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**The crystal structure of  $\text{Ag}_8\text{Ca}_3$ .**\* By L. D. CALVERT and CYNTHIA RAND,† *Division of Applied Chemistry, National Research Council, Ottawa, Canada*

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### Preparation and identification

Silver calcium alloys were made from 99.997% silver granules, with an analysis comparable to the spectroscopic standard for silver, and calcium, distilled from high purity granules (Dominion Magnesium Ltd) with a representative analysis, after distillation, of Mg 2 ppm, Fe 0.2 ppm, Si 0.2 ppm, Sr 0.2 ppm, Ba and other metals not visible; analysis gave nitrogen at the 0.01% level. The components were melted together in a mild steel crucible under purified argon, after which a representative analysis for nitrogen was at the 0.1% level.

A silver-calcium alloy made in this manner and containing 22.2 at.% Ca was wrapped in iron foil, sealed in a silica tube under  $\sim 250$  torr of purified argon, annealed at 695 °C for four days and fast-quenched into water-free oil. The ingot was crushed in a dry inert atmosphere and single-crystal fragments of an unknown phase were obtained. X-ray specimens were protected by a coating of Saran-F220 resin (Dow Chemical Co., Sarnia, Ontario). Precession photographs (Mo  $K\alpha$  radiation,  $\lambda K\alpha = 0.7107$  Å,  $\mu = 20^\circ$ ) of the zero and first levels of the reciprocal lattice nets perpendicular to [001], [1 $\bar{1}$ 0] and [1 $\bar{1}$ 1] showed the crystals to be cubic, with diffraction symbol  $m\bar{3}m I...$ ,  $a = 9.81$  Å. The possible space groups are  $I432 (O_h^5)$ ,  $I\bar{4}3m (T_d^2)$  and  $Im\bar{3}m (O_h^3)$ . An X-ray powder photograph of the ingot revealed a mixture of free silver plus the unknown phase. The density of the quenched alloy was  $7.33 \text{ g.cm}^{-3}$  and chemical analysis confirmed that no change of composition had occurred during the annealing. Thus the unknown compound has a maximum density of  $7.33 \text{ g.cm}^{-3}$  and a minimum calcium content of 22.2 at.%. Assuming atomic volumes for silver and calcium derived from known silver-calcium compounds (Calvert, Dunsmore, Kuhl & Tse, 1957; Rand & Calvert, 1962) the cell contents were calculated to be  $\text{Ag}_{32}\text{Ca}_{12}$ , corresponding to 27.2 at.% Ca and  $D_x = 6.9 \text{ g.cm}^{-3}$ .

### Structure determination and refinement

The observed intensities were corrected for absorption by assuming a sphere of radius  $3.5 \times 10^{-2}$  mm for the roughly cube-shaped fragment used. The intensities were corrected for Lorentz-polarization and scaled by Wilson's method (Wilson, 1942). From the intensities of  $h00$ ,  $330$  and  $550$  and the known atomic sizes a trial structure was derived with 12 Ca in  $12(e)$ ,  $x00$  with  $x = 0.26$ , 8 Ag(1) in  $8(c)$ ,  $xxx$  with  $x = 0.25$  and 24 Ag(2) in  $24(g)$ ,  $xxz$  with  $x = 0.15$  and  $z = 0.5$  in the space group  $I43m$ . Fourier and difference syntheses for the [001] and [1 $\bar{1}$ 0] projections were used to refine the trial coordinates, until there were no further significant changes. The standard deviations of the coordinates were estimated by Cruickshank's method (Cruickshank, 1949) and are given below

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in Å. The final scaling was by comparison of observed and calculated structure factors using the same isotropic temperature factor ( $B = 2 \text{ Å}^2$ ) for both atoms. Final values of  $R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$  were 6% for the 20 accessible independent  $hkl$  reflexions and 6% for the 28  $hhl$  reflexions. The four  $hhl$  and two  $hk0$  reflexions which were unobserved were taken as threshold/2. After this refinement the atomic coordinates could be referred to the space group  $Im\bar{3}m$ .

### Crystal structure

$\text{Ag}_8\text{Ca}_3$  is cubic,  $Im\bar{3}m (O_h^3)$ , with 12 Ca in  $12(e)$ ,  $x00$  with  $x = 0.255$ ,  $\sigma = 0.02$  Å, 8 Ag(1) in  $8(c)$   $\frac{1}{4}\frac{1}{4}\frac{1}{4}$  and 24 Ag(2) in  $24(h)$ ,  $0xx$  with  $x = 0.653$ ,  $\sigma = 0.01$  Å;  $a = 9.81 \pm 0.02$  Å,  $B = 2 \text{ Å}^2$ ,  $U = 944 \text{ Å}^3$ , F.W. = 983.28,  $Z = 4$ ,  $D_x = 6.9 \text{ g.cm}^{-3}$ ,  $\mu_l = 189 \text{ cm}^{-1}$  (Mo  $K\alpha$ ).

The structure (Fig. 1) can be described as follows. Each Ag(1) lies at the centre of a slightly puckered hexagon of 6 Ag(2) at 2.80 Å; there are 6 Ca next nearest neighbours at 3.47 Å arranged at the apices of a trigonal antiprism. When viewed along a [111] direction this array can be recognized as a form of close-packing of unlike spheres, symbolized  $AbCAbC$  in the usual convention. Because of the overall symmetry this descrip-

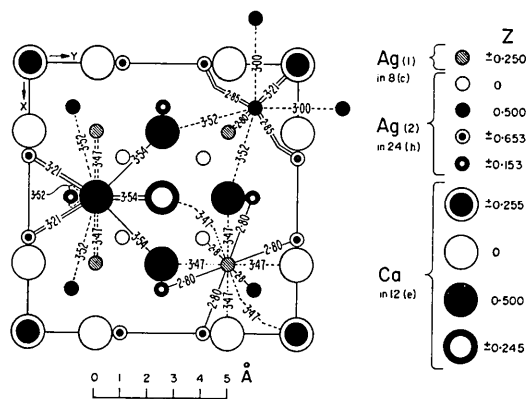


Fig. 1. Projection of the  $\text{Ag}_8\text{Ca}_3$  structure onto (001). The nearest neighbours around each crystallographically different atom are shown by full lines connecting the atoms; next nearest neighbours are indicated by dotted lines. The interatomic distances are given in Å.

tion does not apply to the structure as a whole but only to those atoms in the immediate neighbourhood of the Ag(1) atoms lying along a particular [111] axis. The structure as a whole can best be visualized by noting that the units of 12 atoms around each Ag(1) are lined up along the cube diagonals and share edges to form the octahedral array of 6 Ca atoms around the lattice points at  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$  and 000. The arrangement around the other atoms is less regular. Each Ca lies inside an irregular

square antiprism with vertices defined by 4 Ag(2) at 3.21 Å and 4 Ca at 3.54 Å; next nearest neighbours are 4 Ag(1) at 3.47 Å and 4 Ag(2) at 3.52 Å. Similarly the Ag(2) atoms lie inside an irregular square prism defined by 2 Ag(1) at 2.80 Å, 4 Ag(2) at 2.85 Å and 2 Ca at 3.21 Å with next nearest neighbours 2 Ag(2) at 3.00 Å and 2 Ca at 3.52 Å. Thus the total coordination numbers are 12 each for Ag(1) and Ag(2) and 16 for Ca.

This structure can be regarded as showing some formal resemblances to the  $D_{8h-3}$  structures and also to that of  $U_2F_9$ . For example it can be derived from the  $D_{8h}$  structure ( $\gamma$ - $Cu_3Zn_8$ ) by omitting Cu(1) in 8(c) and making appropriate changes in the parameters of the other atoms.

We are grateful to Dr W. A. Alexander of this Division who kindly prepared the original alloy.

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*Acta Cryst.* (1964). **17**, 1176

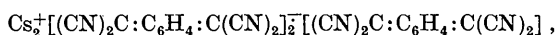
### Structural data on electrically conductive caesium tetracyanoquinodimethane,

$Cs_2[(NC)_2CC_6H_4C(CN)_2]_3$ . By PAUL ARTHUR, JR., *Central Research Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware, U.S.A.\**

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Electronic conductivity remarkably high for organic solids is observed in a series of salts formed from 7,7,8,8-tetracyanoquinodimethane (TCNQ) (Acker, Harder, Hertler, Mahler, Melby, Benson & Mochel, 1960). Theoretical and experimental aspects of electronic conduction and interaction in these compounds have been studied by several researches (Kepler, Bierstedt & Merrifield, 1960; Chesnut, Foster & Phillips, 1961; Chesnut & Phillips, 1961; Chesnut & Arthur, 1962; Jones & Chesnut, 1963). This communication reports a limited X-ray investigation of the molecular arrangements in one of these conducting crystals.

The 7,7,8,8-tetracyanoquinodimethane anion-radical salt with caesium,



prepared from CsCl and TCNQ (Melby, Harder, Hertler, Mahler, Benson & Mochel, 1962) crystallizes in the monoclinic system in the space group  $P2_1/c$  ( $C_{2h}^2$ ) with

$$a = 7.32 \pm 0.03, \quad b = 10.43 \pm 0.03, \quad c = 21.96 \pm 0.04 \text{ \AA};$$

$$\beta = 97.0^\circ \pm 0.1, \quad \text{cell volume} = 1664 \pm 15 \text{ \AA}^3, \quad Z = 2,$$

$$\text{formula} = Cs_2(C_{12}H_4N_4)_3,$$

observed density  $1.753 \pm 0.005 \text{ g.cm}^{-3}$ , X-ray density  $1.759 \text{ g.cm}^{-3}$ , 31 atoms per asymmetric unit, 124 atoms per unit cell.

The [100], [010] and [001] Patterson projections were used to determine the approximate position of the heavy caesium atom. Calculation of structure factors using only the caesium atom contribution produced trial signs for use with the observed structure factors. The signed factors were used to compute electron density distribution projections which were interpreted with the aid of a model planar TCNQ unit consistent with chemical and bond-distance information. The preliminary lighter atom positions were then used in conjunction with the caesium

atom positions to recalculate structure factor signs for use with the observed values.

The atomic positions of Table 1 and Fig. 1 resulted from adjustment of the caesium and TCNQ model positions according to successive  $\rho(x, z)$ ,  $\rho(y, z)$ , and  $\rho(x, y)$  maps until the discrepancy value  $R$  was reduced to 0.18 for the  $F(h0l)$ , 0.28 for the  $F(0kl)$ , and 0.29 for the  $F(hk0)$  values without corrections for absorption,

Table 1. Atomic parameters for  $Cs_2/(TCNQ)_2^+/(TCNQ)$

Atom	$x$	$y$	$z$
N(1)	0.618	0.960	0.150
C(1)	0.768	0.995	0.147
C(2)	0.956	0.039	0.143
C(3)	0.089	0.028	0.197
N(2)	0.198	0.019	0.240
C(4)	0.001	0.087	0.091
C(5)	0.239	0.160	0.033
C(6)	0.863	0.126	0.037
C(7)	0.195	0.108	0.083
N(3)	0.567	0.317	0.115
C(8)	0.717	0.352	0.112
C(9)	0.905	0.396	0.108
C(10)	0.038	0.385	0.162
N(4)	0.147	0.376	0.205
C(11)	0.950	0.444	0.056
C(12)	0.812	0.483	0.002
C(13)	0.144	0.465	0.048
N(5)	0.516	0.674	0.080
C(14)	0.666	0.709	0.077
C(15)	0.854	0.753	0.073
C(16)	0.987	0.742	0.127
N(6)	0.096	0.733	0.170
C(17)	0.899	0.801	0.021
C(18)	0.093	0.822	0.013
Cs	0.514	0.275	0.2645

The six hydrogen positions are not included since they were not involved in the calculations.

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