

The Crystal Structure of Amminecopper(II) Tellurate(IV) Monohydrate $\text{Cu}(\text{NH}_3)\text{TeO}_3 \cdot \text{H}_2\text{O}$

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Single crystals of $\text{Cu}(\text{NH}_3)\text{TeO}_3 \cdot \text{H}_2\text{O}$ have been prepared by hydrothermal synthesis. The space group is $C2/c$ with $a = 12.988$ (4), $b = 7.333$ (1), $c = 10.022$ (3) Å, $\beta = 97.18$ (3)°. The structure parameters were refined to an R of 0.040 with 1283 independent reflexions. The structure contains pyramidal TeO_3^- ions with Te–O distances of 1.867–1.881 Å. The Cu^{II} coordination is square planar with three O atoms at 1.947–1.958 Å, while the fourth corner is occupied by an ammonia molecule with Cu–N = 1.993 Å. The Te and Cu atoms share O atoms thus forming a layer structure. The water of crystallization is situated between the layers.

Introduction

Previous structure investigations of Cu^{II} tellurates(IV) comprise $\text{CuTeO}_3 \cdot 2\text{H}_2\text{O}$ (Zemann & Zemann, 1962), CuTeO_3 (Lindqvist, 1972) and CuTe_2O_5 (Hanke, Kupčik & Lindqvist, 1973).

CuTeO_3 and CuTe_2O_5 were both prepared from $\text{CuO}-\text{TeO}_2$ melts, and the crystals had complicated three-dimensional network structures. The strong covalent connexions result in irregular Te and Cu polyhedra. In the mineral teinite ($\text{CuTeO}_3 \cdot 2\text{H}_2\text{O}$), on the other hand, the presence of water of crystallization permits a more regular arrangement of O around the metal atoms, *i.e.* threefold pyramidal for Te^{IV} and square planar for Cu^{II} .

The Cu^{II} tellurate(IV) crystals used in this study were prepared by Dr Jacques Moret, Montpellier, by hydrothermal synthesis from CuO and TeO_2 in $\text{NH}_3(\text{aq.})$. The crystals were suspected to contain both water and ammonia molecules.

Experimental

Unit-cell dimensions and space-group extinctions were investigated with a Weissenberg camera. Accurate cell dimensions (Table 1) were obtained from a Guinier powder film exposed with KCl as internal standard. The cell constants were refined by least squares based on 41 $\sin^2 \theta$ values (*POWDER*; Lindqvist & Wengelin, 1967).*

* Lists of structure factors, anisotropic thermal parameters and Guinier powder data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32482 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The crystal used for data collection was mounted along **b** (Fig. 1) on a two-circle Paired diffractometer. $\text{Mo } K\alpha$ radiation, monochromated with a graphite crystal, was used. The reflexions were measured with the ω -scan technique and a scan speed of $2.5^\circ \text{ min}^{-1}$ over scan intervals in the range $3.0-6.0^\circ$, depending on μ and 2θ . The background was measured for 24 s at each end of the scan interval. The $h0l-h, 10, l$ reflexions

Table 1. Crystallographic data for $\text{Cu}(\text{NH}_3)\text{TeO}_3 \cdot \text{H}_2\text{O}$

a 12.988 (4) Å	Formula weight	274.2
b 7.333 (1)	Density D_x	3.87 g cm ⁻³
c 10.022 (3)	Space group	$C2/c$ or Cc
β 97.18 (3)°	Absorption coefficient	97.5 cm ⁻¹
V 942.2 Å ³	$\mu(\text{Mo } K\alpha)$	
Z 8	Crystal habit	Blue plates

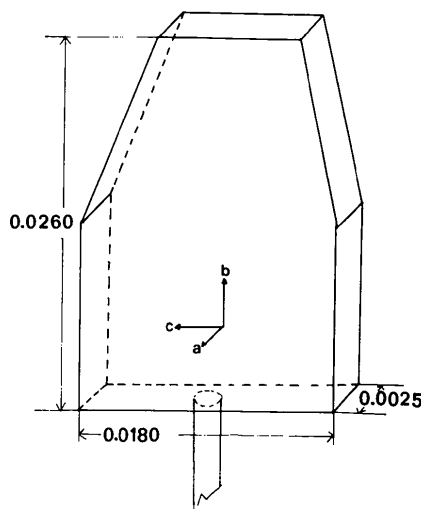


Fig. 1. The crystal used in data collection.

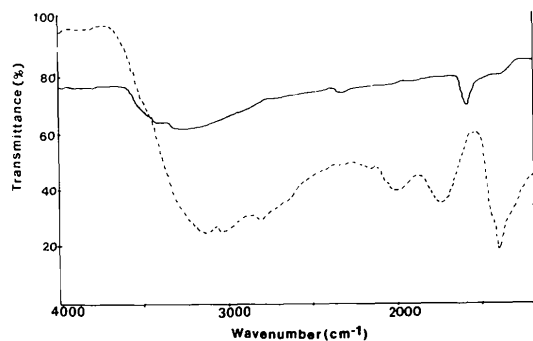


Fig. 2. IR spectra of $\text{Cu}(\text{NH}_3)\text{TeO}_3 \cdot \text{H}_2\text{O}$ (full curve) and NH_4Cl (dotted curve).

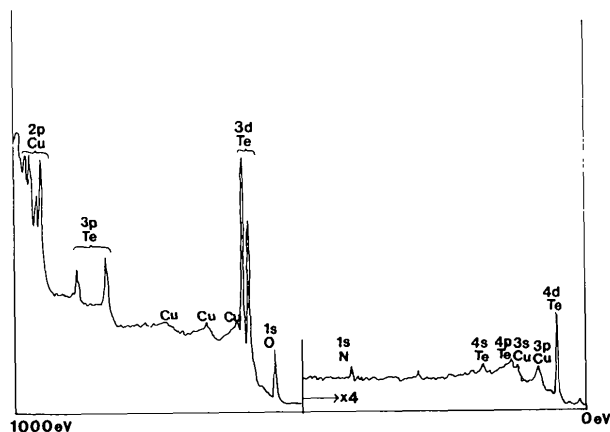


Fig. 3. ESCA spectrum of $\text{Cu}(\text{NH}_3)\text{TeO}_3 \cdot \text{H}_2\text{O}$.

with $2\theta < 70^\circ$ were registered, and 1283 intensities with $\sigma(I)/I < 0.2$ were regarded as significant. Corrections for Lorentz and polarization effects were performed with the program *DATAP1* (O. Lindgren, Göteborg).

At the commencement of the X-ray study, the structural roles of the water and ammonia molecules were not obvious. To confirm the X-ray investigation, spectroscopic and thermogravimetric measurements were also made. The IR spectrum (Fig. 2) was obtained with a Perkin-Elmer 337 spectrophotometer with KBr as internal standard. The chemical analysis was carried out with a Hewlett-Packard ESCA apparatus. The heights of the O(1s) and N(1s) peaks (Fig. 3) indicated a N:O atomic ratio of 1:4.

Determination of the structure

The Te atoms were found to occupy the general position $8(f)$ from the Patterson function, and the other non-hydrogen atoms were located from successive electron density calculations. The Fourier summations were carried out with the program *FFT* (Ten Eyck, 1973). A preliminary least-squares refinement

gave an R of 0.11. It was, however, apparent that the reflexions suffered from absorption. After a correction had been performed (*DATAP2*; Coppens, Leiserowitz & Rabinovich, 1965), R dropped to 0.05. No significant extinction effects were present.

The least-squares refinement was carried out with the block-diagonal approximation program *BLOCK* (O. Lindgren, Göteborg). In the final cycles, the refinement was extended to include anisotropic temperature factors, and the resulting positional parameters are given in Table 2.* Scattering factors for Te were obtained from Cromer & Waber (1965), while those given by Doyle & Turner (1968) were used for Cu, O and N. The observations were weighted according to $w = (20.0 + F_o + 0.004F_o^2)^{-1}$. Interatomic bond distances and angles (Tables 3 and 4) were calculated with the program *DISTAN* (A. Zalkin, Berkeley).

According to the ESCA results and the atomic positions obtained, the chemical formula might be either $\text{NH}_4\text{Cu}(\text{OH})\text{TeO}_3$ or $\text{Cu}(\text{NH}_3)\text{TeO}_3 \cdot \text{H}_2\text{O}$.

* See previous footnote.

Table 2. Positional parameters for $\text{Cu}(\text{NH}_3)\text{TeO}_3 \cdot \text{H}_2\text{O}$

Standard deviations are given in parentheses.

	x	y	z
Te	0.24441 (4)	0.21261 (7)	0.31340 (5)
Cu	0.3332 (1)	0.0941 (1)	0.0302 (1)
N	0.4396 (7)	0.2660 (13)	-0.0244 (8)
O(1)	0.3044 (6)	0.2823 (9)	0.1594 (7)
O(2)	0.3604 (5)	-0.0872 (9)	-0.1036 (7)
O(3)	0.2298 (5)	-0.0636 (9)	0.0977 (7)
O(4)	$\frac{1}{2}$	0.0454 (20)	$\frac{3}{4}$
O(5)	$\frac{1}{2}$	0.4740 (20)	$\frac{1}{4}$

Table 3. Coordination distances (\AA) and angles ($^\circ$) around Te^{IV} and Cu^{II}

Te-O(2)	1.870 (7)	Cu-O(2)	1.950 (8)
Te-O(3)	1.877 (7)	Cu-O(3)	1.958 (7)
Te-O(1)	1.885 (8)	Cu-O(1)	1.960 (9)
Te-O(3')	2.950 (7)	Cu-N	1.998 (7)
Te-O(3'')	3.082 (7)	Cu-O(1')	2.602 (9)
Te-O(1')	3.236 (9)	Cu-O(4)	3.066 (6)
O(1)-Te-O(2)	96.1 (4)	N-Cu-O(1)	86.1 (3)
O(1)-Te-O(3)	94.7 (3)	N-Cu-O(2)	92.9 (3)
O(2)-Te-O(3)	97.6 (3)	N-Cu-O(3)	175.3 (3)
O(1)-Te-O(1')	116.1 (3)	O(1)-Cu-O(2)	178.0 (4)
O(1)-Te-O(3')	65.3 (3)	O(1)-Cu-O(3)	89.5 (3)
O(1)-Te-O(3'')	159.1 (3)	O(2)-Cu-O(3)	91.5 (3)
O(1')-Te-O(2)	68.8 (3)	N-Cu-O(1')	90.9 (3)
O(1')-Te-O(3)	146.9 (3)	N-Cu-O(4)	87.5 (3)
O(1')-Te-O(3')	52.9 (2)	O(1)-Cu-O(1')	93.8 (3)
O(1')-Te-O(3'')	62.7 (2)	O(1)-Cu-O(4)	86.4 (4)
O(2)-Te-O(3')	87.9 (3)	O(1)-Cu-O(2)	84.4 (4)
O(2)-Te-O(3'')	63.4 (3)	O(1)-Cu-O(3)	91.1 (3)
O(3)-Te-O(3')	159.8 (2)	O(1)-Cu-O(4)	178.4 (3)
O(3)-Te-O(3'')	84.3 (3)	O(2)-Cu-O(4)	95.4 (3)
O(3)-Te-O(3''')	115.4 (1)	O(3)-Cu-O(4)	90.5 (3)

Table 4. Distances (Å) and angles (°) for possible hydrogen bonding

N—O(4)	2.96 (1)	Cu—N—O(4)	97.1 (4)
N—O(2)	3.05 (1)	Cu—N—O(2)	101.3 (3)
N—O(3)	3.12 (1)	Cu—N—O(3)	90.8 (3)
N—O(5)	3.16 (1)	Cu—N—O(5)	99.8 (3)
N'—O(5)	3.13 (1)	Cu—N'—O(5)	145.8 (3)
$2 \times \text{O}(4)\text{—O}(2)$	2.66 (1)	N—O(4)—N	113.9 (6)
		N—O(4)—O(2)	60.9 (2)
		N—O(4)—O(2)	152.3 (4)
		O(2)—O(4)—O(2)	137.0 (8)
$2 \times \text{O}(5)\text{—O}(1)$	2.95 (1)	N—O(5)—N	122.3 (5)
		N—O(5)—N'	73.9 (2)
		N—O(5)—N'	150.0 (3)
		N'—O(5)—N'	104.9 (5)
		N—O(5)—O(1)	52.4 (3)
		N—O(5)—O(1)	98.6 (4)
		N'—O(5)—O(1)	110.6 (2)
		N'—O(5)—O(1)	103.2 (2)
		O(1)—O(5)—O(1)	123.1 (6)

However, the colour of the crystals, which are bright blue instead of green, like CuTeO_3 , CuTe_2O_5 and $\text{Cu}(\text{OH})\text{IO}_3$ (*Handbook of Chemistry and Physics*, 1968), and the IR spectrum (Fig. 2), suggest that the formula is $\text{Cu}(\text{NH}_3)\text{TeO}_3 \cdot \text{H}_2\text{O}$.

As indicated in Table 2, O(4) and O(5) occupy special positions in $C2/c$, on twofold axes. Since, both O(4) and O(5) correspond to water of crystallization, they could not possibly occupy these positions in a fully ordered structure. The structure was therefore also refined in Cc , but no significantly different results were obtained. Neither did a difference synthesis based on the $C2/c$ model show any anomalies. The highest peaks, corresponding to $1.3 \text{ e } \text{Å}^{-3}$, occurred near the heavy-atom positions. We therefore decided to describe the structure as belonging to $C2/c$ with the exception of the water H atoms, which may be arranged in a disordered way, or in accordance with Cc symmetry.

Discussion

The structure is built up from TeO_3 pyramids bonded *via* O bridges to three Cu atoms. The Cu^{II} coordination is square planar with three corners of the square occupied by O atoms from different TeO_3 groups and the fourth by an ammonia molecule. This arrangement results in infinite sheets (Fig. 4) separated by water of crystallization (Fig. 5).

The Cu^{II} coordination distances are normal (Table 3). The Cu—O distances are very close to those found in CuTe_2O_5 (Hanke, Kupčik & Lindqvist, 1973) in which they range from 1.950 (3) to 1.969 (3) Å. The Cu—N distance of 1.997 (7) Å falls well within the range 1.97–2.07 Å observed in other ammine Cu^{II} complexes (Meyer, Singh, Hatfield & Hodgson, 1972). The deviations from the planar configuration of 0.03 Å in tetrahedral directions (Table 5) are significant. In addition to the four planar bonds, there are two longer Cu—O interactions of 2.602 (7) and 3.066 (7) Å completing a distorted octahedron.

In the ideal case of $\text{Te}^{\text{IV}}\text{—O}$ threefold coordination, the TeO_3^{2-} ion ought to possess a threefold axis through the inert Te 5s electron pair and the centre of the Te atom. The bond distances and angles in $\text{Cu}(\text{NH}_3)\text{TeO}_3 \cdot \text{H}_2\text{O}$ (Table 3) correspond well to this geometry: three Te—O distances not significantly different from the mean value of 1.880 Å, and angles slightly different from the mean value of 96.15° . In $\text{BaTeO}_3 \cdot \text{H}_2\text{O}$ (Nielsen, Hazell & Rasmussen, 1971), which is evidently ionic, the corresponding bond distances are 1.847–1.859 (6) Å and the angles are $96.5\text{--}102.7 (3)^\circ$, with average values of 1.855 Å and 99.32° . Neither $\text{BaTeO}_3 \cdot \text{H}_2\text{O}$ nor $\text{Cu}(\text{NH}_3)\text{TeO}_3 \cdot \text{H}_2\text{O}$ contain any significant 'backbonding', *i.e.* one to three weak bonds opposite to the pyramidal Te—O bonds. This also supports the presence of TeO_3^{2-} ions in the two structures.

There are several $\text{N}\cdots\text{O}$ and $\text{O}\cdots\text{O}$ distances in $\text{Cu}(\text{NH}_3)\text{TeO}_3 \cdot \text{H}_2\text{O}$ which could be consistent with hydrogen bonding (Table 4). With respect to the angles around N, the N—O(2), N—O(4) and N—O(5) dis-

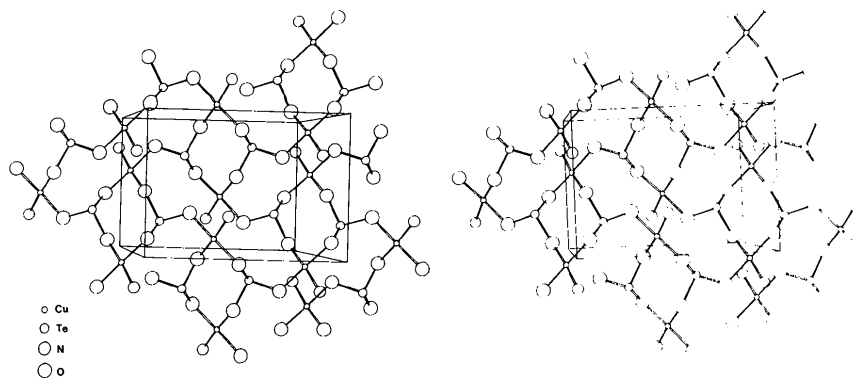


Fig. 4. A stereoscopic drawing of one $\text{Cu}(\text{NH}_3)\text{TeO}_3$ layer (ORTEP, Johnson, 1965).

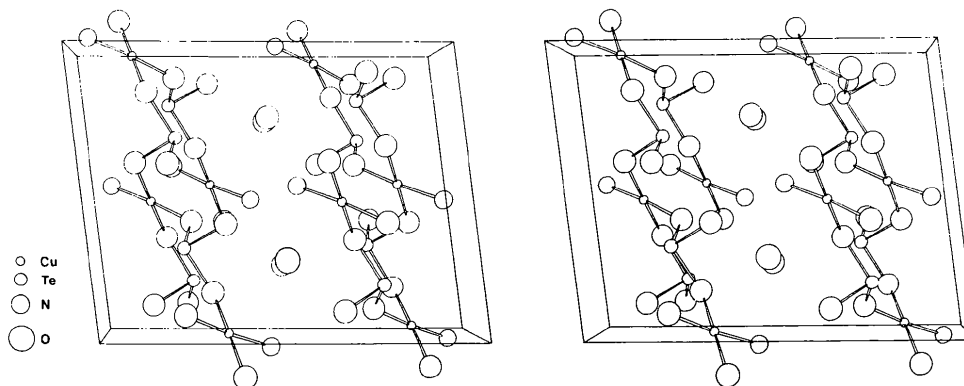


Fig. 5. The $\text{Cu}(\text{NH}_3)\text{TeO}_3 \cdot \text{H}_2\text{O}$ structure seen along the layers (ORTEP, Johnson, 1965).

Table 5. Deviations (Δ) from a least-squares plane through the Cu planar coordination

	Δ (Å)		Δ (Å)
Cu	0.000	O(2)	0.029
N	-0.030	O(3)	-0.030
O(1)	0.031		

tances of 3.045, 2.963 and 3.156 Å respectively, ought to correspond to N—H...O hydrogen bonds. Since the H atoms attached to the water molecules do not conform to the $C2/c$ structure, no definite conclusions can be drawn concerning the O—H...O (or O—H...N) hydrogen bonds. However, it is possible that the true space group is Cc with all but the water H atoms being in agreement with $C2/c$ symmetry. In this case, the water molecules could be hydrogen bonded according to O(1)...H—O(5)—H...O(1) and O(2)...H—O(4)—H...O(2) (Table 4).

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