

Short Communication

Luminescence of Dimeric Tl(I)-Complexes: Metal-Metal Interaction in the Electronically Excited State

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Summary. Dimeric diethyldithiocarbamatethallium(I) $[Et_2NCS_2Tl]_2$ shows a red emission at $\lambda_{max} = 608$ nm which undergoes a huge Stokes shift with regard to the excitation maximum at $\lambda = 246$ nm. It is suggested that the emission originates from a sp excited state which is characterized by strong metal-metal bonding.

Keywords. Dialkyldithiocarbamatethallium(I); Luminescence; Metal-metal interaction.

Lumineszenz von dimeren Tl(I)-Komplexen: Metall-Metall-Wechselwirkung im elektronisch angeregten Zustand (Kurze Mitt.)

Zusammenfassung. Dimeres Thallium(I)diethyldithiocarbamat $[Et_2NCS_2Tl]_2$ zeigt eine rote Emission mit $\lambda_{max} = 608$ nm und eine große Stokes'sche Verschiebung im Bezug auf das Anregungsmaximum von $\lambda = 246$ nm. Die Emission wird einem sp angeregten Zustand zugeordnet, der durch eine starke Metall-Metall Wechselwirkung charakterisiert ist.

The nature and extent of metal-metal interactions in dimeric Tl^I compounds has been controversially discussed in recent years [1, 2]. If both s^2 metal centers are close enough an overlap of s and p orbitals will generate bonding and antibonding σ_s and also σ_p MOs. This simple approach does not yield any metal-metal bonding since the s-derived molecular orbitals are completely filled. However, sp orbital mixing may lead to a certain stabilization of σ_s^b and σ_s^* orbitals. As a result a weak metal-metal bonding could result. This situation is further complicated by relativistic effects [3]. Recent calculations have suggested that metal-metal bonding in $(Tl^I)_2$ dimers is probably rather weak [2].

On the contrary, relatively strong metal-metal bonding (formal bond order of one) should occur in the lowest-energy sp excited state since an electron is promoted from an antibonding s to a bonding p orbital. Since Tl^I compounds are frequently luminescent [4] emission spectroscopy is an excellent tool to study the metal-metal interaction in the excited state. For the present study we selected the dimeric $(Tl^I)_2$ complexes diethyldithiocarbamatethallium(I) ($[Et_2NCS_2Tl]_2$, $Et = CH_3CH_2$, **1**) and

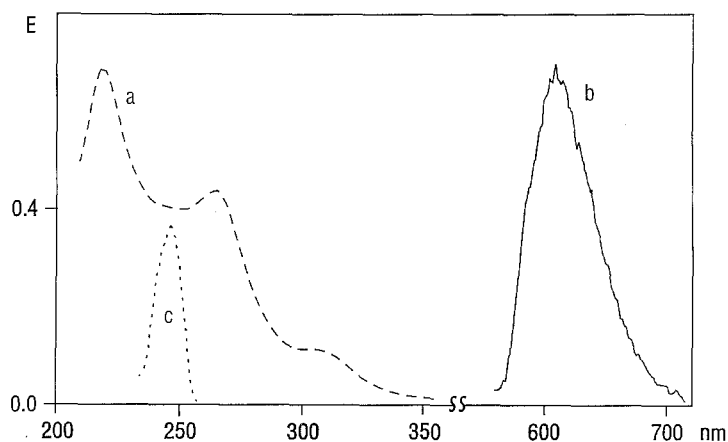


Fig. 1. Electronic absorption (a), emission (b) and excitation spectra (c) of $[Et_2NCS_2Tl]_2$ (**1**) in relative units. Absorption: $c = 1.1 \cdot 10^{-5} M$, CH_3CN , 1 cm cell. Emission: $c = 3.1 \cdot 10^{-6} M$, CH_3CN , 1 cm cell, $\lambda_{exc} = 240$ nm, room temperature. Excitation: $c = 3.1 \cdot 10^{-6} M$, CH_3CN , 1 cm cell, $\lambda_{em} = 610$ nm, room temperature

di(*n*-propyl)dithiocarbamatethallium(I) ($[(n-Prop)_2NCS_2Tl]_2$, *n-Prop* = $CH_3CH_2CH_2$, **2**). In both compounds the Tl^I-Tl^I distances are quite different [5]. A comparison of the electronic spectra of both complexes is thus expected to yield important information on the sp excited (Tl^I)₂ dimers.

The absorption spectra of the complexes **1** (Fig. 1) and **2** in CH_3CN display bands at $\lambda_{max} = 306, 266, 244,$ and 218 nm ($\epsilon = 10\,400, 35\,400, 32\,600,$ and $59\,700$ $cm^{-1} M^{-1}$ for **1**, $\epsilon = 9\,200, 34\,300, 29\,800,$ and $58\,600$ $cm^{-1} M^{-1}$ for **2**). The free ligands Et_2NCS_2Na and $(n-Prop)_2NCS_2Na$ absorb in CH_3CN at $\lambda_{max} = 300, 264, 220,$ and 206 nm ($\epsilon = 11\,900, 10\,800, 9\,650,$ and $14\,500$ $cm^{-1} M^{-1}$) and $\lambda_{max} = 300, 264, 226,$ and 202 nm ($\epsilon = 12\,100, 11\,300, 6\,850,$ and $12\,000$ $cm^{-1} M^{-1}$).

The emission of **1** in CH_3CN at room temperature appears at $\lambda_{max} = 608$ nm (Fig. 1) while **2** was not emissive under these conditions [6]. The excitation spectrum of **1** shows a maximum at 246 nm (Fig. 1). In methanol both complexes emitted at $\lambda_{max} = 356$ nm. Since this emission was nearly identical to that of Tl⁺ ions in methanol (TlNO₃, $\lambda_{max} = 360$ nm) it is assumed that the dimeric complexes break off in this solvent. The luminescence of Tl⁺ ions in methanol was quenched by the addition of CH_3CN .

In the complexes **1** and **2** both Tl^I ions are bridged by two dialkyldithiocarbamate ligands. The four coordinating sulfur atoms form nearly a square which is completed to a distorted octahedron by the Tl⁺ ions. While the Tl^I-Tl^I distance of **1** is 3.6 Å, it is much longer (4.0 Å) for **2** [5]. These distances may be compared to those of the metal (3.4 Å in α -thallium [7]) and to the van der Waals radius of the Tl atom (1.96 Å) [8]. In less polar solvents the dimeric structures are preserved [9]. According to our observations the dimers are also present in CH_3CN while they are split into monomers in CH_3OH .

The absorption spectra of **1** and **2** are rather similar. The bands near 310, 270, and 220 nm are assigned to intraligand transitions since these bands appear also in the spectrum of the free ligand. Both complexes show an additional weak absorption at 240 nm (Fig. 1) which is assigned to the $^1S_0 \rightarrow ^3P_1$ transition of Tl^I. This

sp absorption is displayed by Tl^+ ions in methanol at somewhat shorter wavelength ($TlNO_3$, $\lambda_{max} = 215$ nm, $\epsilon = 8\,600$ $cm^{-1} M^{-1}$ [10]). In the case of **1** this sp absorption coincides also with the excitation band (Fig. 1). Since the energy of the sp transition is almost independent of the Tl^I-Tl^I distance it is concluded that the metal-metal interaction in the ground state of the dimeric complexes is rather small.

However, both complexes **1** and **2** are quite different with regard to their luminescence properties. The emission behavior of **2** is rather similar to that of Tl^+ ions. The Tl^I-Tl^I distance of **2** is apparently so large that the Tl^I centers do not show any interaction even in the excited state. On the contrary, **1** is characterized by an emission at very long wavelength (Fig. 1). This emission is assumed to originate from the sp excited state of the $(Tl^I)_2$ dimer. The large Stokes shift of $\Delta\bar{\nu} = 24\,540$ cm^{-1} is an indication of a strong metal-metal interaction in the electronically excited complex since this shift is only $\Delta\bar{\nu} = 18\,730$ cm^{-1} for the solvated Tl^+ ion. The Stokes shift of **1** is caused by a considerable structural change in the excited state. We suggest that the Tl^I-Tl^I distance becomes much shorter since in the sp excited state a strong metal-metal interaction leads to stabilization. The short metal-metal distance is associated with a large splitting of s (and p) orbitals in σ_s^b and σ_s^* (and σ_p^b and σ_p^* , respectively). While there is no metal-metal bond in the ground state it is then quite strong in the sp excited state. In the dimer **2** the distance between both Tl^I centers is apparently too large to enable this type of interaction.

It is quite interesting that this type of excited state interaction is not restricted to dimers such as **1**. Two polynuclear s^2 complexes, $[TlOCH_3]_4$ [10] and $[Sn_6O_4(OCH_3)_4]$ [11] have been reported to show an emission behavior quite similar to that of **1**. Moreover, the luminescence of cluster compounds of d^{10} metals [12] such as Cu^I [13], Ag^I [14], and Au^I [15] can be explained by an analogous approach. Both, s^2 and d^{10} metals, are characterized by a filled subshell with spherical electron distribution.

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