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Photochemistry of $[MCo_2(CO)_8]$ (M = Zn, Cd, Hg) induced by metal to metal charge transfer excitation *

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Abstract

The electronic absorption spectra of the complexes $[(OC)_4Co^{-I}M^{II}Co^{-I}(CO)_4]$ with M = Zn, Cd, and Hg display an intense long-wavelength band which is assigned to the allowed $\Sigma u^+ \rightarrow \Sigma g^+$ transition from a non-bonding σ to an antibonding σ orbital of the Co–M–Co moiety. This transition is shifted to higher energies and gains an increasing charge transfer (CT) contribution in changing M in the order M = Hg, Cd, and Zn. In a limiting description the $\sigma^n \rightarrow \sigma^*$ transition can be regarded as a metal to metal (MM) CT transition from Co^{-I} to M^{II}. MMCT excitation induces a photoredox reaction: $[(OC)_4Co^{-I}–M^{II}–Co^{-I}(CO)_4] \rightarrow M^0 + [Co_2^0(CO)_8]$. The quantum yields are $\phi = 0.45$ ($\lambda_{irr} = 333$ nm) for M = Hg and $\phi = 0.03$ ($\lambda_{irr} = 313$ nm) for Cd.

Introduction

Polynuclear transition metal complexes which contain a reducing and an oxidizing metal are characterized by optical metal-to-metal charge transfer (MMCT) transitions [1]. The observation of MMCT bands in the absorption spectra has been exclusively restricted to complexes in which the metal–metal interaction is facilitated by bridging ligands ($M_{red}–L–M_{ox}$). In many cases MMCT excitation is associated with photoactivity [1]. However, optical MMCT should occur also in complexes which contain a reducing and an oxidizing metal connected by a direct metal–metal bond. In this case the metal–metal bond must be polar. This bond polarity requires a difference between the electronegativities of the metals which form the metal–metal bond (dative or donor/acceptor metal–metal bond). Although many complexes of this type are known [2–6], their absorption spectra were generally neither recorded nor discussed with regard to the possible occurrance of

* Dedicated to Prof. Dr. Dr. h.c. mult. Ernst Otto Fischer, on the occasion of his 70th birthday.

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MMCT transitions, despite the fact that some of these compounds are known to be light-sensitive [6]. Recently we studied the complex $[PPh_3Au-Co(CO)_4]$ as a first example representing a polar metal–metal bond which can be cleaved photochemically by MMCT excitation [7]. The present work is an extension of this investigation. Special attention is paid to the variation of bond polarity and its effect on the MMCT transition in a related series of compounds.

Experimental

Materials. $[MCo_2(CO)_8]$ with M = Zn, Cd, and Hg were prepared by published procedures [8,10]. Their electronic absorption spectra agreed fairly well with those reported previously [11]. Tetrahydrofuran (THF) used in the photochemical experiments was dried then saturated with argon.

Photolyses. The light source was an Osram HBO 100 W/2 lamp. The mercury lines at 254, 313, and 333 nm were selected by Schott PIL/IL interference filters. Solutions of the complexes were photolyzed in 1-cm spectrophotometer cells at room temperature. For quantum yield determinations the concentrations of the complex were such as to give 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) equipped with an 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 wavelength.

Results

The absorption spectra of $[MCo_2(CO)_8]$ in THF (Fig. 1) contain an intense long-wavelength absorption which is blue-shifted in the series M = Hg (λ_{max} 328 nm, ϵ 25100) [11], Cd (302 nm, 18900) [11], and Zn (284 nm, 14900).

The complex $[HgCo_2(CO)_8]$ in THF underwent an efficient photolysis upon irradiation into the long-wavelength absorption (λ_{irr} 333 nm). The spectral changes which accompany the photolysis (Fig. 2) seem not to be very informative. However, an important feature is an increase of the extinction at all wavelengths. This is due to light scattering by a suspension of small mercury droplets which are formed during the photolysis. When the irradiation was carried out at higher complex concentrations ($> 10^{-2}$ *M*) larger mercury drops precipitated out. Besides mercury $[Co_2(CO)_8]$ was formed as photochemical product. Owing to the rather featureless electronic spectrum of cobalt carbonyl [12], its formation is not apparent from the absorption spectrum of the photolyzed solution. However, the generation of $[Co_2(CO)_8]$ was confirmed by its IR spectrum (ν(CO) 2070, 2042, and 1860 cm^{-1}, in THF). The decrease of the concentration of $[HgCo_2(CO)_8]$ was followed by measuring the extinction at λ_{max} 328 nm, taking into account a residual extinction of $\epsilon = 3800$ for the photolysis product. At λ_{irr} 333 nm $[HgCo_2(CO)_8]$ disappeared with a quantum yield of $\phi = 0.45$.

The basic pattern of the spectral changes which accompanied the photolysis (λ_{irr} 313 nm) of $[CdCo_2(CO)_8]$ in THF (Fig. 3) is very similar to that observed for $[HgCo_2(CO)_8]$. Elemental cadmium and $[Co_2(CO)_8]$ were identified as products of

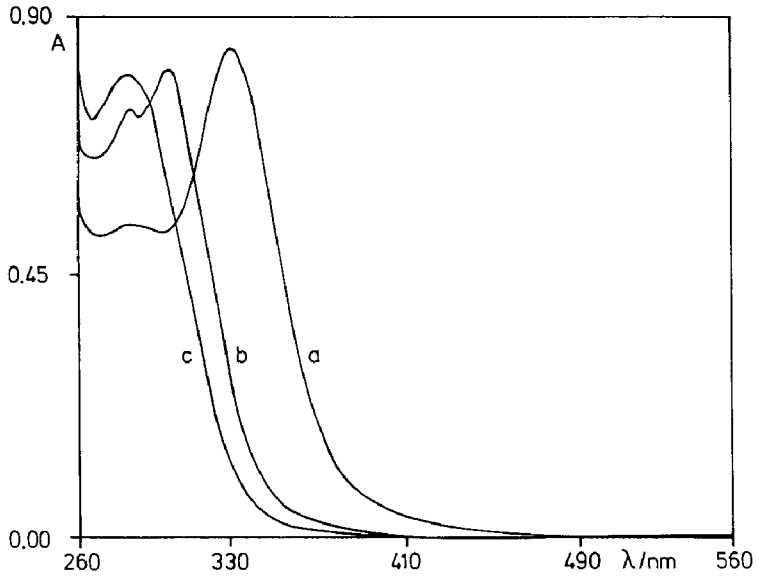

Fig. 1. Electronic absorption spectra of (a) 3.39×10^{-5} *M* $[HgCo_2(CO)_8]$, (b) 4.27×10^{-5} *M* $[CdCo_2(CO)_8]$, (c) 5.37×10^{-5} *M* $[ZnCo_2(CO)_8]$ in THF (saturated with argon) at room temperature; 1 cm cell.

the photolysis of $[CdCo_2(CO)_8]$. The irradiation of the cadmium complex at higher concentration ($> 10^{-2}$ *M*) led to a dark-brown coloration of the solution. This was apparently due to the formation of colloidal cadmium, which could be separated by centrifuging. Elemental cadmium was dissolved in diluted HCl and precipitated as yellow CdS upon addition of H_2S. The formation of $[Co_2(CO)_8]$ was again confirmed by IR spectroscopy. At later stages of the photolysis the isosbestic points

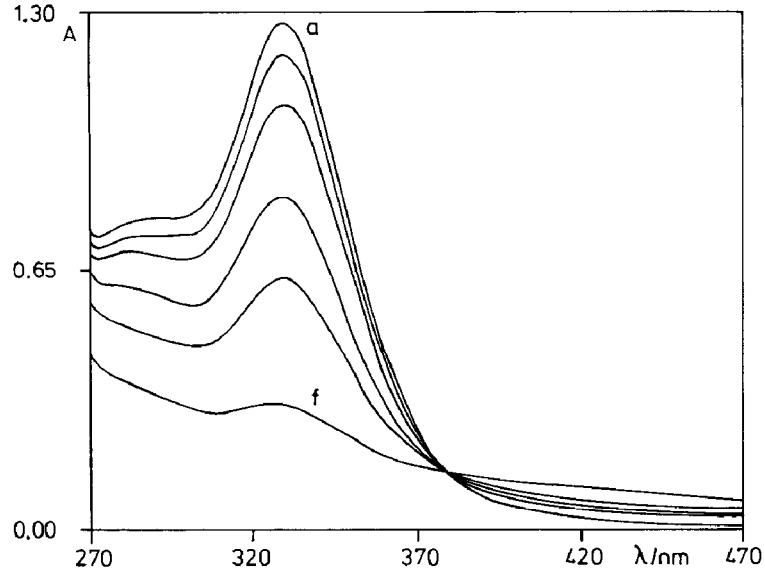

Fig. 2. Spectral changes during the photolysis of 5.06×10^{-5} *M* $[HgCo_2(CO)_8]$ in THF at (a) 0 and (f) 10 min irradiation time, with λ_{irr} 333 nm and a 1 cm cell.

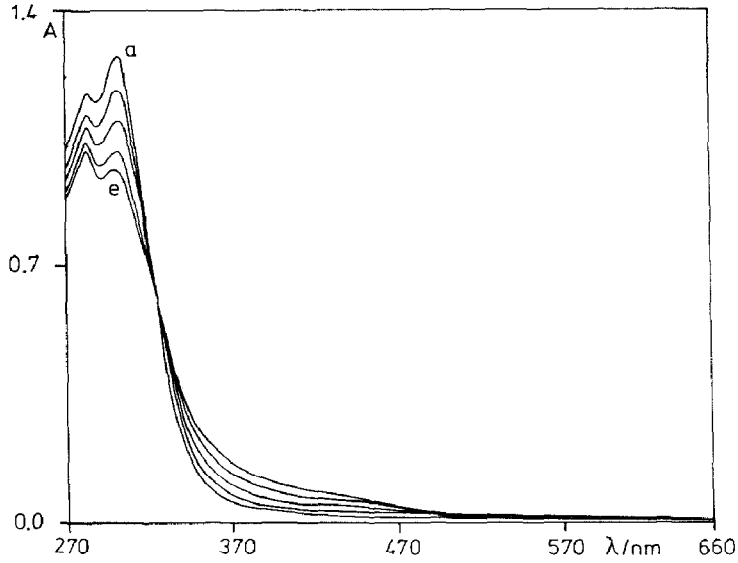

Fig. 3. Spectral changes during the photolysis of 6.73×10^{-5} *M* $[CdCo_2(CO)_8]$ in THF at (a) 0 and (e) 40 min irradiation time, with λ_{irr} 313 nm and a 1 cm cell.

in the absorption spectrum (Fig. 3) disappeared indicating a secondary photolysis. The formation of $[Co_2(CO)_8]$ was monitored by measuring the extinction at 400 nm ($\epsilon = 1720$ for $Co_2(CO)_8$). At this wavelength $[CdCo_2(CO)_8]$ absorbs only slightly ($\epsilon = 1300$). The quantum yield for the formation of $[Co_2(CO)_8]$ was $\phi = 0.03$ at λ_{irr} 313 nm.

The complex $[ZnCo_2(CO)_8]$ in THF was also light-sensitive (λ_{irr} 254 nm). The photolysis was accompanied by a darkening of the initially colorless solution. However, $[ZnCo_2(CO)_8]$ underwent a rather rapid thermal reaction which interfered seriously with the photolysis. For this reason the photoreaction was not further studied.

Discussion

The complexes $[(OC)_4Co\text{-}M\text{-}Co(CO)_4]$ with M = Zn, Cd, and Hg have a linear Co-M-Co structure [10]. The compounds are assumed to contain M^{II} and Co^{-I}. The intense long-wavelength absorption of all three complexes is assigned to the Co^{-I} to M^{II} MMCT transition. A detailed picture can be developed from the following considerations. The metal–metal interaction is essentially facilitated by the overlap of the 4*s* (Zn), 5*s* (Cd), and 6*s* (Hg) valence orbitals of M and the $3d_{z^2}$ orbital of Co with Co–M–Co taken as *z*-axis. The *s* orbitals of M are certainly not very stable and increase in energy from Hg to Zn [13]. The orbital overlap between M and Co thus leads to the simplified MO scheme shown in Fig. 4.

Since the energy difference between the *s* (M) and d_{z^2} (Co) orbitals increases from Hg to Zn the orbital overlap decreases in the same direction (Fig. 4). Consequently, the bonding electron pair in the σ^b orbital becomes more and more localized at both cobalt atoms in going from Hg to Zn. This assumption is consistent with results of independent experiments [2]. In contrast, the *s* (M) orbital

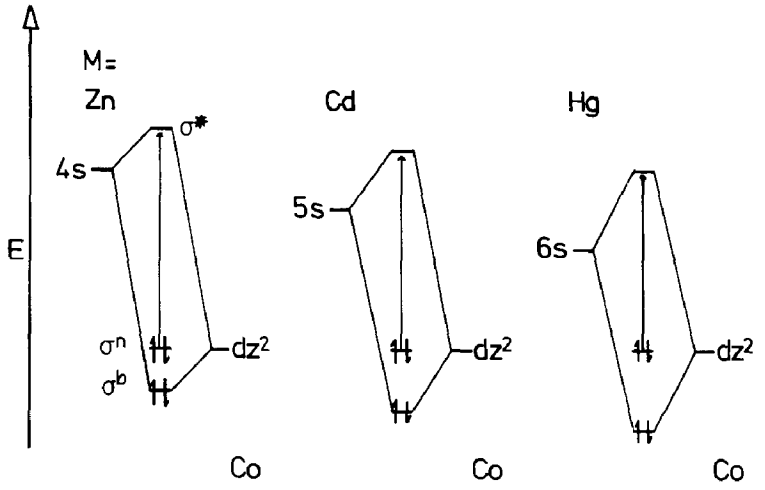

Fig. 4. Qualitative MO scheme for the linear Co–M–Co moiety of $[MCo_2(CO)_8]$ with M = Zn, Cd, and Hg.

increases its contribution to the antibonding σ-MO from Hg to Zn. The non-bonding σ-orbital is composed of d_{z^2} orbitals of both cobalt centers.

The lowest-energy electronic transition of the Co–M–Co moiety is the $\sigma^n \rightarrow \sigma^\star$ transition (Fig. 4), which possesses a substantial CT contribution. As an alternative description this transition can thus be defined as a MMCT transition from Co^{-I} to M^{II}. The CT contribution increases form Hg to Zn. The $\sigma^n \rightarrow \sigma^\star$ transition which is allowed ($\Sigma u^+ \rightarrow \Sigma g^+$ in $D\infty h$ symmetry) is then logically assigned to the intense long-wavelength absorption bands of $[MCo_2(CO)_8]$.

The photolysis of all three complexes induced by Co^{-I} to M^{II} MMCT excitation proceed according to the equation:

$$[M^{II}Co_2^{-I}(CO)_8] \rightarrow M^0 + [Co_2^0(CO)_8]$$

For the mercury complex qualitative observations of this photolysis had been made before [10]. The much lower quantum yield of the cadmium compared to the mercury complex may reflect the efficiency of the thermal back reaction that regenerates the starting complex.

A final question concerns the molecular mechanism of the photolysis. The optical MMCT transition is a one-electron process while product formation is a two-electron redox reaction with regard to M and both cobalt atoms. The reaction may then proceed by the following pathway

$$[(OC)_4Co\text{–}M\text{–}Co(CO)_4] \xrightarrow{h\nu} [(OC)_4Co\cdot] + [\cdot MCo(CO)_4] \rightarrow M + [Co_2(CO)_8]$$

The radicals shown could be formed as real intermediates. However, if the activation energy for the secondary step is rather low the lifetime of the intermediates is very small, and experimental distinction between this mechanism and a concerted formation of $[Co_2(CO)_8]$ may be very difficult and has not yet been attempted.

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References

1 (a) A. Vogler, A.H. Osman, and H. Kunkely, Coord. Chem. Rev., 64 (1985) 159; (b) A. Vogler, A.H. Osman, and H. Kunkely Inorg. Chem., 26 (1987) 2337 and ref. cited herein.
2 T.B. Brill and D.C. Miller, Inorg. Chem., 16 (1977) 1689.
3 F.W.B. Einstein, R.K. Pomeroy, P. Rushman, and A.C. Willis, Organometallics, 4 (1985) 250 and ref. cited therein.
4 W.C. Mercer, R.R. Whittle, E.W. Burkhardt, and G.L. Geoffroy, Organometallics, 4 (1985) 68.
5 F.A. Cotton and R. Poli, Inorg. Chem., 26 (1987) 590 and ref. cited therein.
6 J.M. Burlitch, In G. Wilkinson, F.G.A. Stone, and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Pergamon Press, Oxford, Vol. 6, (1982) p. 983.
7 A. Vogler and H. Kunkely, submitted for publication.
8 W. Hieber, E.O. Fischer, and E. Böckly, Z. Anorg. Allgem. Chem., 269 (1952) 308.
9 R.B. King, J.J. Eisch and R.B. King (Eds.), Organometallic Synthesis, Academic Press, New York, Vol. 1. 1965, p. 101.
10 J.M. Burlitch and A. Ferrai, Inorg. Chem., 9 (1970) 563.
11 W. Hieber and K.-K. Hofmann, Z. Anorg. Allgem. Chem., 270 (1952) 49.
12 H.B. Abrahamson, C.C. Frazier, D.S. Ginley, H.B. Gray, J. Lilienthal, D.R. Tyler, and M.S. Wrighton, Inorg. Chem., 16 (1977) 1554.
13 L.E. Orgel, J. Chem. Soc., (1958) 4186.