Photoluminescence of Tellurium(IV) Chloride Complexes in Solution

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We wish to describe and discuss our observations on the photoluminescence of $TeCl_5^-$ and $TeCl_6^{2-}$ in solution. While low-temperature photoemissions of $TeCl_6^{2-}$ and related Te(IV) complexes in the solid state have been observed before,[1-3] here we report for the first time luminescence from a simple compound of an element of group 16 under ambient conditions. Moreover, our results are of general importance with regard to the nature of excited states of s^2 complexes. In recent years we observed the solution luminescence of complexes of the type MCl_3^{n-}, MCl_4^{n-}, and MCl_6^{n-} with the s^2 metal ions Ge^{2+}, Sn^{2+}, Pb^{2+}, Sb^{3+}, and Bi^{3+}.[4,5] We developed a general concept in order to characterize the emitting sp excited states. The luminescence of $TeCl_5^-$ is the first example of an emission from a pentacoordinate s^2 complex. Our findings serve to check the validity of our previous assumptions.

The absorption spectrum of $TeCl_6^{2-}$ in acetonitrile (Figure 1) agrees with that reported previously.[6,7] The long-wavelength absorptions of this octahedral complex are assigned to sp transitions: A band ($^1S_0 \rightarrow {}^3P_1$ or $^1A_{1g} \rightarrow {}^3T_{1u}$ in O_h symmetry), λ_{max} = 407 nm (sh), ϵ = 800 M^{-1} cm^{-1}, and 385 nm, ϵ = 1500; B band ($^1S_0 \rightarrow {}^3P_2$ or $^1A_{1g} \rightarrow {}^3E_u$, $^3T_{2u}$), λ_{max} = 320 nm, ϵ = 2500, C band ($^1S_0 \rightarrow {}^1P_1$ or $^1A_{1g} \rightarrow {}^1T_{1u}$), λ_{max} = 298 nm, ϵ = 7100, 287 nm, ϵ = 8200, and 273 nm, ϵ = 7300. Upon dilution $TeCl_6^{2-}$ was converted to $TeCl_5^-$,[6] which exists as a discrete ion with a square-pyramidal structure even in the solid state[8,9] in accord with the VSEPR model.[10] The A band of $TeCl_5^-$ (λ_{max} = 291 nm, ϵ = 1600) appears at much shorter wavelength compared to that of $TeCl_6^{2-}$.[6] Addition of chloride to this dilute solution led to a complete recovery of the spectrum of $TeCl_6^{2-}$ (Figure 1). The isosbestic points which occur during the spectral variations indicate the presence of only two species, $TeCl_5^-$ and $TeCl_6^{2-}$. The equilibrium constant ($TeCl_5^- + Cl^- \rightleftarrows TeCl_6^{2-}$) was determined to be $K = 1.5 \times 10^2$ M^{-1}.

$TeCl_6^{2-}$ in CH_3CN shows a red emission at λ_{max} = 603 nm with $\phi = 1 \times 10^{-4}$ at λ_{exc} = 388 nm (Figure 2). The excitation spectrum matched the absorption spectrum rather well. The spectral features of $TeCl_6^{2-}$ in solution (λ_{max} of the $^1S_0 \leftrightarrow {}^3P_1$ transition in absorption and emission, Stokes shift ΔE = 9400 cm^{-1}) are quite similar to those of $TeCl_6^{2-}$ in the solid state (emission: λ_{max} = 632 nm at 150 K; ΔE = 10 100 cm^{-1}).[2] In analogy to other s^2 complexes and in accord with results on $TeCl_6^{2-}$ in the solid state, the emission of $TeCl_6^{2-}$ in solution is assumed to originate from the metal-centered sp excited state $^3P_1$ ($^3T_{1u}$ in O_h symmetry) which undergoes a moderate excited-state distortion.

$TeCl_5^-$ in CH_3CN shows a green luminescence at λ_{max} = 538 nm with $\phi = 8 \times 10^{-3}$ at λ_{exc} = 280 nm (Figure 2). The excitation spectrum agreed with the absorption spectrum. The emitting excited state is certainly again the sp triplet $^3P_1$. However, the

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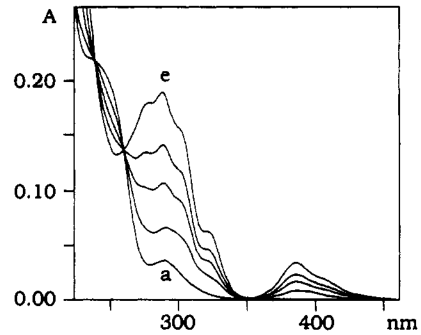

Figure 1. Electronic absorption spectra of $[NBu_4][TeCl_5]$ in acetonitrile at room temperature (1-cm cell). Absorption: 2.18×10^{-5} M without NBu_4Cl (a) and in the presence of 7.08×10^{-4}, 1.39×10^{-3}, 2.08×10^{-3}, and 4.14×10^{-3} M (e) NBu_4Cl.

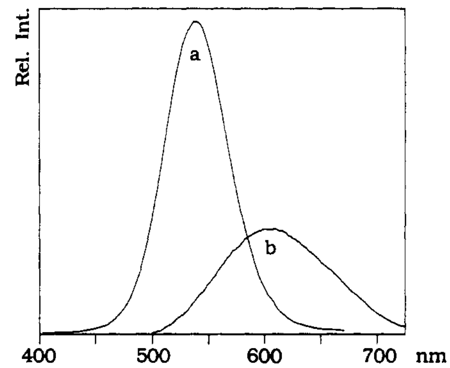

Figure 2. Emission spectra of $[NBu_4][TeCl_5]$ ($c = 2.18 \times 10^{-5}$ M, λ_{exc} = 280 nm (a)) and $[NBu_4]_2[TeCl_6]$ ($c = 1.58 \times 10^{-4}$ M, λ_{exc} = 400 nm (b)) in acetonitrile at room temperature.

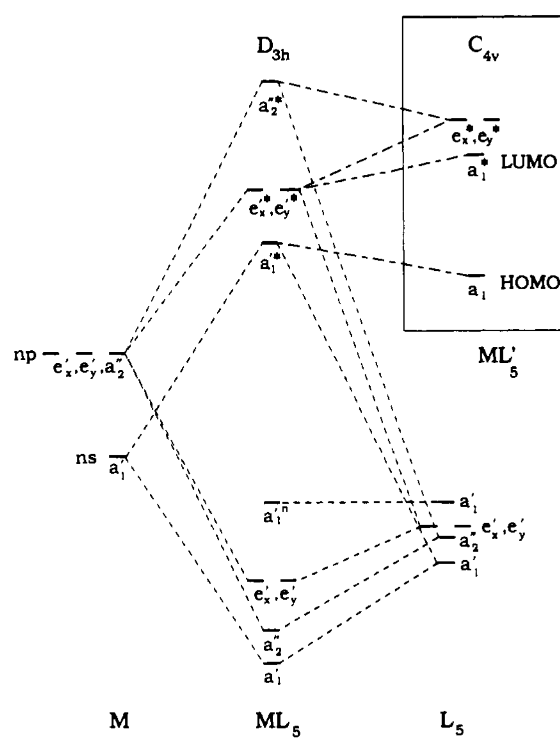

Figure 3. Qualitative MO scheme (Walsh diagram) of a trigonal-bipyramidal complex (D_{3h}) and its distortion to a square-pyramidal structure (C_{4v}). The π-orbitals of the ligands are omitted.

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Stokes shift of the $^1S_0 \leftrightarrow {}^3P_1$ transition (ΔE = 15 700 cm^{-1}) is much larger than that of $TeCl_6^{2-}$. Accordingly, $TeCl_5^-$ undergoes a much larger structural rearrangement in the excited state compared to $TeCl_6^{2-}$.

$TeCl_5^-$ might be expected to have a trigonal-bipyramidal ground state structure (D_{3h}). However, the s^2 electron pair would then occupy a strongly antibonding $a_1'^*$ orbital (Figure 3). As a consequence, a distortion to a square-pyramidal structure (C_{4v}) takes place, because it is associated with an sp hybridization which lowers the energy of $TeCl_5^-$ by configuration interaction of the a_1 orbitals (Figure 3).[11] The HOMO is thus stabilized and becomes stereochemically active as a lone pair in agreement with the VSEPR model.

In the $a_1a_1^*$ sp excited state this stabilization of $TeCl_5^-$ is lost because the a_1^* orbital becomes now the HOMO. We suggest that the complex relaxes then to the stereochemically less demanding trigonal-bipyramidal structure. Such a geometrical change is in accordance with the large Stokes shift observed for $TeCl_5^-$. This explanation is consistent with a general concept which has been developed to characterize the emitting sp excited states of s^2 complexes.[12,13]

The octahedral structure of $TeCl_6^{2-}$ [14] is an exception from the VSEPR rules possibly because there is no space left for a distortion which must provide an open coordination site for the lone pair. In the case of $TeCl_5^-$ the lower coordination number facilitates a distortion in accord with the VSEPR model.

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