

Another structure which can be similarly described is acetato(dimethyl)indium(III) (Einstein, Gilbert & Tuck, 1973), in which In bonds to two methyl groups, an acetate group perpendicular to the  $\text{InMe}_2$  plane, and two O atoms from neighbouring acetate groups above and below the  $\text{InMe}_2$  plane. Similar results have been reported for  $(\text{C}_2\text{H}_5)_2\text{In}(\text{O}_2\text{CCH}_3)$  (Hausen, 1972). By analogy with the above discussion, these  $R_2\text{In}(\text{O}_2\text{CCH}_3)(\text{O}')_2$  structures involve five-coordinate In, with the  $\text{C}_2\text{In}(\text{O}_2\text{CCH}_3)$  moiety accepting two pairs of electrons from neighbouring acetate ligands, which are rotated through  $90^\circ$  relative to the position of the benzoate group in  $\text{Cl}_2\text{In}(\text{O}_2\text{CC}_6\text{H}_5)\text{py}_2$ . An equally valid description is that both are adducts of parent molecules  $R_2\text{In}(\text{O}_2\text{CR}')$  in which In has the planar three-coordinate  $\text{MX}_3$  stereochemistry, and the donor atoms (pyridine N, acetate O atoms) occupy the apical sites to give the five-coordinate stereochemistry which we believe correctly describes these species.

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## Reinvestigation of the Structure of Calcium Copper Acetate Hexahydrate, $\text{CaCu}(\text{C}_2\text{H}_3\text{O}_2)_4 \cdot 6\text{H}_2\text{O}^*$

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**Abstract.**  $M_r = 447.89$ , tetragonal,  $I4/m$ ,  $a = 11.152(2)$ ,  $c = 16.240(1) \text{ \AA}$ ,  $U = 2019.7(5) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_m = 1.465$ ,  $D_x = 1.473 \text{ g cm}^{-3}$ ,  $\lambda(\text{Mo } K\alpha) =$

$0.71069 \text{ \AA}$ ,  $\mu(\text{Mo } K\alpha) = 13.2 \text{ cm}^{-1}$ ,  $F(000) = 932$ ,  $T = 295 \text{ K}$ ,  $R = 0.026$  for 841 observed reflections with  $I > 2.5\sigma(I)$ . The structure consists of infinite acetato-bridged chains of alternate metal ions that are linked together *via* water molecules which form twelve-membered water cages in the structure.

\* Poly[(diaquacalcium)-bis- $\mu$ -(acetato- $O:O,O'$ )-copper-bis- $\mu$ -(acetato- $O'',O''':O''''$ )] tetrahydrate.

**Introduction.** The title compound is an example of an incongruently saturating double salt (Findlay, 1951), *i.e.* an attempt to recrystallize it from an aqueous solution results initially in the deposition of the single salt  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  and not of the double salt again. However, a study of the ternary  $\text{Cu}(\text{OAc})_2$ – $\text{Ca}(\text{OAc})_2$ – $\text{H}_2\text{O}$  system indicates that the double salt may be obtained by isothermal evaporation after the addition of an additional amount of the  $\text{Ca}(\text{OAc})_2$  component (Holden & Singer, 1960). The present paper reports the detailed crystal structure of the double salt as part of a study of the structures that underlie the ternary system. Although the essential coordination features of the structure were reported in a preliminary communication by Langs & Hare (1967), neither explicit coordinate data nor information on hydrogen atoms was given.

The crystal structure of copper acetate has been reported previously by Van Niekerk & Schoening (1953) and refined by de Meester, Fletcher & Skapski (1973). The structure of calcium acetate will be presented in due course (Klop, Schouten, van der Sluis & Spek, 1983).

**Experimental.** Enraf–Nonius CAD-4F diffractometer, Zr-filtered  $\text{Mo K}\alpha$  radiation, block-shaped crystal,  $0.50 \times 0.75 \times 1.50$  mm, 1568 reflections measured,  $\omega/2\theta$  scan,  $\theta < 30^\circ (+h, +k, +l)$ , four reference reflections ( $224, \bar{2}24, \bar{2}24, 224$ ), decay of 4.5%; cell dimensions from the setting angles of twelve reflections, reflection data corrected for Lorentz, polarization and absorption effects (Gauss; minimum and maximum transmission: 0.33 and 0.53) and averaged ( $R_{\text{int}} = 2.6\%$ ), 1332 unique reflections, 841 reflections with  $I > 2.5\sigma(I)$  used in structure determination. Metal-atom positions located with *MULTAN80* (Main, 1980),

structure completed for non-hydrogen atoms with *DIRDIF* (Beurskens *et al.*, 1981), refined on *F* by full-matrix least squares, anisotropic for non-hydrogen atoms, hydrogen atoms of water molecules located from difference Fourier map (refined isotropic). The observed rotational disorder in methyl-group hydrogen atoms was analysed by rigid-group refinement in terms of two mutually staggered conformations (final site-occupation factors 0.57 and 0.43). One reflection was excluded because it apparently suffered from extinction (040). An empirical extinction correction was applied [ $F(\text{cor}) = F(1 - 0.0001gF^2/\sin\theta)$ ,  $g = 0.001(1)$ ];  $R = 0.026$ ,  $R_w = 0.030$ ,  $w^{-1} = [\sigma^2(F) + 0.001F^2]/0.496$ ,  $S = 1.69$ ,  $(\Delta/\sigma)_{\text{max}} = 0.01$ , min/max  $\Delta\rho$  excursions in final difference Fourier map 0.34 and  $0.40 \text{ e } \text{\AA}^{-3}$ ; scattering factors from Cromer & Mann (1968) and anomalous dispersion corrections from Cromer & Liberman (1970).<sup>\*</sup> All calculations carried out on the CDC-Cyber-175 of the University of Utrecht with the programs of the *SHELX76* (Sheldrick, 1976) and *EUCLID* (Spek, 1982) packages.

**Discussion.** The final values of the parameters are given in Table 1. Fig. 1 gives a view of the unit-cell contents along with the adopted numbering scheme. The twelve-membered water cage that cross-links four infinite linear acetato-bridged Cu, Ca chains is shown in Fig. 2. Relevant data on the geometry are given in Table 2.

<sup>\*</sup> Lists of structure factors, anisotropic thermal parameters, bond lengths and angles and a drawing of the projection of the structure down the *c* axis have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38671 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final coordinates and equivalent isotropic thermal parameters*

The labels *A* and *B* denote the disorder in the hydrogen atom positions of the methyl moiety.

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}(\text{\AA}^2)^*$
Cu	0.5	0.0	0.25	0.0264 (1)
Ca	0.5	0.0	0.5	0.0308 (3)
<i>W</i> (1)†	0.5462 (2)	0.3299 (2)	0.3581 (1)	0.0457 (6)
<i>W</i> (2)	0.5779 (3)	0.1951 (2)	0.5	0.057 (1)
O(1)	0.6591 (1)	−0.0744 (1)	0.2626 (1)	0.0376 (5)
O(2)	0.6242 (2)	−0.0545 (2)	0.3942 (1)	0.0616 (7)
C(1)	0.6889 (2)	−0.0876 (2)	0.3375 (1)	0.0339 (6)
C(2)	0.8069 (2)	−0.1468 (3)	0.3550 (2)	0.0535 (9)
H(1 <i>A</i> )	0.8591 (2)	−0.0768 (3)	0.3783 (2)	0.062 (7)
H(1 <i>B</i> )	0.8384 (2)	−0.1452 (3)	0.4107 (2)	0.062 (7)
H(2 <i>A</i> )	0.8367 (2)	−0.1955 (3)	0.3082 (2)	0.062 (7)
H(2 <i>B</i> )	0.8713 (2)	−0.1057 (3)	0.3080 (2)	0.062 (7)
H(3 <i>A</i> )	0.7814 (2)	−0.2068 (3)	0.4097 (2)	0.062 (7)
H(3 <i>B</i> )	0.7961 (2)	−0.2413 (3)	0.3295 (2)	0.062 (7)
H(4)	0.555 (3)	0.283 (3)	0.324 (2)	0.070 (8)
H(5)	0.489 (3)	0.352 (3)	0.361 (2)	0.070 (8)
H(6)	0.567 (2)	0.240 (3)	0.458 (2)	0.064 (9)

$$* U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

† *W* indicates the O atom of a water molecule.

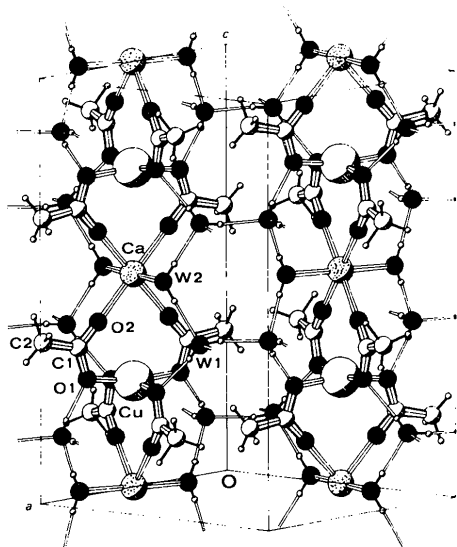


Fig. 1. Crystal structure of  $\text{CaCu}(\text{OAc})_4 \cdot 6\text{H}_2\text{O}$  with the adopted numbering scheme.

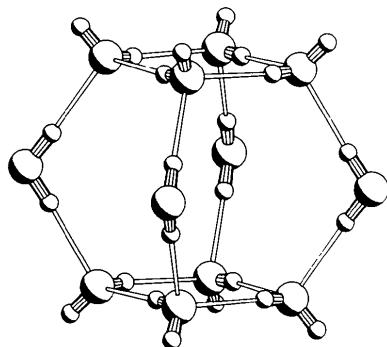


Fig. 2. The twelve-membered 'water cage'.

Table 2. Relevant data on the geometry of  $\text{CaCu}(\text{OAc})_4 \cdot 6\text{H}_2\text{O}$ 

Bond distances (Å)			
Cu—O(1)	1.969 (1)	Ca—W(2)	2.343 (2)
Cu—O(2)	2.289 (2)	C(1)—O(1)	1.227 (3)
		C(1)—O(2)	1.499 (3)

Bond angles (°)			
O(1)—Cu—O(1 <sup>b</sup> )	168.1 (1)	O(2)—Ca—W(2)	91.3 (1)
O(1)—Cu—O(1 <sup>a</sup> )	90.6 (1)	O(1)—C(1)—O(2)	122.0 (2)
O(2)—Ca—O(2 <sup>b</sup> )	82.7 (1)	O(1)—C(1)—C(2)	117.5 (2)
O(2)—Ca—O(2 <sup>a</sup> )	97.3 (1)	O(2)—C(1)—C(2)	120.4 (2)

Hydrogen bonds (Å, °)							
	O...O	O—H	H...O	∠O—H...O	∠H...O—X	X	
W(1)—H(4)...	O(1 <sup>b</sup> )	2.751 (2)	0.77 (3)	1.98 (3)	178 (4)	121 (1)	C(1 <sup>b</sup> )
W(1)—H(5)...	W(1 <sup>a</sup> )	2.780 (3)	0.69 (4)	2.11 (4)	168 (4)	121 (3)	H(4 <sup>b</sup> )
						102 (3)	H(5 <sup>b</sup> )
W(2)—H(6)...	W(1)	2.774 (2)	0.85 (3)	1.93 (3)	175 (3)	104 (3)	H(4)
						104 (3)	H(5)

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

The bond distances and angles from this analysis are in good agreement with the values reported by Langs & Hare (1967). The acetato-bridged Cu...Ca distance [4.060 (1) Å] is much longer than the corresponding distance in  $[\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}]_2$  with Cu—Cu = 2.616 (1) Å (de Meester, Fletcher & Skapski, 1973). The coordination sphere of Cu consists of the eight oxygen atoms of four acetate ligands; four O atoms coordinated in an approximate square-planar configuration with a short Cu—O distance of 1.969 (1) Å and four O atoms coordinated tetrahedrally with a

much longer Cu...O distance of 2.788 (2) Å. The Ca atoms are octahedrally surrounded by four oxygen atoms of four acetato ligands and two oxygen atoms of water molecules. The water molecules in the structure are arranged on the corners of decahedrons with exact  $4/m$  symmetry, the centres of which are at sites (0,0,0) and  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ . Sixteen hydrogen atoms of this water cluster form hydrogen bridges which are directed along the edges of the decahedron. The eight remaining hydrogen atoms are directed outward from the cage and are hydrogen bonded to the acetate O(1) atoms. The decahedron shares four O atoms with the Ca octahedra which are part of the four surrounding chains. There is a void with a diameter of about 3 Å within the water cage.

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## Dimer of (2, 2', 2''-Nitrilotriethanolato)(2-propanolato)titanium(IV), [Ti<sub>2</sub>(C<sub>6</sub>H<sub>12</sub>NO<sub>3</sub>)<sub>2</sub>(C<sub>3</sub>H<sub>7</sub>O)<sub>2</sub>]

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**Abstract.**  $M_r = 506.31$ , monoclinic,  $C2/c$ ,  $a = 91.65$  (1) Å,  $V = 2356$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.427$  g cm<sup>-3</sup>,  $12.240$  (1),  $b = 13.379$  (2),  $c = 14.394$  (1) Å,  $\beta = 90.0$  (1)°,  $\lambda = 0.71069$  Å,  $\mu = 7.5$  cm<sup>-1</sup>,  $F(000) = 1072$ ,

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