

Electronic Spectra and Photochemistry of Hexakis(trichlorostannyl)ruthenate(II)

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Coordination compounds which contain bonds between transition metals and main group metals have attracted considerable attention in recent years. Such compounds have been termed "inorganometallic" complexes^{1,2} in distinction to organometallic and classical Werner-type complexes. In contrast to the general interest in inorganometallic complexes, the photophysical and photochemistry of these compounds remains largely unexplored although there are a few exceptions.^{3,4} Particularly Balch et al. made some remarkable observations on the luminescence of compounds which are characterized by a bond between a transition and a main group metal.⁴

For the present study we selected the complex $[\text{Ru}(\text{II})-(\text{Sn}(\text{II})\text{Cl}_3)_6]^{4-}$.⁵ This choice was stimulated by our recent studies of the optical properties of s^2 complexes.^{6,7} Anions such as SnCl_3^- show an intriguing emission behavior.^{6c} Moreover, the assembly of several Sn(II) complex fragments to an octahedral metal cluster such as $[\text{Sn}_6\text{O}_4(\text{OCH}_3)_4]$ leads to luminescence properties which reflect the metal-metal interaction in the $(\text{Sn}^{2+})_6$ octahedron.⁸ The incorporation of a transition metal into such a Sn_6 octahedron should further affect the optical properties. This is apparently the case. A large variety of homo- and heteroleptic transition-metal complexes with SnCl_3^- as ligand⁹⁻¹¹ are characterized by suspicious colors.⁹ Irrespective of the metal and its oxidation state, intense long-wavelength absorptions are shown by these compounds⁹ including $[\text{Ru}(\text{SnCl}_3)_6]^{4-}$. The colors seem thus to be related to the presence of the $(\text{SnCl}_3^-)_n$ ligand sphere, while the central transition-metal ion has a smaller influence.

Solutions of $[\text{Ru}(\text{SnCl}_3)_6]^{4-}$ in acetonitrile display absorption bands at $\lambda_{\text{max}} = 455$ (sh, $\epsilon = 150 \text{ M}^{-1} \text{ cm}^{-1}$), 365 (2500), 295 (64 000), and $\sim 235 \text{ nm}$ (sh, 19 000) (Figure 1). At room temperature these solutions were not emissive. However, in low-temperature glasses, $[\text{Ru}(\text{SnCl}_3)_6]^{4-}$ showed a luminescence at $\lambda_{\text{max}} = 670 \text{ nm}$ (Figure 1). The excitation spectrum matched the absorption spectrum rather well. The luminescence decayed with $\tau = 70 \mu\text{s}$.

Solutions of $[\text{Ru}(\text{SnCl}_3)_6]^{4-}$ in CH_3CN were thermally quite stable. Upon standing for several days or more rapidly upon

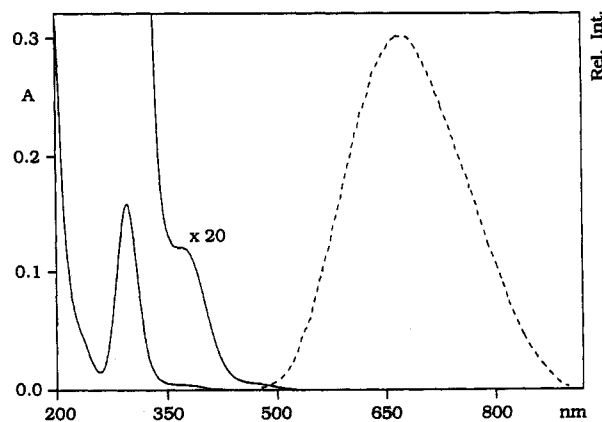


Figure 1. Electronic absorption (left) and emission (right) spectra of $(\text{Et}_4\text{N})_4[\text{Ru}(\text{SnCl}_3)_6]$. Absorption: $5 \times 10^{-6} \text{ M}$ in acetonitrile at room temperature, 1-cm cell. Emission: in ethanol/acetonitrile (9:1) at 77 K, $\lambda_{\text{exc}} = 370 \text{ nm}$, intensity in arbitrary units.

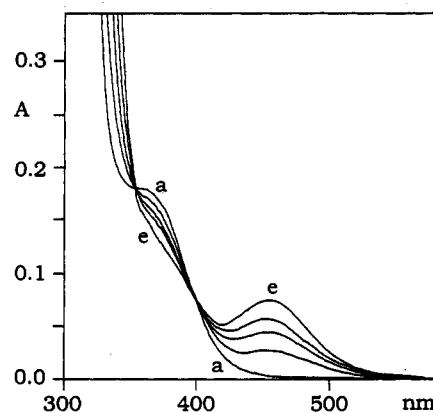


Figure 2. Spectral changes during the photolysis of $5.8 \times 10^{-5} \text{ M}$ $(\text{Et}_4\text{N})_4[\text{Ru}(\text{SnCl}_3)_6]$ in acetonitrile at (a) 0 s and (e) 25 s irradiation time with $\lambda_{\text{irr}} = 366 \text{ nm}$ (Osram HBO 200-W/2 lamp, 1-cm cell).

heating, the complex underwent a substitution with formation of $[\text{Ru}(\text{SnCl}_3)_5\text{CH}_3\text{CN}]^{3-}$.¹² The photolysis of $[\text{Ru}(\text{SnCl}_3)_6]^{4-}$ led to different results. The irradiation was accompanied by spectral changes (Figure 2) which clearly indicated the formation of $[\text{Ru}(\text{SnCl}_3)_5\text{Cl}]^{4-}$ ¹² with $\lambda_{\text{max}} = 458$ ($\epsilon = 2500$), 400 (1900), 314 (36 100), and 240 nm (sh, 39 000). This reaction was very efficient with $\phi = 0.85$ at $\lambda_{\text{irr}} = 366 \text{ nm}$. At longer irradiation times, the isobestic points at 395 and 355 nm were lost due to a secondary photolysis.

Reliable assignments of the absorption bands of $[\text{Ru}(\text{SnCl}_3)_5\text{Cl}]^{4-}$ are not yet available and may be achieved only on the basis of appropriate calculations. However, a tentative explanation accounts for several observations. As mentioned above, a variety of homo- and heteroleptic transition-metal complexes with SnCl_3^- as ligand⁹⁻¹¹ display intense long-wavelength absorptions as a common feature.⁹ We suggest that these bands belong to transitions of the $(\text{SnCl}_3^-)_n$ clusters which provide the ligand sphere for the central transition-metal ion.

The lowest-energy sp band of the isolated SnCl_3^- ion at $\lambda_{\text{max}} = 292 \text{ nm}$ ^{6c} should be shifted to longer wavelength by metal-metal interaction in the $\text{Sn}(\text{II})_6$ octahedron in analogy to $[\text{Sn}_6\text{O}_4(\text{OCH}_3)_4]$,⁸ since the overlap of the valence s as well as of the p orbitals generates bonding, nonbonding, and antibonding MOs ($6 \times s$, a_{1g} , t_{1u} , e_g ; $18 \times p$, a_{1g} , t_{2g} , $2t_{1u}$, t_{2u} , t_{1g} , e_g).^{8,13} The HOMO/LUMO gap is thus diminished. Jørgensen pointed out that this effect could shift the absorptions into the visible region,

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leading to colored s^2 clusters.¹⁴ However, these compounds are generally colorless, presumably because the metal-metal interaction in the ground state is too weak due to rather long metal-metal distances. In the case of $[\text{Ru}(\text{SnCl}_3)_6]^{4+}$, the Ru^{2+} cation could attenuate the repulsion of the SnCl_3^- fragments and mediate their interaction. Accordingly, the longest-wavelength absorptions of $[\text{Ru}(\text{SnCl}_3)_6]^{4+}$ may be assigned to internal sp transitions of the $(\text{SnCl}_3)_6^{6-}$ cluster. These transitions are certainly modified by the interaction of Ru^{2+} with the $(\text{SnCl}_3)_6^{6-}$ cluster sphere.

Of course, ligand field (LF) transitions should occur in the same energy range. Accordingly, the long-wavelength bands may be also of the LF type. However, the high intensity of the absorptions of $[\text{Ru}(\text{SnCl}_3)_6]^{4+}$ is not consistent with such an assignment. Generally, LF bands of octahedral $\text{Ru}(\text{II})$ complexes (e.g., $\text{Ru}(\text{H}_2\text{O})_6^{2+}$, $\text{Ru}(\text{en})_3^{2+}$) have extinction coefficients smaller than 100.¹⁵ Consequently, a traditional LF assignment is not appropriate for $[\text{Ru}(\text{SnCl}_3)_6]^{4+}$. However, a mixture of LF and intraligand transitions might account for the band intensities.

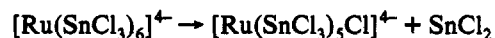
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Nevertheless, this picture does not seem to be very different from the view expressed above.

The emission of $[\text{Ru}(\text{SnCl}_3)_6]^{4+}$ should then originate from the lowest-energy sp/LF excited state. In agreement with the rather long luminescence lifetime, the emitting state is suggested to be of triplet multiplicity.

The photolysis proceeds according to the equation



This is a unique photoreaction which supports the assumption that the reactive excited state has some intraligand character.

While the present work reveals several intriguing features of the electronic spectra and photochemical behavior of this type of inorganometallic complexes, further studies are needed to better understand their excited-state properties. Toward this end we are currently investigating various substituted complexes $[\text{Ru}(\text{SnCl}_3)_5\text{L}]^{4+}$ and their osmium analogues.

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