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Crystal Structure of Dipotassium *catena*-μ-[Tetraacetatocuprato(II)]-[tetrakis-μ-(acetato-*O,O'*)dicopper(II)]†

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The crystal structure of $K_2[Cu_2(CH_3COO)_4][Cu(CH_3COO)_4]$ was determined by single-crystal X-ray diffraction. The compound crystallizes in the monoclinic space group $C2/c$, with $a = 17.956(4)$, $b = 14.312(3)$, $c = 12.443(2)$ Å, $\beta = 98.85(3)°$ and $z = 4$. The structure was refined by full-matrix least-squares methods to an R-factor of 0.038. The compound consists of polymeric chains formed by alternating $Cu_2(CH_3COO)_4$ dimers and $Cu(CH_3COO)_2$ monomers, which are linked by *syn–anti* bridging acetates.

Since the crystal structure determination of copper(II) acetate monohydrate,[1] which was the first tetracarboxylate-bridged copper(II) dimer, adducts of dimeric copper(II) carboxylates have become well known for a variety of ligands, and their preparation, structural, magnetic and spectral properties have been reported.[2] Most copper acetate compounds exist as discrete dimers [as a copper(II) acetate acetic acid adduct] with oxygen or nitrogen donor atom groups as apical ligands, while in a few structures the bifunctional oxygen or nitrogen donor ligands extend the dimers into polymeric chains.[3–7]

In several studies the factors that influence the formation of either binuclear or mononuclear complexes of copper(II) carboxylate adducts have been investigated, but still no clear understanding exists.[8] In general the tendency towards formation of monomeric copper(II) carboxylate compounds increases as the acidity of the carboxylate groups or the basicity of the ligands increases. The steric factors of the ligands have also been found to affect the structural properties of copper carboxylate adducts.[9] The structures of monomeric copper(II) acetate adducts, reported up to the present, contain monodentate nitrogen donor ligands as bis-adducts with *cis* or *trans* square-planar CuN_2O_2 chromophores.[10–13]

Here we report the crystal structure of $K_2[Cu_2(CH_3COO)_4][Cu(CH_3COO)_4]$, which contains both dimeric and monomeric units of copper(II) acetate in a polymeric chain.

Experimental

Preparation. The compound was prepared by addition of stoichiometric amounts of copper(II) acetate monohydrate and potassium cyanate in a hot methanolic solution containing an excess of 1-diethylamino-2-propanol. Recrystallization from methanol gave light-green, prismatic, rod-shaped crystals.

Data collection. A summary of crystal data, intensity collection and structure refinement is given in Table 1. The unit cell parameters were determined on the basis of 15 well centered reflections measured on a Nicolet P3F diffractometer.

Intensity data were collected in the ω-scan mode using graphite-monochromatized Mo $K\alpha$ radiation. The intensities of three reference reflections, recorded after every 100 measurements, remained essentially constant throughout the data collection. The intensities of eight strong reflections (with χ near 90°) as a function of ψ-angle showed less than 5% variation. Consequently, no correction was made for absorption.

Structure determination. Systematic absences indicated space groups Cc and $C2/c$. The solution using direct methods and refinement of the structure by a full-matrix least-squares analysis confirmed the centrosymmetric choice. All the calculations were performed with Release 4.1 of SHELXTL PC version and a 486-based ADC microcomputer. Neutral atom scattering factors,[14] including corrections for anomalous dispersion, were used as they were given in the program. The figures were drawn using the same program package.

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Table 1. Summary of crystal data, intensity collection and structure refinement for $K_2[Cu_2(CH_3COO)_4][Cu(CH_3COO)_4]$.

Formula	$K_2[Cu_2(CH_3COO)_4][Cu(CH_3COO)_4]$
Formula weight	741.2
Crystal size/mm	0.20 × 0.15 × 0.10
Color, habit	Light green, prismatic, rod-shaped
Crystal system	Monoclinic
Space group	*C*2/*c* (No. 15)
Unit-cell dimensions	*a* = 17.956(4) Å
	b = 14.313(3) Å
	c = 12.443(2) Å
	β = 98.85(3)°
Volume/Å^3	3160(2)
Z	4
d_{calc}/g cm^{-3}	1.615
Absorption coefficient/mm^{-1}	2.324
F(000)/e	1492
Diffractometer used	Nicolet P3F
Radiation	Mo *K*α (λ = 0.710 69 Å)
Monochromator	Graphite crystal
2θ-Range/°	3.0–52.0
Scan type	ω-scan
Scan rate/° min^{-1}	3.0–29.3
Standard reflections	3 measured every 100 reflections
Variation in standard intensities	±3%
Index ranges	$0 \leqslant h \leqslant 22$, $0 \leqslant k \leqslant 17$, $-15 \leqslant l \leqslant 15$
No. of reflections collected	3119
No. of observed reflections	1955 ($\|F_o\| > 6.0\sigma\|F_o\|$)
Absorption correction	None
No. of variables	170
$R = \Sigma(\|F_o\| - \|F_c\|)/\Sigma\|F_o\|$	0.038
$R_w = \Sigma[(\|F_o\| - \|F_c\|)w^{1/2}]/\Sigma\|F_o\|w^{1/2}$ [a]	0.042
Residual electron density/e Å^{-3}	0.70
T/K	294

[a] $w = 1/[\sigma^2(F_o) + 0.0004F_o^2]$.

The hydrogen atoms bonded to carbon atoms were included at the calculated positions, and the final refinement with anisotropic thermal parameters for all non-hydrogen atoms gave $R = 0.038$.

The atomic coordinates and equivalent isotropic thermal parameters for non-H atoms are given in Table 2.

Results and discussion

Description of the structure. The compound consists of infinite zigzag chains extending in the unit cell parallel to the [101] direction. The chains are formed by $Cu_2(CH_3COO)_4$ dimers, bridged by tetraacetatocuprato(II), $[Cu(CH_3COO)_4]^{2-}$, anions. The two counter K^+ ions are located between the polymeric chains. A stereoview of the structure of $K_2[Cu_2(CH_3COO)_4][Cu(CH_3COO)_4]$ showing the unit cell content is given in Fig. 1.

In the $Cu_2(CH_3COO)_4$ dimer (Fig. 2) the coordination sphere around Cu(1) is a distorted square-pyramidal, with four oxygen atoms from the *syn–syn* bridging acetate groups at distances of 1.952(4)–1.983(4) Å and the fifth oxygen atom, O(5), in the *syn–anti* bridging acetate group

Table 2. Atomic coordinates (×10^4) and equivalent isotropic temperature factors (×10^3 Å^2) for $K_2[Cu_2(CH_3COO)_4][Cu(CH_3COO)_4]$.

Atom	*x*	*y*	*z*	*U* [a]
K(1)	659(1)	5834(1)	5135(1)	42(1)
Cu(1)	2035(1)	7092(1)	4218(1)	40(1)
Cu(2)	0	4843(1)	2500	32(1)
O(1)	1270(2)	7573(3)	5070(3)	51(1)
O(2)	2940(2)	6717(3)	3636(3)	62(1)
O(3)	2175(2)	6007(2)	5215(3)	47(1)
O(4)	2027(2)	8301(3)	3492(3)	59(1)
O(5)	1194(2)	6314(2)	3173(2)	44(1)
O(6)	490(2)	5752(2)	1702(2)	36(1)
O(7)	809(2)	3912(3)	2394(3)	51(1)
O(8)	749(2)	4139(3)	4125(3)	47(1)
C(1)	1419(3)	8069(4)	5908(5)	54(2)
C(2)	759(4)	8412(5)	6396(6)	90(2)
C(3)	2603(3)	6003(4)	6103(4)	50(2)
C(4)	2666(4)	5122(5)	6742(5)	87(2)
C(5)	947(3)	6348(4)	2182(4)	39(2)
C(6)	1182(4)	7116(4)	1508(4)	82(2)
C(7)	1057(3)	3789(4)	3397(4)	49(3)
C(8)	1735(4)	3196(6)	3674(5)	112(3)

[a] Equivalent isotropic *U*, defined as one third of the trace of the orthogonalized U_{ij} tensor.

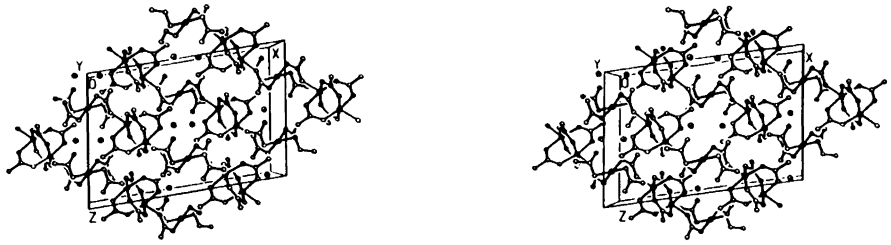

Fig. 1. Stereoscopic drawing of the structure showing the unit-cell content.

at 2.148(3) Å (Table 3). Cu(1) is displaced by 0.20 Å from the basal plane towards the apical oxygen atom. The sixth position is screened by the proximity of the neighboring Cu(1)^{ii} at a distance of 2.633(1) Å.† This, as well as the bond distances in the $[Cu(CH_3COO)_2]_2$ dimer, are comparable to those in copper(II) acetate monohydrate or in its adducts.[1,5,9,15]

Cu(2) is located on the crystallographic two-fold axis at 0, *y*, 1/4. The coordination sphere of Cu(2) consists of a pair of oxygen atoms from the two bidentate acetates at a distance of 1.990(4) Å and the other pair from the two bridging acetates at a distance of 1.929(3) Å. The angles of O(7)–Cu(2)–O(7)^{i} and O(6)–Cu(2)–O(6)^{i} are 96.0(2) and 95.1(2)°, respectively. The two remaining oxygen atoms from the bidentate acetate groups with weak interactions are situated 2.464(3) Å from Cu(2) and the angle between O(8)–Cu(2)–O(8)^{i} is 131.8(2)°. The distance Cu(2)–O(8) is significantly shorter than those in calcium copper acetate hexahydrate, $CaCu(CH_3COO)_4 \cdot 6H_2O$,[16] the *trans* square-planar copper(II) monochloroacetate α-picoline adduct, $Cu(ClCH_2COO)_2(\alpha\text{-picoline})_2$,[17] or *trans* square-planar copper(II) acetate compounds with CuN_2O_2 chromophores,[10–12] but is in close agreement with those in *cis* square-planar $Cu(CH_3COO)_2$-(1,2-dimethylimidazole)$_2$ and $Cu(CH_3COO)_2$(2-methylimidazole)$_2$ complexes.[13] The longer bond length of C(7)–O(7) [1.272(5) Å] suggests that C(7)–O(8) [1.236(6) Å] has more double-bond character, which is the expected trend.

The bidentate and *syn–anti* bridging acetate groups are planar, but Cu(2) is displaced from the O(8)–C(7)–C(8)–O(7) plane by 0.21 Å and by 0.30 Å from the O(6)–C(5)–O(5)–C(6) plane, which is more than in $Cu(ClCH_2COO)_2(\alpha\text{-picoline})_2$.[17] The deviations of the oxygen atoms from the O(7)–O(7)^{i}–O(6)–O(6)^{i} least-squares plane are in the range 0.46–0.49 Å, which is significantly larger than in monomeric *cis* square-planar copper(II) acetate imidazole adducts (0.30–0.33 Å)[13] or in $CaCu(CH_3COO)_4 \cdot 6H_2O$, in which the four nearest acetate oxygen atoms around the copper ion form almost a square plane.[16] In our compound the dihedral

† Symmetry codes: (i) $-x$, y, $\frac{1}{2}-z$; (ii) $\frac{1}{2}-x$, $\frac{3}{2}-y$, $1-z$; (iii) x, $1-y$, $\frac{1}{2}+z$; (iv) $-x$, $1-y$, $1-z$.

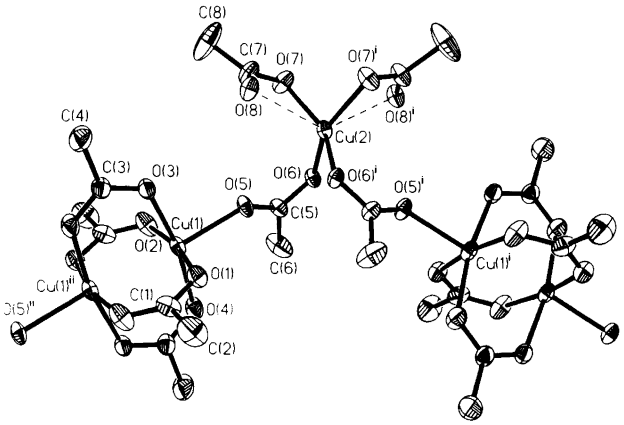

Fig. 2. Schematic drawing of the copper chain showing also the atomic labeling and coordination spheres around copper atoms. Symmetry codes: (i) $-x$, y, $\frac{1}{2}-z$; (ii) $\frac{1}{2}-x$, $\frac{3}{2}-y$, $1-z$.

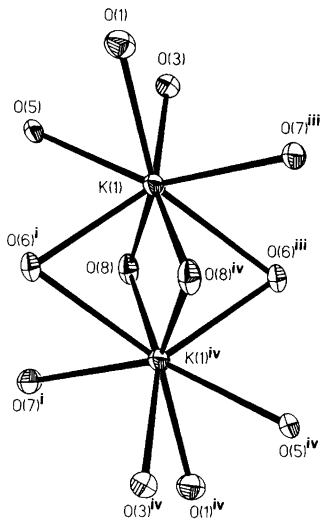

Fig. 3. The coordination around the potassium ions. Symmetry codes: (i) $-x$, y, $\frac{1}{2}-z$; (iii) x, $1-y$, $\frac{1}{2}+z$; (iv) $-x$, $1-y$, $1-z$.

Table 3. Interatomic distances (in Å) and angles (in °) with standard deviations in parentheses.[a]

K(1)–O(1)	2.728(4)	O(1)–Cu(1)–O(2)	167.8(1)
K(1)–O(3)	2.720(4)	O(1)–Cu(1)–O(3)	89.1(2)
K(1)–O(5)	2.842(3)	O(1)–Cu(1)–O(4)	89.0(2)
K(1)–O(6)^{i}	2.836(3)	O(1)–Cu(1)–O(5)	91.3(1)
K(1)–O(7)^{i}	2.806(3)	O(2)–Cu(1)–O(3)	89.1(2)
K(1)–O(6)^{iii}	3.038(3)	O(2)–Cu(1)–O(4)	91.1(2)
K(1)–O(8)	2.748(4)	O(2)–Cu(1)–O(5)	100.4(1)
K(1)–O(8)^{iv}	2.821(4)	O(3)–Cu(1)–O(4)	167.8(1)
Cu(1)–O(1)	1.983(4)	O(3)–Cu(1)–O(5)	89.0(1)
Cu(1)–O(2)	1.952(4)	O(4)–Cu(1)–O(5)	103.0(1)
Cu(1)–O(3)	1.978(4)	Cu(1)–O(1)–C(1)	124.4(4)
Cu(1)–O(4)	1.952(4)	Cu(1)–O(2)–C(1)^{ii}	121.9(4)
Cu(1)–O(5)	2.148(3)	Cu(1)–O(3)–C(3)	124.2(4)
Cu(1)··Cu(1)^{ii}	2.633(1)	Cu(1)–O(4)–C(3)^{ii}	123.4(3)
Cu(2)–O(6)	1.929(3)	Cu(1)–O(5)–C(5)	133.6(3)
Cu(2)–O(7)	1.990(4)	O(1)–C(1)–C(2)	116.3(5)
Cu(2)–O(8)	2.464(3)	O(1)–C(1)–O(2)^{ii}	125.6(6)
O(1)–C(1)	1.256(7)	C(2)–C(1)–O(2)^{ii}	118.1(5)
O(2)–C(1)^{ii}	1.242(7)	O(3)–C(3)–C(4)	117.7(5)
O(3)–C(3)	1.245(6)	O(3)–C(3)–O(4)^{ii}	124.5(5)
O(4)–C(3)^{ii}	1.259(7)	C(4)–C(3)–O(4)^{ii}	117.7(5)
O(5)–C(5)	1.245(5)	O(6)–Cu(2)–O(6)^{i}	95.1(2)
O(6)–C(5)	1.268(6)	O(6)–Cu(2)–O(7)	91.3(1)
O(7)–C(7)	1.272(5)	O(6)–Cu(2)–O(7)^{i}	151.7(1)
O(8)–C(7)	1.236(6)	O(6)–Cu(2)–O(8)	117.6(1)
C(1)–C(2)	1.494(10)	O(6)–Cu(2)–O(8)^{i}	95.1(1)
C(3)–C(4)	1.485(9)	O(7)–Cu(2)–O(7)^{i}	96.0(2)
C(5)–C(6)	1.482(8)	O(7)–Cu(2)–O(8)	57.9(1)
C(7)–C(8)	1.481(9)	O(7)–Cu(2)–O(8)^{i}	89.1(1)
		O(8)–Cu(2)–O(8)^{i}	131.8(2)
		Cu(2)–O(6)–C(5)	121.7(3)
		Cu(2)–O(7)–C(7)	100.2(3)
		Cu(2)–O(8)–C(7)	79.3(3)
		O(5)–C(5)–O(6)	123.1(5)
		O(5)–C(5)–C(6)	120.0(4)
		O(6)–C(5)–C(6)	116.9(4)
		O(7)–C(7)–O(8)	122.3(5)
		O(7)–C(7)–C(8)	117.3(5)
		O(8)–C(7)–C(8)	120.4(4)

[a] Symmetry codes: (i) $-x, y, \frac{1}{2}-z$; (ii) $\frac{1}{2}-x, \frac{3}{2}-y, 1-z$; (iii) $x, 1-y, \frac{1}{2}+z$; (iv) $-x, 1-y, 1-z$.

angle between the planes Cu(2)–O(7)–O(7)^{i} and Cu(2)–O(6)–O(6)^{i} is 38.5°, which indicates the strong deviation from the planar coordination around the copper atom.

The counter K^+ ions form a network with close contacts to the surrounding oxygen atoms. The K^+ ion occupies a site with distorted (4 + 3 + 1) arrangement with oxygens (all contacts up to 3.22 Å being considered). Two K^+ ions form a centrosymmetric arrangement with four bridging oxygen atoms [O(6)^{i}, O(6)^{iii}, O(8), O(8)^{iv}], leading to a short distance of 3.341(2) Å between potassium ions (Fig. 3).

The distance between Cu(1) and Cu(2) in the same chain is 5.088(1) Å and the shortest distance between Cu(1) and Cu(2)^{iii} in the two separate chains is 6.503(1) Å. In a closely related structure in which the chains are formed by alternating $Cu_2(CH_3COO)_4$ and $[Cu_2(CH_3COO)_2(2,2'\text{-bipyridine})_2]^{2+}$ units, linked by *syn–anti* bridging acetates, the distance between Cu(1) and Cu(2) is 5.441(1) Å.[7]

Conclusions

To our knowledge, this is the first single-crystal study of a structure containing both binuclear and mononuclear units of copper(II) acetate. In order to study the magnetic coupling between the copper atoms, magnetic measurements are in progress.

References

1. van Niekerk, J. N. and Schoening, F. R. L. *Acta Crystallogr. 6* (1953) 227.
2. Mehrotra, R. C. and Bohra, R. *Metal Carboxylates*, Academic Press, New York 1983.
3. Morosin, B., Hughes, R. C. and Soos, Z. G. *Acta Crystallogr., Sect. B31* (1975) 762.
4. Pickardt, J. *Acta Crystallogr., Sect. B37* (1981) 1753.
5. Rao, V. M., Sathyanarayana, D. N. and Manohar, H. *J. Chem. Soc., Dalton Trans.* (1983) 2167.
6. Smith, G., Kennard, C. H. L. and Byriel, K. A. *Polyhedron 10* (1991) 873.

7. Perlepes, S. P., Libby, E., Streib, W. E., Folting, K. and Christou, G. *Polyhedron 11* (1992) 923.
8. Melnik, M. *Coord. Chem. Rev. 36* (1981) 1.
9. Doedens, R. J. *Progr. Inorg. Chem. 21* (1976) 209.
10. Simonov, Yu. A., Ablov, A. V. and Malinowski, T. I. *Kristallografiya 8* (1963) 270.
11. Henriksson, H. Å. *Acta Crystallogr., Sect B33* (1977) 1947.
12. Heimer, N. E. and Ahmed, I. Y. *Inorg. Chim. Acta 64* (1982) L65.
13. Abuhijleh, A. L., Woods, C. and Ahmed, I. Y. *Inorg. Chim. Acta 190* (1991) 11.
14. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1974, Vol. IV.
15. de Meester, P., Fletcher, S. R. and Skapski, A. C. *J. Chem. Soc., Dalton Trans.* (1973) 2575.
16. Langs, D. A. and Hare, C. R. *Chem. Commun.* (1967) 890.
17. Davey, G. and Stephens, F. S. *J. Chem. Soc. A* (1971) 1917.

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