Monatshefte für Chemie 135, 1–4 (2004)
DOI 10.1007/s00706-003-0103-4

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

Optical Properties of Thallium(I) Perrhenate. Thallium-Localized Phosphorescence

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Received August 13, 2003; accepted August 14, 2003
Published online October 20, 2003 © Springer-Verlag 2003

Summary. The salt $Tl^+ReO_4^-$ shows a strong luminescence at $\lambda_{max} = 400$ nm which originates from the lowest-energy sp triplet of Tl^+. A low-energy $Tl^I \rightarrow Re^{VII}$ metal-to-metal charge transfer excited state has not been observed.

Keywords. Electronic spectra; Charge transfer; Luminescence; Thallium; Rhenium.

Introduction

Heterobimetallic compounds are frequently characterized by properties which cannot be attributed to the separate metal centers but are caused by metal–metal interaction. In particular, combinations of two quite dissimilar metals (*e.g.* early/late transition metals [1, 2] or main group/transition metals [3, 4]) have attracted much attention. In this context, optical properties of salts which contain a s^2 cation such as Pb^{2+} and Bi^{3+} and a d^0 anion including VO_4^{3-} and WO_4^{2-} have been studied in some detail [5, 6]. Owing to the presence of an electron-donating s^2 and an accepting d^0 configuration, MMCT (metal-to-metal charge transfer) transitions may occur at relatively low energies. Indeed, combinations such as $BiVO_4$ or $PbWO_4$ display long-wavelength absorptions which have been assigned to $s^2 \rightarrow d^0$ MMCT transitions [5, 6]. Moreover, these MMCT excited states are emissive. Accordingly, a new family of luminescent compounds is available. However, it is quite surprising that MMCT of this type does not need much higher energies since, for example, Pb^{2+} is only a weak reductant and WO_4^{2-} a weak oxidant. In addition, s^2 ions are generally treated as two-electron reductants while electronic transitions are normally restricted to one-electron processes. It follows that the removal of one electron from Pb^{2+} and Bi^{3+} requires even more energy. These considerations cast some doubt on the existence of $s^2 \rightarrow d^0$ MMCT transitions at low energies. It is also conceivable that strong covalent Pb^{II}–O and Bi^{III}–O bonding modifies the electronic structure extensively. As a consequence,

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efficient electronic coupling could create new low-energy electronic transitions between highly delocalized orbitals. However, under suitable conditions these problems may be avoided. We explored this possibility and selected the salt $Tl^+ReO_4^-$ for the present study. The structure of this compound is well known [7]. Moreover, owing to the low charge and large size of Tl^+, bonding to anions is largely ionic. In addition, Tl^+ is generally a stronger reductant and consequently a more powerful CT donor than Pb^{2+} and Bi^{3+} while Re^{VII} in perrhenate is a stronger electron acceptor than W(VI) in wolframate as indicated by the energy of the $O^{2-} \rightarrow d^0$ LMCT bands of these oxo anions [8, 9]. Accordingly, $s^2 \rightarrow d^0$ MMCT transitions of $TlReO_4$ are expected to occur at lower energies than those of other s^2/d^0 systems. Another advantage of Tl^+ is the rather high energy of its sp transitions [10, 11] which are less likely to interfere with MMCT transitions. In the case of Pb^{2+} and Bi^{3+} sp bands appear at much longer wavelength [10, 11] and might obscure other bands of different origin. It follows that the electronic spectra of $TlReO_4$ should provide important information about the metal–metal interaction in related $M(s^2)^{n+}[M(d^0)O_4]^{n-}$ compounds in general.

Results

The salt $TlReO_4$ is only slightly soluble in water [12]. The absorption spectrum of a saturated aqueous solution of $TlReO_4$ consists of the superposition of the spectra of Tl_{aq}^+ with $\lambda_{max} = 213$ nm ($\varepsilon = 5600\,M^{-1}\,cm^{-1}$) [10] and ReO_4^- with $\lambda_{max} = 207$ (6100) and 228 nm (3600) [8, 9]. The emission spectrum of $TlReO_4$ in water shows the typical luminescence of Tl_{aq}^+ at $\lambda_{max} = 368$ nm [10]. The excitation spectrum matches the absorption spectrum of Tl_{aq}^+.

The electronic spectrum of solid $TlReO_4$ was measured as scattered transmission spectrum (Fig. 1). It shows two maxima at $\lambda = 205$ and 244 nm. $TlReO_4$ displays a strong luminescence (Fig. 2) at $\lambda_{max} = 400$ nm. The excitation spectrum at $\lambda = 243$ nm coincides with the second maximum of the scattered transmission spectrum, but the excitation band (Fig. 2) is rather narrow and covers only a small part of the transmission spectrum.

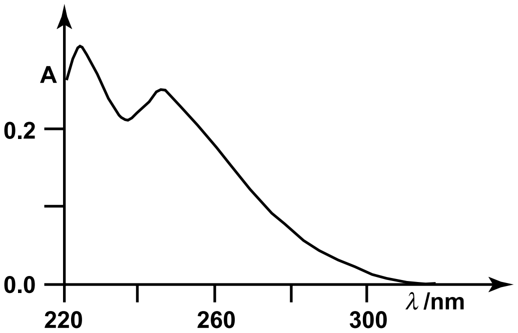

Fig. 1. Scattered transmission spectrum of finely powdered $Tl^+ReO_4^-$ in *n*-hexane at room temperature, 1 cm cell

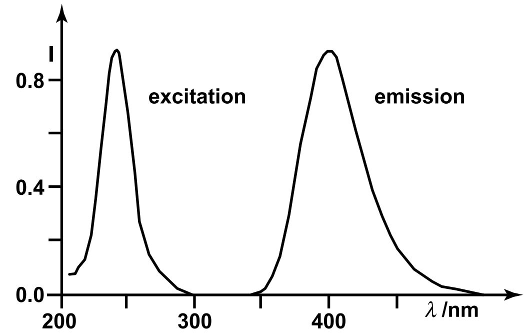

Fig. 2. Electronic emission ($\lambda_{em} = 400\,nm$) and excitation ($\lambda_{exc} = 250\,nm$) spectrum of solid $Tl^+ReO_4^-$ at room temperature, intensity in arbitrary units

For the purpose of comparison the spectra of solid Tl_2SO_4 were also measured. The emission ($\lambda_{max} = 401\,nm$) and excitation ($\lambda_{max} = 244\,nm$) spectra of solid Tl_2SO_4 are nearly identical to those of $TlReO_4$.

Discussion

The structure of $TlReO_4$ consists of isolated ReO_4 tetrahedra and TlO_8 as well as TlO_9 polyhedra [7]. With regard to the environment of Tl^+ the structure of $TlReO_4$ is comparable to that of Tl_2SO_4 [13, 14] which exists in the β-K_2SO_4 structure [15]. Solid Tl_2SO_4 is thus also characterized by distinct SO_4 tetrahedra and TlO_8 polyhedra.

The absorption of sulfate is negligible above $\lambda = 200\,nm$ and SO_4^{2-} is not luminescent. Accordingly, the electronic spectra of Tl_2SO_4 can be unambigously attributed to those of the Tl^IO_8 polyhedron. The excitation ($\lambda_{max} = 244\,nm$) and luminescence ($\lambda_{max} = 401\,nm$) spectra are very similar to those of Tl_{aq}^+, but are shifted to longer wavelength. The excitation of Tl^+ belongs to a spin-forbidden sp transition $^1S_0 \rightarrow {}^3P_1$ [10, 11]. Since the luminescence originates from the $^3P_1$ sp excited state it is a phosphorescence.

The excitation and luminescence spectra of $TlReO_4$ are nearly identical to those of Tl_2SO_4. Accordingly, the emission of $TlReO_4$ originates also from the lowest sp triplet state. Moreover, this triplet can be selectively excited. This excitation maximum is also observed as a distinct maximum in the scattered transmission spectrum of $TlReO_4$.

It follows from these observations that the emissive sp triplet of Tl^+ is not quenched by excited state electron transfer to ReO_4^-. Of course, such an electron transfer would lead to the population of the $Tl^I \rightarrow Re^{VII}$ MMCT state. The absence of electron transfer quenching is also consistent with the absence of a long-wavelength $Tl^I \rightarrow Re^{VII}$ MMCT absorption which does apparently not appear in the transmission spectrum. Nevertheless, such a MMCT state should exist, but must be located at energies well above the Tl^+ sp triplet. Unfortunately, the detection of a new MMCT absorption at shorter wavelength is hampered by the presence of the internal bands of Tl^+ and ReO_4^- which would obscure new MMCT absorptions of lower intensity.

Conclusions

$TlReO_4$ is characterized by an emissive sp triplet of Tl^+. A low-energy $Tl^I \rightarrow Re^{VII}$ MMCT state is apparently not present. This observation does not support the assumption that other s^2/d^0 combinations such as $BiVO_4$ or $PbWO_4$ provide MMCT states as lowest-energy excited states.

Experimental

Materials

The salts Tl_2SO_4 and NH_4ReO_4 are commercially available from Strem. The compound $TlReO_4$ was easily prepared by a literature procedure [12], but can be also purchased from Aldrich. All solvents used for spectroscopic measurements were of spectrograde quality.

Instrumentation

Absorption spectra were measured with a Varian Cary 50 or a Kontron Uvikon 860 spectrophotometer. Emission and excitation spectra were recorded on a Hitachi 850 spectrofluorometer equipped with a Hamamatsu 928 photomultiplier for measurements up to $\lambda = 900\,\text{nm}$. The luminescence spectra were corrected for monochromator and photomultiplier efficiency variations.

Acknowledgements

Financial support by the Fonds der Chemischen Industrie is gratefully acknowledged.

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