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LETTER

Absorption and emission spectrum of $[TlOCH_3]_4$

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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 $[TlOCH_3]_4$ since it has a simple composition and structure [8]. In addition, the Tl^+ ion is a strong emitter in solution under ambient conditions [3].

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The absorption spectrum of $[TlOCH_3]_4$ 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 $[TlOCH_3]_4$ 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 $[TlOCH_3]_4$ consists of a Tl_4O_4 cubane core which contains a tetrahedral Tl_4 cluster [8]. The metal–metal interaction can be explained

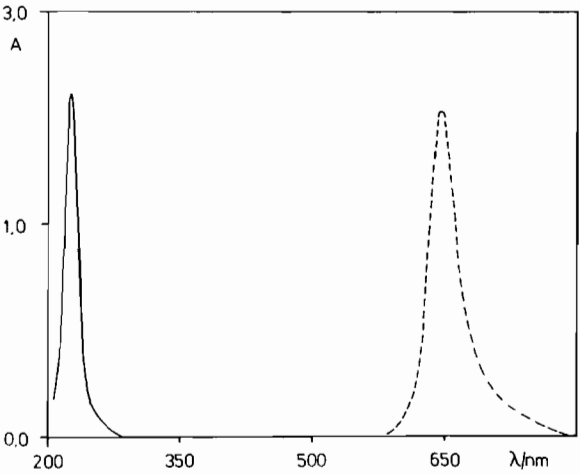

Fig. 1. Electronic absorption (——) and emission (·····) spectra of $[TlOCH_3]_4$ in methanol at room temperature; 1 cm cell. Absorption: 4.93×10^{-5} M. Emission: 10^{-3} M; $\lambda_{exc} = 280$ nm; intensity in arbitrary units.

*Owing to the low solubility of $[TlOCH_3]_4$ 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 $\Delta\tilde{\nu} = 12\,150\ cm^{-1}$ 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.

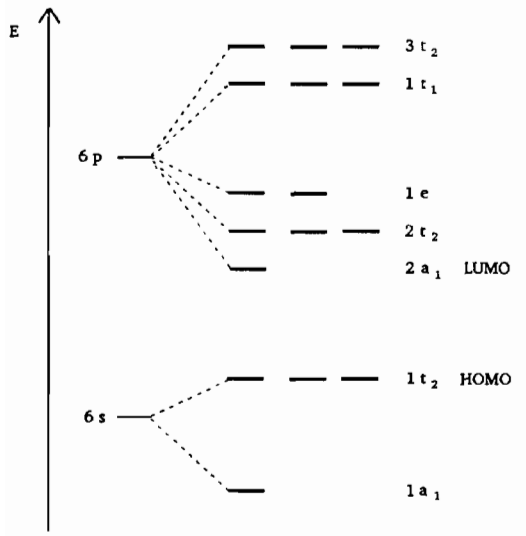

Fig. 2. Qualitative MO diagram of the tetrahedral $(Tl^+)_4$ moiety.

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

Acknowledgements

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References

1 (a) N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon, Oxford, 1984; (b) F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, New York, 5th edn., 1988.
2 (a) C. Janiek and R. Hoffmann, *Angew. Chem., Int. Ed. Engl., 28* (1989) 1688; (b) *J. Am. Chem. Soc., 112* (1990) 5924.
3 A. Vogler, A. Paukner and H,. Kunkely, *Coord. Chem. Rev., 97* (1990) 285.
4 (a) P. K. Mehrotra and R. Hoffmann, *Inorg. Chem., 17* (1978) 2187; (b) K. M. Merz and R. Hoffmann, *Inorg. Chem., 27* (1988) 2120; (c) A. Dedieu and R. Hoffmann, *J. Am. Chem. Soc., 100* (1978) 2074; (d) Y. Jiang, S. Alvarez and R. Hoffmann, *Inorg. Chem., 24* (1985) 749.
5 V. W.-W. Yam, T.-F. Lai and C.-M. Che, *J. Chem. Soc., Dalton Trans.*, (1990) 3747, and refs. therein.
6 (a) A. Vogler and H. Kunkely, *J. Am. Chem. Soc., 108* (1986) 7211; (b) K. R. Kyle, J. DiBenedetto and P. C. Ford, *J. Chem. Soc., Chem. Commun.*, (1989) 714; (c) A. Vogler and H. Kunkely, *Chem. Phys. Lett., 158* (1989) 74; (d) A. Vogler and H. Kunkely, *Chem. Phys. Lett., 150* (1988) 135.
7 (a) C. W. M. Timmermans and G. Blasse, *Phys. Status Solidi B, 118* (1983) 353; (b) A. Wolfert and G. Blasse, *Mater. Res. Bull., 19* (1984) 67.
8 L. F. Dahl, G. L. Davis, D. L. Wampler and R. West, *J. Inorg. Nucl. Chem., 24* (1962) 357.
9 G. Steffen and K. Sommermeyer, *Biophysik, 5* (1968) 192.
10 (a) R. Osman, P. Coffey and J. R. van Wazer, *Inorg. Chem., 15* (1976) 287; (b) A. F. Cuthbertson and C. Glidewell, *Inorg. Chim. Acta, 49* (1981) 91.
11 C. D. Garner, in B. F. G. Johnson (ed.), *Transition Metal Clusters*, Wiley, New York, 1980.
12 C. O. Quicksall and T. G. Spiro, *Inorg. Chem., 9* (1970) 1045.