Photoluminescence of $[Sn_6O_4(OCH_3)_4]$

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The hexameric complex $[Sn_6O_4(OCH_3)_4]$ shows a low-temperature (77 K) photoluminescence of moderate intensity at $\lambda_{max}=565$ nm. This emission is assumed to originate from a metal-centered sp excited state which is modified by metal–metal interaction in the octahedral $Sn(II)_6$ cluster.

1. Introduction

Hexameric metal compounds which contain an octahedral M_6 cluster and eight triply bridging ligands at the faces of the octahedron constitute an important class of polynuclear complexes [1,2]. The absorption and luminescence spectra of transition metal complexes of this type such as $M_6X_8^{4+}$ with M = Mo, W and X^- = halide have been investigated extensively [3]. On the contrary, the optical properties of the isostructural main-group metal compounds $[Bi_6O_4(OH)_4]^{6+}$[#1] [4,5], $[Sn_6O_4(OH)_4]$ [6], and $[Sn_6O_4(OCH_3)_4]$ [7] have not yet been studied although their electronic spectra should be of considerable interest as Jørgensen pointed out already 20 years ago [8]. These clusters are anticipated to be luminescent since compounds which contain s^2 ions such as Tl^+, Sn^{2+}, Pb^{2+}, Sb^{3+}, and Bi^{3+} are generally photoemissive [9–11].

Electronic spectroscopy may help to elucidate the nature of the metal–metal interaction in these s^2 clusters. Although the filled s subshell favors a nonbonding interaction weak metal–metal bonds may result from sp hybridization [12]. In distinction to the ground state the metal–metal bonds may become quite strong in the lowest excited state. The electronic spectra of the tetrameric cluster $[Tl_4(OCH_3)_4]$ have been recently interpreted on the basis of this assumption [13]. If this conception is correct it should also apply to other s^2 clusters. We explored this possibility and selected the octahedral cluster $[Sn_6O_4(OCH_3)_4]$ for the present study.

2. Experimental

The compounds $[Sn_6O_4(OCH_3)_4]$ [7] and $[Sn(benzoylacetonate)_2]$ [14] were prepared according to published procedures. Since the compounds were air sensitive all solvents were deaerated by argon. 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 toluene 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

The absorption spectrum of $[Sn_6O_4(OCH_3)_4]$ in *n*-hexane (fig. 1) displays band maxima at $\lambda=325$ nm (shoulder, 298 nm (sh), 264 nm, 225 nm (sh) and 208 nm. Owing to the low solubility of the compound a precise determination of the molar extinction coefficients was not possible but ϵ was estimated to be approximately 20000 at 208 nm. The compound was photoluminescent only at low temperatures (77 K). While the emission was rather weak in

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[#1] This ion [5] was originally assumed to be $[Bi_6(OH)_{12}]^{6+}$ [4].

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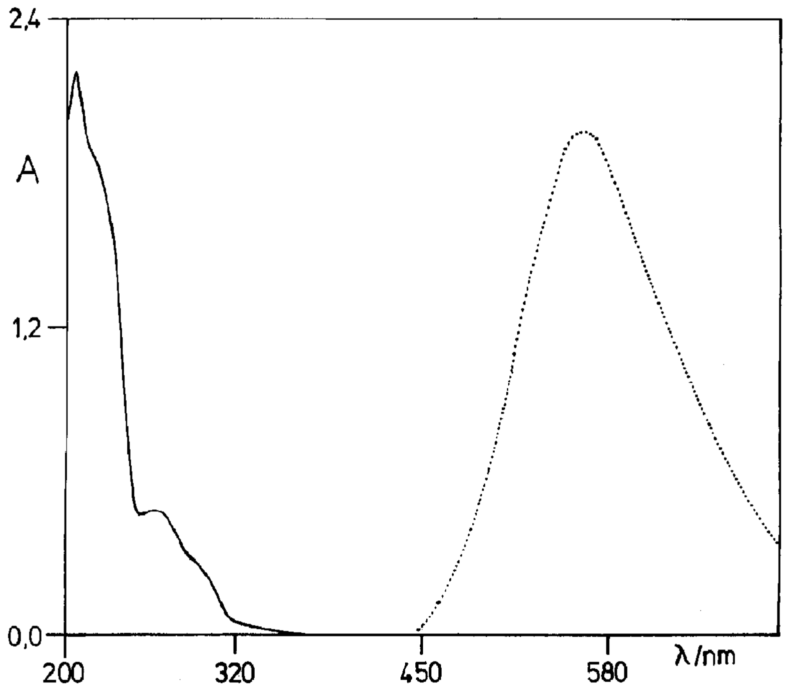

Fig. 1. Electronic absorption (——) and emission (· · ·) spectra of $[Sn_6O_4(OCH_3)_4]$. Absorption: ≈ 10^{-4} M in *n*-hexane at room temperature, 1 cm cell. Emission: in the solid state at 77 K; $\lambda_{exc}=300$ nm, intensity in arbitrary units.

toluene glasses the solid material showed a yellow luminescence of intermediate intensity at $\lambda_{max}=565$ nm (fig. 1). The excitation spectrum agreed quite well with the absorption spectrum.

For comparison the electronic spectra of $[Sn(benzoylacetonate)_2]$ were also measured. The longest wavelength absorption of this compound in benzene appeared at $\lambda_{max}=310$ nm. An emission was also observed only at low temperatures (77 K). In toluene glasses the luminescence occurred at $\lambda_{max}=480$ nm ($\lambda_{exc}=300$ nm).

4. Discussion

The compound $[Sn_6O_4(OCH_3)_4]$ consists of a slightly distorted $Sn(II)_6$ octahedron [7]. The faces of this octahedron are triply bridged by four oxide and four methoxide ligands. The hexameric cluster is thus composed of six mononuclear ML_4 components which have a distorted seesaw structure similar to that of $[Sn(benzoylacetonate)_2]$ [7,15]. The metal–metal interaction in the Sn_6 moiety can be explained by a qualitative MO scheme [16,17] (fig. 2) which includes the 5s and 5p valence orbitals of tin.

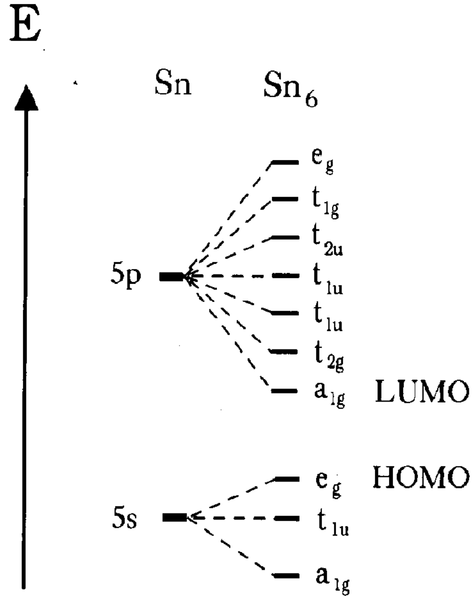

Fig. 2. Qualitative MO scheme of the octahedral $Sn(II)_6$ moiety.

In O_h symmetry the s orbitals generate one a_{1g} bonding, three t_{1u} non-bonding and two e_g anti-bonding orbitals. The overlap of the p orbitals gives 18 bonding, non-bonding, and anti-bonding MOs. Since Sn^{2+} has a closed s^2 subshell all molecular orbitals which originate from s orbitals are occupied. The compensating effect of the filled bonding and anti-bonding MOs should not yield any metal–metal bonding. However, weak metal–metal bonding may result from a stabilization of these s orbitals by sp mixing with p orbitals of the same symmetry (fig. 2). In addition, the a_{1g}, t_{1u}, and t_{2g} orbitals are destabilized by the triply bridging ligands which have orbitals of the same symmetry [16].

It is assumed that in the ground state of $[Sn_6O_4(OCH_3)_4]$ the metal–metal interaction is quite weak and hence the splitting of the s and p orbitals according to fig. 2 rather small. The absorption spectrum should then display low-energy sp bands in analogy to other mononuclear Sn^{2+} compounds. We assign the longest-wavelength band of $[Sn_6O_4(OCH_3)_4]$ at $\lambda_{max} = 325$ nm (fig. 1) to the $^1S_0 \rightarrow {}^3P_1$ sp transition of the free Sn^{2+} ion. Blasse and his group identified this sp transition (A band) of Sn^{2+} in a variety of oxide environments at comparable energies [18]. The less intense absorptions of $[Sn_6O_4(OCH_3)_4]$ at shorter wavelength should be also of the sp type while the higher-intensity bands near 200 nm may belong to ligand to metal charge transfer transitions terminating at the empty p orbitals of Sn^{2+}.

In the low-energy sp excited states of $[Sn_6O_4(OCH_3)_4]$ the metal–metal interaction and thus the splitting of the s and p orbitals (fig. 2) may become quite large since an anti-bonding s electron is promoted to bonding p orbitals. As a consequence of this increased metal–metal bonding the Sn_6 cluster is expected to undergo a contraction in the excited state. This structural change should be reflected by a large Stokes shift of the emission. The luminescence at $\lambda_{max} = 565$ nm is assigned to the $^3P_1 \rightarrow {}^1S_0$ transition of the Sn^{2+} ion. The Stokes shift of $\Delta\bar{\nu} = 13074$ cm^{-1} occurs in an energy range which has been also observed for Sn^{2+} in some oxidic matrices [18]. However, this shift of $[Sn_6O_4(OCH_3)_4]$ seems indeed to be rather large when it is compared with that of its mononuclear components. Unfortunately, $[Sn^{II}O_2(OCH_3)_2]^{4-}$ does not exist as a separate complex, but $[Sn^{II}(\text{benzoylacetonate})_2]$ is characterized by the same structural features including the coordination of Sn^{2+} by four oxygen atoms in a seesaw geometry [7,15]. This compound emits at $\lambda_{max} = 480$ nm from the intraligand (IL) excited state of the coordinated benzoylacetonate [19]. The sp excited state must then lie above the emitting IL state. The much lower energy of the sp excited state of $[Sn_6O_4(OCH_3)_4]$ is now assumed to be caused by the strong metal–metal interaction in the excited cluster.

Finally, a certain analogy between s^2 and d^{10} clusters should be pointed out. In both cases a filled s^2 or d^{10} subshell prevents strong metal–metal bonding in the ground state but favors it in the excited state. The emission spectra of d^{10} clusters of transition metals such as Cu(I) [20,21], Ag(I) [22] and Au [23,24] can be explained by the same type of excited state distortion which we considered here for s^2 clusters.

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