

Novel Mixed Hexahalotellurates(IV)

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The optical spectra of heavy metal ions with s^2 electron configuration doped in alkali halide crystals have been widely investigated in the past two decades. Information about analogous molecular systems like Sb(III) or Te(IV) complexes, on the other hand, is very rare. Electronic spectra of low symmetry hexacoordinated tellurium(IV) complexes are not reported to date, although several mixed halide compounds have been known for some time [1, 2]. The present work reports the synthesis of novel tetragonal $\text{TeCl}_5\text{X}^{2-}$ complexes which are obtained by the reaction of TeCl_5^- with alkyl ammonium halides. The infrared transition and electronic absorption properties of these complexes are discussed.

Experimental

Preparation

The tetraethylammonium salt of TeCl_5^- was obtained from TeCl_4 and $(\text{C}_2\text{H}_5)_4\text{NCl}$ as previously described [3]. For preparing $\text{TeCl}_5\text{Br}^{2-}$ to a suspension of $(\text{Et}_4\text{N})[\text{TeCl}_5]$ in dichloromethane a stoichiometric amount of Et_4NBr was added. The resulting mixture was refluxed for 12 h, cooled to room temperature, and filtered. The yellow precipitate was recrystallized from dichloromethane and dried *in vacuo*. All preparations were performed under strictly anhydrous conditions.

The $\text{TeCl}_5\text{I}^{2-}$ complex was prepared in an analogous manner using tetraethylammonium iodide as starting material.

By this procedure other alkylammonium salts of both tellurium complexes were synthesized likewise, e.g. by the use of triethyl- and tetrabutylammonium halides. These compounds will not be described here, for their spectroscopic properties are only negligibly different.

Elemental Analysis

Calc. for $\text{C}_{16}\text{H}_{10}\text{N}_2\text{Cl}_5\text{BrTe}$: C, 29.78; H, 6.25; N, 4.34; Cl, 27.47; Br, 12.38. Found: C, 29.5; H, 6.1; N, 4.5; Cl, 27.4; Br, 12.3%.

Calc. for $\text{C}_{16}\text{H}_{10}\text{N}_2\text{Cl}_5\text{ITe}$: C, 27.76; H, 5.82; N, 4.05; Cl, 25.61; I, 18.30. Found: C, 28.2; H, 5.7; N, 4.0; Cl, 25.4; I, 18.2%.

Physical Measurements

Absorption measurements of CH_2Cl_2 solutions were performed on a Beckman model 25 UV–Vis spectrometer. Far-infrared spectra for polyethylene pellets were recorded using a Beckman FIS 720 interferometer equipped with a specially designed vacuum chamber for low temperature measurements.

Results and Discussion

The tetragonal hexahalogenotellurates(IV) $\text{TeCl}_5\text{Br}^{2-}$ and $\text{TeCl}_5\text{I}^{2-}$, abbr. [Br] and [I], respectively, can be prepared in high yield by the reaction of pentachlorotellurate(IV) salts with various tetraalkyl halides in hot organic solvents. The stability of these compounds against moisture and ligand substitution is comparable with TeCl_6^{2-} in contrast to the reactive TeCl_5^- ion. The synthesis of the analogous monofluoro complex did not succeed by this method which mainly leads to reactions giving TeCl_6^{2-} and metallic tellurium.

Figure 1 shows far-infrared spectra at low temperature which clearly reflect the presence of tetragonal $\text{TeCl}_5\text{X}^{2-}$ anions in both compounds. Only this spectral region must be considered, for all of the metal–halogen stretching and bending vibrations occur below 400 cm^{-1} . Bands due to the tetraethylammonium cation do not interfere with these transitions, except for some lattice modes which may appear in the low frequency part of these spectra. Assuming that the complexes possess regular C_{4v} point symmetry the normal vibrations transform as

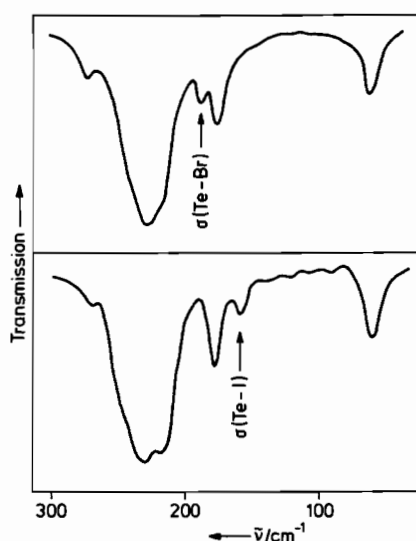


Fig. 1. Far-infrared spectra of $\text{TeCl}_5\text{X}^{2-}$, X = Br, I, as polyethylene pellets at $T = 100\text{ K}$.

$4a_1 + 2b_1 + b_2 + 4e$ with only three modes ($2b_1$ and b_2) being infrared inactive. From the vibrational assignments of the parent TeX_6^{2-} ions [4] the $\sigma(\text{Te}-\text{Cl})$ stretching modes are expected to be observed between 200 and 300 cm^{-1} , whereas $\sigma(\text{Te}-\text{Br})$ and $\sigma(\text{Te}-\text{I})$ should appear at somewhat lower frequencies. The prominent band at 228 cm^{-1} is assigned to the equatorial tellurium chlorine stretching vibration of e -symmetry, which is split by the actual lower symmetry due to either a not strictly tetragonal molecular geometry or the crystalline surrounding. The axial $\text{Te}-\text{X}$ stretching mode (a_1) was found at 187 ([Br]) and 158 ([I]) cm^{-1} . The weak absorption at *ca.* 270 cm^{-1} may be attributed to the axial $\text{Te}-\text{Cl}$ stretching vibration (a_1), for this mode was observed as the highest frequency band in the similar spectra of the corresponding mixed hexahaloosmates(IV) [5].

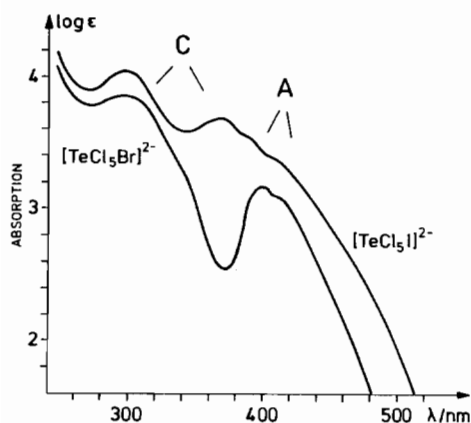


Fig. 2. Electronic absorption spectra of $\text{TeCl}_5\text{X}^{2-}$, $\text{X} = \text{Br}, \text{I}$, measured at room temperature from dichloromethane solutions.

As for the octahedral hexahalotellurium(IV) complexes the bending modes were found to produce relatively weak bands. Comparing these spectra with the normal vibrations of TeCl_6^{2-} [4], the transitions at 178 ([Br]) and 176 ([I]) cm^{-1} are assigned to the equatorial bending deformation $\delta(\text{Cl}-\text{Te}-\text{Cl})$. The medium strong band at *ca.* 70 cm^{-1} is tentatively assigned to a lattice mode, although bending modes of e -symmetry may appear in this spectral region. To provide a more quantitative interpretation of the vibrational structure a normal coordinate analysis, which includes information from Raman measurements, is required.

The electronic absorption spectra of the mixed halide complexes are presented in Fig. 2. The spectrum of [Br], which mainly consists of a dominant

peak at 298 nm with a shoulder at higher wavelength and a doublet structure around 400 nm, shows strong resemblance to the spectrum of the parent TeCl_6^{2-} [6, 7]. The electron configuration of Te^{4+} is $5s^2$ which corresponds to $^1A_{1g}$ ground state (in O_h notation). The first excited configuration is $5s5p$ giving triplet states $^3A_{2u}, ^3T_{1u}, ^3T_{2u}, ^3E_u$ and a singlet state $^1T_{1u}$ in order of increasing energy [8]. Transitions to $^3T_{1u}$ and $^1T_{1u}$ cause the well-known absorption bands A and C, respectively, where the former is made allowed by spin-orbit interaction. Transitions to the other multiplets are electric dipole forbidden.

Also in the case of C_{4v} symmetry the cubic selection rules are unchanged with the exception of $^1A_1 \rightarrow ^3E(^3T_{2u})$ becoming dipole allowed when spin-orbit coupling is operative. However, the main physical effect of symmetry lowering is that the T_{1u} states are both split giving singlet and triplet A_1 and E states. The most intense band at 33 600 cm^{-1} is then assigned to a $^1A_1 \rightarrow ^1E$ corresponding to the $s^2 \rightarrow sp_x, sp_y$ transition (34 700 cm^{-1} in TeCl_6^{2-}). The other spin-allowed transition to 1A_1 , which is derived from $s^2 \rightarrow sp_z$ excitation, is expected at somewhat lower energy and is assigned to the shoulder at 29 500 cm^{-1} . The underlying ordering $p_x, p_y > p_z$ is reasonable considering that bromide and iodide produce lower crystal fields than chloride ligands. In the A band region two well separated transitions are found likewise, which are reasonably assigned to the tetragonal components of $^3T_{1u}$.

The analogous monoiodo complex also shows strong absorption in the region of A-C transitions. Although a drastic broadening of the bands is observed, it seems likely that the maxima are due to the singlet and triplet components of the excited $5s5p$ electron configuration. Larger energy splittings are expected in this case due to the different positions of chloride and iodide ligands in the spectrochemical series. Accordingly, the transitions to the tetragonal components of $^1T_{1u}$ and $^3T_{1u}$ are observed as well separated bands split by *ca.* 6500 and 1700 cm^{-1} , respectively (Fig. 2). The position of the highest $s^2 \rightarrow sp$ transition is almost unchanged in both complexes with regard to the octahedral TeCl_6^{2-} confirming the level ordering as given above. The higher transition probabilities are explained by mixing of the metal localized states with the near-by charge transfer states. The A band intensity relation reflects the influence of spin-orbit coupling which mainly depends on the magnitude of the off-diagonal perturbation matrix element ($\xi/\sqrt{2}$) intermixing $^1T_{1u}$ and $^3T_{1u}$ wave functions [9]. In the case of metal compounds with heavier halogen ligands unusual high values for the coupling parameter ξ may be explained within the framework of LCAO-MO theory by a relativistic nephelauxetic effect [10, 11]. Accordingly, the ordering of the A/C intensity relation was observed as $[\text{I}] > [\text{Br}] > \text{TeCl}_6^{2-}$.

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