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Photophysics and photochemistry of mercury complexes

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Contents

Abstract

The absorption and emission spectra as well as the photochemistry of mercury and various mercury compounds in solution are reviewed. Special attention is paid to atomic mercury, the clusters Hg_2^{2+}, Hg_3^{2+}, Hg_3^{4+}, and a variety of Hg(II) complexes of the type HgX_2, HgX_3^- and HgX_4^{2-} with X = halide or organometallic fragment. © 1997 Elsevier Science S.A.

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1. Introduction

The light sensitivity of mercury compounds has been known for more than a century [1]. Despite these early observations progress has been rather slow in this field [1,2]. In 1988 we started a systematic investigation of the photochemistry and photophysics of mercury compounds. The present report is a short account of this work which reveals a variety of interesting optical and photochemical properties of these compounds.

Mercury is placed at the borderline between the transition and post-transition (or

main group) metals. Accordingly, its electronic configuration varies from d^9 in Hg(III) to s^2 in Hg(0) although Hg(III) is not yet well characterized [3,4]. Our studies covered the oxidation states 0, 2/3, 1, 4/3 and 2 which are represented by the mercury atom, the cluster cations Hg_3^{2+}, Hg_2^{2+}, Hg_3^{4+} and complexes of Hg^{2+}. The 5d, 6s and 6p orbitals can be considered as valence orbitals of mercury. However, for a simplified picture of the bonding interactions it is mostly sufficient to take into account only the mercury 6s orbitals. It follows that Hg, Hg_3^{2+}, Hg_2^{2+}, Hg_3^{4+} and Hg^{2+} can be nicely compared to H^-, H_3^-, H_2, H_3^+ and H^+ with regard to the electronic and geometric structure. On the other side a much closer analogy exists between mercury and the post-transition metals [5–7]. While atomic mercury (s^2) corresponds to Tl^+, Hg^{2+} (s^0) has much in common with Tl^{3+}.

2. Structure and bonding

Elemental mercury dissolves in many solvents including alkanes and water. However, saturated solutions do not exceed concentrations of about 10^{-7} M Hg. Owing to this low solubility it is difficult to study mercury in solution. Despite this limitation the absorption spectrum of elemental mercury in various solvents [8–11] has been measured and shown to be rather similar to that of mercury in the gas phase [12]. These solutions apparently contain mercury atoms which are perturbed by the solvent. With its closed 6s subshell, atomic mercury corresponds to other main group metal ions with an s^2 electron configuration such as Tl^+ or Pb^{2+} [5–7]. Hg(I) occurs in the cation Hg_2^{2+} which represents the best known example of a binuclear complex with a simple metal-to-metal σ-bond [3,4]. It results from the overlap of the 6s orbitals of both mercury cations and the occupation of the bonding MO by two electrons [13].

Three mercury atoms may be combined to a linear or trigonal planar arrangement. The stability depends on the number of valence electrons. In the case of Hg_3^{2+}, four electrons are available which stabilize a linear structure [14], while for Hg_3^{4+} two electrons favor a trigonal-planar geometry [15] (Fig. 1). Both clusters are kept together by one metal–metal bond. Two additional electrons of Hg_3^{2+} are accommodated in a non-bonding orbital which does not exist for the linear structure. The interdependence of both structures can be also described by a different explanation. The trigonal planar geometry of Hg_3^{4+} simply undergoes a distortion to the linear arrangement of Hg_3^{2+} if the degenerate e' orbitals of Hg_3^{4+} are occupied by two additional electrons (Fig. 1).

Hg(II) with a $d^{10}s^0$ electron configuration forms a variety of mononuclear complexes with coordination numbers of 2, 3 and 4 and linear, trigonal planar, and tetrahedral structures, respectively [16]. Halomercurate(II) complexes are typical examples of kinetically labile species, i.e., the complexes of different coordination numbers exist in equilibria (with each other) depending on the free ligand concentration. Generally, the higher the number of ligands, the lower the stepwise complex formation constant is, as shown by the data of Table 1.
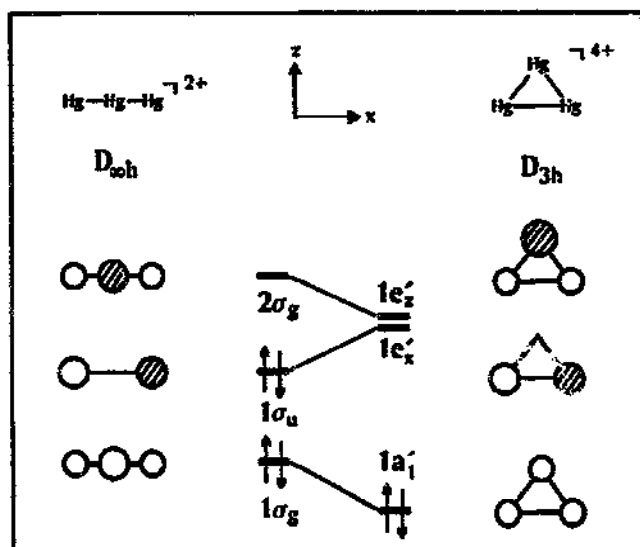
Fig. 1. Frontier orbitals of $Hg_3^{2+/4+}$ generated by overlap of the Hg 6s orbitals (adopted from T.A. Albright, J.K. Burdett and M.-H. Whangbo, Orbital Interactions in Chemistry, Wiley, New York, 1985, p. 97).

Table 1
Complex formation constants of halomercurates(II) in acetonitrile [17][a]

Complex	$HgCl_i^{(i-2)-}$	$HgBr_i^{(i-2)-}$	$HgI_i^{(i-2)-}$
$lg\beta_2$	35.1	35.4	38.2
lgK_3	6	7	8
lgK_4	4.2, 4.03[b]	3.8	2.8, 3.09[c]

Measured by [a]potentiometry, [b]spectrophotometry [18] and [c]spectrophotometry [19].

While the binary halides HgX_2 are typical examples of two-coordinate complexes, X may also be a transition metal complex anion. $[Hg^{II}Co_2^{-I}(CO)_8]$ [20] and $[Hg^{II}Co_2^{I}(CN)_{10}]^{6-}$ [21] are such complexes. They contain linear Co–Hg–Co moieties with polar metal–metal bonds.

Hg(II) forms also polynuclear complexes with ligand-bridged metal centers. For example, $Hg(CN)_2$ reacts with $[Fe(CN)_6]^{4-}$ to generate $[(CN)_2Hg(\mu-NC)-Fe(CN)_5]^{4-}$ [22]. The complexes $[Hg(pyph)Cl]_4$ [23] with pyph = 2-pyridylphenyl and $[Hg_4(SPh)_6(PPh_3)_4]^{2+}$ [24] are composed of mononuclear units which are bridged by chloride and thiophenolate ligands, respectively. It has been suggested that in these rectangular and tetrahedral Hg_4^{II} clusters a weak metal–metal bonding exists which is based on d–s orbital mixing [25] in analogy to cluster compounds of Cu(I), Ag(I) and Au(I) [26].

3. Electronic spectra

3.1. Absorption

The absorption spectrum of atomic mercury is well known from gas phase studies. From its s^2 ground state ($^1S_0$) it can be excited to various sp states ($^3P_0$, $^3P_1$, $^3P_2$, $^1P_1$) [12]. The longest-wavelength absorption line at 254 nm is assigned to the spin-forbidden sp transition $^1S_0 \rightarrow {}^3P_1$. In solution this absorption line is broadened to a narrow band [9–11] (Fig. 2), which is an indication for the perturbation of the atom by the solvent. Metal complexes with s^2 metal ions such as Tl^+, Sn^{2+}, Pb^{2+}, Sb^{3+}, Bi^{3+} also display long wavelength $^1S_0 \rightarrow {}^3P_1$ sp absorptions [5–7].

The Hg_2^{2+} ion which exists as diaquo complex in water shows an intense absorption at $\lambda_{max} = 237$ nm [13,27]. This band is assigned to the $\sigma_g^+ \rightarrow \sigma_u^+$ transition from the metal–metal bonding MO to the corresponding antibonding orbital.

The cluster ions Hg_3^{2+} and Hg_3^{4+} which exist as the ligand-bridged complex $[Hg_3(dppm)_3]^{4+}$ with dppm = diphenylphosphinomethane are also characterized by low-energy metal-centered transitions from a nonbonding σ_u (Hg_3^{2+}) or a bonding a_1' orbital (Hg_3^{4+}) to the antibonding MOs σ_g or e', respectively (Fig. 1). The accompanying absorptions appear at $\lambda_{max} = 323$ nm for Hg_3^{2+} [14] and 332 nm for $[Hg_3(dppm)_3]^{4+}$ [15].

Mercury(II) complexes such as HgX_2, HgX_3^- and HgX_4^{2-} with X = Cl [18], I [19] and N_3 [28] display long-wavelength absorptions in the UV which are only of the ligand-to-metal charge transfer (LMCT) type (Table 2). In all cases, the 6s orbital of mercury is assumed to be the acceptor orbital. If X is $[Co^{-I}(CO)_4]^-$ or $[Co^I(CN)_5]^{4-}$ the corresponding "LMCT" transitions involve $Co(-I)$ or $Co(I)$ as donor. It follows that according to the general terminology the longest-wavelength bands of $[HgCo_2(CO)_8]$ ($\lambda_{max} = 328$ nm) [29] and $[HgCo_2(CN)_{10}]^{6-}$ ($\lambda_{max} = 361$ nm) [30] are assigned to metal-to-metal charge transfer (MMCT) transitions.
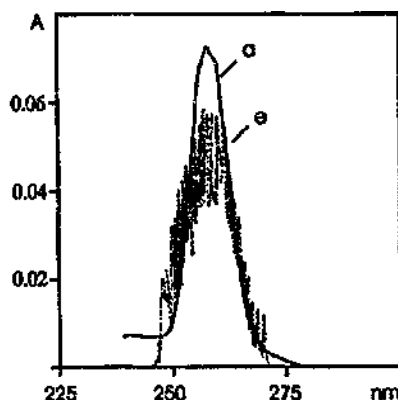

Fig. 2. Electronic absorption (a) and emission (e) spectra of elemental mercury at room temperature in cyclohexane, 1-cm cell.

Table 2
Longest-wavelength LMCT absorption maxima of various Hg(II) complexes in CH₃CN

Complex	$HgCl_2$	$HgCl_3^-$	$HgCl_4^{2-}$	HgI_2	HgI_3^-	HgI_4^{2-}	$Hg(N_3)_2^-$
λ (nm)	~200	240	234	266	301	329	246[a]
ϵ (M⁻¹ cm⁻¹)	2100	21200	41800	5200	16100	22400	5600

[a] In ethanol.

While these complexes contain polar metal–metal bonds, MMCT transitions occur also when reducing and oxidizing metals are bridged by suitable ligands.

The heterobinuclear complex $[(CN)_2Hg^{II}(\mu\text{-NC})Fe^{II}(CN)_5]^{4-}$ shows a MMCT ($Fe^{II}{\rightarrow}Hg^{II}$) absorption at $\lambda_{max} = 265$ nm [30]. In addition to these inner-sphere CT transitions, mercury(II) may also serve as acceptor site in intermolecular or outer-sphere (OS) CT transitions. The ion pair $[Hg(cyclam)]^{2+}[Co(CO)_4]^-$ with cyclam = 1,4,8,11-tetraazacyclotetradecane displays such an OS MMCT absorption at $\lambda_{max} = 288$ nm [31].

3.2. Emission

In the gas phase, elemental mercury consists of atoms which show the well-known emission line at 254 nm [12]. This emission which is used as a UV light source in mercury lamps originates from the $^3P_1$ sp-excited state. In accordance with the general behaviour of atoms elemental mercury absorbs and emits in the gas phase at the same wavelength. In the condensed phase, elemental mercury absorbs also near 254 nm [8–11]. This is an indication that the mercury atoms are only slightly perturbed by the solvent. We expected, then, to see a resonance emission of Hg also in solution. We searched for this emission and detected a very weak luminescence which indeed coincides with the absorption (Fig. 2) [32]. Unfortunately, owing to experimental limitations it was necessary to use exciting light corresponding to the absorption band of mercury in cyclohexane. The emission might have been an artifact caused by scattering of the exciting light. However, this luminescence was not observed when the emission cell was filled only with cyclohexane. Moreover, the emission did not change at all when the monochromator for the exciting light was scanned over the absorption band of Hg in cyclohexane from 230 to 250 nm. If the emission would have been caused by scattering of the exciting light, at least a change of the shape of the emission band should have been observed. Accordingly, we assume that the detected luminescence (Fig. 2) is a genuine emission of elemental mercury. The low intensity may be related to the photoreactivity of atomic mercury. In a zeolite matrix, elemental mercury was shown to emit a blue luminescence [33] which seems to be indicative of a stronger interaction between mercury and the matrix.

The cation Hg_2^{2+} is not emissive since the excitation leads to an efficient dissociation of the metal–metal bond [27]. On the contrary, both trimeric clusters, Hg_3^{2+} [14] as well as $[Hg_3(dppm)_3]^{4+}$ [15] are luminescent. The excitation affects also the
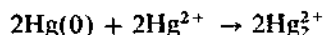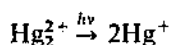
metal–metal bonding. It was suggested that the clusters undergo considerable structural rearrangements in the excited state, as indicated by the large Stokes shifts of these ions [14,15]. In this context it is quite interesting that the well-known orange photoluminescence of solid Hg_2Cl_2 was also attributed to the emission of Hg_3^{2+} [14]. Since Hg_2Cl_2 undergoes a photodisproportionation to $Hg(0)$ and Hg^{2+} the cluster cations Hg_3^{2+} and Hg_3^{4+} could be formed by the addition of $Hg(0)$ and Hg^{2+} to unreacted Hg_2Cl_2. While Hg_3^{2+} shows its orange emission at r.t. [14], Hg_3^{4+} is only emissive at low temperatures [15].

Simple $Hg(II)$ compounds, including halide complexes, are apparently not emissive. However, the $Hg(II)$ clusters $[Hg(2\text{-pyridylphenyl})Cl]_4$ and $[Hg_4(SPh)_6(PPh_3)_4]^{2+}$ display a photoluminescence [25]. It was assumed that this luminescence originates from a LMCT state which is mixed with a metal-centered ds excited state. It was concluded that in analogy to other d^{10} clusters [26] the metal–metal interaction is modified in the excited state. In a recent study the emission of a $Hg(II)$ complex which contains cyclometalated 2,9-diphenyl-1,10-phenanthroline was assigned to an intraligand transition [34].

4. Photochemistry

Atomic mercury serves as photocatalyst for the dehydrodimerization of various organic compounds. In the gas phase this photocatalysis can be used for application in organic synthesis [35]. In solution the study and utilization of the photochemistry of elemental mercury [8,36] is hampered by its low solubility. Although the excited state processes of mercury atoms with organic substrates have not yet been identified, an exciplex mechanism was invoked [35]. In aqueous solution elemental mercury is also photoreactive. Upon irradiation the absorption of $Hg(0)$ at $\lambda_{max}=254$ nm disappeared [37]. Owing to the low solubility of mercury in water (3.2×10^{-7} M) [38], details of this photolysis could not be revealed. As a tentative explanation it is assumed that $Hg(0)$ is photooxidized to $Hg(II)$ by water or oxygen which could not be completely removed by deaeration. Excited mercury atoms are certainly strong reductants in analogy to isoelectronic metal ions such as Tl^+ or Sb^{3+} [5,6].

Aqueous Hg_2^{2+} undergoes a homolysis of the metal–metal bond by $\sigma\sigma^*$ excitation [27]. In the presence of air the Hg^+ radicals are intercepted by oxygen. Finally, Hg^{2+} and H_2O_2 are formed. In deaerated alcoholic solution Hg^+ is reduced to elemental mercury [39]. A unique photoreaction takes place when this photolysis is carried out in the presence of Hg^{2+}. The results are consistent with the following mechanism:

$$Hg_2^{2+} \xrightarrow{h\nu} 2Hg^+$$

$$2Hg^+ + 2e^-(\text{alcohol}) \rightarrow 2Hg(0)$$

$$2Hg(0) + 2Hg^{2+} \rightarrow 2Hg_2^{2+}$$

$$\text{overall: } Hg_2^{2+} + 2Hg^{2+} + 2e^- \xrightarrow{h\nu} 2Hg_2^{2+}$$

This photochemical self-generation of Hg_2^{2+}, which leads to an accumulation of the photoreactive species, seems to be without precedent.

The cluster ions Hg_3^{2+} and $[Hg_3(dppm)_3]^{4+}$ are hardly photosensitive. Only at longer exposure to UV light does $[Hg_3(dppm)_3]^{4+}$ decompose with the formation of elemental mercury [15]. Although this reaction was not studied in any detail it was assumed that the photolysis occurs according to the equation: $Hg_3^{4+} \to Hg(0) + 2Hg^{2+}$. The ejection of a mercury atom may be initiated by an excited state distortion of Hg_3^{4+} which resembles an atom bound to a dimer. A similar demercuration was observed for $[Os_{18}Hg_3C_2(CO)_{42}]^{2-}$ [40]. This huge cluster contains also a triangular Hg_3 moiety.

The photochemistry of HgX_n^{2-n} complexes ($X = Cl$, Br, I, CN, and N_3; $n = 2$ with CN, 2–4 with Cl, Br, and I, and 3 with N_3) is characterized by LMCT behaviour. Ultraviolet irradiation of these compounds in solution (mostly in water or acetonitrile) led to the formation of Hg(I) species and $X^\bullet$ radicals as primary products. The halogen radicals were detected as X_2^- in ligand excess by flash photolysis both in aqueous [41] and in CH_3CN solutions [18,19] of halomercurate(II) complexes. In the case of the aqueous solution of mercury(II) cyanide spin-trapping technique was utilized for identification of the $\overset{\bullet}{CN}$ radicals formed in the primary photoreaction [42].

The subsequent reactions of these radicals depend on their reactivity and the conditions. While continuous irradiation of HgI_2 in deaerated acetonitrile results in no permanent change, indicating a very efficient back-reaction of the $HgI^\bullet$ and $I^\bullet$ formed [19], in the photolysis of $HgCl_2$ the reduction of the metal center is observed, accompanied with the formation of insoluble Hg_2Cl_2 [18]. In the latter system $Cl^\bullet$ formed in the primary photoreaction, and being a very oxidative radical is quantitatively reduced back to Cl^- in a possible redox reaction with the solvent. Thus, an increase in the $Cl^-/Hg(II)$ concentration ratio shifts the complex equilibria towards the formation of species with higher numbers of ligands. The main photoinduced and thermal reactions characterizing the photochemistry of chloromercurate(II) complexes are as follows [18]:
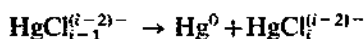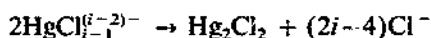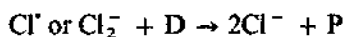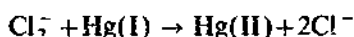
$$HgCl_i^{(i-2)-} \overset{h\nu}{\to} 2HgCl_{i-1}^{(i-2)-} + Cl^\bullet$$

$$2HgCl_{i-1}^{(i-2)-} + Cl^\bullet \to HgCl_i^{(i-2)-}$$

$$Cl^\bullet + Cl- \to Cl_2^-$$

$$Cl_2^- + Hg(I) \to Hg(II) + 2Cl^-$$

$$Cl^\bullet \text{ or } Cl_2^- + D \to 2Cl^- + P$$

$$2HgCl_{i-1}^{(i-2)-} \to Hg_2Cl_2 + (2i-4)Cl^-$$
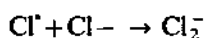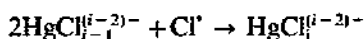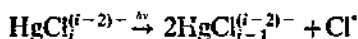
$$HgCl_{i-1}^{(i-2)-} \to Hg^0 + HgCl_i^{(i-2)-}$$

Table 3
Quantum yields for the photoinduced reduction of chloro- and iodomercurate(II) complexes in aceto-
nitrile [18,19][a]

| Condition	$10^2\phi$				
	$HgCl_2$	$HgCl_3^-$	$HgCl_4^{2-}$	HgI_3^-	HgI_4^{2-}
Ar	5.5	1.35	0.95	6.5	2.0
Air	3.1	0.56	0.21	1.5	1.5

[a]Irradiation wavelengths: 254 nm for the chloro- and 333 nm for the iodo-complexes.

where D is a reducing agent (e.g., the solvent itself) and P designates the oxidation product. Disproportionation is considerable only in ligand excess.

In the presence of an efficient reductant such as alcohol, the quantum yields for the disappearance of the chloromercurate(II) species are considerably higher than in pure CH_3CN. This is primarily a consequence of the reaction between the alcohol and the Hg(I) species formed, leading to the formation of elemental mercury, as was also shown in the photochemistry of Hg_2^{2+} [39]. Such a reaction may play a role in the photolysis of $Hg(N_3)_3^-$ in ethanol [28].

In the presence of air reoxidation of Hg^0 is also significant, and in the chloro-mercurate(II) system Hg_2Cl_2 will be the final product. The quantum yields for the photoreduction of Hg(II) in iodomercurate(II) complexes are also diminished by oxygen, as can be seen from the data of Table 3. Since I_2^- is significantly less oxidative than Cl_2^-, its main reaction (beside the back-reaction) is recombination giving I_3^- as final product:

$$I_2^- + I_2^- \rightarrow I_3^- + I^-$$
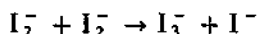
The trinuclear Hg(II) complexes $[HgCo_2(CO)_8]$ [29] and $[HgCo_2(CN)_{10}]^{6-}$ [30] are also light sensitive in solution. Upon MMCT excitation they undergo a photoredox decomposition with the formation of Hg(0) and $Co_2(CO)_8$ or $[Co(CN)_5]^{3-}$, respectively. The ligand-bridged binuclear complex $[(CN)_2Hg^{II}(\mu-NC)Fe^{II}(CN)_5]^{4-}$ is also characterized by a reactive MMCT excited state [30]. The photolysis yields Hg(0) and $[Fe(CN)_6]^{3-}$. In the ion pair $[Hg(cyclam)]^{2+}[Co(CO)_4]^-$ an OS MMCT transition leads to the generation of Hg^+ and $Co(CO)_4$ radicals which facilitate the formation of $[HgCo_2(CO)_8]$ as photoproduct [31].

Acknowledgements

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