

catena-Poly[disodium [[diformato-tricopper(II)]-di- μ_3 -formato-tetra- μ_2 -formato]]: a new mode of bridging between binuclear and mononuclear formate-copper(II) units

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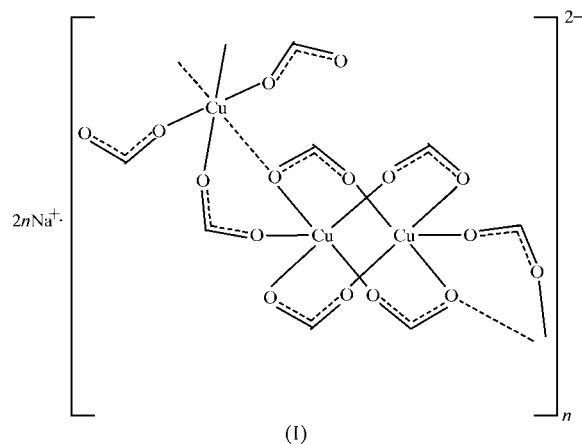
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The novel title polymeric copper(II) complex, $\{\text{Na}_2[\text{Cu}_3(\text{CHO}_2)_8]\}_n$, consists of sodium cations and infinite anionic chains, in which neutral dinuclear $[\text{Cu}_2(\text{O}_2\text{CH})_4]$ moieties alternate with dianionic $[\text{Cu}(\text{O}_2\text{CH})_4]^{2-}$ units. Both metal-containing moieties are located on crystallographic inversion centers. The *syn-syn* bridging configuration between the mononuclear and dinuclear components yields a structure that is significantly more dense than the structures previously reported for mononuclear–dinuclear copper(II) carboxylates with *syn-anti* or *anti-anti* bridging modes.

Comment

Although a large number of dimeric copper(II)–carboxylate complexes of the paddle-wheel-cage type have been structurally characterized, only nine structures of formate derivatives are known (Bernard *et al.*, 1979; Bukowska-Strzyzewska, 1966; Uekusa *et al.*, 1989; Yamanaka *et al.*, 1991; Goodgame *et al.*, 1969; Cejudo *et al.*, 2002; Sapina *et al.*, 1994). In only one of these (Bukowska-Strzyzewska, 1966) are dimeric formate–copper(II) units found to be linked into a polymeric structure. Not only is the title compound, (I), a new example of such an extended structure, it is also the first formate–copper(II) structure that contains both mono- and dinuclear carboxylate–copper(II) units. A view along the *a* axis of the cell is given in Fig. 1. Infinite chains, formed by $[\text{Cu}_2(\text{O}_2\text{CH})_4]$ dimers bridged by $[\text{Cu}(\text{O}_2\text{CH})_4]^{2-}$ anions, propagate along the $[011]$ direction. The charge is balanced by sodium cations, located between the polymeric chains. Fig. 2 shows the coordination of formate ligands around the metal ions. The dimeric unit is centrosymmetric, with four bidentate formate *syn-syn* bridges between Cu1 atoms, which are in a 4+1 environment. The basal coordination of atom Cu1 is formed by four coplanar O atoms from two pairs of symmetry-related formate anions, with an average Cu–O_{basal} distance of 1.968 Å (Table 1). The

apical distance, Cu1–O42, is significantly longer [2.104 (5) Å]. The distortion of the square-pyramidal arrangement of the O atoms around atom Cu1 is very small; τ is 0.005 (Addison *et al.*, 1984). The Cu···Cu separation within the dimer is 2.620 (1) Å. This and the bond distances in the



dimer are comparable to those in other dinuclear copper formates (Bernard *et al.*, 1979; Bukowska-Strzyzewska, 1966; Uekusa *et al.*, 1989; Yamanaka *et al.*, 1991; Goodgame *et al.*, 1969; Cejudo *et al.*, 2002; Sapina *et al.*, 1994). The apical formate ligand is coordinated through atom O41 to the second copper ion, Cu2, thus bridging dimeric and monomeric units to form the polymeric chain. The coordination polyhedron of atom Cu2, which is also located on an inversion centre, is an axially elongated octahedron of O atoms from the three pairs of symmetry-related formate anions. This coordination may be viewed as 4+2, which is quite typical and expected for six-coordinate Cu^{II} in view of Jahn–Teller effects (Hathaway, 1987). The equatorial O atoms (O41 from the bridging formate and O31 from the only formate ligand that is not coordinated to Cu1) are closer than 2 Å to Cu2. Two O atoms, *viz.* O11 and its symmetry equivalent, which lie at a significantly longer distance [2.492 (5) Å], are part of the bridging

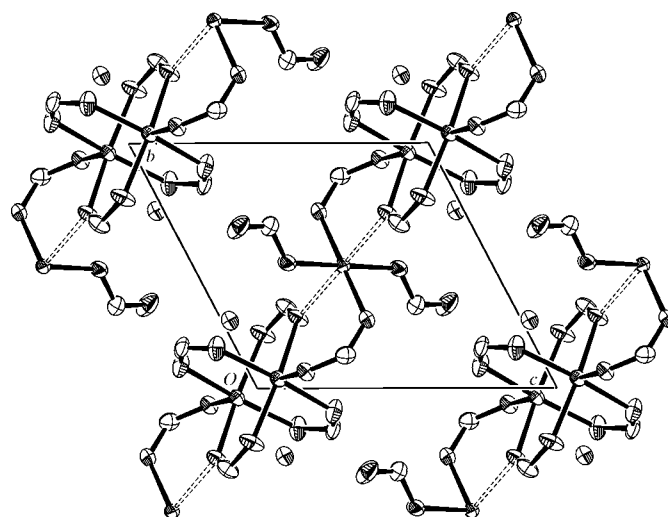


Figure 1
The packing of the title compound, viewed along the *a* axis.

formate groups from the dimeric $[\text{Cu}_2(\text{O}_2\text{CH})_4]$ unit and form a second bridge between the monomeric and dimeric units. This additional bridge is possible because the first mode of bridging between dimer and monomer (through bonds $\text{Cu1}-\text{O42}$ and $\text{Cu2}-\text{O41}$) is *syn-syn*. A *syn-anti* or *anti-anti* mode of bridging could not have brought the units close enough for such additional stabilization. The consequence of this new mode of bridging is that the density (2.275 Mg m^{-3}) is significantly greater than the densities of analogous copper(II) structures (Wang *et al.*, 2000; Valigura *et al.*, 1986; Escuer *et al.*, 1999; Hökelek *et al.*, 1998; Zubkowski *et al.*, 1997; Chiari *et al.*, 1993; Valo & Nasakkala, 1994; Petrenko & Kiosse, 2000; Kani *et al.*, 2000; Neels *et al.*, 1995; Dunaj-Jurčo *et al.*, 1995) with *syn-anti* or *anti-anti* bridging modes between mono- and dinuclear units. In the latter, the densities are less than 1.79 Mg m^{-3} . For instance, in $\{\text{K}_2[\{\text{Cu}_2(\text{O}_2\text{CCH}_3)_4\}\{\text{Cu}(\text{O}_2\text{CCH}_3)_4\}]\}_n$ (Valo & Nasakkala, 1994), whose formula is very similar to that of the title compound, but in which the bridging mode between monomeric and dimeric units is *syn-anti*, the density is only 1.558 Mg m^{-3} . Also, the intra-chain distance between atoms Cu1 and Cu2 in $\{\text{K}_2[\{\text{Cu}_2(\text{O}_2\text{CCH}_3)_4\}\{\text{Cu}(\text{O}_2\text{CCH}_3)_4\}]\}_n$ is $5.088(1) \text{ Å}$. The corresponding distance in the title compound is $3.7103(7) \text{ Å}$. On the other hand, the shortest inter-chain distances between copper ions are similar in the two structures, *viz.* $6.503(1) \text{ Å}$ in $\{\text{K}_2[\{\text{Cu}_2(\text{O}_2\text{CCH}_3)_4\}\{\text{Cu}(\text{O}_2\text{CCH}_3)_4\}]\}_n$ and $6.526(1) \text{ Å}$ in the title compound.

The *syn-syn* bridging mode between dimeric and monomeric units is novel among copper carboxylates and is probably sterically feasible only for formates. This notion is supported by the fact that such a structural motif (within metal carboxylates) has only been observed in one structure, *viz.* $[\text{Cr}_3(\text{O}_2\text{CH})_6 \cdot 2\text{H}_2\text{O}]$, also a formate compound (Cotton *et al.*, 1978).

The sodium cations are surrounded by seven formate O atoms at distances ranging from $2.319(9)$ to $2.699(9) \text{ Å}$. The sodium coordination polyhedra are connected through

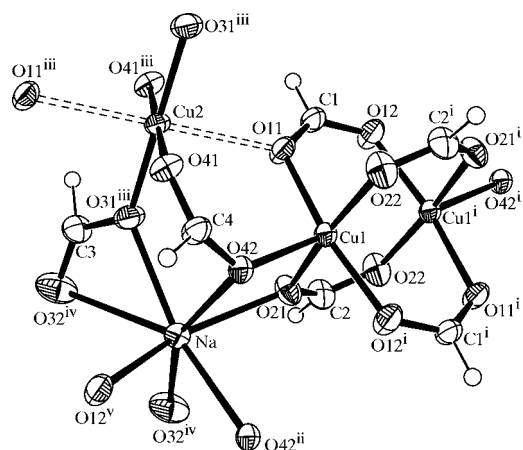


Figure 2

An ORTEP-3 drawing (Farrugia, 1997), with displacement ellipsoids shown at the 50% probability level. Dashed lines depict the additional connections between binuclear and mononuclear formate copper(II) units. [Symmetry codes: (i) $-x+2, -y, -z$; (ii) $-x+1, -y, -z$; (iii) $-x+2, -y+1, -z+1$; (iv) $-x+1, -y+1, -z$; (v) $x-1, y, z$.]

$\text{O42} \cdots \text{O42}(-x+1, -y+1, -z)$ and $\text{O32} \cdots \text{O32}(-x+1, -y+1, -z)$ edges into infinite chains, which run along the *b* axis.

Experimental

Sodium formate was prepared by evaporating an equimolar aqueous solution of methanoic acid and sodium hydroxide to dryness. Sodium formate (1.09 g , 16 mmol) was dissolved with stirring in a mixture of methanol (50 ml) and distilled water (2 ml) acidified with a few drops of methanoic acid. The solution obtained was filtered into a solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.68 g , 4.0 mmol) in acidified methanol (10 ml). The solution was left to stand at 278 K for 24 h . The green crystalline product was filtered off and dried over KOH in a desiccator overnight. The average yield from the synthesis was 87% . The same product was obtained in lower yields using a similar procedure if $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ or anhydrous copper formate (α form) were used as starting materials. All samples were checked by powder X-ray diffraction, which gave *d* spacings and relative intensities in agreement with the values calculated from the single-crystal structure analysis. Single crystals, stable in air and suitable for structural analysis, were obtained by the above procedure using more dilute solutions.

Crystal data

$\text{Na}_2[\text{Cu}_3(\text{CHO}_2)_8]$
 $M_r = 596.76$
 Triclinic, $P\bar{1}$
 $a = 7.6594(2) \text{ Å}$
 $b = 7.7717(1) \text{ Å}$
 $c = 8.7972(2) \text{ Å}$
 $\alpha = 113.248(1)^\circ$
 $\beta = 108.653(1)^\circ$
 $\gamma = 97.495(1)^\circ$
 $V = 435.61(2) \text{ Å}^3$

$Z = 1$
 $D_x = 2.275 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 1672 reflections
 $\theta = 2.9\text{--}27.5^\circ$
 $\mu = 3.76 \text{ mm}^{-1}$
 $T = 293 \text{ K}$
 Prism, green
 $0.12 \times 0.10 \times 0.07 \text{ mm}$

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor 1997)
 $T_{\min} = 0.64$, $T_{\max} = 0.77$
 5090 measured reflections

1966 independent reflections
 1775 reflections with $F^2 > 2\sigma(F^2)$
 $R_{\text{int}} = 0.038$
 $\theta_{\max} = 27.5^\circ$
 $h = -9 \rightarrow 9$
 $k = -10 \rightarrow 10$
 $l = -9 \rightarrow 11$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.052$
 $wR(F^2) = 0.152$
 $S = 1.04$
 1775 reflections
 148 parameters

H atoms treated by a mixture of independent and constrained refinement
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 1.77 \text{ e Å}^{-3}$
 $\Delta\rho_{\min} = -1.72 \text{ e Å}^{-3}$

Table 1

Selected geometric parameters (Å , $^\circ$).

$\text{Cu1}-\text{O11}$	1.965 (5)	$\text{Cu1}-\text{O42}$	2.104 (5)
$\text{Cu1}-\text{O12}^i$	1.987 (6)	$\text{Cu2}-\text{O11}$	2.492 (5)
$\text{Cu1}-\text{O21}$	1.965 (6)	$\text{Cu2}-\text{O31}$	1.937 (6)
$\text{Cu1}-\text{O22}^i$	1.956 (7)	$\text{Cu2}-\text{O41}$	1.987 (6)
$\text{O11}-\text{Cu1}-\text{O12}^i$	168.7 (2)	$\text{O21}-\text{Cu1}-\text{O22}^i$	169.0 (3)
$\text{O11}-\text{Cu1}-\text{O21}$	88.9 (2)	$\text{O21}-\text{Cu1}-\text{O42}$	93.6 (2)
$\text{O11}-\text{Cu1}-\text{O22}^i$	89.7 (3)	$\text{O22}^i-\text{Cu1}-\text{O42}$	97.4 (3)
$\text{O11}-\text{Cu1}-\text{O42}$	101.9 (2)	$\text{O11}-\text{Cu2}-\text{O31}$	90.2 (2)
$\text{O12}^i-\text{Cu1}-\text{O21}$	90.3 (2)	$\text{O11}-\text{Cu2}-\text{O41}$	95.1 (2)
$\text{O12}^i-\text{Cu1}-\text{O22}^i$	88.9 (3)	$\text{O31}-\text{Cu2}-\text{O41}$	92.1 (2)
$\text{O12}-\text{Cu1}-\text{O42}$	89.4 (2)		

Symmetry code: (i) $-x+2, -y, -z$.

The positions of all H atoms were obtained from the difference Fourier map. Full-matrix least-squares refinement on F^2 was employed with isotropic displacement parameters for H atoms. The exception was the H atom bonded to C1 whose isotropic displacement parameter was set to be equal to $1.2U_{eq}(C1)$. A Regina weighting scheme (Wang & Robertson, 1985) using a normal equation of 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 $V(F) = F_{obs}^2/F_{obs}^2(\max)$, $F_{obs}^2(\max) = 12638$, $V(S) = (\sin\theta/\lambda)/[(\sin\theta/\lambda)(\max)]$ and $(\sin\theta/\lambda)(\max) = 0.6497$; the parameters are $A(0,0) = 3200.667$, $A(1,0) = 22.59881$, $A(0,1) = -2802.914$, $A(2,0) = -0.0017726$, $A(1,1) = -14.87134$ and $A(0,2) = -7847.764$. The highest peak in the final difference Fourier map is located between atoms Na and O32 [1.723 (3) Å from Na and 1.255 (7) Å from O32], and the deepest hole is between atoms Cu1 and O32 [1.2329 (8) Å from Cu1 and 1.030 (8) Å from O22].

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *Xtal3.6* (Hall *et al.*, 1999); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *Xtal3.6* and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1173). Services for accessing these data are described at the back of the journal.

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