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Acta Cryst. (1985). C**41**, 1152–1154

Structure of Cadmium Tellurate(IV), $CdTeO_3$

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(*Received 5 November* 1984; *accepted* 19 *April* 1985)

Abstract. $M_r = 288·0$, monoclinic, $P2_1/c$, $a = 7·790$ (1), $b = 11·253$ (2), $c = 7·418$ (1) Å, $\beta = 113·5$ (1)°, $V = 596·5$ Å^3, $Z = 8$, $D_m = 6·41$ (1), $D_x = 6·41$ g cm^{-3}, λ(Ag $K\alpha$) = 0·56083 Å, $\mu = 80·3$ cm^{-1}, $F(000) = 992$, room temperature; final $R = 0·034$ for 3231 independent observed reflections. The structure consists of isolated slightly distorted trigonal TeO_3 pyramids (mean Te—O distance 1·89 Å) which are connected by Cd atoms; the resulting Cd—O coordination polyhedra are a trigonal prism [Cd—O 2·197 (6)–2·476 (6) Å] and an octahedron [Cd—O 2·284 (6)–2·365 (6) Å] both being rather distorted.

Introduction. Many tellurites of the type MTeO$_3$ (M: alkaline earths, Ni, Zn, Cd, Hg, Pb, *etc.*) have been extensively studied because of their promising nonlinear optical properties (Bergman, Boyd & Ashkin, 1969). Contrary to tellurites with small metal ions (Hanke, 1967; Kohn, Inoue, Horie & Akimoto, 1976) or large ones like Sr^{2+}, Ba^{2+}, Pb^{2+} (Burckhardt, Koçak, Külcü & Trömel, 1984; Folger, 1975; Young, 1979), there is a lack of knowledge concerning the structure of tellurites with medium-sized ions like Cd^{2+} (Hanke, 1983). Some other reasons for a structure determination of $CdTeO_3$ and $HgTeO_3$ were given in a previous paper (Brandt & Moritz, 1985) where both compounds were regarded as constituents of native oxide films on (Cd,Hg)Te semiconductor material; moreover, structural details are needed for the interpretation of their XPS spectra (Seelmann-Eggebert, Brandt & Richter, 1984).

Markovskii & Pron (1968) first prepared $CdTeO_3$ by precipitation and reported a cubic structure as well as a hexagonal modification above 770 K. Robertson, Shaw & Young (1978), when studying the system CdO–TeO_2, did not find the cubic phase, but two monoclinic phases with an irreversible phase transition from α- into β-$CdTeO_3$ at about 973 K. Comparison of the d values indicates that the α-phase of Robertson *et al.* (1978) is probably identical to the 'hexagonal' phase of Markovskii & Pron (1968). In addition, Wrobsewska, Erb, Dobrowolski & Freundlich (1979) gave lattice parameters of two $CdTeO_3$ modifications quite different from those of the former investigators.

In order to obtain an insight into the polymorphism of $CdTeO_3$, preliminary annealing and quenching experiments as well as DTA studies of mixtures of CdO and TeO_2 near the 1:1 composition were performed which confirmed the melting point of $CdTeO_3$ at 1068 K, but no indications of a phase transition between room and melting temperature could be encountered. SHG measurements showed no positive signals which is in accordance with the given space group. The lattice parameters correspond roughly to those of the β-phase of Robertson *et al.* (1978).

In this paper we present the structure of $CdTeO_3$; the structure of $HgTeO_3$ will be reported later.

Experimental. From a colourless Czochralski-grown crystal a single crystalline fragment (100 × 200 × 500 μm) was obtained. Automatic four-circle diffractometer (Enraf–Nonius CAD-4), graphite-mono-

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chromatized Ag $K\alpha$ radiation, lattice parameters from refinement of 20 reflections, reflection conditions $h0l$: $l = 2n$, $0k0$: $k = 2n$, scan width 1·2°, ω–2θ scan mode, $2\theta < 60°$, h 0 to 13, k 0 to 20, l −13 to +13; *SHELX*76 (Sheldrick, 1976) and *XRAY*76 systems (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976); two standard reflections; no significant variation; 6910 total reflections, 3526 independent, 3231 with $I > 3\sigma(I)$, $R_{\text{int}} = 0·047$ (2982 contributors); corrections for Lorentz–polarization, absorption (A^* 2·036 to 6·031), and extinction effects ($g = 4·8 \times 10^{-5}$). A starting set of heavy atoms was selected from an E map calculated with direct methods (*SHELX*76); remaining atoms from successive Fourier syntheses; $\sum w(\Delta F^2)$ minimized, unit weights. Refinement of positional and anisotropic thermal parameters resulted in a final $R = 0·034$;† $(\Delta/\sigma)_{\max} = 6·4 \times 10^{-5}$, $(\Delta/\sigma)_{\text{av}} = 1·4 \times 10^{-5}$; $(\Delta\rho)_{\max} = +4·0$, $(\Delta\rho)_{\min} = -5·3$ e Å^{-3}; scattering factors of neutral atoms used and corrected for anomalous dispersion.

Discussion. Atomic coordinates are listed in Table 1, bond lengths in Table 2. A view of the structure is displayed in Fig. 1. All atoms occupy general positions. Te(1) and Te(2) form with their oxygen neighbours slightly distorted trigonal TeO_3 pyramids with mean Te—O distances of 1·89 Å; the TeO_3 pyramids are mutually isolated and linked by the Cd atoms. Both Cd atoms exhibit a sixfold coordination by O atoms; Cd(1) forms a distorted trigonal prism and Cd(2) forms a distorted octahedron as shown in Fig. 2; the Cd(1)—O distances range from 2·197 (6) to 2·476 (6), the Cd(2)—O distances from 2·284 (6) to 2·365 (6) Å. The rather short Cd(1)—O(5) distance of 2·197 (6) Å of the Cd(1)O_6 prism represents a crystal-chemical peculiarity of some Cd—O compounds as described *e.g.* for $Cd_3(AsO_4)_2$ (Engel & Klee, 1970), Cd_2SiO_4 (Mehrotra, Hahn, Eysel, Röpke & Illguth, 1978), and Cd_3TeO_6 (Burckhardt, Platte & Trömel, 1982). However, in these compounds two opposite Cd—O distances of a distorted octahedron are contracted to about 2·20 Å.

The authors express their gratitude to Dr D. S. Robertson (RSRE, Great Malvern, Worcestershire, England) for supplying the crystal sample as well as to Dr E. Keller for the intensity collection and *SCHAKAL* plots. Numerical calculations were performed on the Sperry 1100 computer of the Rechenzentrum der Universität Freiburg.

Table 1. *Fractional atomic coordinates* (×10^4) *and equivalent isotropic thermal parameters* (×10^2) *with e.s.d.'s in parentheses*

$$U_{\text{eq}} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}(Å^2)
Cd(1)	2699 (1)	89 (1)	3096 (1)	1·08 (2)
Cd(2)	42 (1)	2327 (1)	9750 (1)	0·95 (2)
Te(1)	5056 (1)	2555 (1)	1206 (1)	0·94 (1)
Te(2)	8328 (1)	8 (1)	2386 (1)	0·79 (1)
O(1)	9536 (7)	4096 (5)	1145 (8)	1·3 (2)
O(2)	2996 (8)	3199 (6)	1550 (10)	1·9 (2)
O(3)	9918 (8)	1303 (5)	2368 (8)	1·2 (2)
O(4)	6996 (7)	3311 (5)	3296 (8)	1·3 (2)
O(5)	5128 (8)	1270 (5)	4409 (8)	1·5 (2)
O(6)	1960 (8)	4249 (5)	4958 (7)	1·3 (2)

Table 2. *Bond distances* (Å) *with standard deviations in parentheses*

Cd(1)—O(5)	2·197 (6)	Cd(2)—O(6)	2·284 (6)
O(6)	2·288 (6)	O(3)	2·293 (6)
O(4)	2·307 (6)	O(4)	2·296 (5)
O(1)	2·319 (6)	O(3′)	2·318 (6)
O(3)	2·433 (6)	O(1)	2·349 (6)
O(5′)	2·476 (6)	O(2)	2·365 (6)
Te(1)—O(2)	1·869 (7)	Te(2)—O(6)	1·869 (6)
O(4)	1·882 (5)	O(1)	1·888 (5)
O(5)	1·894 (6)	O(3)	1·916 (6)

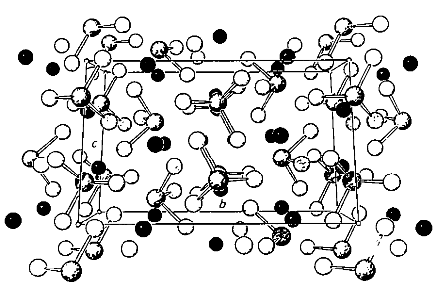

Fig. 1. View of the unit cell along [100] with surrounding atoms showing TeO_3 pyramids and Cd atoms (black) as drawn with *SCHAKAL* (Keller, 1980).

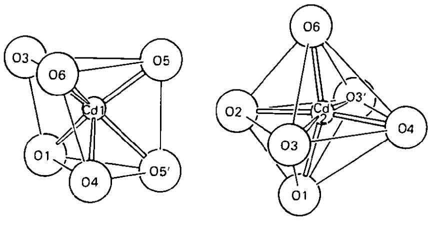

Fig. 2. The oxygen coordination of Cd(1) and Cd(2) (*SCHAKAL*, Keller, 1980).

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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 42179 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1985). C**41**, 1154–1157

Structure du Tétrachlorure de Baryum et de Cadmium Tétrahydraté, $BaCdCl_4.4H_2O$

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(*Reçu le* 15 *novembre* 1984, *accepté le* 26 *avril* 1985)

Abstract. $M_r = 463{\cdot}59$, $P\bar{1}$, $a = 8{\cdot}9938\,(6)$, $b = 8{\cdot}7475\,(9)$, $c = 6{\cdot}9028\,(6)$ Å, $\alpha = 98{\cdot}634\,(8)$, $\beta = 102{\cdot}316\,(7)$, $\gamma = 98{\cdot}919\,(7)°$, $V = 514{\cdot}63$ Å^3, $Z = 2$, $D_x = 2{\cdot}986$ Mg m^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0{\cdot}71069$ Å, $\mu = 6{\cdot}95$ mm^{-1}, $F(000) = 424$, $T = 293$ K, $R = 0{\cdot}019$ for 4675 reflections with $I \geq 3\sigma(I)$. The Cd atom is octahedrally coordinated to six Cl atoms. The Ba atom is surrounded by five Cl atoms and four O atoms (from water molecules) located at the vertices of a monocapped Archimedean antiprism. Edge-sharing $CdCl_6$ octahedra and $BaCl_5(H_2O)_4$ form endless ribbons along the [001] direction. The ribbons are connected by Cl—Cl edges belonging to two $BaCl_5(H_2O)_4$ so that they form puckered layers parallel to the (100) plane. Layers are held together by hydrogen bonds.

Introduction. Les chlorures doubles hydratés dont l'un des cations est le cadmium ont des structures dans lesquelles l'enchaînement des polyèdres de coordination des cations est très varié. Faisant suite à l'étude des chlorures doubles de cadmium et potassium (Ledésert & Monier, 1983), nous avons entrepris celle des composés de cadmium et baryum. Le système $CdCl_2$–$BaCl_2$–H_2O a été exploré par divers auteurs, en particulier par Benrath & Lechner (1940) à différentes températures et par Moshinskii & Tikhomirova (1975) à 323 K. Les sels doubles obtenus à 298 K sont $BaCd_2Cl_6.5H_2O$ et $BaCdCl_4.4H_2O$. La structure cristalline de $BaCdCl_4.4H_2O$ a été déterminée en vue notamment d'étudier les polyèdres de coordination des cations, leur mode d'enchaînement ainsi que la coordination des molécules d'eau.

Partie expérimentale. Cristaux obtenus par évaporation d'une solution aqueuse de $CdCl_2$ et $BaCl_2$ dans le rapport de 3 à 2 mol. Etudes préliminaires radiocristallographiques menées sur chambre de précession. Paramètres affinés par moindres carrés sur diffractomètre CAD-4 Enraf–Nonius à partir de 21 réflexions (θ compris entre 6,2 et 26,8°). Paramètres de la maille et morphologie sont en accord avec les déterminations de Swaryczewski & Stępień (1971): cristaux allongés suivant **c**, limités par les formes $\{100\}$ et $\{010\}$ les plus développées, accompagnées de $\{110\}$ $\{\bar{1}10\}$, $\{\bar{1}01\}$, $\{0\bar{1}1\}$ et $\{001\}$. Cristal de 0,10 × 0,10 × 0,26 mm; radiation Mo $K\bar{\alpha}$, monochromateur de graphite, $2 \leq \theta \leq 40°$, $-16 \leq h \leq 16$, $-15 \leq k \leq 15$, $0 \leq l \leq 12$. Trois réflexions de référence ($0\bar{1}\bar{2}$, $\bar{1}1\bar{3}$, 430) mesurées toutes les 2000 s sans variation significative. 4696 réflexions d'intensité non nulle, 4675 avec $I \geq 3\sigma(I)$ retenues pour l'affinement. Corrections de Lorentz–polarisation et absorption en tenant compte de la forme du cristal, programme *AGNOSTC* (Coppens, Leiserowitz & Rabinovich, 1965; de Meulenaer &

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