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Crystal Structure and Molecular Motion of Tetramethylammonium Hexaiodotellurate(IV)-Iodine (1/1) Compound

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The crystal structure of the title compound was determined by means of X-ray diffraction. The crystal data and the final R value are: $[(CH_3)_4N]_2TeI_6{\cdot}I_2$, tetragonal $I4_1/acd$, a=20.356 (3) and c=27.571 (5) Å, V=11,424 (3) Å^3, Z=16, R=0.082 for 1562 observed unique reflections. The structure consists of discrete $[TeI_6]^{2-}$ anions and Me_4N^+ cations in an arrangement analogous to the K_2PtCl_6 structure and of additional I_2 molecules bridging adjacent complex anions. The TeI_6 octahedron is considerably distorted with Te–I distances of 2.933 (2), 3.017 (2), and 2.857 (2) Å, owing to different interaction with the surrounding I_2 molecules. Two of three independent Me_4N^+ cations are orientationally disordered and distributed over each two positions. A phase transition was found at 234 K from DTA and its molar enthalpy was estimated to be approximately 2.4 kJ mol^{-1} from DSC. Proton NMR studies offered direct evidences for threefold reorientation of CH_3 groups and overall rotation of Me_4N^+ cations taking place consecutively far below room temperatures. At 234 K the spin-lattice relaxation time T_1 changes discontinuously by about one order of magnitude, suggesting the first order of transition. The activation energies of such composite reorientation in the fast regions ($\omega\tau_c \ll 1$) are 5.4 and 14.2 kJ mol^{-1} in the high- and low-temperature phases, respectively.

A large family of methylammonium hexahalometallate(IV) complexes, $[(CH_3)_nNH_{4-n}]_2MX_6$ where M=Pd, Pt, Sn, Te, X=Cl, Br, I, and n=1, 2, 3, 4 exhibit one or more phase transitions associated with molecular motion of cation groups or complex anions.[1,2] Most of them have the typical K_2PtCl_6 type structure, but some tellurate complexes of the series, especially their iodo analogues, are characterized by the unique structures different from the others.[3,4] In order to develop our study on methylammonium hexaiodotellurate(IV), $[(CH_3)_nNH_{4-n}]_2TeI_6$, the complex for n=4 was tried to prepare, but the obtained crystals did include extra iodine atoms, as encountered in $(Me_3NH)_2TeI_7$.[4] The crystal structure of the resulting octaiodotellurate complex was determined by X-ray diffraction methods to elucidate the role of extra iodine atoms and the dynamic process of cations was revealed by ^{1}H NMR experiments to connect with the phase transition newly found.

Experimental

Preparation. A saturated aqueous solution of tetramethylammonium iodide added dropwise with stirring into a hydrogen iodide solution of tellurium dioxide in a stoichiometric molar ratio yielded black precipitates. The product showed broad X-ray powder patterns because of its poor crystallinity. Most of the reflections could be roughly indexed on the basis of a cubic K_2PtCl_6 cell (space group $Fm3m$) with a=14.2 Å, but some of them remained unindexed. In order to obtain single crystals suitable for X-ray use, the precipitate was dissolved into a hot, dilute (ca. 3%) HI solution and black cubooctahedron-like crystals were grown from the filtrate. These crystals were identified with the source material from the X-ray powder patterns and confirmed to be $(Me_4N)_2TeI_8$ by chemical analyses. Unlike $(Me_3NH)_2TeI_7$, the recrystallization from an HI solution did not change the chemical constitution, therefore the original precipitate also being not hexaiodide but octaiodide.

X-Ray Structure Determination. The density was measured by pycnometry with o-xylene at 20°C; the lattice parameters and the space group were previously determined with a Weissenberg camera, reflection conditions hkl: $h+k+l=2n$, $hk0$: $h,k=2n$, $0kl$: $k,l=2n$, hhl: $2h+l=4n$, $00l$: $l=4n$ leading to $I4_1/acd$; crystal 0.2×0.2×0.25 mm^3 in size was mounted with c coincident with the goniostat axis; Rigaku AFC-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation (λ=0.7107 Å), 40 kV-200mA; unit cell parameters were refined by least-squares method using 25 2θ values (20° <2θ <24°); intensity measurement was made up to 2θ =55° ($0 \leq h \leq 18$, $0 \leq k \leq 26$, $0 \leq l \leq 34$), ω—2θ scan technique, all intensities monitored by three standard reflections (0, 0, 16; 6, 4, 10; 800) every 50 reflections throughout experiments; 3629 unique reflections were measured. 1569 reflections classified as observed $[|F_o| > 3\sigma(F_o)]$ used for the structure determination; Lorentz-polarization factors and absorption were corrected, empirical correction factors on F 0.996—1.091;[5] the possible positions of Te and I deduced from the E map were confirmed by the Patterson function, starting with these positions the other non-hydrogen atoms located on electron density maps, the structure refined by full-matrix least-squares on F with anisotropic thermal parameters for Te and I, and isotropic ones for N and C; H atoms were not found in difference maps and omitted in refinement, $\sum w(|F_o|-|F_c|)^2$ minimized for 72 parameters, seven reflections with low angles and strong intensities removed to avoid possible extinction effects, $w=[\sigma^2(F_o)]^{-1}$; final R=0.082, R_w=0.056 and goodness of fit S=1.86 for unique 1562 reflections, $(\Delta/\sigma)_{max}$=0.48 for Te and I, but 2.28 for C and N, maximum positive and negative electron densities, $(\Delta\rho)_{max}$ and $(\Delta\rho)_{min}$, in final difference fourier syntheses 1.90 and −2.52 e Å^{-3}, respectively.

Neutral atom scattering factors and anomalous dispersion terms were taken from International Tables for X-Ray Crystallography.[6] UNICS Program System,[7] Finger Computing System,[8] and their modifications were used for calculations at the Computation Center, Osaka University and later at the Information Processing Center, Kobe University.

Crystal Data: $[(CH_3)_4N]_2TeI_6{\cdot}I_2$, F.W.=1291, tetragonal, space group $I4_1/acd$, a=20.356(3), c=27.571(5) Å, V=11, 424 Å^3, D_m(20 °C)=3.01, D_x(20°C)=3.00 Mg m^{-3}, Z=16, F(000)=8992, μ(Mo $K\alpha$)=9.6 mm^{-1}.

Proton NMR Experiments. For NMR measurements, the polycrystalline sample was sealed in a glass tube with a small amount of helium gas for heat exchange. The continuous wave (CW) absorption spectrum was observed with a bridge-type spectrometer (homemade) operated at 19.4 MHz, while the spin-lattice relaxation time T_1 was measured by an induction type of pulse spectrometer (homemade) adjusted at 10.5 MHz. A conventional pulse sequence of 90°$_{\mathrm{comb}}$-τ-90° or 180°-τ-90° was selectively used. The temperature of the specimen was kept constant within ±0.5 K for the CW experiments and ±1 K for the pulse one. It was measured with a Chromel-Constantan thermocouple above 15 K and with a germanium resistance thermometer or an Au(Fe)-Chromel thermocouple below 15 K.

Thermal Analyses. Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) were carried out with a Rigaku DTA & DSC apparatus. Carbontetrachloride CCl_4 of "extra pure" grade was used as a standard to calibrate the DSC scale.

Table 1. Fractional Coordinates and Equivalent or Isotropic Thermal Parameters (Å^2) with Their e.s.d.'s in Parentheses

Atom	x	y	z	$B_{eq}$$^{a)}$/$B_{iso}$
Te	0.03057(8)	0	0.25	2.74(2)$^{a)}$
I(1)	0.02912(9)	0.00119(16)	0.35637(5)	6.47(2)$^{a)}$
I(2)	0.14876(9)	0.17235(10)	0.49773(13)	7.21(5)$^{a)}$
I(3)	0.14760(7)	0.12349(8)	0.00229(11)	5.58(4)$^{a)}$
I(4)	0.04410(7)	0.05109(7)	0.49947(8)	3.83(2)$^{a)}$
N(1)	0	0.25	0.125	1.9(13)
N(2)	0.271(1)	0.021(1)	0.375	4.1(7)
N(3)	0	0.25	0.375	7.9(26)
C(11)	0.029(5)	0.196(5)	0.098(4)	13.9(30)
C(12)	0.025(6)	0.297(6)	0.093(4)	17.8(36)
C(21)	0.266(4)	0.018(4)	0.168(3)	10.0(23)
C(22)	0.253(4)	0.089(3)	0.373(2)	8.8(16)
C(23)	0.200(4)	0.005(6)	0.116(4)	13.9(31)
C(24)	0.282(5)	0.083(5)	0.359(4)	8.8(34)
C(3)	0.059(3)	0.231(3)	0.346(2)	12.2(17)

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

Results and Discussion

Crystal Structure. The fractional coordinates and isotropic thermal parameters for non-hydrogen atoms are listed in Table 1.[9] The stereoscopic drawing viewed along $\boldsymbol{a}$ and the (001) projection with the atom numbering scheme of the structure are shown in Figs. 1 and 2, respectively.[10] Selected interatomic distances and angles are given in Table 2.

The crystal consists of octahedral anions $[TeI_6]^{2-}$, cation group Me_4N^+ and iodine molecules. The large unit cell as well as the large Z number causes the structure to appear much complicated. However, the principle of the structure is rather simple and adequately described in terms of the K_2PtCl_6 structure, when the tetragonal deformation arising from the inclusion of dumbbell like I_2 molecules and also slight displacements of all constituents are neglected. As shown in Fig. 2, the tetragonal subcell with $\boldsymbol{a}_s=(\boldsymbol{a}+\boldsymbol{b})/2$(=14.39 Å), $c_s=c/2$ (=13.79 Å) and Z_s=4 is closely related to the antifluorite structure. Octahedral $[TeI_6]^{2-}$

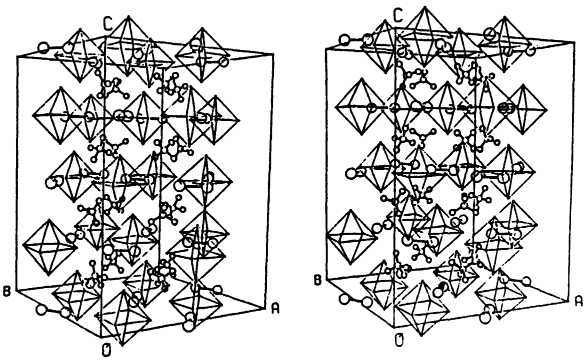

Fig. 1. The *ORTEP* drawing of the structure. Only one of two configurations for each disordered $[(Me)_4N]^+$ cation is given for simplicity.

Table 2. Interatomic Distances (l/Å) and Angles (ϕ/°)

(a) $[TeI_6]^{2-}$ anion

Te–I(1)	2.933(2)	I(1)–Te–I(2)	88.07(9),	91.09(9)
Te–I(2)	3.017(2)	I(1)–Te–I(3)	89.47(8).	91.32(8)
Te–I(3)	2.857(2)	I(2)–Te–I(2)	86.21(8)	
		I(2)–Te–I(3)	90.07(5),	175.50(7)

I(1)···I(4) 4.085(3), 4.376(3)
I(2)···I(4) 3.261(2)
I(3)···I(4) 4.132(2), 4.172(2)

(b) $[(CH_3)_4N]^+$ cation (mean values)
(i) N(1)–C(1) 1.43(6) C(1)–N(1)–C(1) 109(3)
(ii) configuration A: N(2)–C(21′), C(21″), C(22), C(24‴)
N(2)–C(2) 1.41(3) C(2)–N(2)–C(2) 108(2)
configuration B: N(2)–C(22‴), C(23′), C(23″), C(24)
N(2)–C(2) 1.47(5) C(2)–N(2)–C(2) 110(3)
(iii) N(3)–C(3) 1.49(3) C(3)–N(3)–C(3) 109(1)

symmetry code: none, (x, y, z); (′), (x, $-y$, $1/2-z$);
(″), ($1/4-y$, $3/4+x$, $1/4+z$); (‴), ($1/4+y$, $3/4+z$, $3/4-z$).

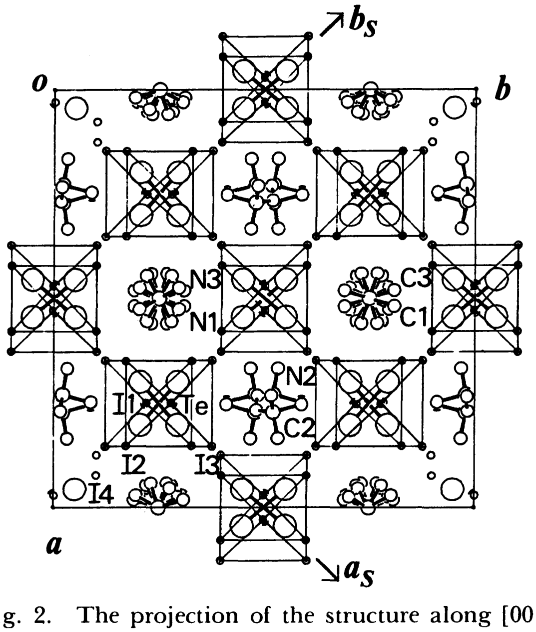

Fig. 2. The projection of the structure along [001] with the atom numbering scheme. Only one orientation for each disordered cation is shown. Atom symbols, for example, I1 denotes I(11) and C2 represents C(21), C(22) and C(24) as listed in Tables 1 and 2.

anions form a tetragonally deformed, face-centered lattice and Me_4N^+ cations occupy the eight tetrahedral holes. The subcell further contains I_2 molecules aligned parallel to a_s or b_s axis at the interstitial sites of twelve edge-centers (1/2, 0, 0) etc. and one body-center (1/2, 1/2, 1/2). Thus, the iodine molecule bridges adjacent complex anions.

Each Te^{IV} atom is coordinated octahedrally by six iodine atoms with Te–I distances of 2.933(2), 3.017(2), and 2.857(2) Å. The average value 2.94 Å is close to the typical one of 2.952(2) Å found in $(Me_3NH)_2TeI_6$.[4] The individual Te–I distances, however, are significantly different from one another, reflecting a variety of interactions with the surroundings. The arrangement of six iodine molecules around a central TeI_6 octahedron is illustrated in Fig. 3. The Te–I(2) bond is parallel to the axis of the neighboring I_2 molecule, while the other two Te–I(1) and Te–I(3) bonds are perpendicular to them. The axial I(1) atom is surrounded by two I(4) atoms with distances of 4.085(3) and 4.376(3) Å. The equatorial I(2) is close to only one I(4) atom with the shortest intermolecular I···I distance 3.261(2) Å, this being much shorter than the corresponding one (3.57 Å) in iodine crystal.[11] The remaining equatorial I(3) has also two I(4) neighbors at distances of 4.132(2) and 4.172(2) Å. A comparison of these I···I separations with the van der Waals contact 4.3 Å suggests that a remarkable interaction such as charge transfer occurs between I(2) and I(4). For this reason the Te–I(2) distance is lengthened than the normal 2.95 Å and consequently the Te–(3) bond may be shortened by some trans effect.

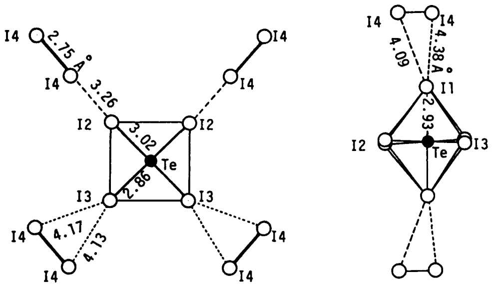

Fig. 3. The arrangement of six I_2 molecules around a central TeI_6 octahedron, (a) viewed along *c*, and (b) viewed along *b* (=*a*).

On the other hand, the intramolecular I–I length 2.748(3) Å is longer than 2.68 Å found in solid iodine. All these facts indicate that the intermolecular I···I interaction is fairly strong in the octaiodo complex relative to iodine crystals. The present X-ray analysis showed that excess iodine atoms are included as iodine molecules in contrast to $(Me_3NH)_2TeI_7$ complex where excess iodine atoms are held together as infinite linear chains.[4] To the best of our knowledge the present complex is the first example for inclusion of iodine molecules in the series of hexaiodometallate(IV) complexes.

There are three kinds of Me_4N^+ cations which are denoted by their central nitrogen atoms in Fig. 2. The N(1), N(2), and N(3) atoms are located at **8b**(222), **16f**(2), and **8a**(4) positions of *I*4$_1$/*acd*, respectively. The cation of N(3) is ordered, whereas those of N(1) and N(2) are orientationally disordered and distributed over each two configurations with the equal probability 0.5. Thus, the occupancy factors of their methyl carbons are 1 for C(3) and 0.5 for the other six from C(11) to C(24). Although the positional parameters of such disordered methyl carbons are less reliable than the ordered ones, the assigned geometry for each cation group appears to be reasonable. The mean C–N distances and the mean C–N–C bond angles around N(1), N(2), and N(3) are 1.43, 1.45, 1.49 Å and 109, 109, 112°, respectively, in agreement with 1.47 Å and the tetrahedral angle in the literature.

Phase Transition. The DTA and NMR results showed that the crystal undergoes a phase transition at 234 K, like some other members of the family. The transition enthalpy was determined approximately to be 2.4 kJ mol^{-1} from DSC. Recently, Matsuo et al. reported the transition enthalpy 1.78 kJ mol^{-1} for $(CH_3NH_3)_2SnCl_6$,[12] where no structural change was disclosed except for slight discontinuities in some lattice parameters.[13] Accordingly, the structural change caused by the transition would not be so much in the octaiodo complex also.

Dynamic Behavior of Me_4N^+ Cation Groups. The ^1H NMR spectra at the lowest temperatures of measurement showed a fine structure characteristic of the static array of nuclei, and it remained fairly well

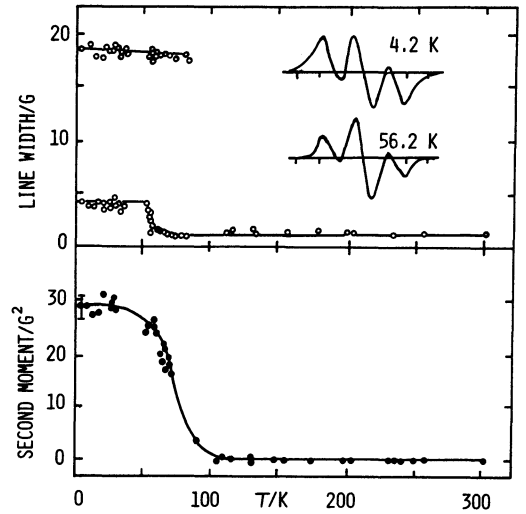

Fig. 4. The temperature dependences of ^{1}H NMR line width and second moment observed for $[(CH_3)_4N]_2TeI_8$.

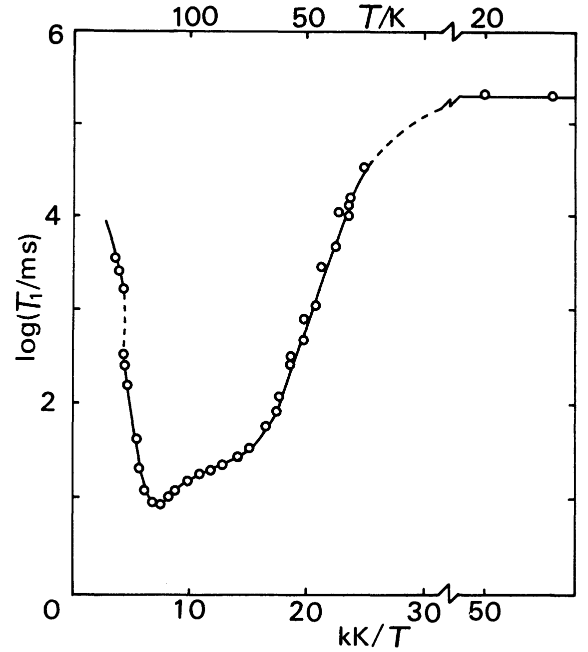

Fig. 5. The temperature variation of proton T_1 measured at 10.5 MHz for $[(CH_3)_4N]_2TeI_8$.

up to about 50 K. The line width δH_{msl} measured on the absorption derivative and the observed second moment M_2 are plotted against temperature in Fig. 4. From liquid helium temperature to 30 K δH_{msl} were 18.4 ± 0.1(outer) and 4.0 ± 0.1 G(inner), and M_2 was $29 \pm 2\,G^2$, these being close to the rigid lattice values expected for Me_4N^+ cations.[14] The spectrum was narrowed strongly between 50 and 100 K, above which the line width and the second moment were again constant at 1.5 ± 0.1 G and 0.5 ± 0.1 G^2, respectively. The M_2 values for various dynamic models of Me_4N^+ cations were calculated in the usual manner based on Van Vleck formula: $M_2 = 30$ G^2 for the rigid lattice; $M_2 = 9$ G^2 for the threefold reorientation of all CH_3 groups; $M_2 = 0.5$ G^2 for the isotropic reorientation of whole cations. In these calculations, the geometry of the cation was taken to be tetrahedral 109°28′ for all the bond angles, 1.47 Å for the C–N bond length and 1.10 Å for the C–H length in all-staggered conformation.[15] A comparison of these calculated values with the experimental ones indicates that all the Me_4N^+ cations reorient rapidly and isotropically far below room temperatures. As seen in Fig. 4, the narrowing process occurs in only a single step, suggesting the three fold reorientation of methyl groups consecutively followed by the overall reorientation of the cations itself.

The spin-lattice relaxation times are plotted in Fig. 5 against reciprocal temperatures. As described previously, the T_1 value changed discontinuously by one order of magnitude at 234 K, indicating the presence of a phase transition which was confirmed by thermal analyses. The T_1 vs. T^{-1} curve exhibits a deep and very broad minimum with a value of 8.5 ms at 133 K. The appearance of a shoulder on the low temperature side of the T_1 minimum may be due to reorientation of methyl groups. However, the T_1 value of the shoulder is longer than that of T_1 minimum in contrast with the usual behavior of methylammonium groups.[16] It is therefore supposed that three or more nonequivalent Me_4N^+ cations set in motion with slightly different motional parameters in the low temperature phase, causing the T_1 minimum to be shallow and consequently to be quite broad. Such a T_1 behavior seems too complicated to analyze, because of many unknown parameters included. Therefore, the activation energy for the threefold (C_3) reorientation of CH_3 groups was tentatively deduced from the positive slope ($\omega\tau_c \gg 1$) in the low temperature side of the T_1 minimum, while the value for the overall reorientation of whole cations from the negative slope ($\omega\tau_c \ll 1$): These are 6.3 and 14.2 kJ mol^{-1}, respectively. The similar T_1 minima were observed in analogous complexes of $(Me_4N)_2MX_6$ (M=Pt, Te, Sn, X=Cl, Br), and each shallow minimum in the low temperature side was successfully explained in terms of a small-angle reorientation of methyl groups of the cations.[17,18] It is not clear whether or not this is the case in the present complex, because of no sufficient evidence for it and also of unusual breadth of the T_1 minimum in comparison with those for the other analogues.

Above T_{tr} (234K), the negative slope of the T_1 curve gives the activation energy 5.4 kJ mol^{-1} for the composite reorientation of cations, which is much smaller than the corresponding value 14.2 kJ mol^{-1} below T_{tr}, reflecting more loose packing in the high temperature phase. This finding together with the discontinuity of T_1 at T_{tr} suggests that the reorientational motion of the cations is associated with the phase transition more or less.

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