theory [1, 23] the energy of a MMCT transition increases with the distance which is much larger in the ion pair.

The photoactivity of the ion pair is another interesting aspect of the present work. MMCT excitation leads to the generation of radicals in the primary step: $[\text{Hg}(\text{II})(\text{cyclam})]^{2+}[\text{Co}(-\text{I})(\text{CO})_4]^- \rightarrow [\text{Hg}(\text{I})(\text{cyclam})]^+ + \text{Co}(\text{O})(\text{CO})_4$.

These reactive intermediates apparently facilitate the formation of Hg-Co bonds. The photolysis of the ion pair is thus associated with the formation of $[\text{HgCo}_2(\text{CO})_8]$ which itself undergoes a further photoredox reaction upon MMCT excitation [12].

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