

## Photoluminescence of Tellurium(IV) Chloride Complexes in Solution

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We wish to describe and discuss our observations on the photoluminescence of  $\text{TeCl}_5^-$  and  $\text{TeCl}_6^{2-}$  in solution. While low-temperature photoemissions of  $\text{TeCl}_6^{2-}$  and related Te(IV) complexes in the solid state have been observed before,<sup>1-3</sup> 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  $\text{MCl}_3^{n-}$ ,  $\text{MCl}_4^{n-}$ , and  $\text{MCl}_6^{n-}$  with the  $s^2$  metal ions  $\text{Ge}^{2+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Sb}^{3+}$ , and  $\text{Bi}^{3+}$ .<sup>4,5</sup> We developed a general concept in order to characterize the emitting sp excited states. The luminescence of  $\text{TeCl}_5^-$  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  $\text{TeCl}_6^{2-}$  in acetonitrile (Figure 1) agrees with that reported previously.<sup>6,7</sup> The long-wavelength absorptions of this octahedral complex are assigned to sp transitions: A band ( $^1\text{S}_0 \rightarrow ^3\text{P}_1$  or  $^1\text{A}_{1g} \rightarrow ^3\text{T}_{1u}$  in  $O_h$  symmetry),  $\lambda_{\text{max}} = 407$  nm (sh),  $\epsilon = 800 \text{ M}^{-1} \text{ cm}^{-1}$ , and 385 nm,  $\epsilon = 1500$ ; B band ( $^1\text{S}_0 \rightarrow ^3\text{P}_2$  or  $^1\text{A}_{1g} \rightarrow ^3\text{E}_u, ^3\text{T}_{2u}$ ),  $\lambda_{\text{max}} = 320$  nm,  $\epsilon = 2500$ ; C band ( $^1\text{S}_0 \rightarrow ^1\text{P}_1$  or  $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1u}$ ),  $\lambda_{\text{max}} = 298$  nm,  $\epsilon = 7100$ , 287 nm,  $\epsilon = 8200$ , and 273 nm,  $\epsilon = 7300$ . Upon dilution  $\text{TeCl}_6^{2-}$  was converted to  $\text{TeCl}_5^-$ ,<sup>6</sup> which exists as a discrete ion with a square-pyramidal structure even in the solid state<sup>8,9</sup> in accord with the VSEPR model.<sup>10</sup> The A band of  $\text{TeCl}_5^-$  ( $\lambda_{\text{max}} = 291$  nm,  $\epsilon = 1600$ ) appears at much shorter wavelength compared to that of  $\text{TeCl}_6^{2-}$ .<sup>6</sup> Addition of chloride to this dilute solution led to a complete recovery of the spectrum of  $\text{TeCl}_6^{2-}$  (Figure 1). The isosbestic points which occur during the spectral variations indicate the presence of only two species,  $\text{TeCl}_5^-$  and  $\text{TeCl}_6^{2-}$ . The equilibrium constant ( $\text{TeCl}_5^- + \text{Cl}^- \rightleftharpoons \text{TeCl}_6^{2-}$ ) was determined to be  $K = 1.5 \times 10^2 \text{ M}^{-1}$ .

$\text{TeCl}_6^{2-}$  in  $\text{CH}_3\text{CN}$  shows a red emission at  $\lambda_{\text{max}} = 603$  nm with  $\phi = 1 \times 10^{-4}$  at  $\lambda_{\text{exc}} = 388$  nm (Figure 2). The excitation spectrum matched the absorption spectrum rather well. The spectral features of  $\text{TeCl}_6^{2-}$  in solution ( $\lambda_{\text{max}}$  of the  $^1\text{S}_0 \leftrightarrow ^3\text{P}_1$  transition in absorption and emission, Stokes shift  $\Delta E = 9400 \text{ cm}^{-1}$ ) are quite similar to those of  $\text{TeCl}_6^{2-}$  in the solid state (emission:  $\lambda_{\text{max}} = 632$  nm at 150 K;  $\Delta E = 10\,100 \text{ cm}^{-1}$ ).<sup>2</sup> In analogy to other  $s^2$  complexes and in accord with results on  $\text{TeCl}_6^{2-}$  in the solid state, the emission of  $\text{TeCl}_6^{2-}$  in solution is assumed to originate from the metal-centered sp excited state  $^3\text{P}_1$  ( $^3\text{T}_{1u}$  in  $O_h$  symmetry) which undergoes a moderate excited-state distortion.

$\text{TeCl}_5^-$  in  $\text{CH}_3\text{CN}$  shows a green luminescence at  $\lambda_{\text{max}} = 538$  nm with  $\phi = 8 \times 10^{-3}$  at  $\lambda_{\text{exc}} = 280$  nm (Figure 2). The excitation spectrum agreed with the absorption spectrum. The emitting excited state is certainly again the sp triplet  $^3\text{P}_1$ . However, the

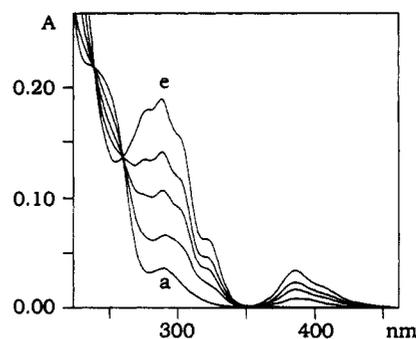


Figure 1. Electronic absorption spectra of  $[\text{NBu}_4][\text{TeCl}_5]$  in acetonitrile at room temperature (1-cm cell). Absorption:  $2.18 \times 10^{-5} \text{ M}$  without  $\text{NBu}_4\text{Cl}$  (a) and in the presence of  $7.08 \times 10^{-4}$ ,  $1.39 \times 10^{-3}$ ,  $2.08 \times 10^{-3}$ , and  $4.14 \times 10^{-3} \text{ M}$  (e)  $\text{NBu}_4\text{Cl}$ .

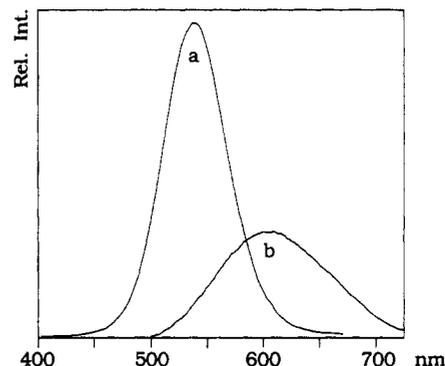


Figure 2. Emission spectra of  $[\text{NBu}_4][\text{TeCl}_5]$  ( $c = 2.18 \times 10^{-5} \text{ M}$ ,  $\lambda_{\text{exc}} = 280$  nm (a)) and  $[\text{NBu}_4]_2[\text{TeCl}_6]$  ( $c = 1.58 \times 10^{-4} \text{ M}$ ,  $\lambda_{\text{exc}} = 400$  nm (b)) in acetonitrile at room temperature.

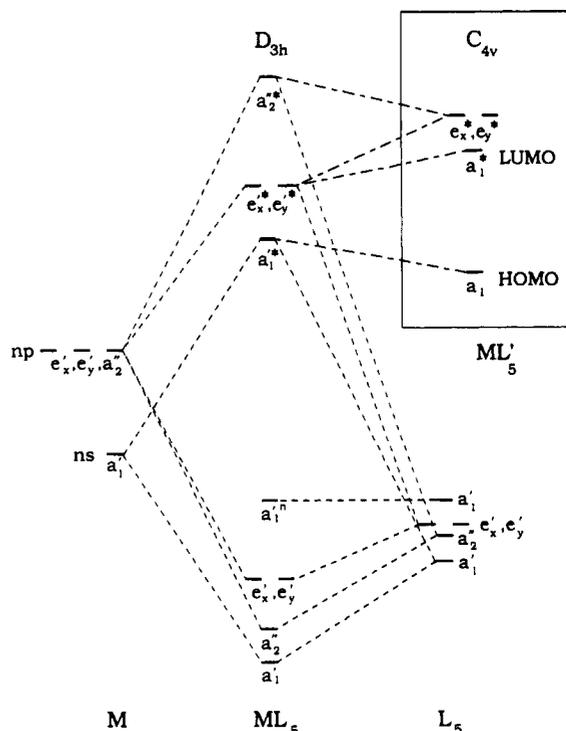


Figure 3. Qualitative MO scheme (Walsh diagram) of a trigonal-bipyramidal complex ( $D_{3h}$ ) and its distortion to a square-pyramidal structure ( $C_{4v}$ ). The  $\pi$ -orbitals of the ligands are omitted.

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Stokes shift of the  $^1S_0 \leftrightarrow ^3P_1$  transition ( $\Delta E = 15\,700\text{ cm}^{-1}$ ) is much larger than that of  $\text{TeCl}_6^{2-}$ . Accordingly,  $\text{TeCl}_5^-$  undergoes a much larger structural rearrangement in the excited state compared to  $\text{TeCl}_6^{2-}$ .

$\text{TeCl}_5^-$  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  $\text{TeCl}_5^-$  by configuration interaction of the  $a_1$  orbitals (Figure 3).<sup>11</sup> 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  $\text{TeCl}_5^-$  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  $\text{TeCl}_5^-$ . This explanation is consistent with a general concept which has been developed to characterize the emitting  $sp$  excited states of  $s^2$  complexes.<sup>12,13</sup>

The octahedral structure of  $\text{TeCl}_6^{2-}$ <sup>14</sup> 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  $\text{TeCl}_5^-$  the lower coordination number facilitates a distortion in accord with the VSEPR model.

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