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Electronic Spectra and Photochemistry of Trichlorostannyl Complexes of Rhodium(III) and Platinum(II)

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ABSTRACT

The absorption spectra of $[Rh(SnCl_3)_4Cl_2]^{3-}$ and $[Pt(SnCl_3)_5]^{3-}$ are characterized by a similar band pattern. It is suggested that the absorption spectra are dominated by bands which are assigned to intraligand transitions. While solid $(NBu_4)_3[Pt(SnCl_3)_5]$ shows a low-temperature emission the rhodium complex is not luminescent. Both complex anions are light sensitive in acetonitrile solution. They undergo an efficient photosubstitution of the trichlorostannyl ligand.

INTRODUCTION

The photochemistry and photophysics of transition metal cluster compounds have been investigated extensively for many years [1-5]. Recently, we extended these studies to cluster complexes of the main group metals [5]. As a combination of both subjects we describe here some observations on the electronic spectra and photochemistry of heteronuclear clusters which are composed of main group and transition metals. This work deals with compounds of the type $M(SnCl_3)_xL_y^{n-}$ with M = transition metal. While in a classical picture the $SnCl_3^-$ anion may be simply regarded as a ligand an alternative description of these compounds as heteronuclear clusters implies a stronger interaction of the Sn^{2+} ions as cluster constituents. Although both approaches should ultimately yield the same results the latter, rather unconventional view may give some new insights. It is based on our previous studies of the electronic spectra of cluster complexes of s^2 metal ions such as $[Sn_6O_4(OCH_3)_4]$ [5,6]. In these compounds the metal-metal interaction is an important feature. The incorporation of a transition metal ion into such a main group metal cluster may then be viewed as a perturbation of the main group metal cluster. Suitable candidates for such studies are trichlorostannyl complexes of transition metals [7-9]. Recently, we reported first observations on the photochemistry and photophysics of $[Ru(SnCl_3)_6]^{4-}$ [10]. Now we describe some observations on the electronic spectra and light sensitivity of Rh(III) and Pt(II) complexes containing $SnCl_3^-$ ligands.

EXPERIMENTAL

The compounds $(NEt_4)_3[Rh(SnCl_3)_4Cl_2]$ [11] and $(NBu_4)_3[Pt(SnCl_3)_5]$ [12] were prepared according to published procedures. Absorption spectra were measured in solution at room temperature on a Shimadzu UV-2100 absorption spectrometer. Emission and

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excitation spectra of the compounds in the solid state, in solution or in ethanol glasses (77 K) were obtained on a Hitachi 850 spectrofluorimeter equipped with a Hamamatsu R 928 photomultiplier. The photolysis procedures have been described elsewhere [13]. All solutions were saturated with argon.

RESULTS

The complex $[Rh(SnCl_3)_4Cl_2]^{3-}$ was originally assumed to be a binuclear anion [14] but this conclusion was later corrected [11]. By elemental analysis we could confirm the corrected composition: $(NEt_4)_3[Rh(SnCl_3)_4Cl_2]$, calculated: C 19,68; H 4,13; N 2,87 %, found: C 19,15; H 4,01; N 2,87 %. The absorption spectrum of $[Rh(SnCl_3)_4Cl_2]^{3-}$ in acetonitrile (Fig. 1) displays bands at $\lambda_{max} = 380$ ($\varepsilon = 25700$ M^{-1} cm^{-1}), 291 (16100), and 227 nm (31900).

The complex did not show any emission at room temperature or at 77 K. Solutions of $[Rh(SnCl_3)_4Cl_2]^{3-}$ in acetonitrile were light sensitive. The photolysis of the complex was accompanied by spectral changes (Fig. 1) which include clear isosbestic points at 321, 258, 253 and 209 nm. The occurence of new spectral features at $\lambda_{max} = 216$, 226 and 236 nm indicated the formation of $SnCl^{3-}$ [15]. In addition, the irradiation led to the appearance of a green luminescence at $\lambda_{max} = 510$ nm which is diagnostic for the presence of free $SnCl^{3-}$ [15]. The quantum yield for the disappearance of $[Rh(SnCl_3)_4Cl_2]^{2-}$ was estimated to be roughly $\phi = 0.18$ at $\lambda_{irr} = 405$ nm.

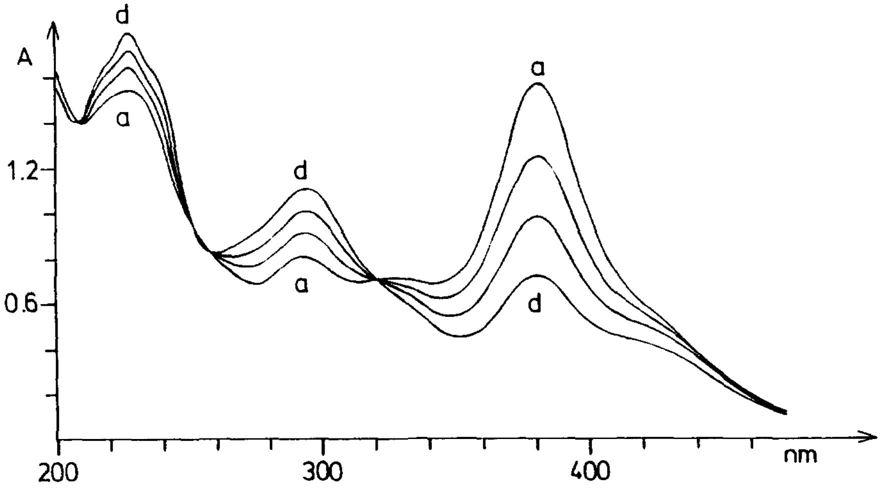

Fig. 1. Spectral changes during the photolysis of 6.11 x 10^{-5} M $(Et_4N)_3[Rh(SnCl_3)_4Cl_2]$ in CH_3CN at (a) 0, and (d) 2 min irradiation time, with $\lambda_{irr} = 405$ nm and a 1 cm cell.

The absorption spectrum of $[Pt(SnCl_3)_5]^{3-}$ in acetonitrile (Fig. 2) shows bands at λ = 480 (sh, 2800), 408 (6000), 312 (26700), 274 (sh, 31000), 258 (34000), and 228 nm (56700).

While at room temperature the complex was not emissive a red luminescence at λ_{max} = 815 nm was observed for the solid salt $(NBu_4)_3[Pt(SnCl_3)_5]$ at 77 K (Fig. 2) [16]. The excitation spectrum matched the absorption spectrum rather well.

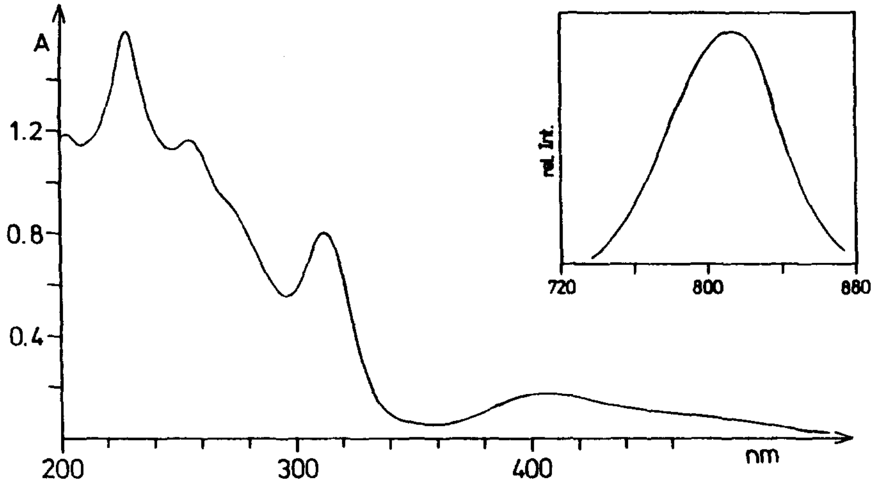

Fig. 2. Electronic absorption and emission (inset) spectra of $(Bu_4N)_3[Pt(SnCl_3)_5]$. Absorption: 2.45 x 10^{-5} M in CH_3CN at room temperature; 1 cm cell. Emission: solid salt at 77 K; λ_{exc} = 400 nm, intensity in arbitrary units.

Solutions of $Pt(SnCl_3)_5]^{3-}$ in acetonitrile were thermally not completely stable. Upon standing a slow decomposition took place. The irradiation of $[Pt(SnCl_3)_5]^{3-}$ in acetonitrile led to an efficient photolysis as indicated by the accompanying spectral variations (Fig. 3). The appearance of a sharp isosbestic point at 221 nm provides evidence for a clean photoreaction. Again, the photolysis led to a liberation of $SnCl^{3-}$ which was identified by its absorption and emission spectrum (see above). $[Pt(SnCl_3)_5]^{3-}$ disappeared with a quantum yield of approximately ϕ = 0.006 at λ_{irr} = 405 nm and 0.7 at 254 nm.

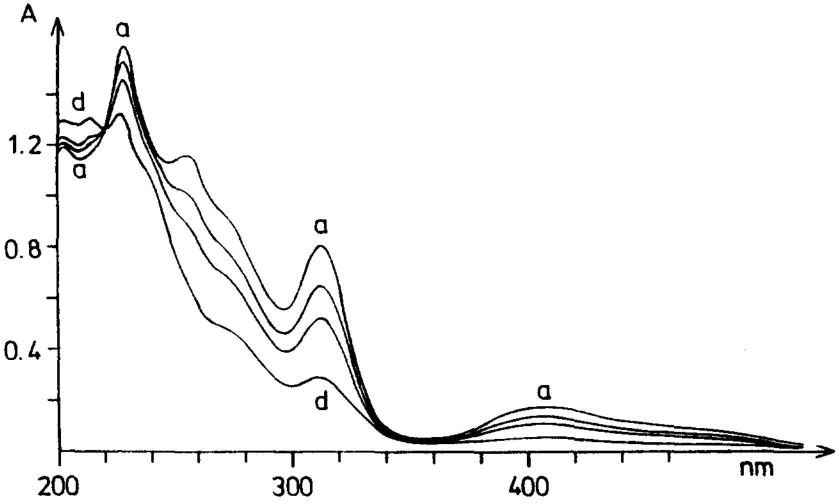

Fig. 3. Spectral changes during the photolysis of 2.82 x 10 $^{-5}$ M $(Bu_4N)_3[Pt(SnCl_3)_5]$ in CH_3CN under argon at (a) O, and (d) 8 min irradiation time, with λ_{irr} = 405 nm;1 cm cell.

DISCUSSION

Trichlorostannyl complexes of transition metals are characterized by striking colors [2]. They are caused by intense absorption bands which are used for the spectrophotometric determination of various transition metals [7]. Moreover, the spectra of $[Rh(SnCl_3)_4Cl_2]^{3-}$ (Fig. 1) and $[Pt(SnCl_3)_5]^{3-}$ (Fig. 2) display a similar pattern with four characteristic bands near 450 nm (sh), 400 nm, 300 nm and 230 nm although both complexes are quite different with regard to their composition, coordination number and electron configuration of the central metal. Accordingly, the absorption spectra seem to be dominated by the presence of the $SnCl^{3-}$ ligands. We suggest that these typical bands including the longest-wavelength absorptions are assigned to transitions which should have considerable intraligand (IL) character.

This seems to be surprising since free $SnCl^{3-}$ absorbs at much shorter wavelength [15]. However, the metal-centered sp transitions may be shifted to lower energies when several Sn^{2+} ions are assembled to clusters, which provide a sufficient metal-metal interaction [6]. The tin-tin interaction could be facilitated by the incorporation of a transition metal ion into the tin cluster. According to these considerations the four typical absorption bands of

$[Rh(SnCl_3)_4Cl_2]^{3-}$ and $[Pt(SnCl_3)_5]^{3-}$ may be assigned to IL sp transitions of the $(SnCl_3^-)_n$ cluster fragment.

While $[Rh(SnCl_3)_4Cl_2]^{3-}$ was not observed to emit $[Pt(SnCl_3)_5]^{3-}$ as the solid tetrabutylammonium salt shows a luminescence at 77 K [16]. It is assumed that this emission originates from the lowest IL triplet of the $(SnCl_3^-)_5$ cluster moiety.

Both complexes $[Rh(SnCl_3)_4Cl_2]^{3-}$ and $[Pt(SnCl_3)_5]^{3-}$, are rather light sensitive in solution. The spectral changes which accompany the photolysis indicate clean reactions. We were not yet able to identify the products which contain the transition metals, but $SnCl_3^-$ was definitely related in the photoreaction. Accordingly, both complexes underwent apparently a simple photosubstitution of the trichlorostannyl ligand.

Generally, photosubstitutions are related to the reactivity of ligand field (LF) excited states. Presently, we cannot exclude the possibility that the photolysis of $[Rh(SnCl_3)_4Cl_2]^{3-}$ and $[Pt(SnCl_3)_5]^{3-}$ is indeed induced by LF excitation. However, other excited states including IL states are also known to initiate photosubstitutions [17]. Our tentative band assignment may indicate that the reactive excited states of these trichlorostannyl complexes are of the IL type. The metal-centered sp excitation of free $SnCl_3^-$ leads to a structural rearrangement from a trigonal-pyramidal to a trigonal-planar geometry [15,18]. In the case of the trichlorostannyl complexes the IL sp excitation could then lead to a photosubstitution since the planar ligand structures should facilitate a dissociation of the $Rh\text{-}SnCl_3$ or $Pt\text{-}SnCl_3$ bond.

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