

Structure of (Benzoato)dichlorobis(pyridine)indium(III), $C_{17}H_{15}Cl_2InN_2O_2$

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Abstract. $M_r = 465.1$, orthorhombic, $Pna2_1$, $a = 20.069$ (6), $b = 10.633$ (3), $c = 9.050$ (2) Å, $V = 1931$ (1) Å³, $Z = 4$, $D_x = 1.599$, $D_m = 1.59$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 13.9$ cm⁻¹, $F(000) = 920$, $T = 295$ K. Final $R = 0.023$ for 1362 unique observed reflections. The possible modes of bonding of the benzoate anion to In are discussed; a three-centre orbital interaction is proposed.

Introduction. In a recent paper (Peppe, Tuck & Victoriano, 1982) we have described some of the synthetic applications of solutions of indium(I) halides in non-aqueous media. One reaction of particular interest corresponds formally to the oxidative insertion of InX ($X = \text{Cl, Br or I}$) into an $A-B$ bond to give species $AInX(B)$. Although such reactions with alkyl halides (*i.e.* $A-B = C-X$) were reported some years ago (Waterworth & Worrall, 1971; Poland & Tuck, 1972), the availability of the solution-phase reaction has now allowed us to extend these investigations to substrates involving elements of Group V and VI. The products of the reaction between $InCl$ and dibenzoyl peroxide in dichloromethane/pyridine solution included the title compound $Cl_2In(O_2CC_6H_5)_2$ (py = pyridine).

We have established the structure of this substance by X-ray crystallographic methods. The results allow some interesting comparisons with results for previously studied indium(III) complexes, and lead to a discussion of the bonding between In and the carboxylate ligand.

Experimental. Equimolar quantities of indium(I) chloride and dibenzoyl peroxide (*ca* 5 mmol) were mixed with 50 ml dichloromethane at 193 K. Pyridine (4 ml) was then added and the temperature allowed to rise slowly to ambient; after being stirred for 5 d, the reaction mixture was a deep-red solution over a brown solid. Addition of diethyl ether to the solution caused the precipitation of further brown solid, which was removed by filtration. The resultant solution slowly deposited a yellow solid, which was removed, and on further standing the filtrate deposited colourless acicular crystals of $Cl_2In(O_2CC_6H_5)_2$, whose composition was established by elemental analysis and

spectroscopy. The overall sequence of reactions will be discussed elsewhere.

Density measured by flotation in CCl_4/CH_3I , $0.08 \times 0.18 \times 0.51$ mm. Syntex $P2_1$ diffractometer, highly oriented graphite monochromator. Data collected and processed as described earlier (Khan, Steevensz, Tuck, Noltes & Corfield, 1980). Intensities of three monitor reflections decreased 20%, scaling factor based on averaged decrease applied. Systematic absences ($0kl$, $k+l = 2n+1$; $h0l$, $h = 2n+1$), choice of two space groups $Pna2_1$ (No. 33) and $Pnam$ (No. 62), space group $Pna2_1$ used, later assumed correct because of successful refinement. 1924 reflections ($2\theta_{\text{max}} = 50^\circ$, h 0–20, k 0–12, l 0–10), 1362 [$I > 2.0\sigma(I)$] unique. Lorentz, polarization, absorption corrections, min. and max. 1.10 and 1.24. Structure solved by heavy-atom method; positions of In and Cl atoms obtained from a sharpened Patterson synthesis, positions of remaining non-H atoms determined from a difference Fourier map. Anisotropic full-matrix least squares, $\sum w(|F_o| - |F_c|)^2$, converged at $R = 0.0292$; difference map at this stage showed peaks at plausible H-atom positions, H atoms included in subsequent refinement in idealized positions and isotropic thermal parameters fixed at 0.01 Å² greater than U of the appropriate C atoms. Final $R = 0.0230$, $R_w = 0.0247$ for 1362 unique observed reflections; $w = [\sigma^2(F) + 0.002F^2]^{-1}$; $S = 0.8$. In final cycle of refinement largest shift/error 0.01. Final difference map had no features of chemical significance, largest peak $0.3 \text{ e } \text{Å}^{-3}$ close to In. Scattering factors for all non-H atoms, including anomalous-dispersion correction for In and Cl, from Ibers & Hamilton (1974), for H from Stewart, Davidson & Simpson (1965). Programs used included *SHELX* (Sheldrick, 1977), *XANADU* (Roberts & Sheldrick, 1975), *ORTEP* (Johnson, 1965), *ABSORB* (Templeton & Templeton, 1973).

Discussion. Positional and thermal parameters are given in Table 1,† interatomic distances and angles in Table 2; Fig. 1 shows the molecule.

† Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and a packing diagram have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38653 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The molecular structure of $\text{Cl}_2\text{In}(\text{O}_2\text{CC}_6\text{H}_5)\text{py}_2$ has a number of interesting features, some of which focus upon the matter of the bonding of the benzoate ligand. We deal with these matters seriatim.

The two pyridine rings are identical within experimental error. The N—C and C—C bond distances are essentially identical to those for free pyridine (Mootz & Wussow, 1981), but there are small increases in the angles at C—N—C and C(12,22)—C(13,23)—C(14,24), corresponding to a slight compression of the coordinated rings along the In—N(2)—C(23) and In—N(1)—C(13) axes.

Table 1. Atomic coordinates and equivalent isotropic thermal parameters

	x	y	z	\bar{U}_{eq}^* ($\text{\AA}^2 \times 10^3$)
In	0.16924 (2)	0.04861 (4)	0.25000	58.8
Cl(1)	0.2838 (1)	0.0657 (2)	0.1805 (3)	85
Cl(2)	0.1361 (1)	-0.1626 (2)	0.1963 (3)	92
O(1)	0.1545 (2)	0.2464 (4)	0.3308 (5)	62
O(2)	0.0696 (2)	0.1191 (4)	0.3382 (5)	63
N(1)	0.1301 (3)	0.1235 (5)	0.0343 (6)	64
N(2)	0.1941 (3)	0.0030 (6)	0.4922 (7)	65
C(1)	0.0932 (3)	0.2278 (6)	0.3564 (7)	53
C(2)	0.0516 (3)	0.3310 (6)	0.4147 (7)	54
C(3)	0.0810 (4)	0.4427 (7)	0.4561 (10)	76
C(4)	0.0433 (6)	0.5383 (10)	0.5141 (17)	105
C(5)	-0.0239 (7)	0.5224 (10)	0.5329 (12)	100
C(6)	-0.0538 (6)	0.4137 (13)	0.4881 (16)	103
C(7)	-0.0158 (4)	0.3160 (7)	0.4308 (9)	75
C(11)	0.1603 (4)	0.2172 (7)	-0.0352 (10)	78
C(12)	0.1340 (6)	0.2687 (9)	-0.1621 (12)	104
C(13)	0.0743 (6)	0.2221 (10)	-0.2137 (9)	109
C(14)	0.0432 (5)	0.1283 (10)	-0.1439 (10)	95
C(15)	0.0725 (4)	0.0805 (8)	-0.0189 (10)	78
C(21)	0.2418 (4)	0.0664 (8)	0.5624 (10)	81
C(22)	0.2594 (5)	0.0443 (9)	0.7074 (10)	97
C(23)	0.2261 (5)	-0.0472 (9)	0.7821 (8)	89
C(24)	0.1758 (5)	-0.1113 (10)	0.7144 (10)	94
C(25)	0.1608 (4)	-0.0842 (8)	0.5695 (11)	85

* \bar{U}_{eq} is calculated from the refined anisotropic thermal parameters (deposited)

$$\bar{U}_{\text{eq}} = \frac{1}{3} \sum_{i=1}^3 (\text{r.m.s.d.}_i)^2;$$

r.m.s.d. values are taken from the ORTEP output.

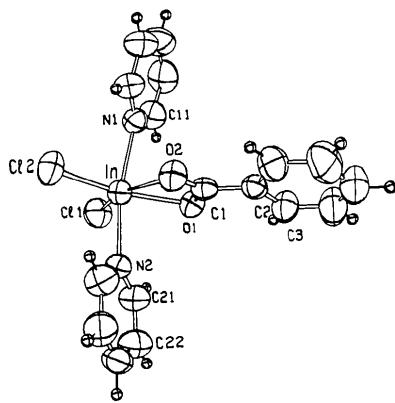


Fig. 1. The stereochemistry of $\text{Cl}_2\text{In}(\text{O}_2\text{CC}_6\text{H}_5)\text{py}_2$; ORTEP diagram, 50% probability for all atoms other than H.

The In—N bond lengths of 2.250 (5) and 2.300 (6) Å can be compared with the values reported for $\text{Cl}_2\text{In}(\text{acac})\text{bipy}$, where In—N *trans* to O is 2.299 (4) Å, and *trans* to Cl 2.276 (4) Å (Contreras, Einstein & Tuck, 1974). For $\text{InCl}_3\cdot\text{terpy}$ (terpy = 2,2':6',2''-terpyridine) (Carty, Dymock & Palenik, 1982) the In—N bond lengths are 2.238 (3), 2.268 (3) and 2.281 (3) Å, all *trans* to Cl. The pyridine N atoms in $[(\text{CH}_3)_2\text{In}(\text{ON}=\text{CHC}_5\text{H}_4\text{N})_2]$ form bonds to In of 2.501 (17) and 2.514 (19) Å (Shearer, Twiss & Wade, 1980), significantly longer than the values just quoted. Given the constraints imposed by the properties of bipy and terpy, it seems that the average length of In—N single bonds involving aromatic nitrogen donors can be taken as 2.28 Å, with variations from this value ascribed to the effect of differing *trans* atoms.

The literature now contains a number of X-ray measurements of In—Cl bond lengths in both inorganic and organometallic compounds (Khan *et al.*, 1980). Although concerned in the main with those compounds which also involve In—N and In—O bonds, we note for the purposes of later discussion that in the series

Table 2. Interatomic distances (Å) and angles (°), with e.s.d.'s in parentheses

In—Cl(1)	2.390 (2)	In—Cl(2)	2.392 (2)
In—O(1)	2.246 (4)	In—O(2)	2.280 (4)
In—N(1)	2.250 (5)	In—N(2)	2.300 (6)
In—C(1)	2.624 (6)	C(1)—C(2)	1.476 (8)
O(1)—C(1)	1.266 (7)	O(2)—C(1)	1.261 (6)
C(2)—C(3)	1.377 (9)	C(2)—C(7)	1.370 (9)
C(3)—C(4)	1.371 (12)	C(4)—C(5)	1.369 (16)
C(5)—C(6)	1.364 (15)	C(6)—C(7)	1.390 (13)
N(1)—C(11)	1.325 (8)	N(2)—C(21)	1.333 (10)
N(1)—C(15)	1.334 (9)	N(2)—C(25)	1.339 (10)
C(11)—C(12)	1.377 (12)	C(21)—C(22)	1.379 (11)
C(12)—C(13)	1.378 (12)	C(22)—C(23)	1.361 (11)
C(13)—C(14)	1.336 (11)	C(23)—C(24)	1.363 (11)
C(14)—C(15)	1.373 (12)	C(24)—C(25)	1.376 (12)
Cl(1)—In—Cl(2)	106.6 (1)	Cl(1)—In—O(1)	98.1 (1)
Cl(1)—In—O(2)	155.6 (1)	Cl(1)—In—N(1)	94.6 (1)
Cl(1)—In—N(2)	93.3 (2)	Cl(1)—In—C(1)	126.9 (1)
Cl(2)—In—O(1)	155.3 (1)	Cl(2)—In—O(2)	97.8 (1)
Cl(2)—In—N(1)	93.4 (1)	Cl(2)—In—N(2)	93.2 (2)
Cl(2)—In—C(1)	126.5 (1)	O(1)—In—O(2)	57.5 (1)
O(1)—In—N(1)	84.5 (2)	O(1)—In—N(2)	85.2 (2)
O(1)—In—C(1)	28.8 (2)	O(1)—C(1)—O(2)	118.9 (6)
O(1)—C(1)—C(2)	119.9 (5)	O(2)—In—N(1)	83.2 (2)
O(2)—In—N(2)	85.7 (2)	O(2)—In—C(1)	28.7 (1)
O(2)—C(1)—C(2)	121.1 (5)	N(1)—In—N(2)	167.8 (2)
N(1)—In—C(1)	81.9 (2)	N(1)—C(11)—C(12)	121.3 (8)
N(1)—C(15)—C(14)	122.8 (8)	N(2)—In—C(1)	85.9 (2)
N(2)—C(21)—C(22)	123.5 (5)	N(2)—C(25)—C(24)	122.3 (9)
In—O(1)—C(1)	92.4 (3)	In—O(2)—C(1)	91.0 (3)
In—C(1)—O(1)	58.8 (3)	In—C(1)—O(2)	60.3 (3)
In—C(1)—C(2)	178.5 (4)	In—N(1)—C(11)	121.3 (5)
In—N(1)—C(15)	119.6 (5)	In—N(2)—C(21)	120.2 (5)
In—N(2)—C(25)	122.4 (5)	C(1)—C(2)—C(3)	119.8 (6)
C(1)—C(2)—C(7)	120.6 (6)	C(2)—C(3)—C(4)	120.5 (7)
C(2)—C(7)—C(6)	119.7 (8)	C(3)—C(2)—C(7)	119.6 (6)
C(3)—C(4)—C(5)	119.9 (10)	C(4)—C(5)—C(6)	120.1 (11)
C(5)—C(6)—C(7)	120.1 (10)	C(11)—N(1)—C(15)	118.9 (6)
C(11)—C(12)—C(13)	118.2 (8)	C(12)—C(13)—C(14)	121.0 (8)
C(13)—C(14)—C(15)	117.7 (8)	C(21)—N(2)—C(25)	117.3 (7)
C(21)—C(22)—C(23)	117.9 (8)	C(22)—C(23)—C(24)	119.9 (7)
C(23)—C(24)—C(25)	119.0 (8)		

Table 3. *Relevant In—Cl and In—O bond distances (Å)*

Molecule	In—Cl*	In—O <i>trans</i> to Cl	Reference
InCl ₄ ⁻	2.345 (3), 2.355 (3)	—	(a)
InCl ₅ ²⁻	2.415 (12), 2.456 (7)	—	(b)
InCl ₆ ³⁻	2.514 (5), 2.538 (5), 2.510 (4)	—	(c)
[InCl ₅ (H ₂ O)]	2.474(3)(<i>trans</i>), 2.486(3), 2.485(3), 2.463 (3)	2.224 (7)	(d)
[InCl ₄ (H ₂ O) ₂] ²⁻	2.485(2)(<i>trans</i>), 2.433 (3), 2.417(3)	2.264 (7)	(e)
InCl ₃ ·3H ₂ O·3dioxane	2.447 (3), 2.420 (3), 2.399 (3)	2.283(7), 2.250(7), 2.199 (7)	(f)
Cl ₂ In(acac)bipy	2.433 (1) (<i>trans</i>), 2.394 (1)	2.164 (3)	(g)

References: (a) Khan & Tuck (1982). (b) Joy, Gaughan, Wharf, Shriver & Dougherty (1975). (c) Contreras, Einstein, Gilbert & Tuck (1977). (d) Wignacourt, Mairesse & Barbier (1976). (e) Ziegler, Schlimper, Nuber, Weiss & Ertl (1975). (f) Whitlow & Gabe (1975). (g) Contreras *et al.* (1974).

* *cis* to In—O bonds unless otherwise indicated.

InCl₄⁻—InCl₅²⁻—InCl₆³⁻ there is a monotonic increase in the In—Cl bond length with increasing coordination number. Table 3 lists the values reported for In—Cl distances in six-coordinate complexes containing oxygen-donor ligands. The unweighted mean length for In—Cl bonds *trans* to O is 2.46 Å, considerably longer than the bond length found for In—Cl in the present compound, a point to which we return below.

The In—O bond lengths in Table 3 (mean 2.23 Å) refer, with one exception, to In—OH₂ bonds which are *trans* to Cl. The exception concerns the acac anion bearing a (formal) single negative charge in Cl₂In(acac)bipy, and here the distances are 2.164 (3) Å *trans* to Cl, and 2.124 Å *trans* to N. The In—O bond lengths in the present case [2.246 (4) and 2.280 (4) Å] are significantly greater than those in Cl₂In(acac)bipy.

There appear to be no reports in the literature of structure determinations for complexes containing either monodentate or bidentate benzoate ligands bonded to an indium(III) cation. The crystal structure of benzoic acid itself was determined some years ago (Sim, Robertson & Goodwin, 1955), and there have been a number of studies of substituted benzoic acids (Colapietro & Domenicano, 1982, and references therein).

The phenyl ring C—C bond distances in Cl₂In(O₂CC₆H₅)₂ are all equal within experimental error (mean value 1.373 Å), and there are none of the variations found in substituted benzoic acids. Similarly, the C—C—C bond angles are all within 1σ of 120°, implying that the structure of the benzene ring is unaffected by the interaction with In. The C(1)—C(2) distance of 1.476 (8) Å is close to those reported for the parent and substituted acids, corresponding to a

significant shortening of the bond due to π-delocalization between ring and COO⁻ orbitals. The C(1)—O(1,2) bond distances are almost equal (mean value 1.263 Å), and close to the average of the C—O distances in *p*-ClC₆H₄COOH [1.247 (3) and 1.283 (3) Å; Colapietro & Domenicano, 1982], confirming that the COO⁻ orbitals are delocalized.

The appropriate description of the bonding between a metal ion and a potentially bidentate ligand has been a matter of much discussion. In the case where such a ligand adopts a bidentate configuration, one is faced

with two possibilities, either the conventional $M \begin{matrix} \diagup O \\ \diagdown O \end{matrix}$,

in which the metal supplies two bonding σ-orbitals, or

$M \begin{matrix} \diagup O \\ \diagdown O \end{matrix}$ in which the three-centre bond involves only one

metal σ-orbital. Particular examples of systems in which these arguments arise are complexes of nitrate (Addison, Logan, Wallwork & Garner, 1971) and nitrite (Bullock & Tuck, 1965). The present case clearly raises the same question, which can be rephrased in terms of whether In is six-coordinate, with an InO₂N₂Cl₂ kernel, or five-coordinate with the carboxylate group being regarded as occupying one coordination site in In(O₂)N₂Cl₂.

We suggest that the following pieces of evidence support this latter description:

(i) The Cl—In—Cl angle of 106.6 (1)° is closer to that required for five-coordination than for a six-coordinate complex.

(ii) The In—Cl bond length (av. 2.391 Å) is significantly lower than the values reported for six-coordinate complexes in which this bond is *trans* to either neutral or charged O (see Table 3). The only exception is one of the bonds in InCl₃·3H₂O·3dioxane (Whitlow & Gabe, 1975) but even here the average In—Cl distance is 2.422 Å. A decreased bond length has been shown to be a feature of the lower coordination numbers in anionic chloroindium complexes (Contreras *et al.*, 1977).

(iii) The O—In—O bond angle [57.5 (1)°] is much lower than would be expected for an octahedral complex.

The explanation which brings these observations together is that the In-atom orbitals involved are essentially those appropriate for five-coordination, and that the In—O₂CC₆H₅ interaction is best described as three-centre (InO₂) bonding. The carboxylate group is not exactly symmetrically sited on the presumed In orbital vector, as shown by the slightly different In—O bond lengths, the In—O(1,2)—C(1) bond angles, and the In—C(1)—C(2) angle. The C—O bonds of the carboxylate group are identical within experimental error, so that the differing In—O bond lengths do not apparently reflect any differences in C—O bond order. Such small distortions can only be ascribed at present to crystal-packing forces.

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 InMe_2 plane, and two O atoms from neighbouring acetate groups above and below the 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° 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 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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References

- ADDISON, C. C., LOGAN, N., WALLWORK, S. C. & GARNER, C. D. (1971). *Q. Rev. Chem. Soc.* **25**, 289–322.
 BULLOCK, J. I. & TUCK, D. G. (1965). *J. Chem. Soc.* pp. 1877–1881.
 CARTY, A. J., DYMOCK, K. R. & PALENIK, G. J. (1982). Private communication to DGT.
 COLAPIETRO, M. & DOMENICANO, A. (1982). *Acta Cryst.* **B38**, 1953–1957.

- CONTRERAS, J. G., EINSTEIN, F. W. B., GILBERT, M. M. & TUCK, D. G. (1977). *Acta Cryst.* **B33**, 1648–1650.
 CONTRERAS, J. G., EINSTEIN, F. W. B. & TUCK, D. G. (1974). *Can. J. Chem.* **52**, 3793–3798.
 EINSTEIN, F. W. B., GILBERT, M. M. & TUCK, D. G. (1973). *J. Chem. Soc. Dalton Trans.* pp. 248–251.
 HAUSEN, H. D. (1972). *J. Organomet. Chem.* **39**, C37.
 IBERS, J. A. & HAMILTON, W. C. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 99, 149. Birmingham: Kynoch Press.
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
 JOY, G., GAUGHAN, A. P., WHARF, I., SHRIVER, D. F. & DOUGHERTY, T. A. (1975). *Inorg. Chem.* **14**, 1796–1801.
 KHAN, M. A., STEEVENSZ, R. C., TUCK, D. G., NOLTES, J. G. & CORFIELD, P. W. R. (1980). *Inorg. Chem.* **19**, 3407–3411.
 KHAN, M. A. & TUCK, D. G. (1982). *Acta Cryst.* **B38**, 803–806.
 MOOTZ, D. & WUSSOW, H. G. (1981). *J. Chem. Phys.* **75**, 1517–1522.
 PEPPE, C., TUCK, D. G. & VICTORIANO, L. (1982). *J. Chem. Soc. Dalton Trans.* pp. 2165–2168.
 POLAND, J. S. & TUCK, D. G. (1972). *J. Organomet. Chem.* **42**, 315–323.
 ROBERTS, P. J. & SHELDRIK, G. M. (1975). *XANADU*. Program for crystallographic calculations. Univ. of Cambridge, England.
 SHEARER, H. M., TWISS, J. & WADE, K. (1980). *J. Organomet. Chem.* **184**, 309–315.
 SHELDRIK, G. M. (1977). *SHELX*. Program for crystal structure determination. Univ. of Cambridge, England.
 SIM, G. A., ROBERTSON, J. M. & GOODWIN, T. H. (1955). *Acta Cryst.* **8**, 157–164.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
 TEMPLETON, D. & TEMPLETON, L. (1973). *ABSORB*. An analytical absorption correction program. Univ. of California, Berkeley.
 WATERWORTH, L. & WORRALL, I. J. (1971). *Chem. Commun.* p. 569.
 WHITLOW, S. H. & GABE, E. J. (1975). *Acta Cryst.* **B31**, 2534–2536.
 WIGNACOURT, J. P., MAIRESSE, G. & BARBIER, P. (1976). *Cryst. Struct. Commun.* **5**, 293–296.
 ZIEGLER, M. L., SCHLIMPER, H. V., NUBER, B., WEISS, J. & ERTL, G. (1975). *Z. Anorg. Allg. Chem.* **415**, 193–201.

Acta Cryst. (1983). **C39**, 1342–1344

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 \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- μ -(acetato- $O:O,O'$)-copper-bis- μ -(acetato- $O'',O''':O''''$)] tetrahydrate.