

Photoluminescence of a triangular Hg_3^{4+} cluster

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The cluster compound $\text{Hg}_3(\mu\text{-dppm})_3(\text{SO}_4)_2$ (dppm=diphenylphosphinomethane) which contains the triangular Hg_3^{4+} moiety shows an intense low-temperature (77 K) photoluminescence at $\lambda_{\text{max}}=658$ nm. This emission is assumed to originate from a metal-centered ss excited state which undergoes a Jahn-Teller distortion.

1. Introduction

The luminescence of mercury clusters in the gas phase has been studied extensively in the past [1]. Mercury vapor shows many emission bands including the ultraviolet ($\lambda_{\text{max}}=335$ nm) and green ($\lambda_{\text{max}}=485$ nm) luminescence which originate from excited dimers Hg_2 and trimers Hg_3 , respectively. In contrast to the gas phase very little is known about the emission of mercury clusters in the condensed phase. We decided to explore this possibility and selected the compound $\text{Hg}_3(\mu\text{-dppm})_3(\text{SO}_4)_2$ [2] (dppm=diphenylphosphinomethane) which contains the triangular moiety Hg_3^{4+} for the present study. With regard to the nature of its electronic structure and excited state this complex is characterized by several interesting features. Although the mercury has the unusual oxidation number $+\frac{4}{3}$ the bonding pattern of the cluster is very simple. In the ground state the Hg_3^{4+} unit is kept together by one bond (see below). In the emitting excited state the electronic structure should be similar to that of the ground-state trimers M_3 ($\text{M}=\text{alkali}, \text{Cu}, \text{Ag}, \text{and Au}$) which were the subject of numerous studies [3-5]. Moreover, the electron configuration of mercury in the Hg_3^{4+} cation is formally intermediate between that of $\text{Hg}(0)$ ($d^{10}s^2$) and $\text{Hg}(\text{II})$ ($d^{10}s^0$). The emission behavior of $d^{10}s^2$ and d^{10} cluster complexes [6,7] including those of $\text{Hg}(\text{II})$ [8] has been studied in some detail quite recently. Finally, the nature of electronically excited Hg_3^{4+} is also of interest with

regard to the photochemical activity of mercury cluster compounds. While the dimer Hg_2^{2+} photodissociates in solution [9], the trimer Hg_3^{4+} is expected to undergo a Jahn-Teller distortion (see below) which might lead to the ejection of one mercury atom. Recently, this type of photoreactivity has been indeed observed. The photolysis of $\text{Os}_{18}\text{Hg}_3\text{C}_2(\text{CO})_{42}^-$ is accompanied by a reversible release of one mercury atom [10]. Unfortunately, the electronic structure of this large cluster which contains a Hg_3 triangle has not been studied.

2. Experimental

The ligand dppm was obtained commercially (Aldrich). The compound $\text{Hg}_3(\mu\text{-dppm})_3(\text{SO}_4)_2$ was prepared according to a published procedure [2]. All solvents were spectro grade. Absorption spectra were measured in solution at room temperature on a Shimadzu UV-2100 absorption spectrometer. Emission and excitation spectra of the compounds in the solid state or in ethanol glasses (77 K) were obtained on a Hitachi 850 spectrofluorimeter equipped with a Hamamatsu R 928 photomultiplier. The luminescence spectra were corrected for monochromator and photomultiplier efficiency.

3. Results

$\text{Hg}_3(\mu\text{-dppm})_3(\text{SO}_4)_2$ underwent a decomposi-

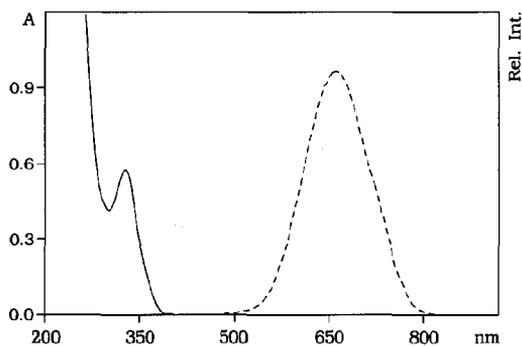


Fig. 1. Electronic absorption (—) and emission (---) spectra of $\text{Hg}_3(\text{DPM})_3(\text{SO}_4)_2$ in ethanol. Absorption: 2.93×10^{-5} M at room temperature, 1 cm. Emission: at 77 K; $\lambda_{\text{exc}} = 310$ nm, intensity in arbitrary units.

tion in acetonitrile but was rather stable in ethanol. The absorption spectrum of $\text{Hg}_3(\mu\text{-dppm})_3(\text{SO}_4)_2$ in ethanol (fig. 1) displays band maxima at $\lambda = 224$ nm ($\epsilon = 9.94 \times 10^4$ l mol $^{-1}$ cm $^{-1}$), 260 nm (shoulder), 280 nm (shoulder), 300 nm (shoulder) and 332 nm (2.04×10^4). The free ligand dppm in CH_3CN absorbs at $\lambda_{\text{max}} = 208$ nm (30200) and 249 (17600).

At room temperature in ethanol $\text{Hg}_3(\mu\text{-dppm})_3(\text{SO}_4)_2$ showed a weak blue emission ($\lambda_{\text{max}} = 450$ nm) which originates from impurities by the free dppm ligand. In ethanol glasses at 77 K the cluster compound emitted a strong orange-red luminescence at $\lambda_{\text{max}} = 658$ nm (fig. 1). The excitation spectrum matched rather well the absorption spectrum. In the solid state $\text{Hg}_3(\mu\text{-dppm})_3(\text{SO}_4)_2$ showed a weak yellow emission ($\lambda_{\text{max}} = 570$ nm) at room temperature and an intense orange luminescence ($\lambda_{\text{max}} = 590$ nm) at 77 K.

4. Discussion

The compound $\text{Hg}_3(\mu\text{-dppm})_3(\text{SO}_4)_2(\text{I})$ contains the triangular cluster cation Hg_3^{4+} with diphenylphosphinomethane (dppm) as bridging ligands [2].

The sulfate counter ions are located perpendicular to the cluster plane. The metal-metal distances (≈ 2.8 Å) are somewhat larger than the Hg-Hg bond length of Hg_2^{2+} (≈ 2.5 Å) [2].

The bonding within the Hg_3^{4+} cluster can be easily

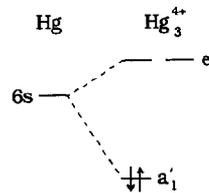


Fig. 2. Qualitative MO scheme of Hg_3^{4+} (D_{3h} symmetry).

described by the interaction of the 6s valence orbitals of mercury (fig. 2). In D_{3h} symmetry the overlap of the s orbitals generates a bonding MO a_1' and two degenerate weakly antibonding orbitals e' [11] (e'_x and e'_y with the z axis perpendicular to the Hg_3 plane). Since the Hg_3^{4+} cluster provides two valence electrons the a_1' orbital is the HOMO. Accordingly, the cluster is kept together by a three-center two-electron bond.

The longest-wavelength absorption band of $\text{Hg}_3(\mu\text{-dppm})_3(\text{SO}_4)_2$ at $\lambda = 332$ nm (fig. 1) is then logically assigned to the metal centered $a_1' \rightarrow e'$ ss transition. An intraligand assignment can be excluded since the free dppm ligand absorbs at much shorter wavelength ($\lambda_{\text{max}} = 249$ nm). The intense $a_1' \rightarrow e'$ band is assigned to a spin-allowed singlet-singlet transition although the spin selection rule does certainly not apply strictly to heavy atoms such as mercury. The corresponding spin-forbidden single-triplet absorption may be hidden under the long-wavelength tail of the spin-allowed $a_1' \rightarrow e'$ band.

The emission of $\text{Hg}_3(\mu\text{-dppm})_3(\text{SO}_4)_2$ at $\lambda_{\text{max}} = 658$ nm is then assigned to the spin-forbidden triplet-singlet $e' \rightarrow a_1'$ transition. This phosphorescence undergoes a very large Stokes shift of at least 11900 cm^{-1} . (The precise shift cannot be determined since the singlet-triplet $a_1' \rightarrow e'$ absorption was not detected). This shift should be caused by a Jahn-Teller distortion which is associated with the population of the degenerate e' orbitals [11] in the excited state. In analogy to the ground state trimers M_3 ($M = \text{alkali}, \text{Cu}, \text{Ag}$ and Au), which are also characterized by the population of the e' orbitals with a single electron, two different distortions are feasible [3-5] (fig. 3).

Although the geometry of the excited Hg_3^{4+} cluster is not known we suggest that it distorts to the isosceles triangle A with a_1 as the HOMO. In the case of the M_3 trimers this distortion was described to

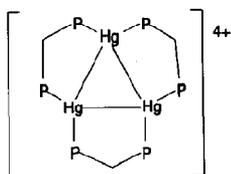
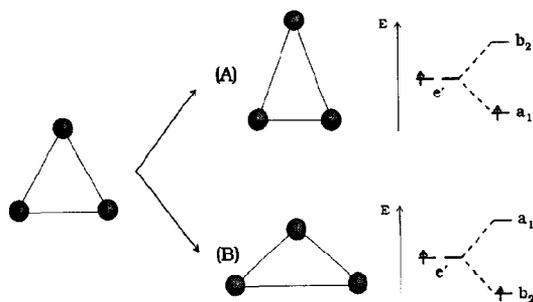


Fig. 3. Jahn-Teller distortion of Hg_3^{4+} in the lowest ss excited state.

roughly resemble an atom bound to a dimer [3–5]. As a consequence, Hg_3^{4+} may be expected to photochemically eject a mercury atom. Although the photolysis of $\text{Hg}_3(\mu\text{-dppm})_3(\text{SO}_4)_2$ was not studied in any detail there is an indication that this photoreaction indeed occurs. At longer irradiation times the photolyzed solutions turned black due to the deposition of metallic mercury. The efficiency of this photoreaction could be limited by the relatively rigid structure of the complex imposed by the bridging

phosphine ligands. The light-induced demercuration of $\text{Os}_{18}\text{Hg}_3\text{C}_2(\text{CO})_{42}^{2-}$ [10] may be initiated by a similar excited-state distortion of the triangular Hg_3 moiety of this huge cluster. On the other side, the presence of the bridging ligands should favor the luminescence of $\text{Hg}_3(\mu\text{-dppm})_3(\text{SO}_4)_2$ in competition with the photochemical splitting of the cluster [9,12].

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