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A Reinvestigation of the Crystal Structure of Diammonium Hexachlorotellurate(IV), $(NH_4)_2TeCl_6$

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The crystal structure of diammonium hexachlorotellurate(IV) has been reexamined by a three dimensional X-ray analysis. The work confirms that the compound has the K_2PtCl_6 structure. The $TeCl_6^{2-}$ ion is a regular octahedron with the Te—Cl bond distance (after correction for thermal vibration) 2.541 Å with standard deviation 0.007 Å.

Gillespie and Nyholm [1] have predicted that hexacoordinated complexes of Te(IV) should have a distorted structure based on seven coordination with a lone pair of electrons occupying the seventh position. However, all structures of this type which have been studied, *e. g.* $(NH_4)_2TeCl_6$,[2] $(C_5H_5NH)_2TeCl_6$,[3] K_2TeBr_6,[4] indicate that such complexes are regular octahedra.

The supposed uronium pentachlorotellurate(IV), $CON_2H_5TeCl_5$ reported by Aynsley and Cambell [5] and to which a random structure of square pyramidal $TeCl_5^-$ ions was assigned by Aynsley and Hazell was later shown [6] to be diammonium hexachlorotellurate(IV). The structure has now been refined, with the correct chemical formulation, to determine the Te—Cl bond length and to see if there is any evidence for distortion of the octahedron.

EXPERIMENTAL AND CRYSTAL DATA

The compound crystallised from HCl as pale yellow octahedra; examination with the polarising microscope showed the crystals to be isotropic. Single crystal X-ray investigation using the oscillation and Weissenberg techniques, and powder photographs with a 19 cm Bradley-Jay camera showed the compound to be cubic with $a = 10.200 \pm 0.005$ Å and with space group $Fm3m$ (O_h^5, No. 225). The lattice dimensions were obtained from the powder photograph using the Nelson-Riley [7] extrapolation method. Cu$K\alpha$ radiation was used.

Three dimensional intensity data were obtained from Weissenberg photographs by the multiple film technique using Cu$K\alpha$ radiation and were estimated visually using a calibration strip, the crystal being mounted about the 100 axis. To obtain a scale factor between the two classes of reflections, *i. e.* those with h, k, and l all even or all odd, a further photograph was taken about the 110 axis. An octahedral crystal of thickness

approximately 0.22 mm was used; since $\mu r = 3.8$ where μ is the linear absorption coefficient, which is 345 cm^{-1} for Cu$K\alpha$ radiation, the intensities were corrected for absorption. Absorption corrections were made by treating the crystals as spherical and using the values tabulated in Vol. III of *International Tables for X-ray Crystallography*.[8]

Chemical analyses were carried out on some of Aynsley's sample, *i. e.* that used for the X-ray work, and on a sample of diammonium hexachlorotellurate(IV) prepared in this laboratory. Aynsley's sample: Found C 0.2; H 2.3; O 0.3; Cl 56.1. $(NH_4)_2TeCl_6$: Found: C 0.3; H 2.3; O 0.3; Cl 56.0. Calc. for $(NH_4)_2TeCl_6$: C 0.0; H 2.1; O 0.0; Cl 56.6; calc. for $CON_2H_5TeCl_5$: C 3.3; H 1.4; O 4.4; Cl 48.5. The analysis on which Aynsley and Cambell [5] based their chemical formulation was: Found: Te 34.9; Cl 47.9; N 7.7.

The compound is thus diammonium hexachlorotellurate(IV) and not uronium pentachlorotellurate(IV).

REFINEMENT

The compound has the K_2PtCl_6 structure with Te at (0,0,0), Cl at (0,0,z) where $z \sim \frac{1}{4}$, and NH_4^+ at ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$). Anisotropic refinement using Grønbæk's block-diagonal least squares programme reduced the R-factor to 0.075 as com-

Table 1. Atomic coordinates and their standard deviations (in Å).

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
Te	0.0	0	0.0	0	0	0
Cl	0.0	0	0.0	0	2.5279	0.0070
N	2.55	0	2.55	0	2.55	0

Table 2. Observed and calculated thermal parameters with the standard deviations of the observed values (in Å^2), only the diagonal elements are given as the off-diagonal terms are zero.

Observed

	u_{11}	$\sigma(u_{11})$	u_{22}	$\sigma(u_{22})$	u_{33}	$\sigma(u_{33})$
Te	0.0632	0.0027	0.0632	0.0027	0.0632	0.0027
Cl	0.0980	0.0025	0.0980	0.0025	0.0594	0.0028
N	0.0804	0.0034	0.0804	0.0034	0.0084	0.0034

Calculated

	u_{11}	u_{22}	u_{33}
Te	0.0608	0.0608	0.0608
Cl	0.0980	0.0980	0.0608
N	—	—	—

pared with $R = 0.12$ when attempting to refine the structure as $CON_2H_5TeCl_5$. The final value of R' was 0.007 where $R' = \sum w(|F_o| - k|F_c|)^2/\sum w|F_o|^2$ and the weighting factor, w, was $1/(|F_o| + 0.03\ F_o^2)$. The atomic scattering factors used were those of *International Tables* [9] approximated by Bassi polynomials [10] calculated from the values of the scattering factor at $\sin\theta/\lambda = 0.1, 0.2, 0.3, 0.5,$ and 0.7. The scattering factor for Te was corrected for the real part of the anomalous scattering correction, $\Delta f' = -1.0$e.[11]

The final three-dimensional map showed no peak greater than 2 e $Å^{-3}$ which was at the tellurium position. There were no peaks greater than 0.5 e $Å^{-3}$ in the neighbourhood of the chlorine atom positions, so there was no evidence for any disordering of the $TeCl_6^{2-}$ ion as might be expected if there was a disordered arrangement of distorted octahedra. From space group considerations the hydrogen atoms should lie on the 3-fold axes; there are two possible ways of orienting the ammonium ion to fulfil this condition, both of which are equally good with regard to packing. The difference map showed peaks of 0.5 e $Å^{-3}$ at each possible hydrogen position but it is doubtful if any significance can be attached to this. An attempt at refining with Webb's [12] scattering curve for a rotating ammonium ion was not successful and gave a negative temperature factor for the ammonium ion.

The final coordinates and thermal parameters are shown in Tables 1 and 2. A comparison of the observed and calculated structure factors is given in Table 3.

THERMAL VIBRATION ANALYSIS

Assuming that the $TeCl_6^{2-}$ ion could be treated as a rigid body Cruickshank's [13] method was used to calculate the molecular librations and vibrations from the individual atomic vibrations. Since the ion has symmetry mmm and the principal axes of the translational, T_{ij}, and vibrational, ω_{ij}, tensors coincided with the crystal axes then $T_{11} = T_{22} = T_{33}$ and $\omega_{11} = \omega_{22} = \omega_{33}$, all the off-diagonal elements being exactly zero. The values obtained were $T_{11} = 0.0608$ Å and $\omega_{11} = 3.3$ deg^2. The u_{ij} calculated from these were in good agreement with the observed values (Table 2) showing that in this case the rigid body approximation is a good one.

As ω_{ij} is isotropic Cruickshank's simplified formula [14] could be used to obtain the correction to be applied to the Te—Cl bond distance. The correction is 0.0127 Å increasing the bond length from 2.528 Å to 2.541 Å.

DISCUSSION

In agreement with earlier X-ray studies and in contradiction to the predictions of Gillespie and Nyholm the $TeCl_6^{2-}$ has been found to be a regular octahedron. The Te—Cl bond length 2.541 s.d. 0.007 Å is similar to that found in other $TeCl_6^{2-}$ compounds.

Table 3.

h k l	F_o	F_c	*h k l*	F_o	F_c
2 0 0	262	245	6 6 6	12	4
4 0 0	418	390	8 6 6	18	17
6 0 0	101	105			
8 0 0	118	136	8 8 6	18	16
10 0 0	28	29			
12 0 0	37	36	1 1 1	229	191
			3 1 1	167	150
2 2 0	114	100	5 1 1	125	115
4 2 0	158	169	7 1 1	70	69
6 2 0	53	53	9 1 1	51	46
8 2 0	82	76	11 1 1	24	21
10 2 0	18	17	13 1 1	12	13
12 2 0	27	24			
			3 3 1	127	123
4 4 0	248	259	5 3 1	99	96
6 4 0	76	82	7 3 1	53	59
8 4 0	102	102	9 3 1	45	40
10 4 0	25	24	11 3 1	20	19
12 4 0	30	28			
			5 5 1	69	77
6 6 0	28	31	7 5 1	46	48
8 6 0	36	41	9 5 1	33	32
10 6 0	11	11	11 5 1	16	15
			7 7 1	30	31
8 8 0	44	45	9 7 1	22	21
10 8 0	15	13	11 7 1	10	10
2 2 2	148	143			
4 2 2	77	86	9 9 1	15	14
6 2 2	30	38			
8 2 2	45	49	3 3 3	106	102
12 2 2	23	19	5 3 3	83	82
			7 3 3	52	51
4 4 2	124	125	9 3 3	34	35
6 4 2	48	46	11 3 3	17	16
8 4 2	65	59			
10 4 2	17	15	5 5 3	62	65
12 4 2	22	19	7 5 3	41	41
			9 5 3	28	28
6 6 2	13	13	11 5 3	15	14
8 6 2	31	28			
			7 7 3	23	27
8 8 2	31	29	9 7 3	19	19
10 8 2	11	10			
			9 9 3	12	12
4 4 4	159	183			
6 4 4	63	65	5 5 5	48	52
8 4 4	69	77	7 5 5	29	34
10 4 4	23	19	9 5 5	21	23
			11 5 5	8	11
6 6 4	28	27			
8 6 4	33	33	7 7 5	26	22
10 6 4	9	9	9 7 5	17	15
8 8 4	35	35	7 7 7	16	15

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