Photoluminescence of Tellurium(IV) Chloride Complexes in Solution

Hans Nikol and Arnd Vogler

Institut für Anorganische Chemie, Universität Regensburg, Universitätsstrasse 31, W-8400 Regensburg, Germany

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We wish to describe and discuss our observations on the photoluminescence of TeCl₅⁻ and TeCl₆²⁻ in solution. While low-temperature photoemissions of TeCl₆²⁻ and related Te(IV) complexes in the solid state have been observed before, 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 s² complexes. In recent years we observed the solution luminescence of complexes of the type MCl₅⁻, MCl₆⁻, and MCl₆⁺ with the s² metal ions Ge²⁺, Sn²⁺, Pb²⁺, Sb³⁺, and Bi³⁺. We developed a general concept in order to characterize the emitting sp excited states. The luminescence of TeCl₅⁻ is the first example of an emission from a pentacoordinate s² complex. Our findings serve to check the validity of our previous assumptions.

The absorption spectrum of TeCl₆²⁻ in acetonitrile (Figure 1) agrees with that reported previously. The long-wavelength absorptions of this octahedral complex are assigned to sp transitions: A band (³S₀ → ³P₁ or ³A₁g → ³T₁u in O₅ symmetry), ³max = 407 nm (sh), ε = 800 M⁻¹ cm⁻¹, and 385 nm, ε = 1500; B band (³S₀ → ³P₂ or ³A₁g → ³E₂g, ³T₁u), ³max = 320 nm, ε = 2500; C band (³S₀ → ³P₁ or ³A₁g → ³T₂u), ³max = 298 nm, ε = 7100, 287 nm, ε = 8200, and 273 nm, ε = 7300. Upon dilution TeCl₆²⁻ was converted to TeCl₅⁻, which exists as a discrete ion with a square-pyramidal structure even in the solid state in accord with the VSEPR model. The A band of TeCl₅⁻ (³max = 291 nm, ε = 1600) appears at much shorter wavelength compared to that of TeCl₆²⁻. Addition of chloride to this dilute solution led to a complete recovery of the spectrum of TeCl₆²⁻ (Figure 1). The isosbestic points which occur during the spectral variations indicate the presence of only two species, TeCl₅⁻ and TeCl₆²⁻. The equilibrium constant (TeCl₅⁻ + Cl⁻ = TeCl₆²⁻) was determined to be K = 1.5 × 10² M⁻¹.

TeCl₅⁻ in CH₃CN shows a red emission at ³max = 603 nm with φ = 1 × 10⁻⁴ at ³exc = 388 nm (Figure 2). The excitation spectrum matched the absorption spectrum rather well. The spectral features of TeCl₅⁻ in solution (³max = 150 K; ³E = 10 100 cm⁻¹) are quite similar to those of TeCl₆²⁻ in the solid state (³max = 632 nm at 150 K; ³E = 10 100 cm⁻¹). In analogy to other s² complexes and in accord with results on TeCl₆²⁻ in the solid state, the emission of TeCl₅⁻ in solution is assumed to originate from the metal-centered sp excited state ³P₁ (³T₁u, in O₅ symmetry) which undergoes a moderate excited-state distortion.

TeCl₅⁻ in CH₃CN shows a green luminescence at ³max = 538 nm with φ = 8 × 10⁻³ at ³exc = 280 nm (Figure 2). The excitation spectrum agreed with the absorption spectrum. The emitting excited state is certainly again the sp triplet ³P₁. However, the

(c) Gillespie, R. J.; Hargittai, I. The VSEPR Model of Molecular Geometry; Allyn and Bacon: Boston, MA, 1991.

Figure 1. Electronic absorption spectra of [NBu₄][TeCl₅] in acetonitrile at room temperature (1-cm cell). Absorption: 2.18 × 10⁻⁵ M without NBu₄Cl (a) and in the presence of 7.08 × 10⁻⁵ M, 1.39 × 10⁻⁵ M, 2.08 × 10⁻⁵ M, and 4.14 × 10⁻⁵ M (e) NBu₄Cl.

Figure 2. Emission spectra of [NBu₄][TeCl₅] (c = 2.18 × 10⁻⁵ M, ³exc = 280 nm (a)) and [NBu₄][TeCl₆] (c = 1.58 × 10⁻⁴ M, ³exc = 400 nm (b)) in acetonitrile at room temperature.

Figure 3. Qualitative MO scheme (Walsh diagram) of a trigonal-bipyramidal complex (D₅h) and its distortion to a square-pyramidal structure (C₅h). The σ-orbitals of the ligands are omitted.
Stokes shift of the $^1S_0 \leftrightarrow ^3P_1$ transition ($\Delta E = 15700$ cm$^{-1}$) is much larger than that of TeCl$_6^{2-}$. Accordingly, TeCl$_5^{2-}$ undergoes a much larger structural rearrangement in the excited state compared to TeCl$_6^{2-}$.

TeCl$_5^{2-}$ 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$_5^{2-}$ 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$_5^{2-}$ 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$_5^{2-}$. 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$_6^{2-}$ 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$_5^{2-}$ the lower coordination number facilitates a distortion in accord with the VSEPR model.

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$^{14}$ A slight dynamic ground-state distortion seems to occur in the solid state: Abriel, W. *Z. Naturforsch.* 1987, 42b, 1273.