

- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- KÁLMÁN, A., ARGAY, G. & CZUGLER, M. (1972). *Cryst. Struct. Commun.* **1**, 375–378.
- MOTHERWELL, W. D. S. (1976). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
- NARDELLI, M. (1978). *LQPARM*. Program for least-squares refinement of lattice parameters. Univ. of Parma, Italy.
- NARDELLI, M. (1979). Proc. 5th Eur. Crystallogr. Meet. Copenhagen, 13–17 August, Abstracts, p. 262.
- NARDELLI, M. (1983). *Comput. Chem.* **7**, 95–98.
- NARDELLI, M., FAVA GASPARRI, G. & CHERICI, I. (1965). *Ric. Sci.* **35**(11-A), 480–481.
- SHELDRIK, G. M. (1976). *SHELX*. Program for crystal structure determination. Univ. of Cambridge, England.
- SPOFFORD, W. A. & AMMA, E. L. (1968). *Chem. Commun.* pp. 405–407.
- UGOZZOLI, F. (1983). *ABSORB*. Program for Walker and Stuart's absorption correction. Univ. of Parma, Italy.
- VIZZINI, E. A. & AMMA, E. L. (1966). *J. Am. Chem. Soc.* **88**, 2872–2873.
- WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.

Acta Cryst. (1987). **C43**, 413–416

Structure of Monomethylammonium Tetrachlorocuprate at 297 and 100 K

BY I. PABST, H. FUESS AND J. W. BATS

Institut für Kristallographie und Mineralogie der Universität, Senckenberganlage 30, D-6000 Frankfurt/Main 1, Federal Republic of Germany

(Received 3 May 1986; accepted 19 September 1986)

Abstract. $[\text{CH}_3\text{NH}_3]_2[\text{CuCl}_4]$, $M_r = 269.48$, monoclinic, $P2_1/a$, $Z = 2$, $F(000) = 270$, $\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$. $T = 297 (1) \text{ K}$: $a = 7.268 (4)$, $b = 7.367 (4)$, $c = 9.971 (3) \text{ \AA}$, $\beta = 110.89 (1)^\circ$, $V = 498.8 (9) \text{ \AA}^3$, $D_x = 1.794 \text{ Mg m}^{-3}$, $\mu = 3.21 \text{ mm}^{-1}$, $R_F = 0.042$ for 879 observed independent reflections. $T = 100 (2) \text{ K}$: $a = 7.155 (4)$, $b = 7.424 (4)$, $c = 9.814 (3) \text{ \AA}$, $\beta = 109.18 (7)^\circ$, $V = 492.4 (3) \text{ \AA}^3$, $D_x = 1.818 \text{ Mg m}^{-3}$, $\mu = 3.26 \text{ mm}^{-1}$, $R_F = 0.040$ for 862 observed independent reflections. The crystal structure is monoclinic in the whole temperature range from 100 to 297 K in contrast to earlier results [Steijger, Frikkee, de Jongh & Huiskamp (1984). *Physica B*, **123**, 284–290] that suggested orthorhombic symmetry at 297 K and a phase transition to monoclinic symmetry at lower temperatures. The Cu^{2+} cations are coordinated by six Cl^- ions with four short and two long Cu–Cl bond distances in a Jahn–Teller distorted octahedron. The methylammonium groups are connected to chloride by hydrogen bonds.

Introduction. Compounds with the general formula $(\text{CH}_3\text{NH}_3)_2\text{MCl}_4$, where M is a divalent metal ($M = \text{Mn}, \text{Cd}, \text{Cu}$ etc.), have been extensively studied in recent years with respect to their magnetic properties and interesting structural phase transitions. The crystal structure may be described as two-dimensional layers of corner-sharing MCl_6 units. The alkylammonium entities are situated between the layers and connected by hydrogen bonds to the Cl^- ions. The crystal structure and the structural phase transitions of $(\text{CH}_3\text{NH}_3)_2\text{CdCl}_4$ (Chapuis, Arend & Kind, 1975; Chapuis, Kind & Arend, 1976) and of the analogous

manganese compound (Heger, Mullen & Knorr, 1975) were studied in great detail. The analogous compound $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$ was studied by X-ray and neutron diffraction powder methods; Steijger, Frikkee, de Jongh & Huiskamp (1984a) reported several structural phase transformations and determined its magnetic properties at low temperatures (Steijger, Frikkee, de Jongh & Huiskamp, 1984b). They found a tetragonal high temperature phase above 348 (1) K and an orthorhombic structure at room temperature. Between 250 and 170 K a coexistence of the orthorhombic room temperature structure and of a low temperature monoclinic phase was derived from the data. These authors confirm the monoclinic phase as stable below 170 K. The present work was undertaken in order to solve the crystal structure of $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$ in its different phases and to elucidate the nature of the coexistence of two structures in the same temperature region by single-crystal X-ray diffraction.

Experimental. Brown crystals were obtained by slow evaporation of an aqueous solution of stoichiometric amounts of $\text{CH}_3\text{NH}_3\text{Cl}$ and $\text{CuCl}_2 \cdot \text{H}_2\text{O}$. The first two crystals examined showed orthorhombic symmetry by precession photographs and on an automatic diffractometer. The structure determination and the refinement (*XRAY* system, Stewart, Kruger, Ammon, Dickinson & Hall, 1972) revealed, however, a domain structure and suggested that the true symmetry is monoclinic and the domains give rise to orthorhombic pseudo-symmetry.

Finally a one-domain crystal of size $0.4 \times 0.9 \times 1.0 \text{ mm}$ of good optical quality was selected and used

for the determination of cell constants and for data collection on an Enraf–Nonius CAD-4 diffractometer. The cell constants were obtained in the non-standard space group $B2_1/a$ from setting angles of 25 reflections with $10.34 < \theta < 29.76^\circ$ (graphite-monochromated Mo $K\alpha$ radiation): $a = 7.279$ (4), $b = 18.648$ (5), $c = 7.370$ (7) Å, $\gamma = 90.46$ (4)° at $T = 297$ K and $a = 7.148$ (6), $b = 18.543$ (6), $c = 7.419$ (4) Å, $\gamma = 92.22$ (5)° at $T = 100$ K. The non-conventional setting was chosen because it facilitates comparison with the orthorhombic symmetry previously suggested. The conversion to the setting $P2_1/a$ is achieved by the transformations $a = a'$, $b = b'$, $c = \frac{1}{2}(c' - a')$, where the unprimed symbols are in $P2_1/a$ (see *Abstract*).

Data were corrected for Lorentz–polarization and absorption (empirical by ψ scans) effects. Data collection by ω scans, variation in intensity of three standard reflections $< 1\%$; 2721 reflections measured in one hemisphere up to $2\theta = 50^\circ$, max. $(\sin\theta)/\lambda = 0.595 \text{ \AA}^{-1}$, range in hkl : $0 \rightarrow \pm 8, \pm 22, \pm 8$; relative transmission range $0.54 - 1.00$. A set of 881 remained after averaging equivalent reflections ($R_{\text{int}} = 0.015$); 879 unique reflections used in refinement, two reflections with $I < \sigma(I)$ were classified as unobserved. An extinction coefficient g according to $|F_o| = F_c [1 / (1 + gI_c)]$ was included in the refinement and $g = 4.12 \times 10^{-6}$ was obtained; $S = 1.32$; unit weights, final $R_F = 0.042$. Data collection at 100K was performed with the same conditions except: range in hkl : $0 \rightarrow \pm 8, \pm 22, + 8$; 1326 reflections collected, 865 after averaging ($R_{\text{int}} = 0.02$), three unobserved as $I < \sigma(I)$ and 862 used in refinement; extinction coefficient $g = 2.64 \times 10^{-6}$, $S = 1.52$, unit weights, final $R_F =$

0.040. The lattice constants were measured as a function of temperature between 100 and 297 K using a cold gas stream device.

The structure was solved in the monoclinic space group $P2_1/a$ by Patterson and Fourier methods. Refinement was based on F , unit weights; atomic scattering factors and values of f' and f'' for anomalous dispersion for Cu and Cl were from *International Tables for X-ray Crystallography* (1974). All calculations on this monodomain crystal were carried out with the *SDP* program package on a PDP11/34 computer (Enraf–Nonius, 1982).

Positional and anisotropic thermal parameters were varied and scale and extinction factors were included (44 parameters at $T = 297$ and 62 parameters at $T = 100$ K). No hydrogen atoms were located from room-temperature data. All of them were, however, detected from difference Fourier maps at 100 K. They were included in the refinement and their positional parameters were varied whereas the thermal parameters were fixed. $(\Delta/\sigma)_{\text{max}} = 0.02$ at both temperatures in last cycle of refinement. Positional and thermal parameters are reported in Table 1 and bond distances and angles in Table 2.* Maximum and minimum heights in the final difference Fourier synthesis were 0.40 and -0.25 e \AA^{-3} .

Discussion. In contrast to previous work (Steijger *et al.*, 1984a), $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$ is monoclinic at 297 K. The lattice constants were determined as a function of temperature between 100 and 297 K. Fig. 1 demonstrates a steady increase of the monoclinic angle with decreasing temperature. In addition we performed differential scanning calorimetry (DSC) measurements between 120 and 400 K, which confirmed the structural phase transition at 348 (1) K but did not indicate any structural change in the low temperature region. We

Table 1. Positional parameters and equivalent values of the anisotropic thermal parameters

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

First row: 100 K. Second row: 297 K. Thermal parameters of H isotropic.

	x	y	z	$U_{\text{eq}}(\text{\AA}^2)$
Cu	0 0 0	0 0 0	0 0 0	0.0085 0.0257
Cl(1)	0.1314 (2) 0.1281 (3)	0.0383 (2) 0.0316 (2)	0.2470 (1) 0.2453 (2)	0.0133 0.0467
Cl(2)	0.2124 (2) 0.2104 (2)	0.2142 (2) 0.2185 (2)	-0.0307 (1) -0.0216 (2)	0.0116 0.0386
N	-0.4045 (6) -0.3916 (7)	0.0268 (6) 0.0204 (7)	0.2240 (4) 0.2228 (5)	0.0142 0.0418
C	0.1850 (8) 0.1880 (10)	0.5352 (9) 0.5260 (10)	0.3724 (6) 0.3739 (8)	0.0253 0.0684
H(1)	0.361 (9)	-0.024 (9)	0.168 (7)	0.0253
H(2)	0.529 (9)	0.015 (10)	0.199 (7)	0.0253
H(3)	-0.397 (9)	0.109 (9)	0.207 (7)	0.0253
H(4)	-0.174 (9)	-0.026 (9)	0.395 (7)	0.0253
H(5)	-0.326 (9)	-0.158 (9)	0.385 (7)	0.0253
H(6)	-0.362 (9)	-0.025 (9)	0.440 (7)	0.0253

Table 2. Bond distances (Å) and angles (°) (e.s.d.'s in parentheses)

	100 K	297 K
Cu–Cl(1) (2×)	2.311 (1)	2.297 (1)
Cu–Cl(2) (2×)	2.287 (1)	2.283 (1)
Cu–Cl(2 ^{II}) (2×)	2.902 (1)	2.907 (1)
C–N	1.460 (6)	1.448 (8)
Cl(1)–Cu–Cl(1)	180	180
Cl(2)–Cu–Cl(2)	180	180
Cl(2 ^{II})–Cu–Cl(2 ^{II})	180	180
Cl(2)–Cu–Cl(2 ^{II})	87.54 (3)	88.95 (10)
Cl(1)–Cu–Cl(2)	90.35 (4)	90.07 (6)
Cl(1)–Cu–Cl(2 ^{II})	87.17 (3)	89.14 (5)

Symmetry codes: (i) x, y, z ; (ii) $\frac{1}{2} + x, y - \frac{1}{2}, z$.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP. 43416 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

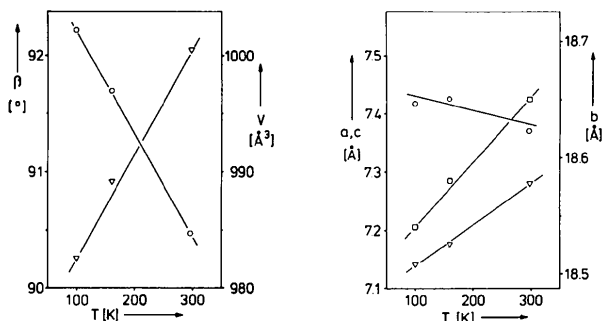


Fig. 1. Lattice parameters as a function of temperature. The steady increase of the monoclinic angle with decreasing temperatures proves the stability of the monoclinic symmetry. (a) \circ Monoclinic angle, ∇ cell volume. (b) Lattice constants: ∇ a; \circ b; \square c.

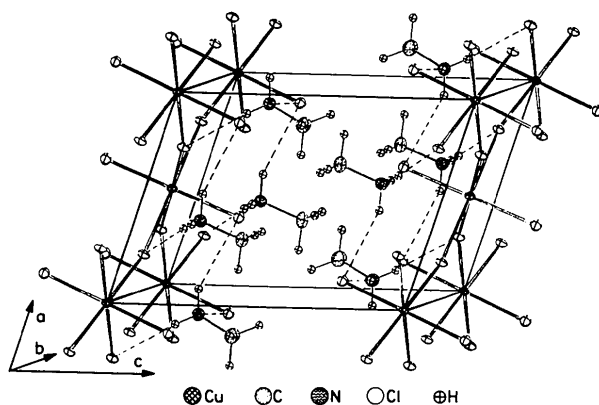


Fig. 2. The structure of $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$ at 100 K. Thermal ellipsoids are at the 50% probability level. Hydrogen bonds indicated by broken lines.

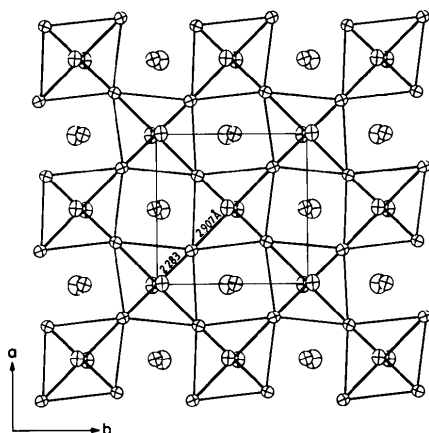


Fig. 3. Schematic projection on the ab layer plane of $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$ at 297 K demonstrating the zigzag arrangement of the CuCl_6 octahedra.

Table 3. Hydrogen-bonding scheme for $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$ at 100 K (distances in Å, angles in $^\circ$)

	N—H	H...Cl	N...Cl	\angle N—H...Cl	Symmetry code
N—H(1)...Cl(2)	0.81 (6)	2.42 (6)	3.226 (4)	171 (5)	$-x, -y, -z$
N—H(2)...Cl(1)	0.85 (6)	2.63 (6)	3.402 (4)	152 (5)	$x-1, y, z$
N—H(3)...Cl(1)	0.65 (7)	2.61 (7)	3.241 (4)	164 (7)	$x-\frac{1}{2}, \frac{1}{2}, y, z$

Table 4. Structural phase transitions in tetrachlorometallates (transition temperature in K)

$(\text{CH}_3\text{NH}_3)_2\text{CdCl}_4$	$I4/mmm$ ⁴⁸⁴	\rightleftharpoons	$Cmca$ ²⁸³	\rightleftharpoons	$P4_2/ncm$ ¹⁷³	\rightleftharpoons	$B2_1/a^*$
$(\text{CH}_3\text{NH}_3)_2\text{MnCl}_4$	$I4/mmm$ ³⁹³	\rightleftharpoons	$Abma$ ²⁵⁶	\rightleftharpoons	$P4_2/ncm$ ⁹⁴	\rightleftharpoons	monoclinic†
$(\text{CH}_3\text{NH}_3)_2\text{FeCl}_4$	$I4/mmm$ ³²⁸	\rightleftharpoons	$Abma$ ²³¹	\rightleftharpoons	$P4_2/ncm$ [‡]		
$(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$	Tetragonal §	\rightleftharpoons	$P2_1/a$ [¶]				

* Chapuis *et al.* (1976). † Heger *et al.* (1975). ‡ Knorr, Jahn & Heger (1974). § Steijger *et al.* (1984 a, b). ¶ This work.

therefore concluded that the previously reported orthorhombic symmetry was due to the presence of domains in the material studied. This conclusion is supported by our own investigation of three different crystals. Two of them exhibited pseudo-orthorhombic symmetry. Their structure was successfully refined by taking domains and their relative volume into account. Distances and angles obtained by these refinements are essentially the same as those reported here from the monodomain monoclinic crystal. The crystal structure (Fig. 2) consists of corner-sharing octahedra which form layers in the ab plane. Two out of the four Cu—Cl distances (bridging) are relatively short and two are long [2.283 (1) and 2.907 (1) Å at room temperature]. The two axial bonds are short with a distance of 2.297 (1) Å at 297 K.

At 100 K the two long Cu—Cl distances appear slightly shorter, whereas the four short ones appear longer, in accordance with a riding-atom model. The two different lengths in the ab plane produce a zigzag arrangement of octahedra in that plane (Fig. 3). The CH_3NH_3^+ groups are situated between the layers and hydrogen bonds are formed between the ammonium group and the axial chloride ligands. The hydrogen-bonding scheme based on the 100 K refinement is described in Table 3.

The C—N groups are almost perpendicular to the ab plane. The direction C—N forms an angle of 88° with the a axis and 75° with the b axis.

A comparison with three other compounds, $(\text{CH}_3\text{NH}_3)_2\text{MCl}_4$ with $M = \text{Cd}, \text{Mn}, \text{Fe}$, shows a different sequence of structural phase transitions than observed for $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$ (Table 4). All four compounds have a tetragonal high temperature structure. At room temperature the compounds with Cd, Mn, Fe all have orthorhombic symmetry followed by a

second tetragonal phase below room temperature. A sequence of phase transitions (Table 4) with decreasing temperature from tetragonal through orthorhombic and a second tetragonal phase to a monoclinic structure is reported for $(\text{CH}_3\text{NH}_3)_2\text{CdCl}_4$ and $(\text{CH}_3\text{NH}_3)_2\text{MnCl}_4$ (Heger *et al.*, 1975). The low temperature structure of tetrachlorocadmate (Chapuis *et al.*, 1976) is described in space group $B2_1/a$ allowing for a direct comparison with high temperature phases. The transformation of positional parameters from $B2_1/a$ to $P2_1/a$ reveals that the room temperature structure of $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$ is isostructural to the low temperature phase of the tetrachlorocadmate. The low temperature form of $(\text{CH}_3\text{NH}_3)_2\text{MnCl}_4$ is reported to be monoclinic but no space group is given in the literature.

Support of this work by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

References

- CHAPUIS, G., AREND, M. & KIND, R. (1975). *Phys. Status Solidi A*, **31**, 449–454.
 CHAPUIS, G., KIND, R. & AREND, M. (1976). *Phys. Status Solidi A*, **36**, 285–295.
 Enraf–Nonius (1982). *Structure Determination Package*. Enraf–Nonius, Delft.
 HEGER, G., MULLEN, D. & KNORR, K. (1975). *Phys. Status Solidi A*, **31**, 455–462.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
 KNORR, K., JAHN, J. R. & HEGER, G. (1974). *Solid State Commun.* **15**, 231–238.
 STEIJGER, J. J. M., FRIKKEE, E., DE JONGH, L. J. & HUISKAMP, W. J. (1984a). *Physica B*, **123**, 284–290.
 STEIJGER, J. J. M., FRIKKEE, E., DE JONGH, L. J. & HUISKAMP, W. J. (1984b). *Physica B*, **123**, 271–283.
 STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. W. & HALL, S. R. (1972). The XRAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Acta Cryst. (1987). **C43**, 416–418

Trimethylbis[2-thenoato(1–)]antimony

BY H. PREUT, M. DOMAGALA AND F. HUBER

Universität Dortmund, Fachbereich Chemie, Postfach 500 500, D-4600 Dortmund 50, Federal Republic of Germany

(Received 12 February 1986; accepted 22 September 1986)

Abstract. $[\text{Sb}(\text{C}_5\text{H}_7\text{O}_2\text{S})_2(\text{CH}_3)_3]$, $M_r = 421.1$, orthorhombic, $Pbca$, $a = 11.197$ (7), $b = 26.026$ (9), $c = 11.224$ (7) Å, $V = 3270.8$ Å³, $Z = 8$, $D_x = 1.710$ Mg m⁻³, $\lambda(\text{Ag } K\alpha) = 0.56083$ Å, $\mu = 1.01$ mm⁻¹, $F(000) = 1664$, $T = 293$ (1) K. Final $R = 0.039$ for 1555 unique observed X-ray diffractometer data and 174 variables. The thiophene ring with the atoms C(5) to C(8) and S(1) is disordered. The positions S(1) and C(6) have been refined with the scattering power of 0.5 S and 0.5 C. Sb is surrounded by three equatorial C(methyl) and two apical O atoms, one from each carboxylate group. The trigonal bipyramid is distorted by weak interaction with the second O of each carboxylate group, both approaching Sb to widen C(1)–Sb–C(2) to 125.11 (4)°.

Introduction. Only two X-ray diffraction studies of triorganoantimony dicarboxylates have been reported: diacetatotriphenylantimony (Sowerby, 1979) and bis-(benzoato)triphenylantimony (Lebedev, Bochkova, Kuzubova, Kuz'min, Sharutin & Belov, 1982) have a distorted trigonal-bipyramidal arrangement of ligands around Sb, the covalently bonding O atoms of the

essentially unidentate carboxylate groups being in apical positions. The distortion was explained by weak interaction between Sb and the carbonyl O atoms of each acetate ligand. In the following a first example of a structure of a trimethylantimony dicarboxylate as well as of a triorganoantimony derivative of a heterocyclic carboxylic acid is described. One object of this study was to examine whether weak coordinative interaction occurs also in a trimethylantimony carboxylate and whether this is similarly accomplished by O atoms or by the heteroatom of the ring in the latter type of ligand as recently found in (2-furoato)trimethyllead (Preut, Röhm & Huber, 1986).

Experimental. Title compound prepared from $(\text{CH}_3)_3\text{Sb}(\text{OH})_2$ and 2-thenoic acid in chloroform. Crystals obtained from CHCl_3 /petroleum ether (b.p. 313–333 K). Crystal size: $0.38 \times 0.22 \times 0.11$ mm. $\omega/2\theta$ scan. Scan speed: $6.7^\circ \text{ min}^{-1}$ in θ . Nonius CAD-4 diffractometer, graphite-monochromated Ag $K\alpha$ radiation; lattice parameters from least-squares fit with 20 reflexions up to $2\theta = 25.1^\circ$; standard reflexions recorded every 2.5 h, only random deviations; 6938