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catena-Poly[disodium [[tris(formato-κO)copper(II)]-μ_2-formato-$\kappa^2 O:O'$]], with partial substitution of formate by acetate, $Na_{2n}[Cu(O_2CH)_{4-x}(O_2CCH_3)_x]_n$ (x = 0.28)

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The structure of the title compound, $Na_2[Cu(CHO_2)_{3.72}(C_2H_3O_2)_{0.28}]$, is built of sodium cations and Cu^{II} complex anions; the latter are linked into infinite chains. The Cu^{II} atoms are coordinated by five O atoms belonging to five formate ligands, forming a distorted square-pyramidal coordination. Four symmetry-independent formate ligands are bonded to the Cu atom with Cu—O distances in the range 1.9370 (10)–1.9886 (8) Å. The fifth formate ligand, bonded to the Cu^{II} atom at a longer distance of 2.2889 (9) Å, forms a bridge to the neighbouring copper(II) ion which is symmetry-related to the original ion by a twofold screw axis. Thus, infinite chains are formed along the *b* axis. One of the terminal formate ligands is disordered; 28.4 (13)% of its sites are occupied by acetate, which was present in the starting material and was not completely displaced in the course of the reaction.

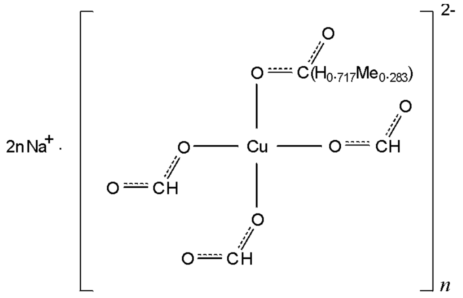
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(O–C) = 0.002 Å
Disorder in main residue
R factor = 0.026
wR factor = 0.018
Data-to-parameter ratio = 12.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Copper carboxylates are well known to form a variety of structures, even with ligands of the same homologous series. One of the objectives of our recent work involved the development of new synthetic methods for the preparation of copper formates, both with and without additional N- or O-donor ligands. Recently, we reported the synthesis and the crystal structure of the new orthorhombic form of a polymeric adduct of copper(II) formate–formic acid (1:2) (Lah *et al.*, 2002). We present here the structure of a new ionic compound, *catena*-poly[disodium[[tris(formato-κO)copper(II)]-μ_2-formato-$\kappa^2 O:O'$]], with partial substitution of formate by acetate, (I).



(I)

The structure of (I) is built of sodium cations and tetraformatocopper(II) complex anions; the latter are linked into infinite chains. The Cu^{II} atom in the anion is coordinated by five O atoms belonging to five formate ligands and forming a distorted square-pyramidal coordination environment (Fig. 1). Distances between the Cu and Oy1 atoms (where y is 1, 2, 3 and 4 for the first, second, third and fourth symmetry-independent formate ligands, respectively) range from 1.9370 (10) to 1.9886 (8) Å. The fifth ligand, which is symmetry-related to

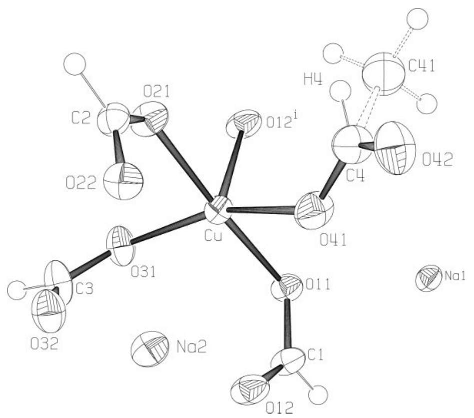


Figure 1
A view of the structure of the title compound, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level [symmetry code: (i) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$]. Dashed lines are to atoms belonging to the minor component of the disorder.

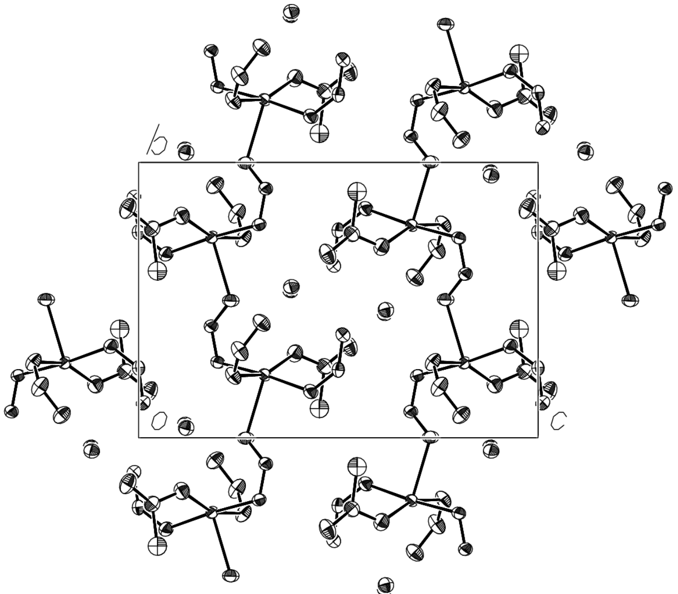


Figure 2
The packing of the title compound, viewed along the *a* axis.

the first formate ion by a twofold screw axis, is bonded to the Cu atom *via* atom O12, at a longer distance of 2.2889 (9) Å, and forms a bridge between two copper(II) ions. The result of such Cu—O11—C1—O12—Cu bridging is infinite chains of connected copper polyhedra along the *b* axis (Fig. 2). The torsion angles around the bridging bonds, Cu—O11—C1—O12 and O11—C1—O12—Cu^i [symmetry code (i): $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$], of 0.73 (15) and −178.54 (9)°, respectively, show that the mode of formate-bridging is *syn–anti* (Sletten & Jensen, 1973). The second O atoms of non-bridging formate ligands are coordinated to the sodium cations. The Na1 and Na2 cations are surrounded by five and six formate O atoms, respectively. The Na—O distances are in the range 2.3559 (11)–2.5398 (12) Å.

One of the terminal formate ligands was found to be disordered. The resolution of the disorder and refinement of the disordered model showed that in 28.4 (13)% of the unit cells the formate group failed to displace the acetate ligand of the starting material.

Experimental

Single crystals of the title compound were prepared by the reaction of copper acetate dihydrate and sodium formate. 1 mmol of $Cu_2(C_2H_3O_2)_4{\cdot}2H_2O$ and 16 mmol of $Na(CHO_2)$ were refluxed with 30 ml of slightly acidified methanol (using formic acid) for one hour. The undissolved solid residue was filtered off and the resulting solution was left to stand at 278 K for 20 h. Blue crystals obtained from the solution were used for X-ray diffraction.

Crystal data

$Na_2[Cu(CHO_2)_{3.72}(C_2H_3O_2)_{0.28}]$
$M_r = 293.58$
Monoclinic, $P2_1/c$
$a = 7.0867$ (4) Å
$b = 9.4514$ (4) Å
$c = 13.8277$ (8) Å
$\beta = 96.993$ (2)°
$V = 919.28$ (8) Å^3
$Z = 4$

$D_x = 2.121$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2160 reflections
$\theta = 1.0$–27.5°
$\mu = 2.49$ mm^{-1}
$T = 293$ K
Prism, blue
0.23 × 0.22 × 0.21 mm

Data collection

Nonius KappaCCD diffractometer
ω scans
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{min} = 0.564$, $T_{max} = 0.593$
12602 measured reflections

2069 independent reflections
1947 reflections with $I > 2\sigma(I)$
$R_{int} = 0.026$
$\theta_{max} = 27.5°$
$h = -9 \rightarrow 9$
$k = -12 \rightarrow 12$
$l = -17 \rightarrow 17$

Refinement

Refinement on F
$R = 0.026$
$wR = 0.018$
$S = 1.27$
2019 reflections
156 parameters

H atoms treated by a mixture of independent and constrained refinement
Weighting scheme: see text
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.52$ e Å^{-3}
$\Delta\rho_{min} = -0.83$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu—O11	1.9616 (9)	Na2—O11^{vi}	2.4702 (9)
Cu—O21	1.9370 (10)	Na2—O22^{vii}	2.4417 (9)
Cu—O31	1.9886 (8)	Na2—O42^{vii}	2.5398 (12)
Cu—O41	1.9798 (9)	O11—C1	1.2592 (14)
Cu—O12^i	2.2889 (9)	O12—C1	1.2374 (16)
Na1—O22^i	2.4176 (10)	O21—C2	1.2597 (16)
Na1—O42^{ii}	2.4198 (11)	O22—C2	1.2356 (15)
Na1—O31^{iii}	2.4274 (10)	O31—C3	1.2598 (16)
Na1—O41^{iv}	2.4980 (11)	O32—C3	1.2312 (17)
Na1—O32^v	2.3559 (11)	O41—C4	1.2472 (16)
Na2—O12	2.4987 (11)	O42—C4	1.2294 (17)
Na2—O22	2.4406 (10)	C4—C41	1.534 (6)
Na2—O32	2.3631 (10)		
O11—Cu—O21	175.40 (4)	O41—Cu—O12^i	113.91 (4)
O11—Cu—O31	89.74 (4)	O11—C1—O12	125.92 (12)
O11—Cu—O41	87.18 (4)	O21—C2—O22	127.74 (12)
O11—Cu—O12^i	84.94 (3)	O31—C3—O32	127.43 (11)
O21—Cu—O31	91.15 (4)	O41—C4—O42	124.50 (14)
O21—Cu—O41	93.57 (4)	O41—C4—C41	112.4 (2)
O21—Cu—O12^i	90.61 (4)	O41—C4—H4	114.6 (18)
O31—Cu—O41	159.16 (4)	O42—C4—C41	118.2 (2)
O31—Cu—O12^i	86.30 (3)	O42—C4—H4	119.7 (19)

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

The structure was found to be disordered in the vicinity of the carboxyl group containing C4. A substantial maximum in the differ-

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ence Fourier map was found at a distance of *ca* 1.5 Å from atom C4, along with the expected peak at the typical C—H distance; the constrained refinement of the H4 and C41 atoms indicated that 28.4 (13)% of the H4-atom sites in the crystal are occupied by a methyl group. The sum of the occupancy parameters of the H4 atom and the atoms of the methyl group was constrained to be 1.0 and their isotropic displacement parameters were set to be equal. The positions of the H atoms of the formate ligands were refined together with the isotropic displacement parameters of these atoms. The coordinates of three H atoms of the disordered methyl group were calculated but not refined. The C—H bond lengths for all refined H atoms are in the range 0.87 (3)–0.97 (2) Å. A *REGINA* (Wang & Robertson, 1985) weighting scheme using the normal equation of the second order was applied for individual reflections so that $w = A(0,0) + A(1,0)V(F) + A(0,1)V(S) + A(2,0)V(F)^2 + A(0,2)V(S)^2 + A(1,1)V(F)V(S)$, where $V(F) = F_{\rm obs}/F_{\rm obs}({\rm max})$, $F_{\rm obs}({\rm max}) = 129.68$ and $V(S) = (\sin\theta/\lambda)/[(\sin\theta/\lambda)({\rm max})]$, $(\sin\theta/\lambda)({\rm max}) = 0.6489$. The parameters were: $A(0,0) = 2713.301$, $A(1,0) = -42.03272$, $A(0,1) = -9979.300$, $A(2,0) = 0.1684363$, $A(1,1) = 70.41786$ and $A(0,2) = 8995.714$.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *Xtal*3.6 (Hall *et al.*, 1999); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *Xtal*3.6.

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