Acta Cryst. (1981). B**37**, 650–652

Structure of Ammonium Sulfate Tellurate $Te(OH)_6.(NH_4)_2SO_4$

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(*Received* 22 *September* 1980; *accepted* 3 *December* 1980)

Abstract. $Te(OH)_6.(NH_4)_2SO_4$, monoclinic, *Cc*, $a = 13·741$ (8), $b = 6·631$ (2), $c = 11·405$ (7) Å, $\beta = 106·75$ (5)°, $V = 995$ (2) Å^3, $Z = 4$, $D_x = 2·415$ Mg m^{-3}. The structure has been determined using the Patterson method and refined to an *R* value of 0·024 with 1035 independent reflections. The main feature of this structure is the presence of two different types of anions in the same crystal. An attempt to locate the protons of the OH groups has been made.

Introduction. Pursuing our study of sulfate tellurate salts, among which we have solved $Te(OH)_6.Na_2SO_4$ (Zilber, Tordjman & Guitel, 1980) and $Te(OH)_6.K_2SO_4$ (Zilber, Durif & Averbuch-Pouchot, 1980), we have grown the title compound out of a solution into particularly well shaped transparent crystals. The chemical preparation and characteristic data are to be described elsewhere.

A piezoelectric test proved to be positive indicating the space group was non-centrosymmetric. A preliminary study using a Weissenberg camera led to the assumption that *Cc* (No. 9) was the correct space group. The crystal used was a small prism of approximate dimensions 0·13 × 0·11 × 0·12 mm. 1447 reflections were recorded on a Philips PW 1100 four-circle diffractometer having a graphite monochromator. The radiation used was that of a silver target (λAg $K\alpha = 0·5608$ Å). The angular range was taken between 3 and 28° (θ), the scan speed was 0·02 s^{-1} and the scan width 1·20°. The background was measured for 10 s at each edge of the scan range. An ω scan was used. The data were processed on a PDP 11 computer using the SDP system. Because of the small size of the crystal and the radiation used, no absorption correction was made. Nevertheless, a Lorentz–polarization correction was applied to the data.

The structure was solved using the heavy-atom method. A Patterson function allowed the positioning of the Te and the S atoms. A Fourier synthesis gave an *R* factor of about 0·40 and allowed the positioning of most of the O atoms. A few more least-squares refinement cycles gave the remaining O atoms. A difference-Fourier function gave one N atom leading to an *R* factor of 0·034. One more difference-Fourier function gave the second N atom bringing *R* down to the value of 0·026 ($R = \sum||F_o| - |F_c||/\sum|F_o|$). $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$ was 0·034. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = \sigma^{-2}(F_o)$ determined by counting statistics. The reflections used in the refinement had $F > 3\,\sigma(F)$.

Table 1. *Proton parameters* [*columns* (1), (2) *and* (3) *explained in the text*]

		(1)	(2)	(3)
H(1)	x	= 0·89	0·889 (8)	0·969 (124) Å
	y	= 0·51	0·527 (19)	
	z	= 0·09	0·128 (10)	
	B_{iso}	= 1·0 Å^2	0·4 (24) Å^2	
H(2)	x	= 0·65	0·615 (10)	1·509 (132)
	y	= 0·65	0·627 (22)	
	z	= 0·36	0·394 (12)	
	B_{iso}	= 1·0 Å^2	1·8 (31) Å^2	
H(3)	x	= 0·17	0·173 (10)	0·796 (159)
	y	= 0·23	0·207 (30)	
	z	= 0·17	0·161 (12)	
	B_{iso}	= 1·0 Å^2	2·0 (34) Å^2	
H(4)	x	= 0·12	0·120 (4)	0·422 (59)
	y	= 0·57	0·602 (9)	
	z	= 0·36	0·422 (5)	
	B_{iso}	= 1·0 Å^2	−0·8 (7) Å^2	
H(5)	x	= 0·22	0·329 (5)	0·817 (73)
	y	= 0·58	0·520 (12)	
	z	= 0·11	0·113 (6)	
	B_{iso}	= 1·0 Å^2	−1·3 (11) Å^2	
H(6)	x	= 0·36	0·313 (12)	0·581 (183)
	y	= 0·32	0·420 (27)	
	z	= 0·86	0·839 (14)	
	B_{iso}	= 1·0 Å^2	5·9 (45) Å^2	

In an attempt to locate the H atoms of the OH groups belonging to the Te octahedra we have applied the results of Brown & Shannon (1973) and of Donnay & Allmann (1970) concerning the bond strength. Assuming that (i) O—H···O is a linear bond, (ii) the average distance O—H is 0·95 Å and locating the H atoms on the shortest distances O(1*j*) — O(*k*), we found a set of six positions [Table 1, column (1)]. These values were introduced into the structure parameters and a few cycles of least-squares refinements were performed. The *R* factor decreased to a value of 0·024.

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* On leave from: Soreq Nuclear Research Centre, Yavne, Israel.

0567-7408/81/030650-03$01.00

Table 2. *Positional parameters with their estimated standard deviations and* B_{eq} *for* $Te(OH)_6.(NH_4)_2SO_4$

$$B_{\text{eq}} = \tfrac{4}{3}\textstyle\sum_i\sum_j \beta_{ij}\,\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq} (Å^2)
Te	$\frac{1}{4}$	0·2486 (6)	0	1·06
S	−0·0011 (5)	0·2405 (5)	0·2454 (5)	2·12
O(1)	0·9202 (5)	0·263 (2)	0·1160 (6)	2·15
O(2)	0·0867 (5)	0·375 (1)	0·2383 (6)	1·88
O(3)	0·0325 (6)	0·029 (1)	0·2528 (8)	2·50
O(4)	0·4566 (6)	0·195 (1)	0·8343 (7)	2·62
O(11)	0·3847 (5)	0·147 (1)	0·0785 (9)	2·79
O(12)	0·2139 (7)	−0·011 (1)	0·9286 (9)	3·43
O(13)	0·2180 (6)	0·159 (2)	0·1402 (8)	3·94
O(14)	0·1143 (5)	0·336 (1)	0·9248 (6)	1·84
O(15)	0·2703 (6)	0·483 (1)	0·1029 (8)	2·33
O(16)	0·3005 (6)	0·386 (1)	0·8786 (7)	2·54
N(1)	0·3980 (6)	0·237 (2)	0·4075 (7)	2·73
N(2)	0·6047 (6)	0·247 (3)	0·1517 (7)	2·54

Table 3. *Interatomic distances and angles*

The distances Te–O(1*j*) and S–O(*i*) in Å are underlined in the diagonals. Below the diagonals the angles O(1*j*)–Te–O(1*k*) and O(*i*)–S–O(*j*) are given in degrees and $\frac{1}{10}$°. Above the diagonals the distances O–O are given in Å. The estimated standard deviations are given in parentheses.

(*a*) TeO_6 octahedron

Te	O(11)	O(12)	O(13)	O(14)	O(15)	O(16)
O(11)	1·931 (7)	2·687 (11)	2·585 (13)	3·834 (9)	2·788 (12)	2·742 (12)
O(12)	88·8 (4)	1·911 (9)	2·650 (14)	2·673 (12)	3·798 (12)	3·010 (13)
O(13)	85·6 (4)	88·9 (4)	1·874 (10)	2·726 (11)	2·346 (14)	3·795 (13)
O(14)	177·0 (4)	89·0 (4)	92·4 (4)	1·904 (7)	2·677 (10)	2·777 (11)
O(15)	92·8 (4)	165·0 (4)	76·4 (4)	88·9 (3)	1·919 (9)	2·784 (13)
O(16)	90·1 (4)	102·7 (4)	167·6 (4)	92·4 (3)	92·2 (4)	1·944 (9)

(*b*) SO_4 tetrahedron

S	O(1)	O(2)	O(3)	O(4)
O(1)	1·565 (8)	2·427 (9)	2·416 (11)	2·410 (10)
O(2)	103·8 (5)	1·520 (10)	2·431 (11)	2·396 (12)
O(3)	105·3 (5)	108·6 (5)	1·473 (9)	2·419 (12)
O(4)	110·1 (6)	111·7 (6)	116·4 (6)	1·373 (11)

(*c*) Surroundings of the N atoms

N(1)–O(1^{iv})	2·309 (11)	N(2)–O(2^{iii})	2·700 (19)
N(1)–O(3^{iii})	3·486 (15)	N(2)–O(3^{iii})	2·540 (7)
N(1)–O(4^{ii})	3·156 (16)	N(2)–O(11^{i})	2·970 (11)
N(1)–O(11^{ii})	3·243 (16)	N(2)–O(13^{iii})	3·161 (20)
N(1)–O(12^{ii})	3·007 (15)	N(2)–O(14^{iv})	3·128 (12)
N(1)–O(13^{i})	3·367 (11)	N(2)–O(15^{iii})	3·049 (16)
N(1)–O(14^{iv})	2·962 (12)	N(2)–O(16^{iv})	2·271 (11)
N(1)–O(16^{ii})	2·813 (16)		

Symmetry code

The Arabic numbers correspond to crystallographically independent atoms. The Roman numbers correspond to the following positions: (i) x,y,z; (ii) $x, \bar{y}, \frac{1}{2}+z$; (iii) $\frac{1}{2}+x, \frac{1}{2}+y, z$; (iv) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$.

The refined parameters appear in Table 1, column (2). Some isotropic factors still remained with negative but small values. The distances O(1*s*)–H(*s*) were also shifted from the assigned value of 0·95 Å, sometimes in a relevant way [Table 1, column (3)].

Nevertheless, we infer that the H atoms are actually located at the refined positions, but the quadratic approximation used for thermal-factor calculations might be insufficient to determine the position of the protons more accurately, especially taking into account the presence of such a heavy atom as tellurium.

Table 2 gives the positional and B_{eq} parameters with their estimated standard deviations for all atoms except H and Table 3 the main interatomic distances and bond angles.*

Discussion. Fig. 1 shows a projection on plane *ac* of $Te(OH)_6.(NH_4)_2SO_4$. A projection on the plane *bc* is

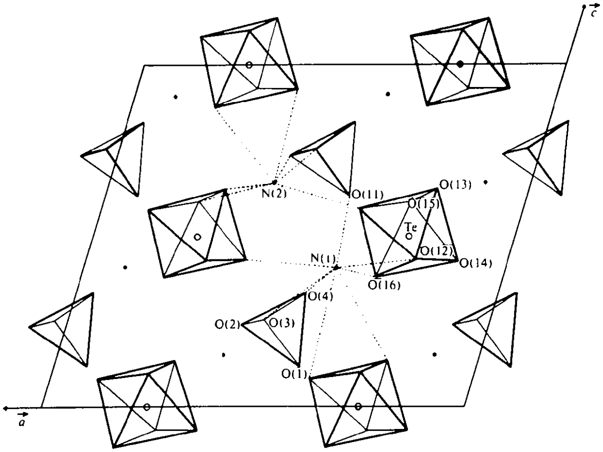

Fig. 1. Projection of $Te(OH)_6.(NH_4)_2SO_4$ on the *ac* plane, along the *b* axis.

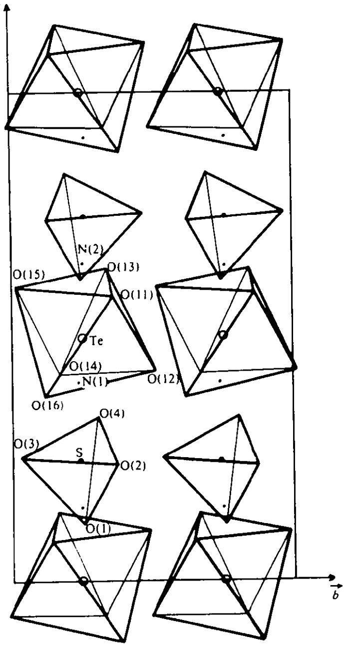

Fig. 2. Projection of $Te(OH)_6.(NH_4)_2SO_4$ on the *bc* plane, along the *a* axis.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35844 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

depicted in Fig. 2. The main feature of this structure is the presence of two different types of anions in the crystal. The structure can be regarded as being built of planes of pure TeO_6 octahedra alternating with planes of pure SO_4 tetrahedra, both families being parallel to the *ab* plane. The same observation holds when the polyhedra are viewed in a direction parallel to the plane *ac*. Also in a direction parallel to the plane *ac* we observe parallel layers, each of them containing both kinds of polyhedra.

An interesting point is, that compared with the already known sulfate tellurate structures, the Te octahedra here are distorted with angles such as O(12)—Te—O(15) = 165·0° and O(13)—Te—O(15) = 76·4°.

The N atoms are distributed on two sites. In one of them the N atom is coordinated by three O atoms belonging to S tetrahedra and five O atoms belonging to Te octahedra. In the second site only four O atoms belonging to Te octahedra participate in the coordination reducing the coordination number of this N atom to seven.

References

Brown, I. D. & Shannon, R. D. (1973). *Acta Cryst.* A**29**, 266–282.

Donnay, G. & Allmann, R. (1970). *Am. Mineral.* **55**, 1003–1015.

Zilber, R., Durif, A. & Averbuch-Pouchot, M. T. (1980). *Acta Cryst.* B**36**, 2743–2745.

Zilber, R., Tordjman, I. & Guitel, J. C. (1980). *Acta Cryst.* B**36**, 2741–2743.

Acta Cryst. (1981). B**37**, 652–654

Structure de l'Hexachlorure de Cadmium et Dimagnesium Dodécahydraté

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(*Reçu le* 2 *juin* 1980, *accepté le* 6 *novembre* 1980)

Abstract. $CdMg_2Cl_6.12H_2O$, hexagonal, $P31c$, a = 9·9809 (9), c = 11·5560 (9) Å, Z = 2, d_m = 1·967 (2), d_c = 1·965 Mg m^{-3}. The structure was refined by least-squares calculations to a final R of 0·030 (R_w = 0·034) for 1292 independent reflexions. The crystal structure consists of $CdCl_6$ and $Mg(H_2O)_6$ octahedra linked by hydrogen bonds. Approximate positions for the H atoms in the four water molecules are proposed.

Introduction. Dans le cadre des travaux effectués au laboratoire sur les sels hydratés nous avons entrepris les déterminations de structures d'hydrates des chlorures mixtes de cadmium et magnésium.

Les cristaux de formule $CdMg_2Cl_6.12H_2O$ (Bassett & Strain, 1952) ont été obtenus par évaporation à température ordinaire d'une solution aqueuse contenant du chlorure de cadmium et du chlorure de magnésium dans le rapport de 1 à 2 mol. Très hygroscopiques et assez isométriques les cristaux de symétrie trigonale présentent les monoèdres (00.1) et $(00.\bar{1})$ bien développés accompagnés des pyramides {10.2} et $\{10.\bar{2}\}$. Le prisme hexagonal {10.0} est moins développé. Les pyramides {10.1} et $\{10.\bar{1}\}$ ainsi que les prismes trigonaux {11.0} et $\{\bar{1}\bar{1}.0\}$ sont peu développés. Les notations que nous employons sont relatives aux données cristallographiques de *l'Abstract.*

Un cristal légèrement allongé suivant c a été scellé dans un tube capillaire en verre de Lindemann contenant de l'huile de paraffine. D'une longueur de 0,22 mm il présente un prisme hexagonal de 0,17 mm de section moyenne.

L'enregistrement du spectre de diffraction a été effectué sur un diffractomètre CAD-4 Enraf–Nonius avec le rayonnement $K\bar{\alpha}$ du molybdène (λ = 0,71069 Å) isolé par un monochromateur à lame de graphite. Les paramètres de la maille ont été obtenus avec un affinement par moindres carrés de 25 réflexions choisies dans l'espace réciproque.

Les mesures des intensités ont été réalisées jusqu'à l'angle de Bragg θ = 40° avec un balayage ω–2θ d'amplitude $(1{,}10 + 0{,}35\ \mathrm{tg}\theta)°$ et une ouverture de compteur $(3{,}00 + 0{,}80\ \mathrm{tg}\theta)$ mm. Les réflexions ayant un $\sigma(I)/I > 0{,}018$ ont été mesurées à nouveau avec une vitesse de balayage ajustée de façon à avoir ou à approcher $\sigma(I)/I < 0{,}018$ pour un temps de mesure limité à 60 s. Le fond continu a été déterminé en augmentant l'intervalle de balayage de 25% de part et d'autre de la réflexion. La mesure de trois réflexions de

0567-7408/81/030652-03$01.00