# Electronic spectra and photochemistry of trichlorostannyl complexes of ruthenium(II) and osmium(II)

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## Abstract

The absorption spectra and photochemistry of trichlorostannyl complexes $[M(SnCl_3)_6]^{4-}$, $[M(SnCl_3)_5Cl]^{4-}$ and $[M(SnCl_3)_5AN]^{3-}$ (M = Ru, Os; AN = acetonitrile) in acetonitrile were investigated. In view of the similarity of all absorption spectra it is suggested that the lowest energy transitions are largely of the intraligand type. The photolysis of these complexes in acetonitrile leads to substitutions of $SnCl_3^-$ or in the case of $[Ru(SnCl_3)_6]^{4-}$ to a ligand fragmentation as primary photoreactions. Owing to secondary processes $[M(SnCl_3)_4(AN)_2]^{2-}$ is the terminal product of all the photoreactions. It is assumed that the photoreactions are initiated by intraligand excitation.

*Keywords:* Electronic spectra; Photochemistry; Ruthenium complexes; Osmium complexes

## 1. Introduction

A large class of coordination compounds comprises complexes which are characterized by bonds between transition and main group metals [1]. These compounds show interesting structural and bonding features. Moreover, they have promising properties for applications in materials science and catalysis. While the general chemistry of such 'inorganometallic' [2] complexes is a rapidly developing branch of coordination chemistry, the photophysics and photochemistry of these compounds are still in their infancy. Nevertheless, some remarkable observations on the photoluminescence [3] and light sensitivity [4] of complexes with bonds between transition and main group metals have been reported in recent years. For a systematic approach to this subject we selected homo- and heteroleptic trichlorostannyl ($SnCl_3^-$) complexes of transition metals since they represent a large family of inorganometallic compounds [5–7]. This choice was based on the expectation that a variation of the complex composition might provide a better insight into the factors which determine their spectral and photochemical properties. As central transition metals we chose Ru(II) and Os(II) since the spectroscopy and photochemistry of coordination compounds of these metals with classical ligands such as

NH$_3$, CN$^-$ or bipyridyl are rather well understood [8]. The present study has been facilitated by our recent work on the excited state properties of $SnCl_3^-$ [9] and related anions [10] which contain a main group metal with an $s^2$ electron configuration. Our interest in trichlorostannyl complexes was also stimulated by a report on the photocatalytic properties of mixtures which contain transition metal ions such as $Ru^{2+}$ and $SnCl_2$ [11]. Recently, we reported initial observations on the electronic spectra and photochemistry of $[Ru(SnCl_3)_6]^{4-}$ [12]. The present investigation is an extension of that work. We describe here details of the electronic spectra and the photochemical behavior of various trichlorostannyl Ru(II) and Os(II) complexes in acetonitrile.

## 2. Experimental

### 2.1. Materials

The compounds $(NEt_4)_4[Ru(SnCl_3)_5Cl]$, $[NEt_4]_3[Ru(SnCl_3)_5AN]$ and $[NEt_4]_4[Os(SnCl_3)_5Cl]$ with AN = acetonitrile were prepared according to published procedures [13,14]. Originally the complex anions $[Ru(SnCl_3)_6]^{4-}$ and $[Os(SnCl_3)_6]^{4-}$ were obtained as tetraphenylphosphonium salts [15]. In the present work they were isolated with tetraethylammonium counter-

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ions which are transparent in the UV region. The purity of all substances was confirmed by elemental analysis.

## 2.2. Syntheses

### 2.2.1. (NEt$_4$)$_2$[ Ru(SnCl$_3$)$_4$(AN)$_2$]xAN

A solution of 50 mg of (NEt$_4$)$_4$[Ru(SnCl$_3$)$_5$Cl] in 50 ml CH$_3$CN was photolyzed ($\lambda_{irr} > 360$ nm) in a quartz flask for 3 h with stirring. The photolyzed solution was concentrated by vacuum evaporation to 2 ml at 40 °C. Purification was achieved by gel chromatography. The solution was run through a column (height 70 cm, diameter 3.3 cm) filled with lipophilic sephadex (LH 20 from Sigma) and eluted with CH$_3$CN. The first fraction which consisted of [Ru(SnCl$_3$)$_5$Cl]$^{4-}$ was discarded while the second fraction was collected and concentrated by vacuum evaporation to 3 ml at 40 °C. After addition of 5 ml of ether, a precipitate separated. It was collected by filtration and washed with ethanol and ether. The yellow solid was dried in a vacuum desiccator over KOH; yield 10 mg (25.7%). *Anal.* Calc. for C$_{22}$H$_{49}$Cl$_{12}$N$_5$OsSn$_4$: C, 19.08; H, 3.57; N, 5.06. Found: C, 18.93; H, 3.40; N, 4.31%.

### 2.2.2. (NEt$_4$)$_2$[ Os(SnCl$_3$)$_4$(AN)$_2$]xAN

This compound was prepared in analogy to the corresponding ruthenium complex; yield 9 mg (22.8%). *Anal.* Calc. for C$_{22}$H$_{49}$Cl$_{12}$N$_5$OsSn$_4$: C, 17.95; H, 3.35; N, 4.75. Found: C, 17.85; H, 3.35; N, 4.23%.

### 2.2.3. (NEt$_4$)$_3$[ Os(SnCl$_3$)$_5$AN]

This compound was prepared in analogy to the corresponding ruthenium complex [13]; yield 76.5%. *Anal.* Calc. for C$_{26}$H$_{63}$Cl$_{15}$N$_4$OsSn$_5$: C, 17.87; H, 3.63; N, 3.21. Found: C, 17.56; H, 3.53; N, 2.86%.

## 2.3. Photolyses

The light source was an Osram HBO 200 W/2 lamp. Monochromatic light was obtained by means of Schott PIL/IL interference filters 366 and 405 nm. The cutoff filter Schott WG 360 ($\lambda_{irr} > 360$ nm) was used to avoid short-wavelength irradiation.

Photolyses were carried out in solutions of acetonitrile (spectrograde) in 1 cm spectrophotometer cells at room temperature. Solutions were air-saturated since deaeration did not affect the results. Progress of the photolyses was monitored by UV–Vis spectrophotometry. The photoproducts were identified by their absorption spectra. The release of SnCl$_3^-$ was detected by its absorption ($\lambda_{max} = 216$, 226 and 236 nm) and emission ($\lambda_{max} = 510$ nm) spectra [9].

The photoproducts were also isolated and identified by elemental analysis and/or spectroscopically. For this purpose the photolyses and the following procedures were performed as described for the synthesis of

(NEt$_4$)$_2$[Ru(SnCl$_3$)$_4$(AN)$_2$]xAN. The complex concentrations were approximately $6 \times 10^{-4}$ M and the irradiation required several hours. Under these conditions thermal reactions and secondary photolyses led sometimes to the formation of additional products. In these cases the spectral variations which were observed in the beginning of the photolysis (see above) showed deviations including the loss of isosbestic points at later stages of the photolysis. The following products were isolated. Photolysis of (NEt$_4$)$_4$[Ru(SnCl$_3$)$_6$] ($\lambda_{irr} > 360$ nm; $t_{irr} = 0.5$ h): (NEt$_4$)$_4$[Ru(SnCl$_3$)$_5$Cl], (NEt$_4$)$_3$[Ru(SnCl$_3$)$_5$AN] and (NEt$_4$)$_2$[Ru(SnCl$_3$)$_4$(AN)$_2$]xAN. (NEt$_4$)$_4$[Ru(SnCl$_3$)$_5$Cl] ($\lambda_{irr} > 360$ nm, $t_{irr} = 3$ h): (NEt$_4$)$_2$[Ru(SnCl$_3$)$_4$(AN)$_2$]xAN. (NEt$_4$)$_3$[Ru(SnCl$_3$)$_5$-AN] ($\lambda_{irr} > 360$ nm, $t_{irr} = 2$ h): (NEt$_4$)$_2$[Ru(SnCl$_3$)$_4$(AN)$_2$]xAN. (NEt$_4$)$_4$[Os(SnCl$_3$)$_6$] ($\lambda_{irr}$ 360 nm, $t_{irr} = 2$ h): (NEt$_4$)$_2$[Os(SnCl$_3$)$_4$(AN)$_2$]xAN. (NEt$_4$)$_4$-[Os(SnCl$_3$)$_5$Cl] ($\lambda_{irr} > 360$ nm, $t_{irr} = 3$ h): (NEt$_4$)$_2$[Os-(SnCl$_3$)$_4$(AN)$_2$]xAN. (NEt$_4$)$_3$[Os(SnCl$_3$)$_5$AN] ($\lambda_{irr} > 360$ nm, $t_{irr} = 2$ h): (NEt$_4$)$_2$[Os(SnCl$_3$)$_4$(AN)$_2$]xAN.

## 2.4. Instrumentation

Absorption spectra were measured with a Shimadzu UV-2100 absorption spectrometer. Emission and excitation spectra were obtained on an Hitachi 850 spectrofluorimeter equipped with an Hamamatsu 928 photomultiplier.

## 3. Results

### 3.1. Electronic spectra

The absorption spectra of the complex anions [Ru(SnCl$_3$)$_6$]$^{4-}$, [Ru(SnCl$_3$)$_5$Cl]$^{4-}$, [Ru(SnCl$_3$)$_5$AN]$^{3-}$ and [Ru(SnCl$_3$)$_4$(AN)$_2$]$^{2-}$ (Table 1) are characterized by the same pattern with four bands near 460 (A band), 380 (B band), 300 (C band) and 240 (D band) nm. The corresponding osmium complexes [Os(SnCl$_3$)$_6$]$^{4-}$, [Os(SnCl$_3$)$_5$Cl]$^{4-}$, [Os(SnCl$_3$)$_5$(AN)]$^{3-}$ and [Os(SnCl$_3$)$_4$-(AN)$_2$]$^{2-}$ display similar absorption spectra (Table 2). For the osmium complexes the A bands appear near 450 nm while the B bands are split into two components which occur at approximately 390 and 350 nm. The C bands are centered around 280 nm and the D bands appear as shoulders in the vicinity of 230 nm.

With the exception of [Ru(SnCl$_3$)$_5$Cl]$^{4-}$, [Os-(SnCl$_3$)$_5$Cl]$^{4-}$ and [Os(SnCl$_3$)$_4$(AN)$_2$]$^{2-}$ the trichlorostannyl complexes of Ru(II) and Os(II) were luminescent, but only in low-temperature glasses (Tables 1 and 2). The excitation spectra matched the absorption spectra rather well. As an example the absorption, excitation and emission spectra of [Ru(SnCl$_3$)$_5$AN]$^{3-}$ are shown in Fig. 1.

Table 1
Absorption and emission data for ruthenium(II) trichlorostannyl complexes

| | Complex | | | |
| --- | --- | --- | --- | --- |
| | $[Ru(SnCl_3)_6]^{4-}$ | $[Ru(SnCl_3)_5Cl]^{4-}$ | $[Ru(SnCl_3)_5AN]^{3-}$ | $[Ru(SnCl_3)_4(AN)_2]^{2-}$ |
| | Absorption [a] $\lambda_{max}$ (nm) ($\epsilon$ (1 mol$^{-1}$ cm$^{-1}$)) | | | |
| A band | ~455 sh (150) | 458 (2500) | ~460 sh (400) | ~460 sh (800) |
| B band | 365 (2500) | 400 (1900) | 380 (2700) | 388 (2200) |
| C band | 295 (64000) | 314 (36100) | 299 (62000) | 304 (27000) |
| D band | ~235 sh (19000) | ~240 sh (39000) | ~236 sh (29300) | ~236 sh (31400) |
| | Emission [b] | | | |
| $\lambda_{exc}$ (nm) | 370 | c | 380 | 385 |
| $\lambda_{max}$ (nm) | 670 | c | 700 | 735 |

[a] In acetonitrile at room temperature.
[b] In ethanol/acetonitrile (9:1) at 77 K.
[c] No emission.

Table 2
Absorption and emission data for osmium(II) trichlorostannyl complexes

| | Complex | | | |
| --- | --- | --- | --- | --- |
| | $[Os(SnCl_3)_6]^{4-}$ | $[Os(SnCl_3)_5Cl]^{4-}$ | $[Os(SnCl_3)_5AN]^{3-}$ | $[Os(SnCl_3)_4(AN)_2]^{2-}$ |
| | Absorption [a] $\lambda_{max}$ (nm) ($\epsilon$ (1 mol$^{-1}$ cm$^{-1}$)) | | | |
| A band | ~443 sh (800) | ~448 sh (1100) | ~450 sh (950) | ~450 sh (300) |
| B band | 391 (1800) | 392 (2400) | 386 (2200) | ~400 sh (800) |
| | ~342 sh (1500) | 348 (1500) | ~346 sh (2300) | 342 (1700) |
| C band | 276 (54800) | 285 (48700) | 278 (55400) | 275 (7200) |
| D band | ~230 sh (46000) | ~235 sh (45000) | ~230 sh (44000) | 224 (90000) |
| | Emission [b] | | | |
| $\lambda_{exc}$ (nm) | 370 | c | 350 | c |
| $\lambda_{max}$ (nm) | 740 | c | 740 | c |

[a] In acetonitrile at room temperature.
[b] In ethanol/acetonitrile (9:1) at 77 K.
[c] No emission.

## 3.2. Photochemistry

The photochemistry of $[Ru(SnCl_3)_6]^{4-}$ in $CH_3CN$ was briefly described in our previous communication [12]. The spectral changes which occurred at the beginning of the photolysis ($\lambda_{irr} = 366$ nm) were simulated by mixtures of $[Ru(SnCl_3)_6]^{4-}$ and $[Ru(SnCl_3)_5Cl]^{4-}$. While this observation confirms the formation of $[Ru(SnCl_3)_5Cl]^{4-}$ in the primary photolysis (process a, Scheme 1), the photolyzed solution contained $[Ru(SnCl_3)_5Cl]^{4-}$, $[Ru(SnCl_3)_5AN]^{3-}$ and $[Ru(SnCl_3)_4(AN)_2]^{2-}$ when the irradiation was carried out for
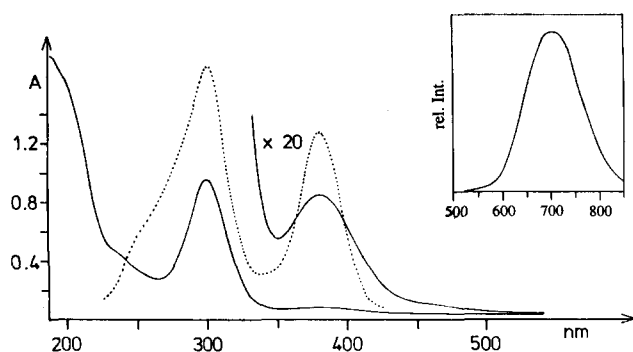
Fig. 1. Electronic absorption (——), excitation (⋯) and emission (inset) spectra of (NEt₄)₃[Ru(SnCl₃)₅AN]. Absorption: $1.55 \times 10^{-5}$ M in acetonitrile at room temperature, 1 cm cell. Emission: in ethanol/acetonitrile (9:1) at 77 K, $\lambda_{exc} = 380$ nm, intensity in arbitrary units. Excitation: $\lambda_{em} = 700$ nm.
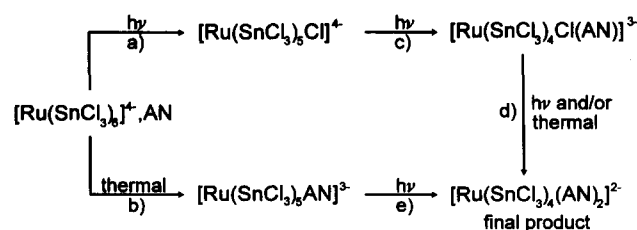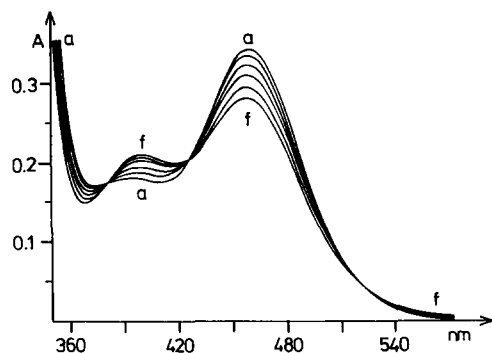


Scheme 1.



Fig. 2. Spectral changes during the photolysis of $1.38 \times 10^{-4}$ M (NEt₄)₄[Ru(SnCl₃)₅Cl] in acetonitrile at 0 (a) and 100 (f) s irradiation time with $\lambda_{irr} = 436$ nm, 1 cm cell.

extended periods. [Ru(SnCl₃)₄(AN)₂]²⁻ was apparently produced by the photolysis of the primary product [Ru(SnCl₃)₅Cl]⁴⁻ (see below). The formation of [Ru(SnCl₃)₅AN]³⁻ is attributed to the thermal substitution of [Ru(SnCl₃)₆]⁴⁻ (process b, Scheme 1).

The photolysis of [Ru(SnCl₃)₅Cl]⁴⁻ in CH₃CN led finally to the formation of [Ru(SnCl₃)₄(AN)₂]²⁻ which was isolated from the irradiated solutions. However, neither [Ru(SnCl₃)₄(AN)₂]²⁻ nor [Ru(SnCl₃)₅AN]³⁻ was the primary product. The clean spectral changes including isosbestic points at 380 and 425 nm which were observed at the beginning of the photolysis (Fig. 2) could not be reproduced by the spectra of mixtures of [Ru(SnCl₃)₅Cl]⁴⁻ and one of these final photoproducts. Since free SnCl₃⁻ was already detected during

the first stages of the photolysis it is assumed that [Ru(SnCl₃)₄Cl(AN)]³⁻ was the primary photoproduct of [Ru(SnCl₃)₅Cl]⁴⁻ (process c, Scheme 1). [Ru(SnCl₃)₄Cl(AN)]³⁻ is apparently not stable but underwent a thermal and/or photochemical substitution of chloride with the formation of [Ru(SnCl₃)₄(AN)₂]²⁻ as the only isolable product (process d, Scheme 1).

The photolysis of [Ru(SnCl₃)₅AN]³⁻ ($\lambda_{irr} = 405$ nm) in CH₃CN was accompanied by spectral changes (Fig. 3) which clearly indicated the formation of [Ru(SnCl₃)₄(AN)₂]²⁻ as the primary product (process e, Scheme 1). After longer irradiation times only this complex could be recovered from the photolyzed solution. In addition, SnCl₃⁻ was released in the photoreaction.

From the photolyzed solutions of [Os(SnCl₃)₆]⁴⁻ only [Os(SnCl₃)₄(AN)₂]²⁻ was isolated. However, according to the spectral variations this was not the primary photoproduct. Moreover, mixtures of [Os(SnCl₃)₆]⁴⁻ and [Os(SnCl₃)₅Cl]⁴⁻ or [Os(SnCl₃)₅AN]³⁻ did not reproduce these spectral changes either. Since SnCl₃⁻ was already detected at the beginning of the photolysis, [Os(SnCl₃)₄Cl(AN)]³⁻ might have been formed as the primary photoproduct which thermally or photochemically underwent a substitution with the formation of [Os(SnCl₃)₄(AN)₂]²⁻ as the final product.

The photolysis of [Os(SnCl₃)₅Cl]⁴⁻ in CH₃CN afforded only [Os(SnCl₃)₄(AN)₂]²⁻ as isolable material. The spectral variations which were observed at the beginning of the photolysis ($\lambda_{irr} = 405$ nm) could not be simulated by mixtures of [Os(SnCl₃)₅Cl]⁴⁻ with [Os(SnCl₃)₅AN]³⁻ or [Os(SnCl₃)₄(AN)₂]²⁻. Again, it is assumed that [Os(SnCl₃)₄Cl(AN)]³⁻ was formed as the primary photoproduct because the emission of free SnCl₃⁻ was seen after short irradiation times. This corresponds to step c (Scheme 1) of the ruthenium complexes.

The photolysis of [Os(SnCl₃)₅AN]³⁻ ($\lambda_{irr} = 405$ nm) led to the formation of [Os(SnCl₃)₄(AN)₂]²⁻ as both
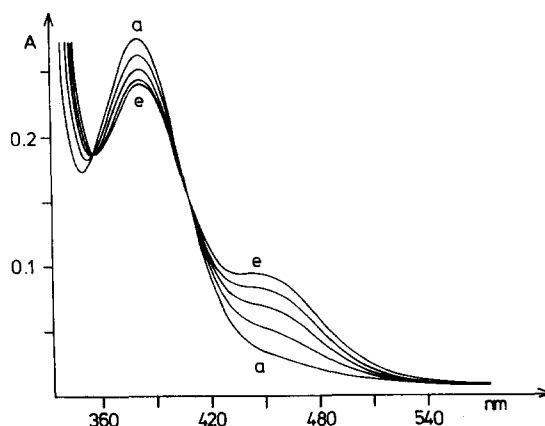


Fig. 3. Spectral changes during the photolysis of $1.0 \times 10^{-4}$ M (NEt₄)₃[Ru(SnCl₃)₅AN] in acetonitrile at 0 (a) and 70 (e) s irradiation time with $\lambda_{irr} = 405$ nm, 1 cm cell.

primary and final product (in analogy to step e, Scheme 1).

## 4. Discussion

### 4.1. Electronic spectra

Generally, trichlorostannyl complexes of transition metals are characterized by striking colors [5] which are caused by strong absorptions in the visible (and UV) region. These absorptions have been used for the colorimetric and spectrophotometric determination of various transition metals, particularly those of the platinum group [5]. According to the results of the present and a previous study on Pt(II) and Rh(III) trichlorostannyl complexes [16], the spectral pattern of all complexes seems to be rather similar irrespective of the metal, its oxidation state, coordination number, and the presence of additional ligands. A conclusive interpretation of these spectra is not yet available and may be achieved only on the basis of an appropriate theoretical calculation. Nevertheless, an attempt is made to provide a tentative explanation taking into account the following considerations.

For the sake of simplicity possible assignments are discussed only for the longest wavelength absorption (A band) which appears for all complexes at approximately 460 nm with an extinction coefficient of roughly $10^3$. The assignment of this band to a regular ligand field (LF) [17] transition does not seem to be appropriate [12,17] in view of its constant energy and relatively high intensity. As an alternative, the A band may be assigned to a metal-to-ligand charge transfer (MLCT) transition which occurs for Ru(II) and Os(II) complexes with suitable ligands at low energies [8,17]. However, MLCT bands should hardly occur at the same wavelength for both metals. Moreover, in the case of the redox-inert $Rh^{3+}$ the assignment of the A band [16] to an MLCT transition can certainly be ruled out.

In view of the similarity of the absorption spectra of quite different trichlorostannyl complexes we propose that the characteristic absorptions have considerable intraligand (IL) character. At this point it is appropriate to discuss the electronic structure of the $SnCl_3^-$ ligand. The interaction of $SnCl_3^-$ with a transition metal can be explained by a simplified MO scheme (Fig. 4) which is based on theoretical considerations advanced by Albright et al. [18]. The overlap of the $2a_1$ lone pair of $SnCl_3^-$ with suitable d orbitals of a transition metal generates molecular orbitals which are used for M–SnCl₃ σ-bonding. The 2e orbitals of $SnCl_3^-$ which are σ-antibonding with respect to the Sn–Cl interaction are available for π-overlap with suitable d orbitals of the transition metal. According to this picture $SnCl_3^-$ is a π-acceptor ligand in analogy to phosphines $PR_3$ [19].
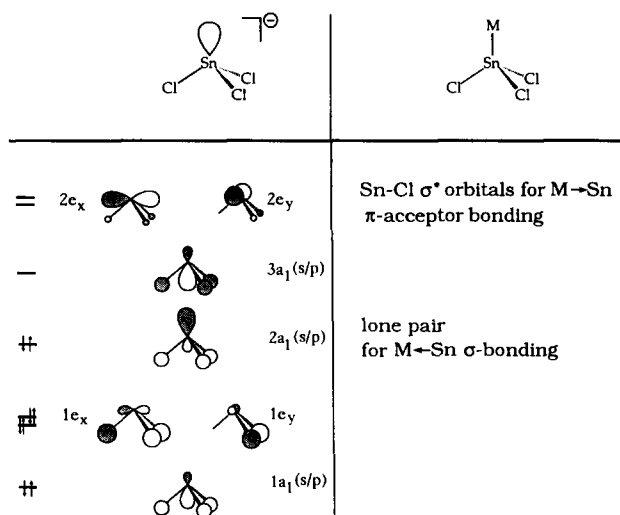


Fig. 4. Qualitative MO diagram of $SnCl_3^-$ ($C_{3v}$ symmetry, π orbitals of Cl are omitted) and schematic representation of the interaction of $SnCl_3^-$ with a transition metal.



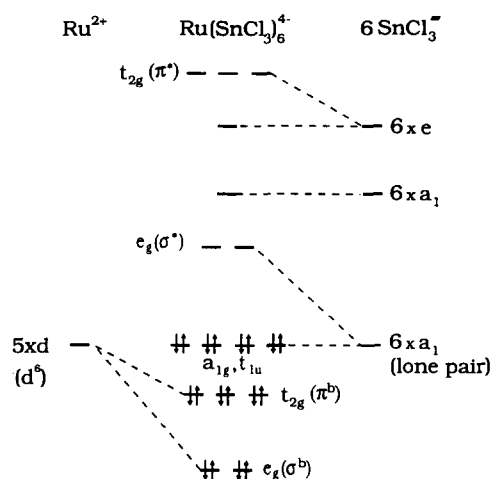Fig. 5. Simplified MO scheme of $[Ru(SnCl_3)_6]^{4-}$ ($O_h$ symmetry).

While the extent of M–SnCl₃ π-bonding is not quite clear the M–SnCl₃ σ-bands are very strong and covalent as indicated by Mössbauer spectroscopy [7]. The lone pair of $SnCl_3^-$ and the d orbitals of Ru(II) and Os(II) are apparently close in energy.

A simplified MO scheme of an octahedral $d^6$ complex $[M(SnCl_3)_6]^{n-}$ provides a qualitative picture of its electronic structure with special reference to the frontier orbitals (Fig. 5). The s and p valence orbitals of the central metal are omitted since their interaction with the ligand orbitals is not expected to affect the ordering of the frontier orbitals. For the same reason the Sn–Cl σ-bonding orbitals are also neglected. For a low-spin $d^6$ complex the lowest energy, parity-allowed transition ($t_{1u} \rightarrow e_g$) is of the ligand-to-metal charge transfer (LMCT) type in the classical sense. Since, however, the $e_g$ σ*-orbitals of $[M(SnCl_3)_6]^{n-}$ have a much larger ligand contribution compared to other ligands with

more stable $\sigma$-orbitals the $t_{1u} \rightarrow e_g$ transition can be considered to be of the IL type with some LMCT character. According to this description the longest wavelength absorption (A band) of $[Ru(SnCl_3)_6]^{4-}$ and $[Os(SnCl_3)_6]^{4-}$ is assigned to this $t_{1u} \rightarrow e_g$ transition. A similar IL/LMCT transition should be also responsible for the appearance of A bands in the absorption spectra of the heteroleptic trichlorostannyl complexes.

The luminescence of the trichlorostannyl complexes (Fig. 1, Table 1) is assumed to originate from the lowest excited triplet states in agreement with the general emission behavior of coordination compounds with singlet ground states [20,21].

### 4.2. Photochemistry

Generally, the trichlorostannyl complexes of Ru(II) and Os(II) undergo a photosubstitution of the $SnCl_3^-$ ligand in the primary photolysis. The photofragmentation of $[Ru(SnCl_3)_6]^{4-}$ may be a related process. The dissociation of an Ru–SnCl$_3$ bond could lead to a linkage isomerization with the intermediate generation of $[Ru(SnCl_3)_5(ClSnCl_2)]^{4-}$ which finally releases $SnCl_2$ and forms $[Ru(SnCl_3)_5Cl]^{4-}$ as the stable photoproduct. In this context it is quite interesting that a silver trichlorostannyl complex exists as such a linkage isomer even in the ground state [22]. Of course alternative reaction steps are feasible at various points of Scheme 1. In particular, Pannell-type $\alpha$-eliminations [4c–f] $\{M–SnCl_3 \rightarrow MCl(SnCl_2)\}$ may lead to the generation of intermediates which undergo an extrusion of $SnCl_2$.

Usually, photosubstitutions of coordination compounds are initiated by LF excitation, but also excited states of different origin [20,21,23] including IL states are known to induce ligand substitutions. According to Fig. 5 the lowest energy transition $t_{1u} \rightarrow e_g$ leads to an IL/LMCT state which simply might be dissociative because this excitation is associated with the population of an M–SnCl$_3$ $\sigma$-antibonding orbital. The dissociative nature of an IL sp excited state could be also related to the excited state properties of $SnCl_3^-$ [9,10]. Since $SnCl_3^-$ becomes planar upon sp excitation it may be released from the complex due to steric hindrance or M–Sn bond weakening. This process may also facilitate the linkage isomerization which could precede the photofragmentation of $[Ru(SnCl_3)_6]^{4-}$.

### Acknowledgements

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