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Crystal Structures of Trimethylammonium Hexaiodotellurate(IV) and Heptaiodotellurate(IV)

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Crystal structures of the title compounds were determined by X-ray diffraction method. The crystal data and the final R values are: $[(CH_3)_3NH]_2TeI_6$, cubic, $Pa3$, a=13.210(2) Å, V=2305.2(9) Å^3, Z=4, R=0.057 for 263 observed unique reflections and $[(CH_3)_3NH]_2TeI_7$, tetragonal, $P4/nmm$, a=13.921(3), c=6.224(2) Å, V=1206.4(8) Å^3, Z=2, R=0.051 for 553 reflections. The structure of hexaiodo complex is a modified K_2PtCl_6 type. The discrete $[TeI_6]^{2-}$ octahedra are practically regular with a Te-I distance of 2.952(2) Å. The trimethylammonium cations lie on the unit cell triad axes and form trifurcated, weak hydrogen bonds of NH···3I. In contrast, the Te^{IV} coordination in the heptaiodo complex is an elongated octahedron with Te-I(1)=2.934(1) and Te-I(2)=3.124(4), 3.100(4) Å. These TeI_6 octahedra form linear trans TeI_5 chains running along c by sharing each pair of opposite vertices. Extra iodine atoms also stack along c with nearly equidistant I-I separations of 3.091(6) and 3.133(6) Å. The trimethylammonium cation is distributed randomly over four configurations in a cavity formed by two $[TeI_5]_n^{n-}$ and two $[I]_{2n}^{n-}$ columns. Thus, the chemical constitution of the heptaiodo complex can be expressed as di-trimethylammonium *catena-μ*-iodo-tetraiodo tellurate(1-) *catena*-diiodide(1-), $[(CH_3)_3NH]_{2n}^{2n+}[TeI_5]_n^{n-}[I]_{2n}^{n-}$.

A series of methylammonium hexahalometallate(IV), $[(CH_3)_nNH_{4-n}]_2MX_6$ where M=Pd, Pt, Sn, Te, X=Cl, Br, I and n=1, 2, 3, 4 has been widely studied so far by means of X-ray diffraction, NMR, NQR, dielectric and thermal analyses in view of structural chemistry focussed on their phase transitions and molecular dynamics.[1–5] Our preliminary report on $(CH_3NH_3)_2TeCl_6$ suggested that tellurate complexes of the series, especially their iodo analogs would be somewhat different from other hexahalometallates in nature.[6] In order to ascertain this suggestion the system of methylammonium hexaiodotellurate(IV), $[(CH_3)_nNH_{4-n}]_2TeI_6$ has been studied by X-ray diffraction and ^{1}H NMR measurements. In this paper, the X-ray results obtained for n=3 are described.

The X-ray powder patterns showed that trimetylammonium (abbreviated as Me_3NH hereinafter) hexaiodotellurate is isostructural with the corresponding hexachlorotellurate complex.[7] Thus, it was found that the structure is an antifluorite type in principle, but the crystal symmetry is lowered from $Fm3m$ to $Pa3$ owing to the presence of Me_3NH^+ cations. At the beginning of the work it was desired to determine the geometry of $[TeI_6]^{2-}$ ion more accurately than those in the literature.[8] Because the Me_3NH complex evidently contains discrete $[TeI_6]^{2-}$ anions, its crystal structure was analyzed by X-ray diffraction.

During preliminary attempts to grow single crystals of $(Me_3NH)_2TeI_6$ suitable for structure determination, a novel complex of formula $(Me_3NH)_2TeI_7$ was obtained by chance. Therefore, the heptaiodo complex was also subjected to an X-ray analysis in order to elucidate such a unique chemical constitution as well as the role of extra iodine atoms.

Experimental

Preparation. A saturated aqueous solution of trimethylammonium iodide added dropwise to a hydrogen iodide solution of tellurium dioxide in a stoichiometric molar ratio yielded black precipitates. The product was cubic from its X-ray powder patterns and was a hexaiodotellurate complex of $(Me_3NH)_2TeI_6$ from elemental analyses. The precipitate was dissolved into a hot, dilute HI solution and then brown-black prismatic crystals were grown from the solution held at ca. 50 °C for several days. These crystals were not identical to the source material of $(Me_3NH)_2TeI_6$, as evidenced by the X-ray powder pattern, and confirmed to correspond to $(Me_3NH)_2TeI_7$ by careful, chemical analyses. Found: C, 6.62; H, 1.84; N, 2.55; I, 79.14%. Calcd for $C_6H_{20}N_2TeI_7$: C, 6.34; H, 1.77; N, 2.47; I, 78.19%.

To avoid such a change in composition, solvents and temperatures were varied upon recrystallization, and the pure hexaiodo complex was successfully recrystallized only from absolute ethanol solution not including HI acid at an optimum temperature near 50 °C. Thus obtained single crystals of $(Me_3NH)_2TeI_6$ were black, octahedral and less than 70 μm, these being used for the present study.

X-Ray Structure Determination. As the X-ray analytical methods used were almost the same for both complexes, the following description is made mainly for $(Me_3NH)_2TeI_7$ and briefly for $(Me_3NH)_2TeI_6$.

$(Me_3NH)_2TeI_7$: The density was measured by pycnometry with petroleum at 20 °C; the lattice parameters and the space group ($P4/nmm$ from systematic absences: $hk0$, $h+k=2n+1$) were previously determined with a Weissenberg camera; crystal 0.12×0.12×0.20 mm^3 in size was mounted with c coincident with the goniostat axis; Rigaku AFC-4 diffractometer, graphite-monochromatized Mo$K\alpha$ radiation, 40 kV-200 mA; unit cell parameters were refined by least-squares methods on the basis of 25 2θ values (18°<2θ<28°, λ=0.71069 Å); intensity measurement was performed up to 2θ=55° ($0 \leq h \leq 12$, $0 \leq k \leq 18$, $-8 \leq l \leq 8$), ω—2θ scan technique, scan rate 4° min^{-1} (ω); all intensities were corrected for some X-ray damage (8.2% decay) by a factor of $a\exp(bN)$, where a=1.0043 and b=0.00011 obtained by least-squares on the basis of the intensity variation of three standard reflections (502, 060, and 004) every 50 reflections through experiments and N the ordinal number of measurements; 1523 reflections including 722 equivalent ones were measured, $R_{int}=\sum||F_o|-\langle|F_o|\rangle|/\sum|F_o|=0.031$, 248 weak reflections classified as unobserved [$|F_o|<3\,\sigma(F_o)$], 553 observed unique reflections used for the structure determination;

Lorentz-polarization factors and absorption were corrected, empirical absorption correction factors on F 0.9986—1.0595; [9] the positions of Te and I were deduced from a Patterson map, starting with these positions the other non-H atoms were determined from electron density maps and refined by full-matrix least-squares on F with anisotropic thermal parameters for Te and I, and isotropic ones for N and C; the H atoms were not found from difference maps, and omitted in the refinement, $\sum w(|F_o|-|F_c|)^2$ minimized for 31 parameters, $w=[\sigma^2(F_o)]^{-1}$; final $R=0.051$, $R_w=0.044$, and goodness of fit $S=[\sum w(|F_o|-|F_c|)^2/(m-n)^{1/2}=1.74$, where m is the number of unique reflections and n the number of refined parameters, ratio of maximum least-squares shift to error, $(\Delta/\sigma)_{\max}$, was 0.3 for C(1) and $(\Delta/\sigma)_{\text{mean}}=0.07$, maximum positive and maximum negative electron densities in final difference Fourier synthesis, $(\Delta\rho)_{\max}$ and $(\Delta\rho)_{\min}$, were 1.24 and -1.46e/Å^3, respectively.

$(Me_3NH)_2TeI_6$: Black, octahedral crystal used was $0.07\times0.07\times0.07$ mm^3 in size; lattice parameters were refined by least-squares methods based on 12 2θ values ($17°<2\theta<22°$, $\lambda=0.71069$ Å); ω scan technique, $2\theta_{\max}=55°$ ($0\leq h\leq17$, $0\leq k\leq17$, $0\leq l\leq17$), 2800 measured reflections, 891 unique reflections, 628 unobserved [$|F_o|<7\sigma(F_o)$], 263 observed unique reflections used for the structure determination; R_{int}(based on F)=0.097, standard reflections 400, 040, 004, intensity variation less than 3.0%, absorption correction neglected because of small size of crystal; structure was solved by heavy atom method and refined by full-matrix least-squares on F with anisotropic thermal parameters for non-H atoms, $\sum w(|F_o|-|F_c|)^2$ minimized for 24 parameters, $w=[\sigma^2(F_o)]^{-1}$; $R=0.057$, $R_w=0.040$, $S=2.04$, $(\Delta/\sigma)_{\max}=0.01$, $(\Delta\rho)_{\max}$ and $(\Delta\rho)_{\min}$ in final difference Fourier synthesis were 1.20 and -1.62 e/Å^3, respectively.

In both cases, neutral atom scattering factors and anomalous dispersion terms were taken from Internationl Tables for X-ray Crystallography[10] and *UNICS* Program System,[11] Finger Computing System[12] and their modifications used for calculations at the Computation Center of Osaka University and later at the Information Processing Center of Kobe University.

The crystal date are summarized in Table 1. The positional and thermal parameters of hexaiodo and heptaiodo complexes are listed in Tables 2 and 3, respectively.[13]

Results and Discussion

The Structure of Hexaiodo Complex, $(Me_3NH)_2TeI_6$. The crystal of hexaiodo complex consists of octahedral anions $[TeI_6]^{2-}$ and group cations $[(CH_3)_3NH]^+$ in an arrangement of the K_2PtCl_6 structure, as shown in Fig. 1. The length of six equivalent Te–I bonds is 2.952(2) Å, and the two I–Te–I bond angles are 89.90(7)° and 90.10(7)°, indicating that the coordination octahedra of Te^{IV} atoms are practically regular. The obtained value of 2.952 Å is more reliable than 2.93 Å found in K_2TeI_6[8] and can be compared to 2.947(2) Å corrected for thermal motion in Rb_2TeI_6.[14] The Me_3NH^+ cations occupy the eight tetrahedral holes at 1/4, 1/4, 1/4 etc. The C–N bond length 1.51(5) Å and the C–N–C bond angle 110(2)° are reasonable in comparison with those in the literature, cf. 1.466—1.487 Å, 110.2—112.1° for $(CH_3)_3NHCl$[15] and 1.478 Å and 111.6° for $(Me_3NH)_2SnCl_6$[16]. The threefold axis of each cation is aligned with the unit cell triad axis and its N–H bond approaches to one iodine triangle of the nearest octahedron with three symmetrical N···I distances of 3.87(3) Å. Then the H···I distance and the N–H–I angle were calculated to be 3.14 Å and 130°, respectively, by assuming the hydrogen position at a distance of 1.02 Å from its attached

Table 1. Crystal Data of Hexaiodo and Heptaiodo Complexes

Compound	$(Me_3NH)_2TeI_6$	$(Me_3NH)_2TeI_7$
Formula	$C_6H_{20}N_2TeI_6$	$C_6H_{20}N_2TeI_7$
Formula weight	1009.3	1136.2
Crystal system	cubic	tetragonal
Space group	*Pa*3	*P*4/*nmm*
a/Å	13.210(2)	13.921(3)
c/Å		6.224(2)
V/Å^3	2305.2(9)	1206.2(8)
D_m/Mg m^{-3}	2.93	3.19
D_x/Mg m^{-3}	2.91	3.13
Z	4	2
μ(Mo $K\alpha$)/mm^{-1}	9.24	10.1

Table 2. Fractional Coordinates and Equivalent Isotropic Thermal Parameters of non-H Atoms in $(Me_3NH)_2TeI_6$

Atom	x	y	z	B_{eq}/Å^2
Te	0	0	0	3.455(1)
I	0.0326(2)	−0.0281(2)	0.2193(2)	4.730(1)
N	0.2071(24)	0.2071(24)	0.2071(24)	6.150(1)
C	0.2184(25)	0.3094(24)	0.1576(27)	5.598(1)

$B_{eq}=(4/3)\sum_i\sum_j\beta_{ij}\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

Table 3. Fractional Coordinates (×10^4) and Thermal Parameters(Å^2) for $(Me_3NH)_2TeI_7$ with Their e.s.d.'s in Parentheses

Atom	p	x	y	z	B_{eq}/B
Te	1.0	2500	2500	0877(4)	3.009(1)*
I(1)	1.0	2500	4607(1)	0918(2)	5.404(2)*
I(2)	1.0	2500	2500	5896(5)	4.790(1)*
I(3)	1.0	7500	2500	2483(5)	6.424(2)*
N	0.5	4731(13)	4731(13)	4539(44)	3.9(6)
C(1)	0.25	4236(56)	5554(52)	5473(118)	6.8(19)
C(2)	0.25	5663(40)	5065(38)	3404(73)	4.3(12)
C(3)	0.25	5158(54)	3962(52)	5870(12)	5.7(17)

p: occupancy factor. *: $B_{eq}=(4/3)\sum_i\sum_j\beta_{ij}\,\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

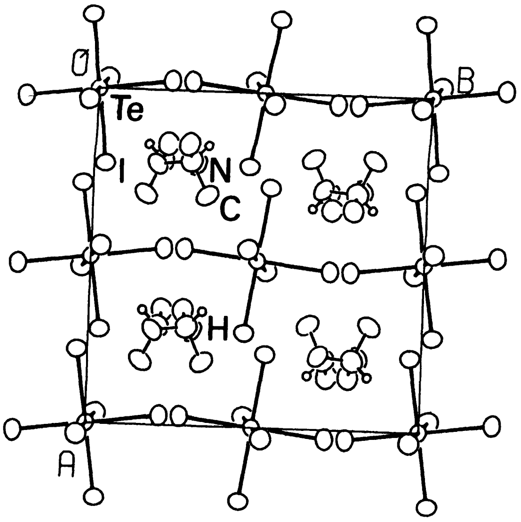

Fig. 1. Crystal structure of $(Me_3NH)_2TeI_6$ projected along [001].

nitrogen with sp^3 hybridization. The scheme of trifurcated hydrogen bonds, N–H···3I, is quite similar to that found in $(Me_3NH)_2TeCl_6$,[7] although H···I distance is only a little shorter than the normal van der Waals approach, 3.4 Å.[17] On the other hand, the CH_3 group is surrounded by five I(1) atoms with distances of 3.84—4.27 Å, less than or near the van der Waals distance 4.2 Å.

The Structure of Heptaiodo Complex, $(Me_3NH)_2TeI_7$. A projetion of the crystal structure along *a* with the numbering of atoms and a stereo pair of structure viewed along *c* are shown in Figs. 2 and 3, respectively. Selected interatomic distances and angles are listed in Table 4.

The Te atom is coordinated by six iodine atoms, 4I(1) and 2I(2), in an elongated octahedral arrangement. These octahedra are connected to each other by sharing two opposite vertices of each octahedron to form a linear trans chain running along *c*. The bond length of Te to terminal I(1), 2.934(1) Å, is shorter than 2.952(2) Å found in cubic $(Me_3NH)_2TeI_6$ and agrees with 2.930(2) Å in Rb_2TeI_6, which is uncorrected for librational motion of $[TeI_6]^{2-}$ ion.[14] The central Te atom is at 0.026(3) Å below or above the coordination plane formed by 4I(1). The Te–I(2) bridging distances of 3.124(4) and 3.100(4) Å are longer than that for the terminal I(1) by 0.18 Å. The lengthening of a bond to a bridging halide ion is quite common: In $[MeAlCl_2]_2$ the Al–Cl distances are 2.25 and 2.05 Å for bridging and terminal chlorine atoms, respectively.[18] Another example is found in $BaFeF_5$, where the mean Fe–F distances are 1.90 Å for bridging atoms and 1.82 Å for terminal fluorine atoms within the linear trans $[FeF_5]_n^{2n-}$ chain.[19] Thus the formed polymeric chain is a previously unknown, newly found chemical species for halotellurate anions and can be described as $[TeI_5]_n^{n-}$.

Another striking feature of the structure is that extra iodine atoms, I(3)'s, are also stacked along *c* to form a linear polyiodide chain within the crystal lattice. More remarkable is the appearance of nearly equal I–I bond lengths with successive values of 3.091(6) and 3.133(6) Å. Both separations are larger than the I–I bond lengths of 2.715(6) Å in crystalline iodine and also of the mean 2.92(1) Å for seventeen compounds including linear, symmetric triiodide ions.[20,21] Such an approximately linear array of equally spaced iodine atoms was first proposed for some polyiodide compounds of starch and cyclodextrin, but later works proved that these results probably correspond to disordered structure.[22,23] On the other hand, recent studies on some metal complexes of α-cyclodextrin polyiodide and also on various stacked organometallic iodide compounds have shown that long polyiodide chains exclusively consist of I_2 and/or $[I_n]^-$ (n=1, 3, and 5) moieties.[24] Consequently, a linear and nearly equidistant array of iodine atoms was first realized in the heptaiodo complex, although its presence had been speculated so far only as an extreme model case or interpreted in terms of a statistical structure or disordered arrangements. In contrast with many other polyiodide compounds, no indication of diffuse scattering or superstructure appearance was disclosed on

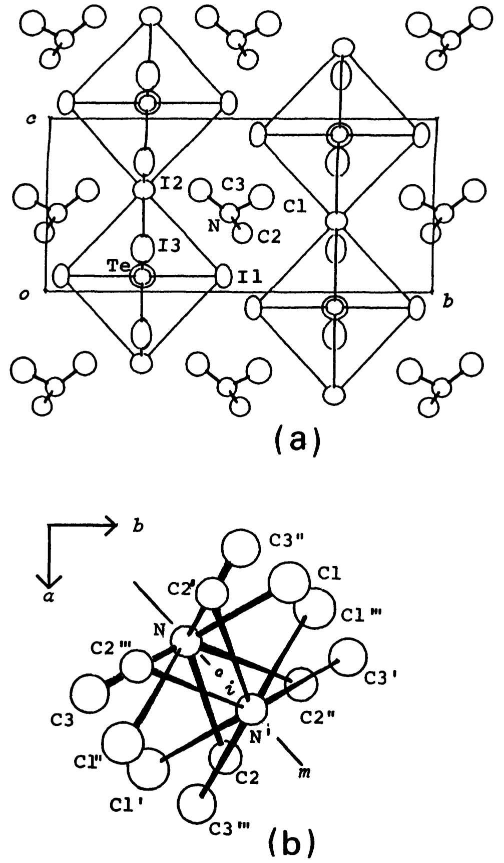

Fig. 2. Crystal structure of $(Me_3NH)_2TeI_7$. (a) The projection along [100], and (b) disordered configurations of the Me_3NH^+ cation. Symbols are: none, (x, y, z); ('), $(\bar{x}, \bar{y}, \bar{z})$; (''), (y, x, z); ('''), $(\bar{y}, \bar{x}, \bar{z})$.

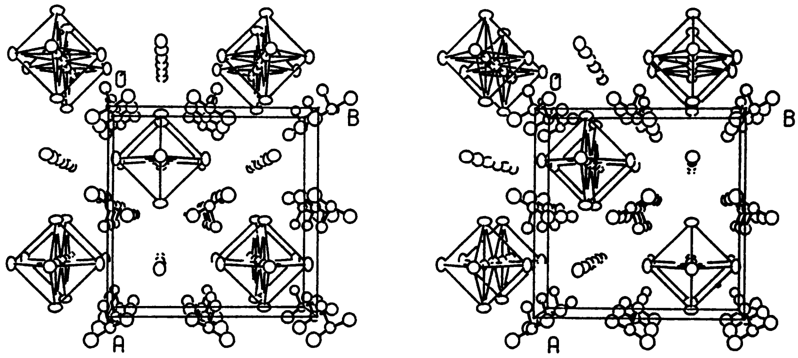

Fig. 3. Stereoscopic view of crystal structure of $(Me_3NH)_2TeI_7$ along the *c* axis. Thermal ellipsoids are shown at 50% probability level.

Table 4. Interatomic Distances (l/Å) and Angles (ϕ/°) in $(Me_3NH)_2TeI_7$

(i) $[TeI_5]^-$ anion				
	Te–I(1)	2.934(1)	I(1)–Te–I(1)	179.0(1)
	Te–I(2)	3.124(4)	I(1)–Te–I(2)	89.5(1)
	Te–I(2′)	3.100(4)	I(1)–Te–I(2′)	90.5(1)
(ii) Polyiodide chain, $[I]^{n-}_{2n}$				
	I(3)–I(3″)	3.133(6)	I(3)–I(3‴)	3.091(6)
(iii) $[(CH_3)_3NH]^+$ cation				
	N–C(1)	1.46(8)	C(1)–N–C(2)	110(4)
	N–C(2)	1.55(6)	C(1)–N–C(3)	122(4)
	N–C(3)	1.48(8)	C(2)–N–C(3)	98(4)
		(mean 1.50)		(mean 110)

Symmetry code: none, (x, y, z); (′), (x, y, $z-1$); (″), (x, y, $1-z$); (‴), (x, y, $-z$).

Weissenberg photographs of the heptaiodo complex. The thermal parameters of I(3) are, in fact, relatively large to those of I(1) and I(2) and more anisotropic with root-mean-square amplitudes of 0.34 Å (at most) parallel to the polyiodide chain and of 0.25 Å perpendicular to it, but there is no sufficient evidence for establishing disordered structure. The appearence of unique iodine array in the present complex may be associated with the fact that the length of repeating unit in $[I]^{n-}_{2n}$ chain is almost the same as that in $[TeI_5]^{n-}_{n}$ chain, which corresponds to the *c* spacing of the unit cell, 6.2 Å.[25]

The Me_3NH^+ cation is inserted between two $[TeI_5]^{n-}_{n}$ and two $[I]^{n-}_{2n}$ columns. The electron density map revealed a statistical arrangement of Me_3NH^+ ions. Four equivalent N atoms in the unit cell are distributed on the special position **8j** of the space group *P4/nmm* with a statistical weight of 0.5, while the methyl carbon atoms, C(1), C(2), and C(3), are located on each individual **16k** positions with a statistical weight of 0.25. Each Me_3NH^+ cation is therefore distributed over four configurations with the equal probability; any two of which are related by either the center of symmetry or the mirror plane as illustrated in Fig. 2(b). The mean C–N bond length of 1.50 Å and the mean C–N–C bond angle of 110° for the disordered Me_3NH^+ cations are comparable to those for the ordered one in the hexaiodide described earlier.

The NH hydrogen positions of cations were calculated on the basis of sp^3 N atoms with N–H distances of 1.02 Å as in hexaiodide. Weak, but significant hydrogen bonds are formed between NH and I atoms with distances of 3.84(2) Å for N···I and 2.90 Å for H···I, and with the angle N–H···I of 154°. The statistical distribution of Me_3NH^+ cation is probably associated with the formation of hydrogen bonds and packing restriction of molecular ions. Some intermolecular CH_3···I distances are less than the sum of the van der Waals radii of 4.2 Å, suggesting weak interaction due to C–H···I hydrogen bonds; their minimum distances are 3.85(7) Å for C(1)–I(3), 3.74(5) Å for C(2)–I(1) and 3.77(7) Å for C(3)–I(1).

In conclusion, the present X-ray analysis together with the neutralization principle of electric charges revealed that the chemical constitution of the newly prepared catena heptaiodo complex is $[(CH_3)_3NH]^{2n+}_{2n}[TeI_5]^{n-}_{n}[I]^{n-}_{2n}$. The presence of such a peculier polyiodide ion of $[I]^{n-}_{2n}$ is interesting in view of the chemical bond.

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