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LETTER

Absorption and emission spectrum of [TlOCH3]4

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It is well known that main group metal ions with an s^2 electron configuration form a large variety of polynuclear coordination compounds [1]. Recently it has been suggested that in these compounds a weak metal–metal bonding may exist which is achieved by sp orbital mixing [2]. In particular, calculations on Tl^+ clusters were used to support this idea. Unfortunately, the metal–metal interaction in polynuclear s^2 complexes has been characterized almost only by structural data. However, since s^2 metal ions are generally luminescent [3], absorption and emission spectroscopy should be well suited for studying the metal–metal interaction in these clusters. This expectation is based on a certain analogy between the electronic structure of s^2 and d^{10} metal clusters. In the ground state of d^{10} clusters a weak metal–metal bonding is accomplished by ds (or dp) orbital mixing [4]. Many polynuclear d^{10} complexes are luminescent [5]. In the ds excited state some tetranuclear clusters seem to undergo a considerable contraction by the promotion of an electron from an antibonding d to a bonding s orbital [6]. As consequence the emission undergoes a large red shift with respect to the absorption. A similar effect can be anticipated for s^2 clusters. This assumption is supported by an observation that dimer formation of Bi^{3+} ions in solid matrices is accompanied by a change of the luminescence of the s^2 ion [7]. For the present study we selected the compound [TlOCH3]4 since it has a simple composition and structure [8]. In addition, the Tl^+ ion is a strong emitter in solution under ambient conditions [3].

The absorption spectrum of [TlOCH3]4 in methanol* (Fig. 1) displays an intense absorption in the UV at $\lambda_{max} = 227$ nm ($\epsilon = 48\,500$). The emission appears at $\lambda_{max} = 640$ nm (Fig. 1). It was independent of the excited wavelength ($\lambda_{exc} < 320$ nm). For comparison the spectra of $TlNO_3$ in methanol were also measured. The absorption spectrum of Tl^+ showed a band at $\lambda_{max} = 215$ nm ($\epsilon = 8600$). Nitrate has a much weaker absorption at this wavelength. The emission of Tl^+ occurred at $\lambda_{max} = 360$ nm. The excitation spectrum agreed rather well with the absorption spectrum.

The electronic spectra of Tl^+ in water are well known [3]. The absorption maximum at $\lambda_{max} = 214$ nm ($\epsilon = 5600$ mol^{-1} dm^3 cm^{-1}) was assigned to the lowest-energy metal-centered $s \rightarrow p$ transition $^1S_0 \rightarrow {}^3P_1$. The corresponding $^3P_1 \rightarrow {}^1S_0$ emission appears at $\lambda_{max} = 368$ nm [9]. The electronic spectra of Tl^+ in methanol are thus very similar to those of Tl^+ in water. Water and methanol as ligands have apparently quite the same effect on the electronic structure of Tl^+. On the contrary, the spectra of [TlOCH3]4 are rather different. While the absorption band of $\lambda_{max} = 227$ nm is shifted only slightly to longer wavelengths the emission at $\lambda_{max} = 640$ nm undergoes a huge red shift when compared with Tl^+ in CH_3OH.

The compound [TlOCH3]4 consists of a Tl_4O_4 cubane core which contains a tetrahedral Tl_4 cluster [8]. The metal–metal interaction can be explained
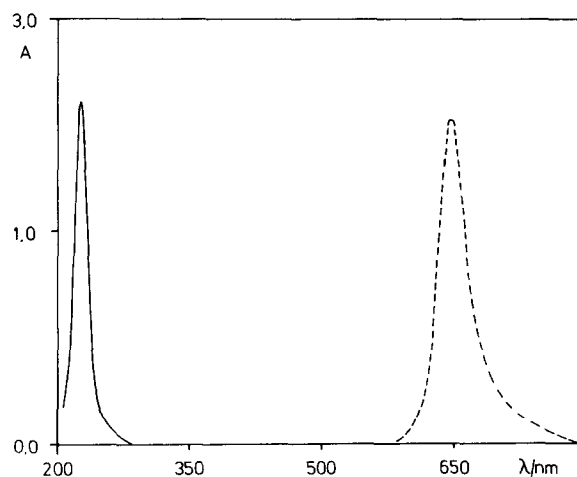

Fig. 1. Electronic absorption (——) and emission (·····) spectra of [TlOCH3]4 in methanol at room temperature; 1 cm cell. Absorption: 4.93×10^{-5} M. Emission: 10^{-3} M; $\lambda_{exc} = 280$ nm; intensity in arbitrary units.

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*Owing to the low solubility of [TlOCH3]4 in methanol the compound was first dissolved in benzene. This solution was then diluted by methanol (1:100 for absorption and 1:10 for emission spectra).

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by a qualitative MO scheme [10] (Fig. 2) which includes the 6s and 6p valence orbitals of thallium. In T_d symmetry the s orbitals yield one bonding a_1 and three antibonding t_2 MOs. The p orbitals generate six bonding (a_1, t_2, e) and six antibonding (t_1, t_2) MOs. It is assumed that the ligand orbitals of CH_3O^- are much more stable and do not change this pattern significantly. Since Tl^+ has a closed s^2 subshell the $1a_1$ and $1t_2$ orbitals are occupied. The compensating effect of the filled bonding and antibonding MOs should not yield any metal–metal bonding. However, the $1a_1$ and $1t_2$ orbitals may be lowered by sp mixing with p orbitals of the same symmetry. Accordingly the $(Tl^+)_4$ cluster can be stabilized by weak metal–metal bonding. The assumption of a rather small metal–metal interaction in the ground state [11] is supported by measurements of the Raman spectrum [12] and an X-ray structural analysis [8] which reveals a relatively long Tl–Tl distance of 3.8 Å. The occurrence of the lowest sp transition of $[TlOCH_3]_4$ and Tl^+ in methanol at comparable energies is also indicative of a small metal–metal interaction in the ground state.

However, the impressive energy difference $\Delta\bar{\nu} = 12\,150\,cm^{-1}$ between the emission of $[TlOCH_3]_4$ and Tl^+ in CH_3OH leads to the conclusion that the metal–metal interaction is quite strong in the sp excited state of the cluster. The $1t_2 \rightarrow 2a_1$ transition of $[TlOCH_3]_4$ is associated with the promotion of an antibonding electron to a bonding MO of the
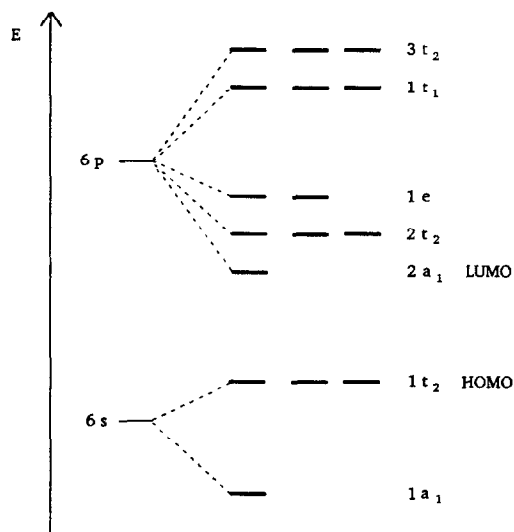
$(Tl^+)_4$ moiety which may then undergo a contraction in the excited state. The large Stoke's shift of the $1t_2 \leftrightarrow 2a_1$ sp transition is simply a consequence of such a considerable structural rearrangement.

In conclusion we anticipate that other cluster complexes of s^2 metal ions may show analogous spectroscopic features.

Acknowledgements

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Fig. 2. Qualitative MO diagram of the tetrahedral $(Tl^+)_4$ moiety.