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CRYSTAL STRUCTURE DETERMINATION AND VIBRATIONAL SPECTRA OF (t-BuNH$_3$)$_2$[TeBr$_6$] AND COMPARISONS WITH OTHER SOLIDS CONTAINING [TeCl$_6$]$^{2-}$ OR [TeBr$_6$]$^{2-}$ IONS

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Abstract—The structure of (t-BuNH$_3$)$_2$[TeBr$_6$] determined by X-ray crystallography reveals the [TeBr$_6$]$^{2-}$ ion to be trigonally distorted with three long bonds of 2.761, 2.735 and 2.780 Å and three short bonds of 2.609, 2.594 and 2.632 Å. The longer set are involved in hydrogen bonds to the t-BuNH$_3^+$ cation. The symmetry of [TeBr$_6$]$^{2-}$ is close to C_{3v} and this model fits the vibrational spectrum which contains Te—Br stretching frequencies of 148, 163, 180 and 201 cm^{-1} active in both IR and Raman spectra. Solutions of TeCl$_4$ in HCl yield, with t-BuNH$_2$, the double salt (t-BuNH$_3$)$_2$[TeCl$_6$]·4t-BuNH$_3$Cl in which the [TeCl$_6$]$^{2-}$ ion is shown by the vibrational spectrum to have a regular octahedral (O_h) structure exhibiting the frequencies ν_1 287, ν_2 247, ν_3 230, ν_4 158 and ν_5 131 cm^{-1}. The spectra of (dapH$_2$)[TeX$_6$] (dap = 1,3-diaminopropane; X = Cl or Br) are reported and examined in relation to known structures.

Tellurium(IV) attains its highest coordination number of six in the halide complexes [TeX$_6$]$^{2-}$ (X = Cl, Br or I).[1,2] These complexes test the valence shell electron pair repulsion (VSEPR) approach to the explanation of structure[3,4] having seven electron pairs one of which can be regarded as a lone pair. In association with simple cations the [TeX$_6$]$^{2-}$ ions tend to be octahedral, although there are unusual features of the electronic absorption and vibrational spectra which demand special treatment.[5] It is now recognized that the structures of the anions [SeCl$_6$]$^{2-}$, [TeCl$_6$]$^{2-}$, the analogous complexes [SbCl$_6$]$^{3-}$, and the corresponding bromides and iodides of Se(IV), Te(IV) and Sb(III), depend strongly on the counterion. Simple or highly symmetric cations enforce an octahedral structure in the solid state, whereas the same anions partnered by less symmetric cations may deviate from O_h towards lower symmetry.[2,6]

The present note describes the crystal structure and vibrational spectra of (t-BuNH$_3$)$_2$[TeBr$_6$] in which the complex anion shows trigonal distortion, with three long and three short Te—Br bonds, giving near C_{3v} symmetry. Although a distortion is predicted by VSEPR theory, the present compound is exceptional because most [TeX$_6$]$^{2-}$ salts (X = Cl, Br or I) have octahedral structures. Another exception contains the cation derived from 1,3-diaminopropane, [H$_3$N(CH$_2$)$_3$NH$_3$][TeCl$_6$], in which the Te—Cl bonds are in three pairs so that the anion has approximate C_{2v} symmetry.[7] The spectra of this compound and the corresponding [TeBr$_6$]$^{2-}$ salt are considered here.

EXPERIMENTAL

Preparative work

(t-BuNH$_3$)$_2$[TeBr$_6$] was prepared by the addition of t-BuNH$_3$Br to a solution of TeBr$_4$ in hydrobromic acid. Crystals suitable for X-ray crystallography formed upon cooling a warm solution of the compound in concentrated HBr and were identified by chemical analysis. Found: C, 12.8; H, 3.1; N, 3.7. Calc. for C$_8$H$_{24}$Br$_6$N$_2$Te: C, 12.7; H,

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3.2; N, 3.7%. $(t\text{-BuNH}_3)_2[\text{TeCl}_6]\cdot 4t\text{-BuNH}_3\text{Cl}$ was obtained on combining t-BuNH$_2$ and $TeCl_4$ in concentrated HCl. Found: C, 31.1; H, 8.0; N, 9.1; Cl, 39.4. Calc. for $C_{24}H_{72}Cl_{10}N_6Te$: C, 31.1; H, 7.8; N, 9.1; Cl, 38.2%. Crystals of $(t\text{-BuNH}_3)_2[\text{SnX}_6]$ (X = Br or Cl) were obtained by adding t-BuNH$_2$ to solutions of $SnBr_4$ or $SnCl_4$ in the appropriate acid, and the literature method was used to prepare $(\text{dapH}_2)[\text{TeX}_6]$ (dap = 1,3-diaminopropane; X = Br or Cl).[7] The compositions were confirmed by C, H, N analysis.

Crystallography

An orange crystal of $(t\text{-BuNH}_3)_2[\text{TeBr}_6]$ measuring $0.2 \times 0.2 \times 0.35$ mm was mounted on a silica fibre on an Enraf–Nonius CAD-4 diffractometer. Unit cell parameters were obtained from a least-squares fit to the four circle coordinates of 25 reflections using monochromatic Mo-K_α radiation (λ = 0.71069 Å). Intensity data were collected using ω–2Θ scans with scan width $0.8 + 0.35 \tan \Theta$, giving 3044 unique reflections in the range $2^\circ < 2\Theta < 55^\circ$. The data were corrected for Lorentz and polarization effects and an absorption correction applied using empirical phi scans.

Crystal data. $C_8H_{24}Br_6N_2Te$, M = 755.06, monoclinic, space group $P2_1/c$, a = 10.307(4), b = 15.876(11), c = 12.907(6) Å, β = 90.25(4)°, U = 2112.0 Å^3, Z = 4, D_o = 2.33, D_c = 2.374 g cm^{-3}, $F(000)$ = 1392, $\mu(Mo\text{-}K_\alpha)$ = 126.5 cm^{-1}.

The structure was solved by conventional Patterson and difference-Fourier techniques and refined by full-matrix least-squares. Non-hydrogen atoms were assigned anisotropic thermal parameters. Hydrogen atoms of the t-butylammonium group were included in calculated positions and allowed to ride on the atom to which they were attached. The final R and R' values were 0.052 and 0.059, respectively, for the 1833 observed data ($I > 3\sigma\{I\}$) and weights $1.0/[\sigma(F^2) + 0.002F^2]$. Final atomic coordinates, thermal parameters and tables of observed and calculated structure factors have been deposited with the Cambridge Crystallographic Data Centre.

Spectroscopy

Far IR spectra were recorded as polythene pressed discs on a Digilab FTS-60 Fourier transform infrared spectrometer employing the FTS-60V vacuum optical bench with a 6.25 μm Mylar film beam splitter, a mercury lamp source and a TGS detector. Raman spectra were measured with a Jobin Yvon U1000 system using the 514 nm line of an Ar^+ laser, or a modified Cary 81 spectrometer using the 647 nm line of a Kr^+ laser as the excitation source.

RESULTS AND DISCUSSION

$[\text{TeBr}_6]^{2-}$ *complexes*

The complex anion of $(t\text{-BuNH}_3)_2[\text{TeBr}_6]$ is shown in Fig. 1, and Table 1 gives the bond distances and angles for $[\text{TeBr}_6]^{2-}$. The anion has a distorted octahedral structure with three long Te—Br bonds having an average length of 2.759 Å and three short bonds averaging 2.612 Å; the difference between short and long sets amounts to 5.6%. The angles between the long bonds average 89.6° and those between the short bonds average 91.8°. All these dimensions are within the ranges found in previous crystallographic studies of hexabromotellurate ions.[6] An irregular structure is sometimes associated with the presence of a large and unsymmetrical counterion. However, in this case the distortion of $[\text{TeBr}_6]^{2-}$ is probably linked to the charge distribution and capacity for hydrogen bonding of the $Me_3CNH_3^+$ ion. Detailed examination of the structure confirms the presence of weak hydrogen bonds. The bromine atoms with long Te—Br bonds make approaches to hydrogen atoms of $—NH_3^+$ groups of 2.47, 2.59 and 2.66 Å. The Br atoms with short Te—Br bonds come no closer than 3.1 Å to H atoms.

Most spectroscopic investigations of crystalline solids containing $[\text{TeBr}_6]^{2-}$ have dealt with compounds in which this ion is octahedral, or at least close to O_h in symmetry. These cases display the familiar spectra from species of the MX_6 type.[8] An example is $(H_9O_4)_2[\text{TeBr}_6]$, isolated as red crystals from a solution of $TeBr_4$ in concentrated HBr.[9] X-ray analysis has established that the anion has a

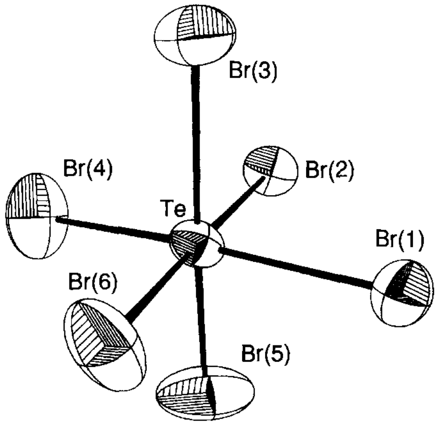

Fig. 1. The $[\text{TeBr}_6]^{2-}$ anion showing distortion from regular octahedral symmetry.

Table 1. Bond distances (Å) and angles (°) for $[\text{TeBr}_6]^{2-}$

Te—Br(1)	2.761(2)	Br(2)—Te—Br(1)	88.8(1)	Br(5)—Te—Br(4)	90.7(1)
Te—Br(2)	2.735(2)	Br(3)—Te—Br(1)	91.1(1)	Br(6)—Te—Br(1)	86.4(1)
Te—Br(3)	2.780(2)	Br(3)—Te—Br(2)	89.5(1)	Br(6)—Te—Br(2)	174.2(1)
Te—Br(4)	2.609(2)	Br(4)—Te—Br(1)	176.6(1)	Br(6)—Te—Br(3)	87.3(1)
Te—Br(5)	2.594(2)	Br(4)—Te—Br(2)	92.5(1)	Br(6)—Te—Br(4)	92.4(1)
Te—Br(6)	2.632(2)	Br(4)—Te—Br(3)	92.0(1)	Br(6)—Te—Br(5)	92.2(1)
		Br(5)—Te—Br(1)	86.1(1)		
		Br(5)—Te—Br(2)	90.7(1)		
		Br(5)—Te—Br(3)	177.3(1)		

regular octahedral structure and the Raman spectrum reveals three bands, 71 w, 151 m, 172 s, in agreement with the aqueous solution frequencies of 73 m, 146 s, 167 s, polarized, cm^{-1}.[9] This spectrum can be assigned with confidence to $[\text{TeBr}_6]^{2-}$ of O_h symmetry. In dichloromethane solution, $[\text{TeBr}_6]^{2-}$ displays the Raman frequencies 170 (ν_1), 148 (ν_2) and 96 (ν_5), along with 180 cm^{-1} (ν_3) in the infrared spectrum.[10]

Against this background the interpretation of the spectrum of the distorted $[\text{TeBr}_6]^{2-}$ ion found in $(t\text{-BuNH}_3)_2[\text{TeBr}_6]$ requires a different treatment. Strictly speaking, the symmetry of the ion in this compound is C_1 and therefore 15 vibrational modes could arise, all of them Raman and IR active. A more realistic approach is to regard the symmetry as C_{3v} which it matches quite closely. The vibrational representation then becomes $4A_1+A_2+5E$. The A_2 vibration is inactive, and the other nine modes should appear in both Raman and IR spectra. The Raman spectrum of $[\text{TeBr}_6]^{2-}$ (Fig. 2) contains six bands. The intense features at 163 and 201 cm^{-1} can be assigned to symmetric Te—Br stretching vibrations (A_1 species) of which the one of lower energy is associated with the set of longer (and hence weaker) bonds, and the other with the stronger bonds. The accompanying bands at 148 and 180 cm^{-1} can be attributed to the degenerate Te—Br stretching modes (E species) of the respective 'TeBr_3' units, while the bands at 69 and 91 cm^{-1} no

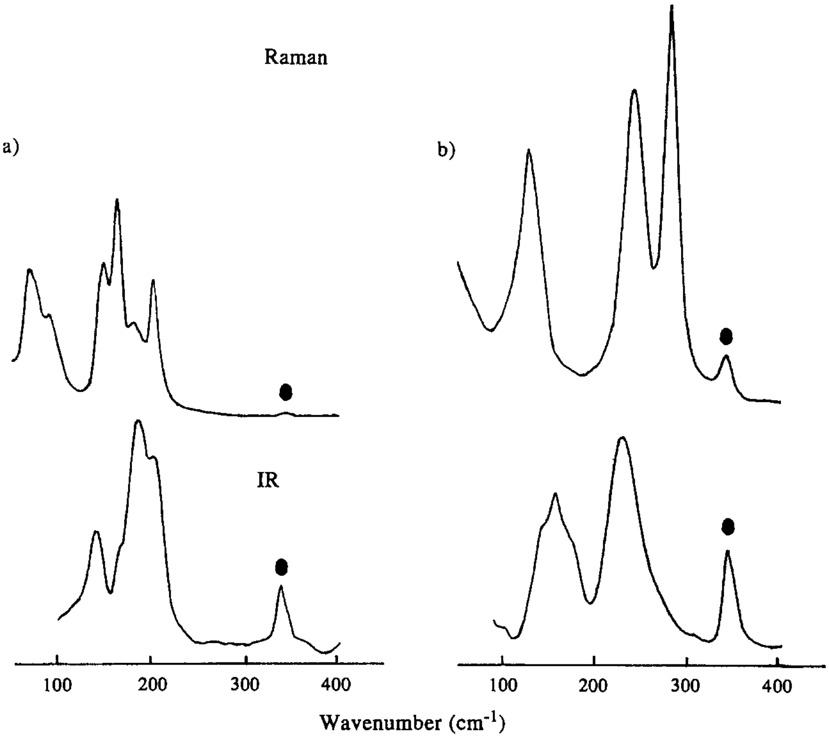

Fig. 2. Raman and far IR spectra of (a) $(t\text{-BuNH}_3)_2$ $[\text{TeBr}_6]$ and (b) $(t\text{-BuNH}_3)_2$ $[\text{TeCl}_6]$. Bands due to the cation are marked by ●.

doubt comprise bending modes of the $[TeBr_6]^{2-}$ ion. This interpretation is supported by the fact that the absorbtion frequencies of the far IR spectrum 141, 165, 185 and 201 cm^{-1} are close to those of the Raman spectrum, while the intensities in the two spectra are complementary to one another.

Shown for comparison are the vibrational spectra of $(dapH_2)[TeBr_6]$ (Fig. 3). The distortion of the halogenotellurate complex in association with this particular cation is considered later, in relation to the spectrum of the $[TeCl_6]^{2-}$ salt.

$[TeCl_6]^{2-}$ *complexes*

The product to crystallize from a solution of $TeCl_4$ in concentrated HCl on adding *t*-$BuNH_2$ had been expected to be a simple salt of $[TeCl_6]^{2-}$, but turned out upon analysis to be a double salt $(t\text{-}BuNH_3)_2[TeCl_6]\cdot 4t\text{-}BuNH_3Cl$. The vibrational spectra of this compound are shown in Fig. 2 and, in contrast to $(t\text{-}BuNH_3)_2[TeBr_6]$, suggest that the octahedral structure of $[TeCl_6]^{2-}$ is preserved. The Raman spectrum has an intense band at 287 cm^{-1} and two other bands at 247 and 131 cm^{-1}, and is analogous to that of $(Me_4N)_2[TeCl_6]$ which displays the Raman frequencies 281 (ν_1), 242 (ν_2) and 136 cm^{-1} (ν_5).[11] The IR spectra also correspond with bands at 230 (ν_3) and 158 cm^{-1} (ν_4) in the present compound and similar bands in the previous work.[11] X-ray crystallographic examination of $(Me_4N)_2[TeCl_6]$ shows the ion to be undistorted.[12] The close similarity with the vibrational spectra of this solid, as well as compliance with the selection rules of O_h symmetry, provides firm evidence of the presence of octahedral $[TeCl_6]^{2-}$ ions in the compound investigated here. Other formulations containing the $[TeCl_5]^-$ ion,[13] or condensed structures like $[Te_2Cl_9]_n^{n-}$ found in the crystals which separate from $TeCl_4$/HCl solutions,[14] can be ruled out.

A crystallographic investigation of the $dapH_2^{2+}$ salt, $[H_3N(CH_2)_3NH_3][TeCl_6]$, has revealed distorted $[TeCl_6]^{2-}$ ions (with Te—Cl distances 2.426 (two), 2.492, 2.558, 2.672 Å (two) giving approximate C_{2v} symmetry).[7] We have prepared this compound and the spectra are given in Fig. 3. $[TeCl_6]^{2-}$ salts in which the anion is octahedral exhibit three Raman frequencies with ν_1 in the range 280–300 cm^{-1} (and tending to be smallest when the accompanying cation is large).[11] In the present case, since the point group permits no degeneracy, six Te—Cl stretching frequencies might be observed. There are Raman bands at 279 and 313 with a broad shoulder at 240 cm^{-1} and it is natural to associate the band at 313 cm^{-1} with symmetric stretching of the short Te—Cl bonds. The IR spectrum contains intense absorbtion centred at 210 cm^{-1} and extending from 330 to 140 cm^{-1}. Shoulders at 280 and 315 cm^{-1} are close to the Raman values and, although the number of frequencies falls

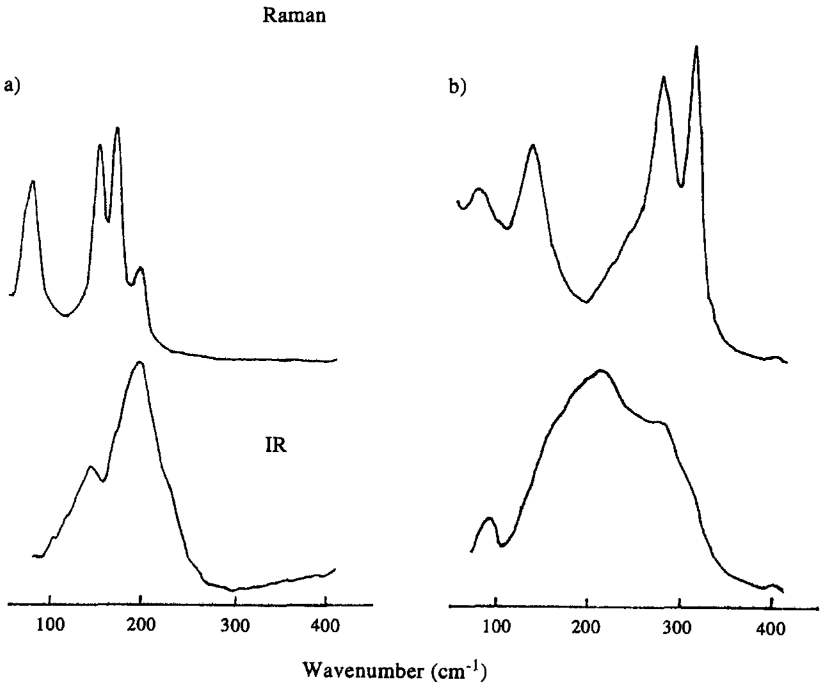

Fig. 3. Raman and far IR spectra of (a) $(dapH_2)_2[TeBr_6]$ and (b) $(dapH_2)_2[TeCl_6]$ (dap = 1,3-diaminopropane).

short of the predicted tally, the spectra are in fair agreement with the C_{2v} model of $[\text{TeCl}_6]^{2-}$.

The spectra of $[\text{TeBr}_6]^{2-}$ in its dapH_2^{2+} salt (of unknown crystal structure) are in Fig. 3. The Raman bands at 146, 164 and 189 cm^{-1}, which are the possible candidates for symmetric Te—Br stretching frequencies, lie outside the range of 168–180 cm^{-1} where ν_1 of octahedral $[\text{TeBr}_6]^{2-}$ has been observed[15,16] and the pattern is not that of an O_h species. IR absorbance features occur at 140, 165sh and 190 cm^{-1} and the close registration of these with the Raman values reinforces the view that the ion has lower than octahedral symmetry.

Concluding remarks

Several previous workers[5,10] have compared the structures and spectra of $[\text{TeX}_6]^{2-}$ salts with those of the $[\text{SnX}_6]^{2-}$ ions partnered by the same cation. We have made a similar comparison by examining the vibrational spectra of $(t\text{-BuNH}_3)_2[\text{SnX}_6]$ (X = Cl or Br). The Raman bands of $[\text{SnCl}_6]^{2-}$ 146m, 232w, 310s, and $[\text{SnBr}_6]^{2-}$ 97m, 147m, 185vs cm^{-1} are those of the regular octahedral Sn(IV) complexes. The far infrared spectra exhibit split ν_3 bands due to $[\text{SnCl}_6]^{2-}$ 158, 175sh; 291, 310sh and $[\text{SnBr}_6]^{2-}$ 115, 125sh; 211, 220sh. The slight splitting can be attributed to the influences of hydrogen bonding to the $[t\text{-BuNH}_3]^+$ counter-ion on the T_2 modes of the anions. In contrast to the behaviour of $[\text{SnX}_6]^{2-}$ which is consistently octahedral, the $[\text{TeX}_6]^{2-}$ ions can exhibit octahedral, trigonal or less regular shapes and there are no simple rules to predict which structure will occur in a given compound.

Recent *ab initio* calculations on $[\text{SeCl}_6]^{2-}$ and $[\text{TeCl}_6]^{2-}$ favour O_h symmetry for the electronic ground states of these ions.[17] Earlier attempts have been made to interpret the structural and spectroscopic behaviour of the six-coordinate complexes of Se(IV), Te(IV), Sb(III) and Bi(III).[2–6] However, the ease with which the vibrational spectra and structure of the hexahalotellurates respond to their environment is a remarkable feature of their chemistry which remains to be fully explained.

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