angles are in the same row. Standard deviations were computed using the entire variance-covariance matrix and include lattice constant errors. The first three angles with copper as the central atom are formed by the three ligands that are nearly coplanar. These angles are similar to those formed by the three coplanar ligands in $KCu(CN)_2$ and $KCu_2(CN)_3 . H_2O$. The last six angles with copper as the central atom are formed by the tetrahedral neighbors. The Cu–NH_3 bond is 0·07 Å longer than the average of 2·00 Å observed for the Cu–N bonds in $KCu(CN)_2$ and $KC_2(CN)_3 . H_2O$; the Cu–NH_3 bond is essentially the same as the Cu–NH_3 (2·04, 2·06 Å) bonds found in $Cu(NH_3)_4SO_4 . H_2O$ (Mazzi, 1955).

The ammonia molecule ought to rotate fairly easily in this environment. Perhaps this is why hydrogen was not found. However, with a heavy atom such as copper, it would be difficult to find hydrogen in any case.

No calculations involving a disordered cyanide group were made. In this structure, the two ends of the cyanide group have such different surroundings that one orientation, whichever it is, must be highly favored.

Essentially planar groups of eight atoms occur in the structure. These planes are formed by two copper atoms, the cyanide group and the four atoms related to these by a symmetry center. The least-squares plane is given in Table 7 and the arrangement is diagrammed in Fig. 4.

Current theories of bonding seem inadequate to account for the structures of these complex cyanides. In $KCu(CN)_2$ and $KCu_2(CN)_3 . H_2O$ the copper atom is perhaps in an sp^2 hybridized state. The three ligands are approximately planar but the bond angles vary considerably from 120°. This also may be the case for the present compound, as far as the N, NH_3 and Cu ligands are concerned. In the present compound it is not clear how the Cu–C bonds are formed from the standpoint of either the copper atom or the carbon atom.

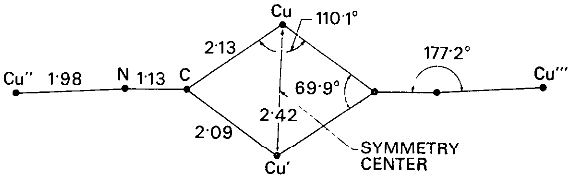


Fig. 4. Eight atom plane occurring in CuCN . NH_3.

All calculations were performed with an IBM-7094 computer using programs written by the authors.

References

CROMER, D. T. (1957). *J. Phys Chem.* **61**, 1388.

CROMER, D. T., DOUGLASS, R. M. & STARITZKY, E. (1957). *Anal. Chem.* **29**, 315.

CROMER, D. T. & LARSON, A. C. (1962). *Acta Cryst.* **15**, 397.

EVANS, H. T. (1961). *Acta Cryst.* **14**, 989.

Gmelins Handbuch der Anorganischen Chemie (1961), No. 60*B*, 854.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

MAZZI, F. (1955). *Acta Cryst.* **8**, 137.

ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139.

Acta Cryst. (1965). **19**, 197

Structures Involving Unshared Electron Pairs: Coordination of Antimony in Racemic Potassium Antimonyl Tartrate.*

BY D. GRDENIĆ AND B. KAMENAR

Laboratory of General and Inorganic Chemistry, Faculty of Science, University of Zagreb, Zagreb, Yugoslavia

(*Received* 16 *November* 1964)

The structure of racemic potassium antimonyl tartrate has been determined by X-ray diffraction methods. The space group is $Pca2_1$ (No. 29) and the unit cell has dimensions $a=8·79$, $b=16·32$, $c=12·19$ Å. The chemical formula is established as $C_4H_4O_7KSb . \frac{1}{2}H_2O$, eight of which are contained in the unit cell. The compound is shown to be based upon the antimonite ion, $[Sb(OH)_4]^-$.

There is an uncertainty about the structural formula of 'tartar emetic' in the chemical literature, but nevertheless the formulation of the compound as potassium antimonyl tartrate in still commonly used. Reihlen & Hezel (1931) proposed another structural formula with the antimony atom coordinated by one carboxylic and two hydroxylic oxygen atoms completed to a tetrahedron by one oxygen atom of a water molecule. On the basis of such a formula, these authors were able to explain why only D- or L-tartaric acid was able to form tartar emetic, while *meso*-tartaric acid was devoid of this property. The chemical behaviour of tartar emetic

---

* Reported at the Sixth Congress of the International Union of Crystallography, Rome, September 1963 (Grdenić & Kamenar, 1963).

in aqueous solutions was also discussed on the assumption of this formula (Chinoporos & Papathanasopoulos, 1961). Thus a tetrahedral coordination of antimony(III) was accepted regardless of the presence of an unshared electron pair which otherwise has been found stereochemically active in all similar instances (Wells, 1962; Grdenić & Šćavničar, 1960; Kamenar & Grdenić, 1961; Kamenar & Grdenić, 1962).

In order to facilitate the structure analysis, we decided to examine the racemic instead of natural tartrate because of the alleged holohedry (Groth, 1910). Still, it turned out that it belonged to the pyramidal class. This class was subsequently confirmed by Kiosse, Golovastikov & Belov (1964*a*) who observed the piezoelectric effect on the crystals. According to the crystallographic data reported by the same authors, the antimony(III) D-tartrates of potassium, rubidium and ammonium belong to one isomorphous group, the racemic antimony(III) tartrates of rubidium and ammonium to the other one, while the racemic potassium antimony(III) tartrate crystallizes in a different way. The data reported by Kiosse *et al.* for racemic potassium antimony(III) tartrate are in perfect agreement with the present data, except as regards the content of water of crystallization; they consider it to be a monohydrate, but a preliminary chemical analysis in this laboratory, as well as the results of the structure analysis, proved the salt examined to be a hemihydrate.

The racemic tartar emetic, with the empirical formula $C_4H_4O_7KSb\frac{1}{2}H_2O$, crystallizes in orthorhombic prismatic crystals elongated along the **c** direction. The unit-cell constants and density are:

$a = 8{\cdot}79 \pm 0{\cdot}02$ Å	$D_m = 2{\cdot}510$ g.cm^{-3}
$b = 16{\cdot}32 \pm 0{\cdot}02$	$D_x = 2{\cdot}508$
$c = 12{\cdot}19 \pm 0{\cdot}02$	$Z = 8$

The systematic absences of the reflexions $0hl$ for l odd and $h0l$ for h odd indicated $Pca2_1$ (C_{2v}^5) or $Pbcm$ (D_{2h}^{11}) as the possible space groups. The final choice of $Pca2_1$ (No. 29) was done in the course of the interpretation of the Patterson (x, 0, z) synthesis. Because $Z=8$, the unit cell contains two symmetrically independent sets of four tartrate formula units and one set of four water molecules.

The $hk0$ and $h0l$ reflexions were recorded on multiple-film Weissenberg photographs taken with nickel-filtered Cu K radiation and the intensities were determined by means of a microdensitometer. The cylindrically ground specimens along the c and b axes allowed an accurate absorption correction ($\mu = 315$ cm^{-1}) to be made. The structure has been determined from the centrosymmetrical (x, y) electron-density projection

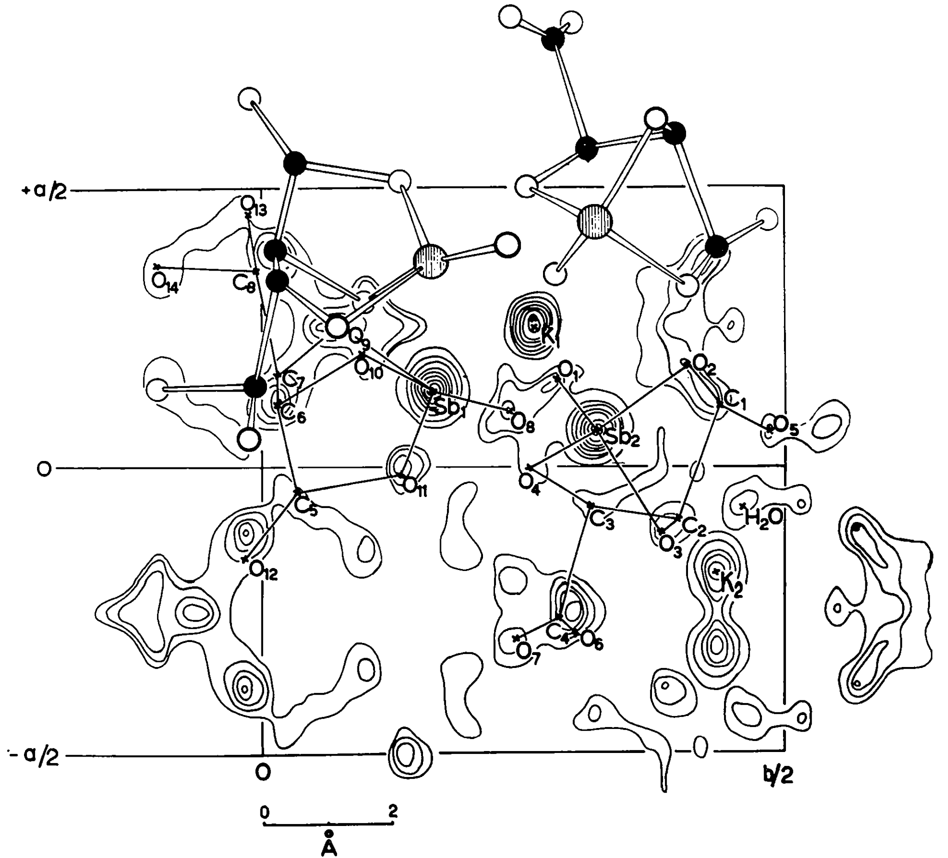


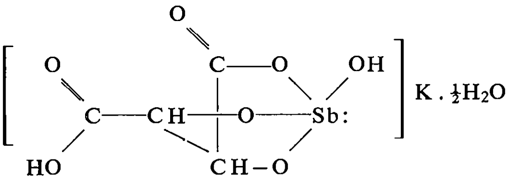
Fig. 1. The (x, y) Fourier synthesis of the electron-density projection in a crystal of racemic potassium antimony(III) tartrate. Contours are drawn on an arbitrary scale. The model of two symmetrically independent molecules as obtained from the preliminary atomic parameters is shown superimposed on the projection.

starting from antimony and potassium atomic coordinates evaluated from the corresponding Patterson projection. It was confirmed during refinement that almost all signs of the structure factors were defined by the antimony and potassium contribution. The reliability index in the present stage of the analysis is $R(hk0) = 0{\cdot}24$.

The (x, y) electron-density projection, with the assumed molecular model superimposed upon it, is shown in Fig. 1. The model is based on the standard interatomic distances and bond angles, as well as on the z parameters derived approximately from the packing conditions. All maxima in the projection are satisfactorily interpreted as concerns their height and position. Accordingly, tartar emetic in the crystalline state is represented by the structural formula

Table 1. *Atomic coordinates obtained from the x, y projection* (Fig. 1)

	x	y		x	y
Sb(1)	0·138	0·164	O(11)	−0·017	0·131
Sb(2)	0·064	0·319	O(12)	−0·162	−0·012
K(1)	0·233	0·210	O(13)	0·453	−0·023
K(2)	−0·191	0·434	O(14)	0·367	−0·083
O(1)	0·161	0·282	O(H_2O)	−0·077	0·458
O(2)	0·194	0·410	C(1)	0·119	0·427
O(3)	−0·120	0·375	C(2)	−0·083	0·406
O(4)	−0·005	0·255	C(3)	−0·062	0·314
O(5)	0·059	0·492	C(4)	−0·254	0·284
O(6)	−0·285	0·303	C(5)	−0·047	0·038
O(7)	−0·302	0·236	C(6)	0·110	0·013
O(8)	0·099	0·238	C(7)	0·170	0·013
O(9)	0·250	0·073	C(8)	0·347	−0·022
O(10)	0·204	0·097			



and the salt is defined as potassium hydroxotartratoantimonite hemihydrate. The compound therefore does not belong to the antimonyl series, but is a derivative of the antimonite ion $[Sb(OH)_4]^-$. The coordination of antimony is a deformed trigonal bipyramid whose four apices are occupied by oxygen while one equatorial apex belongs to the unshared electron pair. The O(1)Sb(2)O(3) as well as the O(8)Sb(1)O(10) angle, as evaluated from the present data, is 165 ± 5° instead of 180° as in a regular trigonal bipyramid. Such a deformation in similar cases has been explained as a consequence of the lone-pair bond pair-repulsion (Gillespie & Nyholm, 1957).

The crystal structure of the analogous racemic ammonium antimony(III) tartrate, as solved by Kiosse, Golovastikov & Belov (1964*b*) differs completely from the structure of racemic tartar emetic. This was to be expected because of the different symmetry and crystal classes, *i.e.* C_{2h} *versus* C_{2v}. However, the coordination of the antimony atom in both structures is not essentially different (in the ammonium derivative four oxygen atoms form the basis of a square pyramid if the unshared electron pair is considered to point towards the apex of the pyramid). As one can see in Fig. 1, the trigonal bipyramid (four oxygen atoms plus one unshared electron pair) should be deformed just in the direction which approximates it to a square pyramid. The final values of the OSbO angles will show whether a deformed trigonal bipyramid or a deformed square pyramid is the more convenient for the description of the actual coordination round the antimony atom.

Further work on the structure will be continued.

The authors are grateful to Rudjer Bošković Institute, Zagreb for experimental facilities.

References

Chinoporos, E. & Papathanasopoulos, N. (1961). *J. Phys. Chem.* **65**, 1643.

Gillespie, R. J. & Nyholm, R. S. (1957). *Quart. Rev. Chem. Soc. Lond.* **11**, 339.

Grdenić, D. & Kamenar, B. (1963). *Acta Cryst.* **16**, A 42.

Grdenić, D. & Ščavničar, S. (1960). *Proc. Chem. Soc.* p. 147.

Groth, P. (1910). *Chemische Kristallographie.* Vol. III, p. 378. Leipzig: Engelmann.

Kamenar, B. & Grdenić, D. (1961). *J. Chem. Soc.* p. 3954.

Kamenar, B. & Grdenić, D. (1962). *J. Inorg. Nucl. Chem.* **24**, 1039.

Kiosse, G. A., Golovastikov, N. I. & Belov, N. V. (1964*a*). *Kristallografiya,* **9**, 402.

Kiosse, G. A., Golovastikov, N. I. & Belov, N. V. (1964*b*). *Doklady Akad. Nauk S.S.S.R.*, **155**, 545.

Reihlen, H. & Hezel, E. (1931). *Liebigs Ann.* **486**, 217.

Wells, A. F. (1962). *Structural Inorganic Chemistry,* 3rd edn., p. 662. Oxford: Clarendon Press.