The Crystal Structure of Calcium Copper Acetate Hexahydrate and its Isomorph Calcium Cadmium Acetate Hexahydrate

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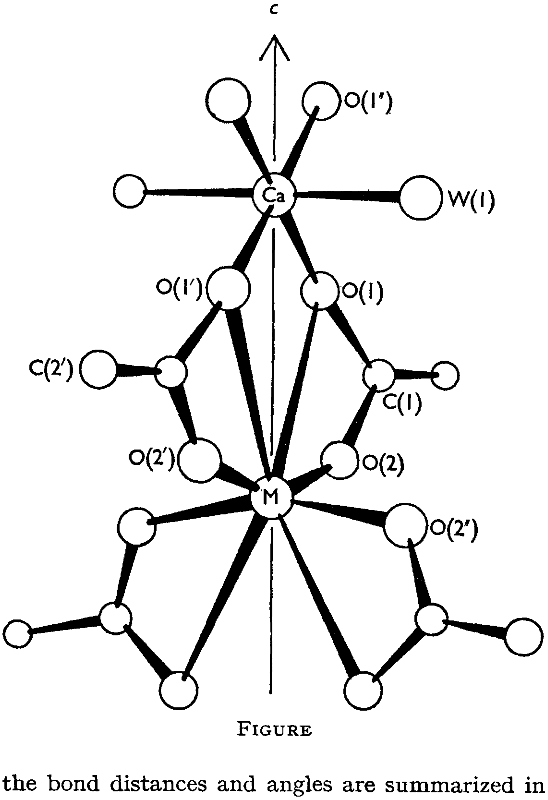
THE crystal structure of copper acetate monohydrate[1] and copper acetate monopyridine[2,3] are unusual in that the acetate ligands are bidentate and bridge such as to form dimeric units of the empirical formula. These crystals are antiferromagnetic as a result of the exchange interactions within the dimeric units. Calcium copper acetate hexahydrate is a normal paramagnetic crystal and may easily be grown as large tetragonal prismatic crystals from solutions of calcium acetate and copper acetate.[4] In view of the current interest in the stereochemistry and bonding of these acetates, a complete crystallographic investigation of $\mathrm{CaCu(OAc)_4,6H_2O}$ and a search for isomorphous crystals was undertaken. Only $\mathrm{CaCd(OAc)_4,6H_2O}$ was found to be isomorphous with $\mathrm{CaCu(OAc)_4,6H_2O}$. The structure of both isomorphs was completely determined. All attempts to prepare other isomorphs by substituting Ba or Sr for Ca and Zn for Cu or Cd met with failure.

Crystal data: $\mathrm{CaCu(OAc)_4,6H_2O}$, $M = 448$. Tetragonal, $a = 11{\cdot}183$, $c = 16{\cdot}277$ Å, $U = 2035$ Å^3, $D_m = 1{\cdot}465$, $Z = 4$, $D_c = 1{\cdot}461$.

$\mathrm{CaCd(OAc)_4,6H_2O}$, $M = 497$. Tetragonal, $a = 11{\cdot}374$, $c = 16{\cdot}084$ Å, $U = 2080$ Å^3, $D_m = 1{\cdot}629$, $Z = 4$, $D_c = 1{\cdot}585$. Space group (in each case): $I\,4/m$ (No. 87).

Intensities were determined, using Mo-K_α radiation ($\lambda = 0{\cdot}7107$ Å), with a G.E. XRD-5 diffractometer. The structure was solved by the heavy-atom method, and refined by electron-density syntheses and anisotropic, block-diagonal, least-squares analysis. Final R-values are 0·041 for 1049 non-zero intensity-terms (Cu salt) and 0·057 for 924 terms (Cd salt).

The co-ordination polyhedra about the Ca and M (Cu or Cd) atoms are depicted in the Figure, and the bond distances and angles are summarized in the Table. The acetate anion is bidentate and acts as a bridging ligand between two metal ions in such a manner as to produce polymeric chains



FIGURE

TABLE

Interatomic distances and angles[a] *of* CaM(OAc)$_4$,6H$_2$O

Atoms	M = Cu Dist. (Å)	M = Cd Dist. (Å)	Atoms	M = Cu Angle, deg.	M = Cd Angle, deg.
M–O(1)	2·790(3)	2·677(8)	O(1)–M–O(1)	65·7(1)	66·3(2)
M–O(2)	1·973(2)	2·289(7)	O(2)–M–O(2″)	90·6(1)	90·7(2)
Ca–O(1)	2·295(3)	2·305(9)	O(1)–Ca–O(1′)	82·5(1)	78·8(3)
Ca–W(1)	2·358(3)	2·356(9)	O(1)–Ca–O(1″)	97·5(1)	101·2(3)
C(1)–C(2)	1·509(5)	1·507(15)	W(1)–Ca–O(1)	91·4(1)	92·2(2)
C(1)–O(1)	1·233(4)	1·262(12)	W(1)–Ca–O(1′)	88·6(1)	87·8(2)
C(1)–O(2)	1·268(4)	1·226(10)	O(1)–C(1)–O(2)	121·5(3)	118·8(8)
O(1)–O(2)	2·182(4)	2·142(10)	O(1)–C(1)–C(2)	121·0(3)	121·7(9)
O(1)–O(1′)	3·025(5)	2·927(13)	O(2)–C(1)–C(2)	117·4(3)	119·4(8)
O(1)–O(1″)	3·452(4)	3·554(13)			
O(2)–O(2″)	2·806(3)	3·258(9)			

[a] The estimated standard deviations in the last significant figure are given in the parentheses.

of alternate metal ions parallel to the *c* axis of the crystal. The water molecules co-ordinate only to the Ca-metal ions and their role in the structure is to fill the void of the lattice and to bind the polymeric chains together. Each water molecule co-ordinated to the Ca is hydrogen-bonded to the remaining water molecules in such a manner as to form a "cluster" of twelve water molecules which has C_{4h} symmetry. The calcium atom occupies a site of $2/m(C_{2h})$ symmetry and is six-co-ordinate with four oxygen [O(1)] atoms from the bridging acetates and two water molecules [W(1)] which are members of different solvent clusters. The M atom occupies the $\bar{4}(S_4)$ site and is co-ordinated to a puckered square of four oxygen atoms [O(2)] at 1·972 Å for Cu and 2·286 Å for Cd. The oxygen atoms [O(1)] which are co-ordinated to calcium are bridging between Ca and M and are 2·787 Å from Cu or 2·682 Å from Cd. Two of these O(1) atoms lie above the puckered square and two below. The O(2) atoms describe a tetrahedrally distorted square plane while the O(1) atoms describe an elongated tetrahedron about the variable metal ion. The symmetry of the resulting co-ordination polyhedron is approximately D_{2d} and is a distorted dodecahedron. In CaCu(OAc)$_4$,6H$_2$O the oxygen atoms of the puckered square make an angle of 96·1° with the *c* axis of the crystal but the angle that adjacent oxygen atoms form with Cu is 90·6°, which differs only slightly from the 90° required for square planar co-ordination.

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