Tableau 6. *Code de symétrie*

(i)	$x-1$	y	z	(iv)	$1-x$	$\bar{y}$	$\bar{z}$
(ii)	$x+1$	y	z	(v)	$\bar{x}-1$	$\bar{y}$	$\bar{z}$
(iii)	$\bar{x}$	$\bar{y}$	$\bar{z}$	(vi)	x	$y+1$	z

4 et 5, les atomes O(1) et O(2) d'une part, H(3) et H(4) d'autre part peuvent être considérés comme équidistants par rapport à ce plan et les angles concernés comme égaux. De plus l'atome H(5) s'éloigne peu de ce plan.

Une seule liaison hydrogène, intéressant l'atome H(2) de la molécule d'eau, est observée avec: $d[O(2^{vi})\cdots H(2)] = 1{,}82$ (9); $d[O(4)\cdots O(2^{vi})] = 2{,}751$ (6) Å et $O(4)-H(2)\cdots O(2^{vi}) = 163$ (9)°.

Le code de symétrie est explicité par le Tableau 6.

Discussion

La bibliographie fait en général état de polyèdres de coordination très dissymétriques pour le cadmium (Harrison & Trotter, 1972). Seul le dihydrogénophosphate de cadmium dihydraté possède un octaèdre CdO_6 presque parfait avec des distances de liaison comprises entre 2,28 et 2,31 Å (Averbuch-Pouchot, Durif, Guitel, Tordjman & Läugt, 1973). Le méthanesulfonate de cadmium dihydraté constitue donc un autre exemple de ce mode de coordination.

Cette structure met en évidence le rôle bicoordinant du groupement méthanesulfonato qui complète ceux de mono-, tri- et pentacoordinant déjà observés dans le cas des complexes avec Cu^{II}, Ca^{II} et Ag^{I} (Charbonnier, Faure & Loiseleur, 1977*a*,*b*,*c*).

Elle montre aussi que la symétrie C_s du groupement $CH_3SO_3^-$ qui avait été notée comme probable à propos du complexe $[Cu(CH_3SO_3)_2(H_2O)_4]$ (Charbonnier, Faure & Loiseleur, 1977*a*) doit vraisemblablement être réelle. L'existence formelle de cette symétrie a d'ailleurs été prouvée dans le méthanesulfonate de césium anhydre (Brandon & Brown, 1967) où le plan de symétrie s'identifie au plan *m* du groupe (*Pnma*).

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Study of the First-Order Phase Transition of $(C_3H_7NH_3)_2CdCl_4$ at 183 K by X-ray Diffraction of the Two Phases

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Bis(propylammonium) tetrachlorocadmate crystallizes in a perovskite-type layer structure. The Cl octahedra centred by Cd atoms form infinite two-dimensional layers which are sandwiched between the propylammonium chains. Two first-order phase transitions have been observed at 156 and 183 K by differential thermal analysis and optical methods. The phases below and above the 183 K transition with space groups *Pbca* and *Abma*, respectively, have been solved by X-ray diffraction analysis. The propylammonium chains are linked by hydrogen bonds to the layers. In the room-temperature phase, a positional disorder of the chains was observed which is interpreted as an oscillation of approximately 74° about the N–C(3) axis. The phase transition is due to the freezing of this movement and only one position remains below the transition temperature. One C atom of the alkyl chain remains, however, disordered. [Crystal data: low-temperature phase, $a = 7{\cdot}581$ (2), $b = 7{\cdot}301$ (1), $c = 25{\cdot}508$ (9) Å, $Z = 4$; room-temperature phase, $a = 7{\cdot}609$ (5), $b = 7{\cdot}367$ (3), $c = 25{\cdot}18$ (1) Å, $Z = 4$.]

1. Introduction

The phase transitions occurring in the systems $(C_nH_{2n+1}NH_3)_2MCl_4$ with M = Mn, Cu, Cd have attracted the attention of many solid-state physicists and are the topic of numerous recent investigations [see, for example, Blinc, Žekš & Kind (1977) and references cited therein].

The bis(alkylammonium) tetrachlorometallates have a structure similar to the perovskite-type compound K_2NiF_4. They form two-dimensional layers of corner-sharing Cl octahedra centred by the metal atoms and held together by the alkylammonium groups situated between them. X-ray and neutron diffraction studies on various systems have shown that the ammonium ends of these chains are always linked to the layer by hydrogen bonds whereas the methyl ends are directed towards the interlayer space. The distance between the chlorometallate layers is thus directly related to the number of C atoms of the alkylammonium ion.

Under various well defined temperatures, these compounds exhibit phase transitions in the solid state. It is known from spectroscopic measurements that they are triggered principally by the dynamic behaviour of the alkylammonium groups (Kind & Roos, 1976). Recently a model based principally on the free energy of the methylammonium groups has been proposed to describe the phase sequence in $(CH_3NH_3)_2CdCl_4$ (Blinc, Žekš & Kind, 1977). The generalization of such a model would be greatly facilitated by the knowledge of additional structural data on analogous systems. We report in this article an X-ray diffraction study of two phases of $(C_3H_7NH_3)_2CdCl_4$ occurring at room and at low temperature. In the following, this compound will be referred to by the shortened symbol C_3Cd for 3 C atoms in the alkylammonium chain and Cd as divalent metal.

2. Experimental

The synthesis of C_3Cd was similar to that reported for the corresponding Mn compound (Arend, Hofman & Waldner, 1973). For our single-crystal diffraction measurements, C_3Cd was obtained by slow evaporation from an aqueous solution. Mechanical deformations of the soft material were avoided by mounting the crystal directly from the solution on a quartz-glass fibre under the microscope.

2.1. *Temperature measurements of the phase transitions*

Differential thermal analysis of C_3Cd gave a very sharp peak at 158 (2) K and a second, slightly larger peak centred at approximately 183 K. Both showed the characteristics of first-order phase transitions. On a freezing-stage polarizing microscope, only a single phase transition occurring at 156·1 (3) K was observed corresponding to the sharp peak of the DTA measurement. The second transition in the temperature region of 183 K was not observed under polarized light.

2.2. *X-ray measurements*

X-ray intensity measurements were obtained on an automatic four-circle diffractometer (Syntex $P2_1$). Both phases were measured with Mo $K\bar{\alpha}$ radiation (λ_{Mo} = 0·71069 Å). We used the XRAY 72 system of programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) for the treatment of data and the refinement of the structures.

The values of the atomic scattering factors for neutral C and N atoms and for Cl^- and Cd^{2+} were those calculated by Cromer & Mann (1968). For H atoms we used the values given by Stewart, Davidson & Simpson (1965). Anomalous dispersion corrections for Cl and Cd atoms were taken from Cromer & Liberman (1970).

2.2.1. *Structure of the low-temperature phase.* A single crystal of C_3Cd with the dimensions 0·068 × 0·234 × 0·032 mm was maintained during the measurements at a temperature of 165 (2) K by means of an open stream of nitrogen gas (modified Syntex LT1 system). Lattice constants were obtained from a least-squares refinement of 12 accurately centred reflections with diffraction angles 2θ lying between 25 and 35°. They are a = 7·581 (2), b = 7·301 (1) and c = 25·508 (9) Å. The orthorhombic space-group symmetry was uniquely determined as

Table 1. *List of atomic coordinates of the low-temperature phase of* C_3Cd

The population parameter (p.p.) is given for each atom.

	p.p.	x	y	z
Cd	1	0·0	0·0	0·0
Cl(1)	1	0·2680 (2)	0·2323 (2)	−0·01314 (6)
Cl(2)	1	0·0554 (2)	−0·0178 (3)	0·09891 (7)
N	1	0·4749 (7)	0·0247 (8)	0·0863 (2)
C(1)	1	0·573 (1)	−0·033 (1)	0·1337 (3)
C(2*a*)	0·5	0·481 (2)	0·006 (3)	0·1825 (7)
C(2*b*)	0·5	0·517 (2)	0·068 (3)	0·1827 (7)
C(3)	1	0·604 (1)	−0·018 (1)	0·2304 (3)
H(1)	1	0·37	−0·02	0·089
H(2)	1	0·52	0·00	0·059
H(3)	1	0·44	0·16	0·084
H(4)	1	0·58	−0·16	0·136
H(5)	1	0·70	0·02	0·132
H(6*a*)	0·5	0·43	0·14	0·182
H(6*b*)	0·5	0·55	0·19	0·179
H(7*a*)	0·5	0·37	−0·07	0·186
H(7*b*)	0·5	0·39	0·05	0·186
H(8)	1	0·61	−0·15	0·232
H(9)	1	0·72	0·03	0·227
H(10)	1	0·55	0·03	0·263

Pbca from systematic absences (*International Tables for X-ray Crystallography*, 1969). The four formula units in the unit cell yielded a calculated density of 1·762 (4) g cm^{-3}; the measured density at 295 K was 1·74 (1) g cm^{-3}. With Nb-filtered radiation, 923 independent reflections were measured up to $(\sin\theta/\lambda)_{max} = 0{\cdot}54$ Å^{-1}, 605 of which had an intensity larger than $3\sigma(I)$ where $\sigma(I)$ represents the standard deviation of the intensity derived from counting statistics and the variations of periodically measured check reflections. Backgrounds were obtained by analysing the $2\theta/\theta$ scan profile (Schwarzenbach, 1977). All the intensities were corrected for absorption by the Gaussian integration method. With the linear absorption coefficient $\mu_{Mo} = 22{\cdot}5$ cm^{-1}, absorption factors ranged from 1·08 to 1·16. The structure was solved by interpretation of the Patterson map. An anisotropic least-squares refinement with unsplit C(2) atoms gave an abnormally large value of one of the diagonalized terms: $u_{I}[C(2)] = 0{\cdot}120$, $u_{II}[C(2)] = 0{\cdot}016$ and $u_{III}[C(2)] = 0{\cdot}035$ Å and the C(1)—C(2) distance of 1·46 (1) Å was also much too short to be accounted for. For this reason this position was split and the corresponding atom was refined isotropically in subsequent refinement cycles. By contrast, the thermal ellipsoids of C(1) and C(3) did not show any characteristic anisotropy. A difference Fourier synthesis revealed all the H atoms except those attached to the disordered C atom. Their positions were generated by assuming a C—H distance of 1 Å. A constant isotropic temperature coefficient ($u = 0{\cdot}06$ Å^2) was assigned to the H atoms bonded to the terminal and disordered C atoms. The final residual based on the $|F|$'s resulting from a full-matrix least-squares refinement was $R = \sum |\Delta F|/\sum |F_o| = 0{\cdot}028$. The weighting scheme was $w = 1/\sigma^2(F) = 1/[\sigma^2_{st}(F) + 3 \times 10^{-4} F^2]$ where σ_{st} represents the standard deviation of F derived from the statistics. Table 1 lists the final atomic parameters.*

2.2.2. *Structure of the room-temperature phase.* The relevant data for the room-temperature phase are: crystal dimensions: 0·017 × 0·030 × 0·0045 mm; temperature of measurements: 220 (3) K; lattice constants calculated from 13 accurately centred reflections; $a = 7{\cdot}609$ (5), $b = 7{\cdot}367$ (3) and $c = 25{\cdot}18$ (1) Å; space-group symmetry: *Abma*; $Z = 4$; ρ_x at 220 K: 1·763 (4) g cm^{-3}; radiation: Mo $K\alpha$, graphite-monochromatized; background: same as for the low-temperature phase; $(\sin\theta/\lambda)_{max} = 0{\cdot}71$ Å^{-1}; total independent measurements: 1117; observed reflections $[I > 3\sigma(I)]$: 869; intensities corrected for absorption with absorption factors ranging from 1·11 to 1·43. The structure was refined by full-matrix least squares on the $|F|$'s. A difference Fourier map revealed strong maxima in the neighbourhood of the two C(1) and C(2) atoms and out of the symmetry plane. The splitting of the two positions symmetrically to the mirror improved the model significantly. The thermal coefficients of the C(3) atom showed also some large motion in a plane parallel to the layer. The diagonalized ellipsoid, however, did not show any trend in a specific direction. Thus, this atomic position was constrained on the mirror plane. Only the ammonium H atoms found on a difference map were included in the structure factor calculations and kept constant during the refinement. The final residual $R = 0{\cdot}051$ was obtained by applying the weighting scheme $w = 1/[\sigma^2_{st}(F) + 6 \times 10^{-4} F^2]$ to the data. The positional parameters for the room-temperature phase of C_3Cd are given in Table 2.*

Table 2. *List of atomic coordinates of the room-temperature phase of* C_3Cd

The population parameter (p.p.) is given for each atom.

	p.p.	x	y	z
Cd	1	0·0	0·0	0·0
Cl(1)	1	0·25	0·25	−0·01266 (8)
Cl(2)	1	0·0540 (3)	0·0	0·09936 (9)
N	1	0·4717 (9)	0·0	0·0853 (3)
C(1)	0·5	0·572 (2)	0·037 (2)	0·1344 (5)
C(2)	0·5	0·499 (2)	−0·057 (3)	0·1820 (8)
C(3)	1	0·613 (2)	0·0	0·2308 (4)
H(1)	1	0·353	0·0	0·090
H(2)	0·5	0·491	−0·126	0·079
H(3)	0·5	0·515	0·060	0·055

3. Results

The orthorhombic low-temperature (OLT) phase of C_3Cd shows a disorder which affects principally the C(2) atom and its H atoms, as seen from Table 1. This disorder would hint at an oscillation of the C(2) atom in a plane normal to the direction defined by the C(1) and C(3) atoms. The N atom is bonded to the Cl octahedra by three H atoms with N—H···Cl distances varying between 3·21 and 3·36 Å (Table 3). Of these three H atoms, two are directed towards *two axial* Cl atoms [Cl(2)] and the third is directed towards one equatorial Cl atom [Cl(1)] as indicated on Fig. 1. This hydrogen-bond configuration has been found also in various bis(alkylammonium) tetrachlorometallates (Chapuis, Kind & Arend, 1976; Heger, Mullen & Knorr, 1976; Depmeier, 1977) and is responsible for a slight tilt of the Cl octahedra relative to the ideal chessboard-like configuration. This displacement amounts to a

* Lists of structure factors and thermal parameters for both phases have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33295 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

* See deposition footnote.

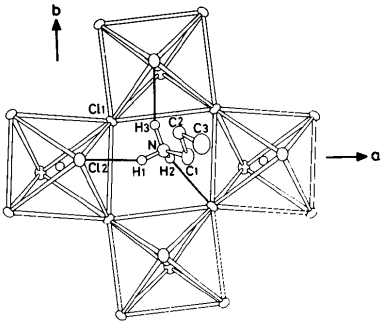


Fig. 1. Projection of the OLT phase of C_3Cd. This figure has been generated by the *ORTEP* plot program (Johnson, 1971) with thermal ellipsoids scaled to include 50% probability for the non-hydrogen atoms. Only one disordered C(2) and the three ammonium hydrogen atoms are shown in this figure.

Table 3. *Bond distances* (Å) *of the low-temperature phase of* C_3Cd

Cd–Cl(1)	2·668 (2)	N–H(1)	0·9 (1)
Cd–Cl(1^{i})	2·651 (2)	N–H(2)	0·79 (8)
Cd–Cl(2)	2·561 (2)	N–H(3)	1·0 (1)
N–C(1)	1·481 (9)	N–H(1)···Cl(2)	3·211 (6)
C(1)–C(2*a*)	1·46 (2)	N–H(2)···Cl(1^{ii})	3·287 (6)
C(1)–C(2*b*)	1·52 (2)	N–H(3)···Cl(2^{iii})	3·363 (6)
C(2*a*)–C(3)	1·55 (2)	N···Cl(1)	3·345 (6)
C(2*b*)–C(3)	1·52 (2)		

Symmetry code

(i) $x-\frac{1}{2}, -y+\frac{1}{2}, -z$
(ii) $-x+1, -y, -z$
(iii) $-x+\frac{1}{2}, y+\frac{1}{2}, z$

Table 4. *Bond angles* (°) *of the low-temperature phase of* C_3Cd

Cl(1)–Cd–Cl(2)	91·78 (5)	H(1)–N–H(2)	109 (9)
Cl(1)–Cd–Cl(1^{i})	93·01 (5)	H(1)–N–H(3)	98 (9)
Cl(2)–Cd–Cl(1^{i})	91·25 (5)	H(2)–N–H(3)	107 (9)
N–C(1)–C(2*a*)	113·5 (9)	H(1)–N–C(1)	107 (7)
N–C(1)–C(2*b*)	113·0 (9)	H(2)–N–C(1)	116 (6)
C(1)–C(2*a*)–C(3)	111 (1)	H(3)–N–C(1)	117 (5)
C(1)–C(2*b*)–C(3)	109 (1)		

Symmetry code

(i) $x-\frac{1}{2}, -y+\frac{1}{2}, -z$

rotation of 5° about the *c* axis and 11° about the *b* axis.

The octahedra have nearly tetragonal symmetry and are contracted along the direction of the non-bonding Cl atoms. None of the Cl–Cd–Cl angles deviates by more than 3° from 90° (Table 4). It is interesting to note that the geometry of the Cl octahedron is identical within error limits to that found in the OLT phase of C_2Cd (Chapuis, 1977). The direction of the propylammonium chain defined by the terminal N and C(3) atoms makes an angle of 15·6° relative to the layer normal (*c* axis). This tilt is a consequence of the three hydrogen bonds constraining the positions of the first two atoms, N and C(1), relative to the layer.

The bond distances and angles of the orthorhombic room-temperature (ORT) phase are given in Tables 5 and 6. This structure shows a disorder which is more important than in the OLT phase. In an ordered model, the propylammonium chain constrained by symmetry to lie on the mirror plane normal to the *b* axis showed very short C–C bonds and large anisotropic thermal coefficients perpendicular to the mirror plane. The splitting of the two C atoms indicates a superposition of

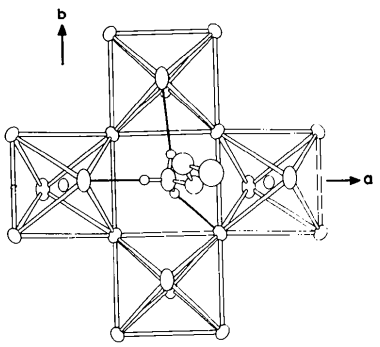


Fig. 2. Projection of the ORT phase of C_3Cd with 50% thermal ellipsoids for the non-hydrogen atoms. Only one single disordered chain is shown in the figure.

Table 5. *Bond distances* (Å) *of the room-temperature phase of* C_3Cd

Cd–Cl(1)	2·667 (1)	N–H(1)	0·91 (8)
Cd–Cl(2)	2·535 (2)	N–H(2)	0·95 (8)
N–C(1)	1·48 (1)	N–H(3)	0·94 (8)
C(1)–C(2)	1·49 (2)	N–H(1)···Cl(2)	3·198 (7)
C(2)–C(3)	1·56 (2)	N–H(2)···Cl(2^{i})	3·706 (5)
		N–H(3)···Cl(1^{ii})	3·350 (6)

Symmetry code

(i) $-x+\frac{1}{2}, -y-\frac{1}{2}, z$
(ii) $-x+1, y, -z$

Table 6. *Bond angles* (°) *of the room-temperature phase of* C_3Cd

Cl(1)–Cd–Cl(2)	90·13 (6)	H(1)–N–C(1)	113 (4)
Cl(1)–Cd–Cl(1^{i})	92·645 (7)	H(2)–N–C(1)	104 (4)
N–C(1)–C(2)	113 (1)	H(3)–N–C(1)	114 (4)
C(1)–C(2)–C(3)	107 (1)	H(1)–N–H(2)	100 (5)
		H(1)–N–H(3)	116 (4)
		H(2)–N–H(3)	105 (5)

Symmetry code

(i) $-x,y,-z$

two statistically equivalent propylammonium chains with terminal atoms occupying the same positions. In Fig. 2, only one of the two symmetrically equivalent chains is represented and a comparison with the same projection of the OLT phase will show the similarity between the chains. In the ORT phase also, the tilt of the whole chain relative to the *c* axis is 16°. By assuming that a specific bonding scheme of the H atoms corresponds to each single chain, the five maxima found in the neighbourhood of the N atom can be accounted for. This leads to the bonding scheme where two H [H(1) and H(2)] are directed towards *two axial* Cl atoms [Cl(2)] and one H [H(3)] is directed towards *one equatorial* Cl atom [Cl(1)]. This bonding scheme is identical with that observed in the OLT phase and is confirmed by the inclination of the N—C(1) bond relative to the layer normal, which angles are very similar in both phases (OLT: 35·8; ORT: 33·4°). The alternative hydrogen-bonding scheme, namely with one axial and two equatorial Cl atoms participating in the bonds, would result in a corresponding N—C(1) bond inclination of nearly 20°. Two of the N—H···Cl distances listed in Table 5 are in agreement with the corresponding values of the OLT phase. The third distance of 3·70 Å is too large in comparison with the values reported for the low-temperature phase, but it can be explained on the basis of the thermal coefficients reported for the N and Cl(2) atoms.* Both atoms have practically identical thermal coefficients with values $u_{22}[\mathrm{Cl}(2)] \simeq u_{22}(\mathrm{N})$ which are more than twice the other diagonal terms. This result is in contrast to the corresponding values found in the low-temperature phase where no significant anisotropy of the thermal coefficients of the N atom could be observed. On this basis, and by assuming that each Cl(2) atom participates only in a single hydrogen bond as in the OLT phase, the large anisotropic thermal coefficients can be interpreted as a result of a superposition of atoms participating in different and equally probable hydrogen-bonding schemes. It is clear that the N and Cl(2) atoms linked by a hydrogen bond will be displaced relative to each other, and the symmetry of the model requires the existence of two alternatives as represented in Fig. 3, a section through the layer.

* See deposition footnote.

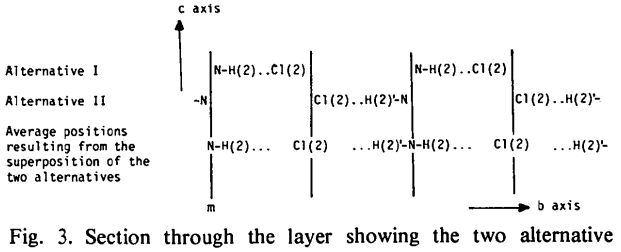


Fig. 3. Section through the layer showing the two alternative hydrogen-bonding schemes.

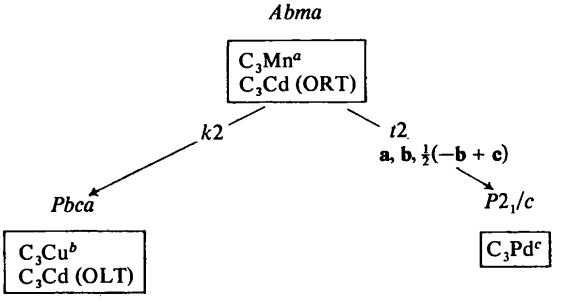
In view of this, the listed distance for N—H(2)···Cl(2) can be reduced by $2\sqrt{u_{22}} \simeq 0{\cdot}5$ Å giving a value comparable to the other distances. The Cl octahedra which are constrained by symmetry on the mirror plane are tilted about the *b* axis by an angle of 9·3°. They have nearly tetragonal symmetry and show the same contraction along the axial Cl atoms as in the OLT phase.

4. Discussion

Knowledge of the structural data below and above the phase transition at 183 K is of great help in understanding its mechanism. The X-ray structure analysis of the ORT phase shows a disordered structure with two statistically occupied and equivalent chain positions. Nuclear resonance analysis (Seliger, Blinc, Kind & Arend, 1976; Blinc, Burgar, Ložar, Seliger, Slak, Rutar, Arend & Kind, 1977) of these compounds has shown this disorder to be of a dynamical nature, *i.e.* the chain flips from one position to the other in the solid state. By assuming that the propylammonium molecule rotates about an axis going through the N and C(3) atoms, the angle of rotation needed to move the chain from one position to the other can be calculated to be 74°. The anisotropic temperature coefficient $u_{22}(\mathrm{N})$ shows, moreover, that the rotation is combined with an additional displacement of the N atom perpendicular to the mirror plane. At the transition temperature, the rotation of the propylammonium molecule is frozen and only one single chain position remains. From the five hydrogen bonds assumed before the transition, only three remain and

Table 7. *Group–subgroup relations in the family of compounds* $(C_3H_7NH_3)_2MCl_4$ *(abbreviated* C_3M*)*

The letter *k* characterizes subgroups belonging to the same crystal class and *t* subgroups with the same translations. The number following these symbols is the index of the subgroup. The basis vectors of the new cell are given as a linear combination of the basis vectors of the space group from which they are derived, if different.



References: (*a*) Peterson & Willett (1972). (*b*) Barendregt & Schenk (1970). (*c*) Willett & Willett (1977).

the tilt of the Cl octahedra changes accordingly. The mirror plane normal to the *b* axis disappears, resulting in a reduction of the symmetry to *Pbca*, a subgroup of index 2 of *Abma*. The geometry of the Cl octahedra does not change at all during the phase transition; only the position of each octahedron relative to its neighbours is altered.

The low-temperature phase, however, is not completely ordered. The C(2) position had to be split as a consequence of the very large anisotropic component parallel to the layer plane. Here, the two positions are related by a rotation of 36° about the C(1)—C(3) axis. This structural disorder is probably connected with the existence of two different proton spin-lattice relaxation times below the transition temperature as observed by NMR (Blinc *et al.*, 1977). It is unfortunately not possible to distinguish between a static or dynamic disorder by diffraction methods. However, the observation of two different C(2) positions is compatible with the existence of ordered domains in the crystal as proposed by nuclear magnetic resonance.

The structure of the ORT phase of C_3Cd is similar to the structure of C_3Mn (Peterson & Willett, 1972). Both have the same space-group symmetry and the same disorder of the propylammonium chain. Although the C(1) and C(2) positions in the Mn compound have not been split, the N—C and C—C distances as well as the anisotropic thermal coefficients reported for this structure show a behaviour of the chain identical with that of the ORT phase of the Cd compound. The Cu derivative of the same type of compound, however, crystallizes in a different space group, namely *Pbca* (Barendregt & Schenk, 1970). Because of the Jahn–Teller deformation of the d^9 ion, the Cu atom has not octahedral but square-planar coordination. The structure of the Cu derivative exhibits also a disordered propylammonium chain and was refined by splitting the C(2) and C(3) but not the C(1) positions. Neglecting the very small separation of the two disordered C(3) sites (0·39 Å), this type of disordered chain can be compared with the propylammonium of the OLT phase of the Cd compound. The separation of the two C(2) sites is 1·24 Å for the Cu derivative at room temperature and 0·6 Å for the low-temperature phase of the Cd derivative. The Pd compound (Willett & Willett, 1977) shows yet another kind of disorder of the chain. In this derivative, the two propylammonium chains are related to each other by a rotation of approximately 180° about the N—C(3) axis. As in the Cu compound, the coordination of the metal is square planar but the symmetry is further reduced to monoclinic. Table 7 gives a short summary of the symmetry relations between the structures found in the bis(propylammonium) tetrachlorometallates (Bärnighausen, 1975).

From the numerous structures of the bis(alkylammonium) chlorometallates known to this date, it seems that the existence of disordered chains is an intrinsic property of these layer compounds at room temperature and above. The chlorometallate layers influence the magnitude of this disorder according to the number of Cl atoms which are in a favourable position to contribute to the formation of H bonds. It is possible to freeze completely the dynamical behaviour of the chains by lowering the temperature. This has been shown in the monoclinic low-temperature phase of C_1Cd and, by analogy, it is highly probable that the C_3Cd phase below the second phase transition at 156 K will show a completely ordered propylammonium chain.

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The Crystal Structure of [4,4,4-Trifluoro-3,3-dihydroxy-1-phenyl-1-butanonato(2–)-*O,O′,O″*]tris(*p*-tolyl)antimony(V)–1,2-Dichloroethane (2/1)

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Crystals of the title compound, $C_{31}H_{28}F_3O_3Sb.\frac{1}{2}C_2H_4Cl_2$, are triclinic, space group $P\bar{1}$, with $a = 11{\cdot}828$ (1), $b = 13{\cdot}851$ (1), $c = 10{\cdot}516$ (1) Å, $\alpha = 103{\cdot}65$ (1), $\beta = 113{\cdot}03$ (1), $\gamma = 84{\cdot}14$ (1)° and $Z = 2$. The structure has been refined by the least-squares method to an R value of 0·028 on the basis of 6159 observed reflexions collected by diffractometry. The Sb complex is monomeric and exhibits a distorted octahedral coordination. The fluorinated ligand is hydrated at the carbonyl group next to the CF_3 group, to form a terdentate ligand, 3,3-dihydroxy-1-ketone, in which three O atoms are bonded to the Sb atom in facial positions. The Sb—O(alcohol) distances are 2·050 (2) and 2·042 (2) Å, and the Sb—O(carbonyl) distance is 2·568 (2) Å. The three Sb—C bonds, 2·122 (3), 2·112 (3) and 2·127 (2) Å, make angles ranging from 101·1 (1) to 103·9 (1)° owing to the repulsions among the three bulky tolyl groups.

Introduction

It is well known that a carbonyl or an aldehyde group attached to an electron-attracting group is liable to hydration to form a *gem*-diol. A typical example is chloral hydrate. However, a metal complex with such an organic ligand had not been reported, although the carbonate ion is a common inorganic *gem*-diol ligand. Recently, the first example of a complex of this type has been found for the reaction product of a triarylantimony(V) compound with trifluoroacetylacetone (Ebina, Ouchi, Yoshino, Sato & Saito, 1977; Ebina, Uehiro, Iwamoto, Ouchi & Yoshino, 1976). In this compound, the β-diketone is hydrated at the carbonyl group next to the trifluoromethyl group, being converted to a 4,4-dihydroxy-2-ketone ligand in which the *gem*-diol moiety forms a four-membered chelate ring with the Sb atom.

In this paper, the structure of the related compound with hydrated benzoyltrifluoroacetone is described.

Experimental

Colourless crystals of the title compound were grown by recrystallization from a mixture of dichloroethane and petroleum spirit. They are unstable in air, losing the solvent of crystallization. Preliminary cell dimensions and the space group were determined from oscillation and Weissenberg photographs. The cell dimensions were refined by least-squares calculations on the basis of 2θ values of higher-order reflexions ($37° < 2\theta < 55°$) measured on a diffractometer. The density was determined by flotation in an aqueous solution of potassium iodide.

The crystal data are: $C_{31}H_{28}F_3O_3Sb.\frac{1}{2}C_2H_4Cl_2$, FW 676·82, triclinic, $a = 11{\cdot}828$ (1), $b = 13{\cdot}851$ (1), $c = 10{\cdot}516$ (1) Å, $\alpha = 103{\cdot}65$ (1), $\beta = 113{\cdot}03$ (1), $\gamma = 84{\cdot}14$ (1)°, $U = 1540{\cdot}6$ (3) Å^3, $Z = 2$, $D_m = 1{\cdot}45$, $D_x = 1{\cdot}46$ g cm^{-3}; space group $P\bar{1}$ (No. 2); μ(Mo $K\alpha$) ($\lambda = 0{\cdot}7107$ Å) = 10·46 cm^{-1}.

The intensity data were collected on a Rigaku