

Photoredox Reactions of $\text{Hg}(\text{CN})_2/[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{HgCo}_2(\text{CN})_{10}]^{6-}$ Induced by Inner-Sphere Metal to Metal Charge Transfer Excitation

H. Kunkely, G. Stochel[†], and A. Vogler*

Institut für Anorganische Chemie, Universität Regensburg,
Universitätsstraße 31, D-8400 Regensburg, FRG

Z. Naturforsch. **44b**, 145–148 (1989); received November 22, 1988

Cyano Complexes of Mercury(II), Iron(II), Cobalt(I), UV Spectra, Photochemistry

In complexes of the type $[(\text{NC})_2\text{Hg}^{\text{II}}\text{NCFe}^{\text{II}}(\text{CN})_5]^{4-}$ which are formed in aqueous mixtures of $\text{Hg}(\text{CN})_2$ and $[\text{Fe}(\text{CN})_6]^{4-}$ both metals are weakly coupled. Optical metal to metal charge transfer (MMCT) excitation from Fe^{II} to Hg^{II} leads to the reduction of Hg^{II} to Hg^0 and the oxidation of $[\text{Fe}(\text{CN})_6]^{4-}$ to $[\text{Fe}(\text{CN})_6]^{3-}$. In the complex $[(\text{NC})_5\text{Co}^{\text{I}}-\text{Hg}^{\text{II}}-\text{Co}^{\text{I}}(\text{CN})_5]^{6-}$ the metals are strongly coupled by direct but polar metal metal bonds. MMCT ($\text{Co}^{\text{I}} \rightarrow \text{Hg}^{\text{II}}$) excitation induces the photoredox reaction: $[\text{HgCo}_2(\text{CN})_{10}]^{6-} \rightarrow \text{Hg}^0 + 2[\text{Co}(\text{CN})_5]^{3-}$.

Introduction

Polynuclear transition metal complexes which contain reducing and oxidizing metal centers are characterized by optical metal to metal charge transfer (MMCT) transitions [1–8]. Two different cases can be distinguished. The interaction of the reducing and oxidizing metal may be facilitated by bridging ligands ($\text{M}_{\text{red}}-\text{L}-\text{M}_{\text{ox}}$) [1–8]. The electronic coupling of both metals may be very weak. Photoredox reactions induced by such MMCT transitions are well known [8, 9]. In addition, the reducing and oxidizing metal of heteronuclear complexes can be connected by a direct metal–metal bond which provides a very strong coupling of the metals. Since the interacting metal orbitals have different energies in this case the metal–metal bond has a certain degree of polarity ($\overset{+}{\text{M}}-\overset{-}{\text{M}}$) and MMCT transitions can occur. The extent of CT contribution to such a transition depends on the polarity of the metal–metal bond. Photoredox reactions induced by this type of inner-sphere MMCT excitation have been discussed only recently [10, 11]. In the present study we describe photoredox reactions initiated by both types of MMCT transitions. While in the system $\text{Hg}^{\text{II}}(\text{CN})_2/[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ the interaction between Hg^{II} and Fe^{II} takes place *via* bridging cyanide the complex $[(\text{NC})_5\text{Co}^{\text{I}}-\text{Hg}^{\text{II}}-\text{Co}^{\text{I}}(\text{CN})_5]^{6-}$ contains polar $\overset{+}{\text{Hg}}-\overset{-}{\text{Co}}$ bonds. In both cases inner-sphere MMCT (Fe^{II} or Co^{I} to Hg^{II}) excitation is associated with a redox photolysis.

Experimental Section

Materials. The compounds $\text{K}_4[\text{Fe}(\text{CN})_6] \times 3\text{Hg}(\text{CN})_2 \times 4\text{H}_2\text{O}$ [12] and $\text{K}_6[\text{HgCo}_2(\text{CN})_{10}]$ [13] were prepared according to published procedures. The electronic absorption spectrum of the latter complex agreed well with that reported previously [13].

Photolyses. The light source was a Hanovia 977 B-1 (1 kW) lamp. The mercury lines at 313 and 366 nm were selected by a Schoeffel monochromator GM 250/1. Solutions of the complexes were photolyzed 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 that was calibrated and equipped with a RkP-345 detector.

Progress of the photolysis was monitored by UV-visible spectral measurements with a Uvikon 860 recording spectrophotometer and a Zeiss PMQ II spectrometer for measurements at selected wavelengths.

Results

$\text{Hg}(\text{CN})_2/[\text{Fe}(\text{CN})_6]^{4-}$

The electronic spectrum of an aqueous solution containing $\text{Hg}(\text{CN})_2$ and $[\text{Fe}(\text{CN})_6]^{4-}$ displays a new absorption band at $\lambda_{\text{max}} = 265 \text{ nm}$ ($\epsilon = 2960$). This band which does not belong to the components $\text{Hg}(\text{CN})_2$ and $[\text{Fe}(\text{CN})_6]^{4-}$ was first observed by Beck and Porzsolt in 1971 [14].

The irradiation of an aqueous solution of 0.25 M $\text{Hg}(\text{CN})_2$ and $2 \times 10^{-4} \text{ M}$ $[\text{Fe}(\text{CN})_6]^{4-}$ into this new

[†] Permanent address: Jagiellonian University, Faculty of Chemistry, 30–060 Krakow, Karasia 3, Poland.

* Reprint requests to A. Vogler.

absorption band ($\lambda_{\text{irr}} = 313 \text{ nm}$) led to the deposition of metallic mercury as a dark-grey precipitate or small shiny droplets. In addition, $[\text{Fe}(\text{CN})_6]^{3-}$ was generated and recognized by its absorption maxima at 260, 300, 320 and 418 nm. The formation of $[\text{Fe}(\text{CN})_6]^{3-}$ was monitored by measuring the increase of extinction at 418 nm ($\epsilon = 1050$). At $\lambda_{\text{irr}} = 313 \text{ nm}$ the Fe(III) complex was formed with the quantum yield $\theta = 0.03$.

Under our experimental conditions about 70% of the incident light was absorbed by the new absorption band while both components $\text{Hg}(\text{CN})_2$ and $[\text{Fe}(\text{CN})_6]^{4-}$ absorbed each about 15%. Light absorption by the components does not seem to interfere with the observed photoredox reaction of the mixture. Aqueous $\text{Hg}(\text{CN})_2$ is not light-sensitive and ligand-field excitation of $[\text{Fe}(\text{CN})_6]^{4-}$ at 313 nm leads to a photoaquation [15].

$[\text{HgCo}_2(\text{CO})_{10}]^{6-}$

The absorption spectrum of $[\text{HgCo}_2(\text{CN})_{10}]^{6-}$ (Fig. 1) is dominated by a very intense long-wavelength band at $\lambda_{\text{max}} = 361 \text{ nm}$ ($\epsilon = 51200$) [13]. The complex is thermally stable only in alkaline solution. Upon irradiation at 366 nm at pH = 13 (NaOH) a very efficient photolysis took place. The photoreaction of an argon-saturated solution was accompanied by spectral changes (Fig. 1) which clearly indicated the formation of $[\text{Co}(\text{CN})_5]^{3-}$. This com-

plex is characterized by absorption maxima at 280 and 967 nm [16–18]. In addition, metallic mercury was formed as a grey precipitate. When the photolysis was carried out at higher concentrations of $[\text{HgCo}_2(\text{CN})_{10}]^{6-}$ ($> 10^{-2} \text{ M}$) the mercury separated as shiny droplets. The concentration of $[\text{HgCo}_2(\text{CN})_{10}]^{6-}$ was monitored by measuring the extinction at the band maximum at 361 nm. The complex disappeared with a quantum yield of $\theta = 0.36$ at $\lambda_{\text{irr}} = 366 \text{ nm}$.

Discussion

$\text{Hg}(\text{CN})_2/[\text{Fe}(\text{CN})_6]^{4-}$

Beck and Porzolt have presented convincing evidence that in aqueous mixtures of $\text{Hg}(\text{CN})_2$ and $[\text{Fe}(\text{CN})_6]^{4-}$ polynuclear complexes of the type $[(\text{NC})_2\text{Hg}^{\text{II}}\mu\text{-NCFe}^{\text{II}}(\text{CN})_5]^{4-}$ are formed [14]. Mercury(II) is well known for the expansion of its coordination number from 2 to 3 and 4. The presence of bridging cyanide is also apparent from the IR spectrum of the solid addition compound $\text{K}_4[\text{Fe}(\text{CN})_6] \times 3\text{Hg}(\text{CN})_2 \times 4\text{H}_2\text{O}$ [12]. The CN stretching vibration of $\text{Hg}(\text{CN})_2$ at 2190 cm^{-1} [19] and $[\text{Fe}(\text{CN})_6]^{4-}$ at about 2050 cm^{-1} [19] appears also in the addition compound which, however, shows a further band at 2070 cm^{-1} . This band which is blue-shifted with regard to $[\text{Fe}(\text{CN})_6]^{4-}$ is a good indication for the presence of bridging cyanide [20–22]. Since the energy of the terminal cyanides is not changed by the formation of the bridged complex mercury and iron interact only weakly.

The assumption that the electronic coupling of both metals of the $\text{Hg}^{\text{II}}\text{NCFe}^{\text{II}}$ moiety is only weak is also supported by other observations. The stability constant for the association of $\text{Hg}(\text{CN})_2$ and $[\text{Fe}(\text{CN})_6]^{4-}$ is rather small ($K = 240 \text{ M}^{-1}$) [14]. In addition the electronic spectrum of $[\text{Fe}(\text{CN})_6]^{4-}$ remains essentially unaffected by the presence of $\text{Hg}(\text{CN})_2$ with the exception of the new absorption band at $\lambda_{\text{max}} = 265 \text{ nm}$. This new band is logically assigned to the MMCT transition from the d_π orbitals of the reducing Fe(II) to the $6s$ orbital of the oxidizing Hg(II). This assignment is also supported by the fact that the electronic spectra of mixtures of $\text{Hg}(\text{CN})_2$ and other transition metal cyano complexes such as $[\text{Ru}(\text{CN})_6]^{4-}$, $[\text{Mo}(\text{CN})_6]^{4-}$, $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Mo}(\text{CN})_6]^{3-}$, $[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{Rh}(\text{CN})_6]^{3-}$, and $[\text{Pd}(\text{CN})_4]^{2-}$ display MMCT absorptions only if the transition metal is reducing (Ru(II) and Mo(IV))

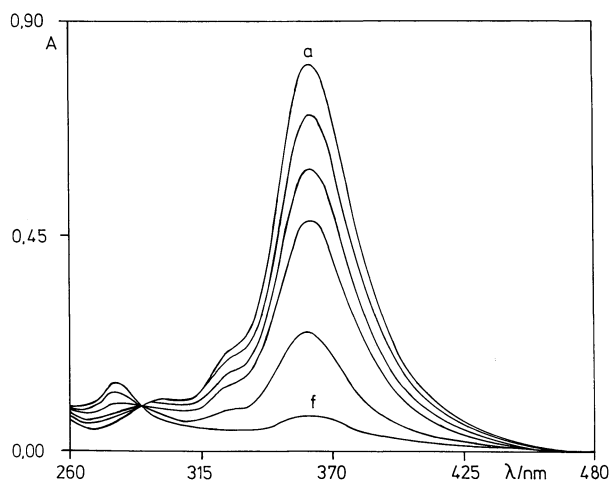
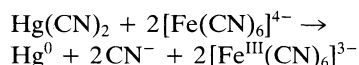


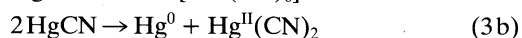
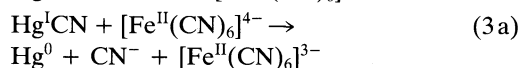
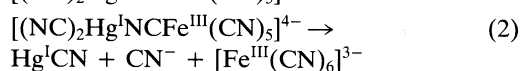
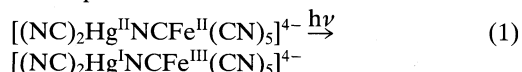
Fig. 1. Spectral changes during the photolysis of $1.58 \times 10^{-5} \text{ M K}_6[\text{HgCo}_2(\text{CN})_{10}]$ in argon-saturated 0.1 M NaOH at (a) 0 and (f) 40 s irradiation time, with $\lambda_{\text{irr}} = 366 \text{ nm}$ and a 1 cm cell.

[14]. In the case of $[\text{Ru}(\text{CN})_6]^{4-}$ the MMCT band occurs at $\lambda_{\text{max}} = 238$ nm. Such a blue shift from Fe(II) to Ru(II) is expected since $[\text{Ru}(\text{CN})_6]^{4-}$ is the weaker oxidant compared with $[\text{Fe}(\text{CN})_6]^{4-}$ [23].

Upon MMCT (Fe^{II} to Hg^{II}) excitation an aqueous mixture of $\text{Hg}(\text{CN})_2$ and $[\text{Fe}(\text{CN})_6]^{4-}$ underwent a photoredox reaction according to the equation:



The mechanism of this reaction was not investigated. However, the following sequence of processes may lead to product formation:



Mercury(I) cyanide is not stable but could exist as a reactive intermediate [19]. It may oxidize Fe(II) (3a) or disproportionate to Hg(0) and Hg(II) (3b).

$[\text{HgCo}_2(\text{CN})_{10}]^{6-}$

The structure of $[\text{HgCo}_2(\text{CN})_{10}]^{6-}$ is not known. But there is little doubt that the trinuclear complex contains a linear Co–Hg–Co moiety in analogy to many other related compounds [24] including $[\text{HgCo}_2(\text{CO})_8]$ [25]. The metal–metal bonds are assumed to be polar. Consequently, the oxidation numbers Co(I) and Hg(II) can be assigned. This assumption is based on the following considerations. Generally, the frequency of the cyanide stretching vibration of cyano complexes decreases with decreasing charge of the metal ion reflecting an increased π -back bonding in this direction. In the IR-spectra of homoleptic cobalt cyanide complexes the lowest-frequency CN bands appear at ~ 2130 cm^{-1} for Co(III) and ~ 2080 cm^{-1} for Co(II) [19].

Although $[\text{Co}^{\text{I}}(\text{CN})_5]^{4-}$ or $[\text{Co}^{\text{I}}(\text{CN})_4]^{3-}$ seem to exist [19, 26] these complexes have never been characterized and their IR spectra are also not known. The complex $[\text{HgCo}_2(\text{CN})_{10}]^{6-}$ exhibits CN bands at 2035, 2072, 2099, and 2128 cm^{-1} [13]. By comparison with Co(III) and Co(II) it is then certain-

ly reasonable to assign the oxidation numbers $[\text{Hg}^{\text{II}}\text{Co}^{\text{I}}_2(\text{CN})_{10}]^{6-}$.

The metal–metal interaction of $[\text{HgCo}_2(\text{CN})_{10}]^{6-}$ can be explained by a qualitative MO diagram (Fig. 2). The frontier orbitals are generated by the overlap of the 6s Hg and 3d 2 Co orbitals of the linear Co–Hg–Co moiety which is located on the z-axis. The 6s(Hg)–3d 2 (Co) energy difference determines the bond polarity. The 6s orbital of mercury occurs at rather high energies [27] and is certainly situated above the d 2 orbital of Co. It follows that the metal–metal bond is polar: $\overset{\delta-}{\text{Co}}-\overset{\delta+}{\text{Hg}}-\overset{\delta-}{\text{Co}}$. The bonding electron pair is then predominantly localized at both Co atoms. This description confirms also the assignment of the oxidation numbers Hg(II) and Co(I). However, in distinction to the system $\text{Hg}(\text{CN})_2/[\text{Fe}(\text{CN})_6]^{4-}$ the electronic coupling of the metals in $[\text{HgCo}_2(\text{CN})_{10}]^{6-}$ is rather strong due to the direct orbital overlap.

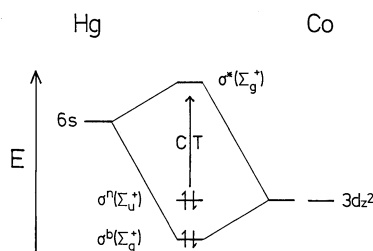
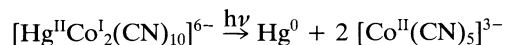


Fig. 2. Qualitative MO diagram of the linear Co–Hg–Co moiety ($D_{\infty h}$ symmetry) of $[\text{HgCo}(\text{CN})_{10}]^{6-}$.

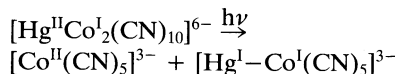
According to the MO scheme (Fig. 2) the lowest-energy electronic transition of $[\text{HgCo}_2(\text{CN})_{10}]^{6-}$ from σ^a to σ^* has a MMCT contribution. Although the extent of this contribution is not known in a limiting description the $\sigma^a \rightarrow \sigma^*$ transition can be viewed as a Co(I) to Hg(II) MMCT transition. This MMCT transition which is allowed ($\Sigma_u^+ \rightarrow \Sigma_g^+$ in $D_{\infty h}$ symmetry) is then logically assigned to the intense long-wavelength absorption of $[\text{HgCo}_2(\text{CN})_{10}]^{6-}$.

Upon MMCT excitation an efficient photolysis takes place according to the equation:



The mechanism of this reaction was not investigated. It is feasible that this stoichiometry represents also the primary photoprocess which proceeds as a reductive elimination at Hg(II) in a concerted fash-

ion. As an alternative the photolysis may first generate intermediates which are formed by the homolytic cleavage of one Hg–Co bond:



The final product formation could then take place by the thermal splitting of the second Hg–Co bond: $[\text{Hg}^{\text{I}}\text{Co}(\text{CN})_5]^{3-} \rightarrow \text{Hg}^0 + [\text{Co}^{\text{II}}(\text{CN})_5]^{3-}$.

Conclusion

The system $\text{Hg}(\text{CN})_2/[\text{Fe}(\text{CN})_6]^{4-}$ adds further evidence to the general significance of photoredox reac-

tions of cyanide-bridged complexes induced by inner-sphere MMCT excitation. A new type of inner-sphere MMCT transition occurs in the trinuclear complex $[(\text{NC})_5\text{Co}^{\text{I}}-\text{Hg}^{\text{II}}-\text{Co}^{\text{I}}(\text{CN})_5]^{6-}$. In this case the reducing and oxidizing metal are connected by a direct metal–metal bond. MMCT excitation leads also to a photoredox reaction.

Support of this research by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. G. S. is indebted to the Humboldt-Foundation for a fellowship.

-
- [1] N. S. Hush, *Progr. Inorg. Chem.* **8**, 391 (1967).
 [2] H. Taube, *Ann. N. Y. Acad. Sci.* **313**, 483 (1978).
 [3] T. J. Meyer, *Ann. N. Y. Acad. Sci.* **313**, 496 (1978).
 [4] T. J. Meyer, *Acc. Chem. Res.* **11**, 94 (1978).
 [5] D. Brown (ed.): *Mixed-Valence Compounds*, Reidel, Dordrecht, The Netherlands (1980).
 [6] C. Creutz, *Progr. Inorg. Chem.* **30**, 1 (1983).
 [7] D. E. Richardson and H. Taube, *Coord. Chem. Rev.* **60**, 107 (1984).
 [8] A. Vogler, A. H. Osman, and H. Kunkely, *Coord. Chem. Rev.* **64**, 159 (1985).
 [9] A. Vogler, A. H. Osman, and H. Kunkely, *Inorg. Chem.* **26**, 2337 (1987).
 [10] A. Vogler and H. Kunkely, *J. Organomet. Chem.* **355**, 1 (1988).
 [11] A. Vogler and H. Kunkely, *Z. Naturforsch.* **44b**, 69 (1989).
 [12] D. Strömholm, *Z. Anorg. Chem.* **84**, 208 (1913).
 [13] H. S. Lim and F. C. Anson, *Inorg. Chem.* **10**, 103 (1971).
 [14] M. T. Beck and E. C. Porzolt, *J. Coord. Chem.* **1**, 57 (1971).
 [15] V. Balzani and V. Carassiti, *Photochemistry of Coordination Compounds*, Academic Press, New York (1970).
 [16] N. N. King and M. E. Winfield, *J. Am. Chem. Soc.* **83**, 3366 (1961).
 [17] J. J. Alexander and H. B. Gray, *J. Am. Chem. Soc.* **89**, 3356 (1967).
 [18] J. M. Pratt and R. J. P. Williams, *J. Chem. Soc. A* **1967**, 1291.
 [19] A. G. Sharpe, *The Chemistry of Cyano Complexes of the Transition Metals*, Academic Press, New York (1976).
 [20] D. A. Dows, A. Haim, and W. K. Wilmarth, *J. Inorg. Nucl. Chem.* **21**, 33 (1966).
 [21] A. Vogler and H. Kunkely, *Ber. Bunsenges. Phys. Chem.* **79**, 301 (1975).
 [22] J. Ribas and A. Escuer, *Trans. Met. Chem.* **10**, 466 (1985).
 [23] J. C. Curtis and T. J. Meyer, *Inorg. Chem.* **21**, 1562 (1982).
 [24] J. M. Burlitsch, *Comprehensive Organometallic Chemistry*, G. Wilkinson, F. G. A. Stone, and E. W. Abel (eds), Pergamon Press, Oxford, Vol. 6, 983 (1982).
 [25] J. M. Burlitsch and A. Ferrari, *Inorg. Chem.* **9**, 563 (1970).
 [26] T. Funabiki, H. Hosomi, S. Yoshida, and K. Tarama, *J. Am. Chem. Soc.* **104**, 1560 (1982).
 [27] L. E. Orgel, *J. Chem. Soc.* **1958**, 4186.