Acta Cryst. (1978). B**34**, 1450–1453

The Crystal Structure of $CuTeO_4$

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(*Received* 3 *November* 1977; *accepted* 9 *December* 1977)

Crystals of $CuTeO_4$ are disordered. The structure has been determined in a unit cell with $a = 5{\cdot}500\ (2)$, $b = 10{\cdot}327\ (7)$, $c = 4{\cdot}704\ (2)$ Å, $\alpha = \beta = \gamma = 90{\cdot}0°$, $Z = 4$. Structural details have been obtained from a refinement in space group $P2_1/n$ ($R = 0{\cdot}048$), and the OD character of the structure is discussed in terms of idealized $[TeO_4]_n^{2n-}$ layers with the plane group symmetry $Pm(n)a$ ($R = 0{\cdot}054$). The Cu atoms have a distorted octahedral coordination of O atoms with Cu–O distances in the range 1·91–2·26 Å. The Te–O coordination is also octahedral; the octahedra are connected by corners forming $[TeO_4]_n^{2n-}$ layers. The Te–O bonds involving terminal and bridging O atoms are 1·87–1·91 and 1·91–2·02 Å respectively.

Introduction

The structures of some Cu^{II} tellurates(IV) have been determined: $CuTeO_3.2H_2O$ (Zemann & Zemann, 1962; Effenberger, 1977), $CuTeO_3$ (Lindqvist, 1972), $CuTe_2O_5$ (Hanke, Kupčik & Lindqvist, 1973), $Cu(NH_3)TeO_3.H_2O$ (Johansson & Lindqvist, 1977). However, information concerning Cu^{II} tellurates(VI) is limited to the structure of Cu_3TeO_6 (Falck, Lindqvist & Moret, 1978) which is built up from Cu^{2+} ions and TeO_6^{6-} ions of C_{3i} symmetry. In $CuTeO_4$ either a tetrahedral Te^{VI}–O coordination, as has been suggested for K_2TeO_4 (Tarte & Leyder, 1971), or, more probably, a polymerization of TeO_6 octahedra, as found in H_2TeO_4 (Moret, Philippot, Maurin & Lindqvist, 1974), is possible.

Experimental

Single crystals of $CuTeO_4$ were prepared by hydrothermal synthesis. From an aqueous solution of 0·5 *M* $CuSO_4$ and 0·5 *M* $Te(OH)_6$, kept at 650°C and 2000 bar for one week, single crystals of Cu_3TeO_6, $CuTeO_4$ and TeO_2 were obtained simultaneously. The $CuTeO_4$ crystals were very small plates. Slightly larger $CuTeO_4$ crystals could be prepared if the time for the hydrothermal synthesis was extended to two months, and the $Te(OH)_6$ concentration was increased to 1 *M*. Some crystallographic data are given in Table 1.

Preliminary investigation with a Weissenberg camera

Table 1. *Crystallographic and powder data for* $CuTeO_4$ (*MDO*$_1$)

The cell parameters were refined with the program *POWDER* (Lindqvist & Wengelin, 1967). The powder data were obtained from a Siemens powder diffractometer.

Crystal habit: yellow plates
Space group: MDO$_1$: $P2_1/n$ (MDO$_2$: $P\bar{1}$)
Plane group symmetry: $Pm(n)a$ (for $[TeO_4]_n^{2n-}$)

$a = 5{\cdot}500\ (2)$ Å	$V = 267{\cdot}2\ (3)$ Å^3
$b = 10{\cdot}327\ (7)$	μ(Mo $K\alpha$) = 193·6 cm^{-1}
$c = 4{\cdot}704\ (2)$	$\rho = 6{\cdot}345$ g cm^{-3}
$\beta = 90{\cdot}0\ (1)°$	$M_r = 255{\cdot}15$
$\alpha = \gamma = 90°$	$Z = 4$

Powder data

h k l	$\sin^2\theta_o$	$\sin^2\theta_c$	d_o (Å)
0 2 0	0·02231	0·02229	5·161
1 0 1	0·04648	0·04650	3·576
1 1 1	0·05220	0·05207	3·374
1 2 1	0·06883	0·06879	2·935
2 1 0	0·08451	0·08415	2·652
0 4 0	0·08923	0·08916	2·581
1 3 1	0·09662	0·09665	2·480
2 2 0	0·10110	0·10087	2·425
0 0 2	0·10772	0·10742	2·349
0 4 1	0·11619	0·11601	2·262
2 2 1	0·12777	0·12772	2·157
2 3 0	0·12866	0·12873	2·149
0 2 2	0·12977	0·12971	2·140
1 1 2	0·13272	0·13264	2·116
2 4 0	0·16791	0·16774	1·881
2 0 2	0·18595	0·18600	1·788
0 4 2	0·19673	0·19658	1·738
3 0 1	0·20392	0·20366	1·707
3 1 1	0·20915	0·20923	1·686

showed that $CuTeO_4$ crystallizes with an OD structure (Dornberger-Schiff, 1966), diffuse intensity streaks being observed in the **b*** direction. The relative intensities of the streaks were very low compared with the intensities of the discrete reflections. Four different crystals were investigated, but all showed weak intensity streaks only in a few places in reciprocal space. This indicated that the stacking sequence corresponding to an ordered structure is relatively seldom broken.

Reflections corresponding to the unit cell given in Table 1 were measured, since the intensity effect of the continuous streaks could be considered as insignificant. The crystal used for data collection was mounted along [101] on a Pailred two-circle diffractometer. Graphite-monochromated Mo $K\alpha$ radiation was used, and the intensities were measured with the ω-scan procedure. The scan speed was 2·5° min^{-1} in ω, and the background was measured for 24 s at each end of the scan interval. Nine layer lines were explored out to $2\theta = 60°$. Reflections with $h + l = 2n + 1$ were very weak, and only 15 such reflections were strong enough to be considered observed. 403 reflections with $\sigma(I)/I < 0{\cdot}3$ were regarded as being observed.

The intensities were corrected for Lorentz and polarization effects with the program *DATAP*1 (Lindgren, 1977) and for absorption with the program *DATAP*2 (Coppens, Leiserowitz & Rabinovich, 1965).

Structure determination

The observed reflections obey the symmetry and extinction rules of $P2_1/n$. The positions of the Te and Cu atoms were obtained from the Patterson function. In the successive electron density calculations, it was possible to find two sets of O atoms that satisfied the intensity data. One such model is shown in Table 2, and the same agreement ($R = 0{\cdot}048$) was obtained if the refinement was carried out with all O atoms shifted by $(\frac{1}{2},0,\frac{1}{2})$. This indicated that the O atoms have higher symmetry than that inherent in $P2_1/n$. In fact the $[TeO_4]_n^{2n-}$ layer, as refined in $P2_1/n$, very closely obeys the plane group symmetry $Pm(n)a$. The O atom positions deviate 0·05–0·2 Å in the **a** direction. The geometry of this idealized layer is determined only by the three parameters $y_{O(01)}$, $y_{O(03)}$ and $z_{O(03)}$ (Table 3). The structure may then be described as built up of such layers stacked according to the translations $\mathbf{L}_0$, $\mathbf{L}_1 = \mathbf{L}_0 + [r,\frac{1}{2},s]$, $\mathbf{L}_2 = \mathbf{L}_1 + [-r,\frac{1}{2},-s] = \mathbf{L}_0 + [0,1,0]$, *etc.*, where r and s are refinable parameters. The coordinates of the Cu ions are completely determined by the translations (Table 3). The refinement of the constrained structure model (Table 3) gave an R of 0·054 with the least-squares program *BLOCK* (Lindgren, 1977). Because the number of positional parameters could be reduced from 15 in the $P2_1/n$ model (Table 2) to 5 in the constrained-layer model (Table 3) the parameter standard deviations were improved in spite of the increase in R. However, the R difference clearly indicates that the unconstrained $P2_1/n$ model is significantly better than the constrained-layer model, and the detailed description of the structure should thus refer to the $P2_1/n$ coordinates (Table 2).

The scattering factors of Cromer & Waber (1965) were used for Te and those of Doyle & Turner (1968) for Cu and O. Correction for the real part of the scattering was applied for Te and Cu (Cromer, 1965). The observations were weighted according to Cruickshank (1970) with $w(hkl) = [50{\cdot}0 + F_o(hkl) + 0{\cdot}01F_o(hkl)^2]^{-1}$.*

Table 2. *Structure solution refined in space group* $P2_1/n$

Equivalent positions: $\pm(x,y,z)$, $\pm(\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2},\frac{1}{2}+z)$; 15 positional and 7 thermal parameters varied; $R = \sum||F_o| - |F_c||/\sum F_o = 0{\cdot}048$.

	x	y	z	B (Å^2)
Te	0·2963 (2)	0·2489 (6)	0·0166 (2)	0·23 (1)
Cu(1)	0	0	0	0·39 (5)
Cu(2)	$\frac{1}{2}$	0	$\frac{1}{2}$	0·55 (6)
O(1)	0·537 (4)	0·320 (2)	0·768 (4)	0·4 (2)
O(2)	0·535 (4)	0·173 (2)	0·267 (4)	0·7 (2)
O(3)	0·271 (3)	0·416 (1)	0·187 (3)	1·0 (2)
O(4)	0·271 (4)	0·088 (2)	−0·164 (4)	0·2 (2)

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33292 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Constrained-layer model of the* $CuTeO_4$ *structure*

The $[TeO_4]_n^{2n-}$ layers have been constrained to the plane symmetry $Pm(n)a$. The Cu atoms only have the (n) glide plane in common with the $[TeO_4]_n^{2n-}$ layers, but their positions are completely determined by the translations r and s. The coordinate table is to be extended according to the (n) symmetry; equivalent positions: (x,y,z), $(\frac{1}{2}+x,-y,\frac{1}{2}+z)$. Five positional and four thermal parameters were varied; $R = 0{\cdot}054$.

	x	y	z	B (Å^2)
Te(0)	0	0	0	B(Te)
O(01)	$\frac{1}{4}$	y(01)	$\frac{3}{4}$	B(01)
O(02)	$\frac{1}{4}$	$-y$(01)	$\frac{1}{4}$	B(01)
O(03)	0	y(03)	z(03)	B(03)
O(04)	0	$-y$(03)	$-z$(03)	B(03)
Cu(1)	$r/2$	$\frac{1}{4}$	$(1+s)/2$	B(Cu)
Cu(2)	$(1+r)/2$	$\frac{1}{4}$	$s/2$	B(Cu)
Te(1)	r	$\frac{1}{2}$	s	B(Te)
O(11)	$r+\frac{1}{4}$	$\frac{1}{2}+y$(01)	$s+\frac{3}{4}$	B(01)
O(12)	$r+\frac{1}{4}$	$\frac{1}{2}-y$(01)	$s+\frac{1}{4}$	B(01)
O(13)	r	$\frac{1}{2}+y$(03)	$s+z$(03)	B(03)
O(14)	r	$\frac{1}{2}-y$(03)	$s-z$(03)	B(03)

where r	= 0·4077 (5)	B(Te) = 0·24 (1)
s	= −0·0331 (6)	B(Cu) = 0·54 (2)
y(01)	= 0·0740 (11)	B(01) = 0·64 (15)
y(03)	= 0·1635 (13)	B(03) = 0·93 (18)
z(03)	= 0·1702 (32)	

Discussion of the structure

Bond distances and angles, both for the unconstrained and the constrained, idealized model, were calculated with *DISTAN* (written by Zalkin, University of California), and are shown in Table 4.

The idealized layer model is useful for the description of possible disorder in the structure. The layer stacking, as described by the parameters in Table 3, is fully ordered with alternating translations $[r,\frac{1}{2},s]$ and $[-r,\frac{1}{2},-s]$. This arrangement thus represents a structure of maximum degree of order (Dornberger-Schiff, 1966), MDO_1. The two types of translations are chemically identical with respect to the contacts between the layers and the Cu coordination. It is therefore possible to build up another structure, MDO_2, in which each translation is positive, *i.e.* with layers $\mathbf{L}_0$, $\mathbf{L}_1 = \mathbf{L}_0 + [r,\frac{1}{2},s]$, $\mathbf{L}_2 = \mathbf{L}_0 + [2r,1,2s]$, *etc.* Schematic representations of the MDO_1 and MDO_2 structures are shown in Fig. 1.

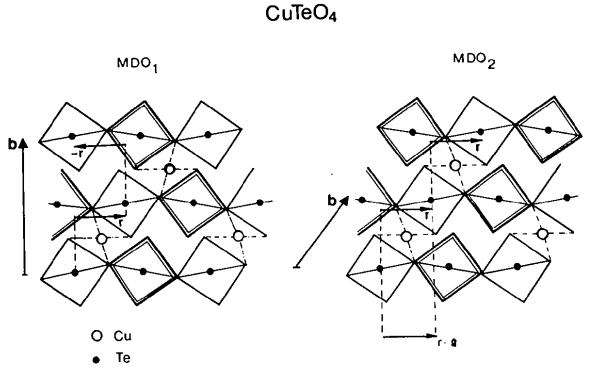

Fig. 1. Schematic picture of the MDO_1 and MDO_2 structure models showing three adjacent $[TeO_4]_n^{2n-}$ layers. MDO_2 has the unit-cell dimensions $a = 5{\cdot}500$, $b = 5{\cdot}632$, $c = 4{\cdot}704$ Å, $\alpha = 90{\cdot}0$, $\beta = 90{\cdot}0$, $\gamma = 66{\cdot}5°$.

Table 4. *Interatomic bond distances* (Å) *and angles* (°) *in* $CuTeO_4$

The columns refer to (*a*) the unconstrained $P2_1/n$ model and (*b*) the constrained $Pm(n)a$ layer model.

	(*a*)	(*b*)
Te–O(4)	1·87 (2)	1·88 (1)
Te–O(3)	1·91 (1)	1·88 (1)
Te–O(1)	1·91 (2)	1·97 (1)
Te–O(2)	1·93 (2)	1·97 (1)
Te–O′(1)	1·99 (2)	1·97 (1)
Te–O′(2)	2·02 (2)	1·97 (1)
Cu(1)–O(4)	2 × 1·91 (2)	2 × 2·05 (1)
Cu(1)–O(3)	2 × 2·12 (1)	2 × 2·17 (1)
Cu(1)–O(1)	2 × 2·26 (2)	2 × 2·14 (1)
Cu(2)–O(3)	2 × 1·94 (2)	2 × 1·99 (1)
Cu(2)–O(2)	2 × 2·11 (2)	2 × 2·22 (1)
Cu(2)–O(4)	2 × 2·22 (2)	2 × 2·05 (1)

O(1)–Te–O′(1)	177·7 (1·0)	O′(1)–Te–O(3)	91·2 (9)
O(1)–Te–O(2)	93·3 (9)	O′(1)–Te–O(4)	84·2 (9)
O(1)–Te–O′(2)	89·1 (8)	O(2)–Te–O′(2)	177·5 (1·2)
O(1)–Te–O(3)	87·7 (8)	O(2)–Te–O(3)	99·2 (8)
O(1)–Te–O(4)	86·5 (9)	O(2)–Te–O(4)	88·1 (9)
O′(1)–Te–O(2)	88·8 (9)	O′(2)–Te–O(3)	92·2 (9)
O′(1)–Te–O′(2)	88·8 (9)	O(3)–Te–O(4)	171·3 (8)

O(1)–Cu(1)–O(3)	96·0 (6), 85·0 (6)
O(1)–Cu(1)–O(4)	103·7 (8), 76·3 (8)
O(3)–Cu(1)–O(4)	90·7 (7), 89·3 (7)
O(2)–Cu(2)–O(3)	102·4 (7), 77·6 (7)
O(2)–Cu(2)–O(4)	94·3 (8), 85·7 (8)
O(3)–Cu(2)–O(4)	94·0 (7), 86·0 (7)

Table 5. *Copper coordination in tellurates*

Compound	Type	Bond distances (Å) Cu–O	σ (Å)	Reference
(*a*) Te(IV)				
$CuTeO_3.2H_2O$	Square planar	1·93, 1·95, 1·96 1·97, 2·35, 3·37	0·01	1
$CuTeO_3$	Irregular	1·94, 1·97, 1·97 1·98, 2·38, 3·33	0·02	2
$CuTeO_3$(h.p.)	Square planar (distorted octahedral)	2 × 1·91, 2 × 2·06, 2 × 2·61	0·02	3
$Cu(NH_3)TeO_3.H_2O$	Square planar	1·950, 1·958, 1·960 1·998,* 2·602, 3·066	0·008	4
$CuTe_2O_5$	Square planar (distorted octahedral)	1·950, 1·952, 1·961 1·969, 2·305, 2·780	0·003	5
(*b*) Te(VI)				
Cu_3TeO_6	Square planar (distorted octahedral)	2 × 1·949, 2 × 2·031, 2 × 2·369	0·002	6
$CuTeO_4$	Octahedral	*cf.* Table 4	0·01	7

References: (1) Effenberger (1977). (2) Lindqvist (1972). (3) Philippot & Maurin (1976). (4) Johansson & Lindqvist (1977). (5) Hanke, Kupčik & Lindqvist (1973). (6) Falck, Lindqvist & Moret (1978). (7) This work.

* Cu–N bond distance.

The reciprocal lattices of the MDO_1 and MDO_2 structures coincide in the *h0l* plane, but the contribution of the MDO_2 structure in the crystal used for the structure determination was too small to appear as a significant increase in the F_o/F_c ratio for the *h0l* reflections, compared with the *hkl* reflections. Even in the other crystals investigated, the MDO_2 arrangement did not seem to occur to more than a few percent, although weak MDO_2 reflections could be detected from one of the crystals.

It should be noted that the refinement in $P2_1/n$ shows that the O atoms deviate slightly (0·05–0·15 Å) from the mirror plane in the plane group symmetry $Pm(n)a$, and $x_{O(01)} = x_{O(02)} = 0{\cdot}241$ and $x_{O(03)} = x_{O(04)} = -0{\cdot}025$, instead of $\frac{1}{4}$ and 0 respectively. In addition, the $[r,\frac{1}{2},s]$ translation does not hold strictly (in the $P2_1/n$ refinement results) for the x coordinates of the O atoms. However, the appearance of diffuse streaks in the **b*** direction confirms the OD character of the investigated crystals.

The results may be interpreted as indicating that the Cu coordination of O atoms tends to distort the $[TeO_4]_n^{2n-}$ layers in a way which is more easily achieved in the MDO_1 than in the MDO_2 type of stacking sequence. In a related structure under investigation, $PbTeO_4$, similar disordered stacking occurs, but the two MDO structures occur to approximately the same extent.

The following discussion of the $CuTeO_4$ structural details refers to the unconstrained $P2_1/n$ model (Table 2).

Octahedral layers of composition $[TeO_4]_n^{2n-}$ have previously been found in Te_2O_5 (Lindqvist & Moret, 1973) and in H_2TeO_4 (Moret, Philippot, Maurin & Lindqvist, 1974). Both these structures are fully ordered and belong to the monoclinic space groups $P2_1$ and $P2_1/n$ respectively. The layers found in $CuTeO_4$ and Te_2O_5 can schematically be described in the same way (Fig. 2). The $Te-O_{bridge}$ bonds in $CuTeO_4$ are slightly longer than those in H_2TeO_4 and Te_2O_5, which have average values of 1·918 and 1·935 Å respectively. The $Te-O_{terminal}$ bonds of 1·87–1·91 Å in $CuTeO_4$ are in good agreement with values (1·83–1·91 Å) found in other tellurates(VI) (Lindqvist, 1973). In Te_2O_5 there are two different $Te-O_{terminal}$ bonds of 1·848 and 1·929 Å, as a result of the different connections with the interlayer Te(IV) atom.

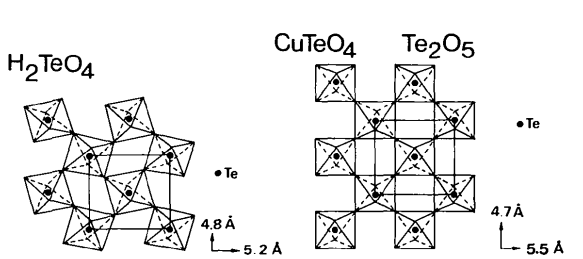

Fig. 2. A comparison of the $[TeO_4]_n^{2n-}$ layers found in H_2TeO_4, $CuTeO_4$ and Te_2O_5.

The Cu coordination in $CuTeO_4$ has been assumed to cause slight distortion of the $[TeO_4]_n^{2n-}$ layers. However, the packing of these layers mainly determines the geometry of the CuO_6 polyhedron, which is a distorted octahedron (Table 4). The Cu coordination in different tellurates is summarized in Table 5.

The authors thank Dr Susan Jagner for valuable comments on the OD character of the structure and for revising the English text. Financial aid has been obtained from the Swedish Natural Science Research Council (NFR).

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