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Bis{(μ-acetato)[μ-bis(salicylidene)-1,3-propanediaminato]copper(II)}copper(II) dioxane solvate[†]

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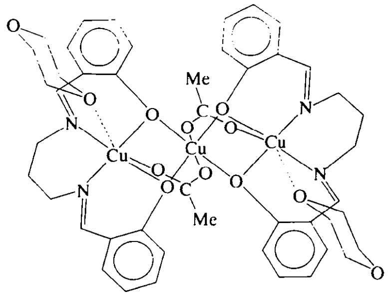
Abstract

The structure of the title compound, $[Cu\{Cu(CH_3CO_2)(C_{17}H_{16}N_2O_2)\}_2]\cdot C_4H_8O_2$, contains a linear homo-trinuclear complex with a central Cu^{II} ion which lies on an inversion centre. It has an irregular octahedral coordination involving four O atoms from two *N,N'*-bis(salicylidene)-1,3-propanediaminato ($SALPD^{2-}$) ligands and two acetate groups. The coordination about each of the two terminal Cu^{II} ions related by the inversion centre comprises two O atoms and two N atoms from an $SALPD^{2-}$ ligand, as well as one acetate O atom. Each acetate anion bridges between a terminal and the central Cu^{II} ion, and these are mutually *trans*. The Cu···Cu bridging distance is 3.1242 (7) Å. Taking into account that the dioxane molecules bridge trinuclear complexes in neighbouring unit cells through Cu2···O5 contacts of 2.649 (3) Å, each terminal Cu^{II} ion possesses irregular octahedral coordination.

Comment

Oxygen-bridged trinuclear linear homo- or heteronuclear complexes exhibit magnetic superexchange interactions between bridged metal ions, and their synthesis and structural characterization is therefore of interest. The ligand stereochemistry around the metal ions and the structure of the O-atom bridges influence the magnetic exchange interactions. The magnetic properties and synthesis of the trinuclear complexes of general formulae $[MCu_2(SALPD)_2(CH_3CO_2)_2]$ ($M = Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}$ or Zn^{2+}) and $[MNi_2(SALPD)_2(CH_3CO_2)_2]$ ($M = Mg^{2+}, Mn^{2+}, Co^{2+}$ or Ni^{2+}), where H_2SALPD represents *N,N'*-bis(salicylidene)-1,3-propanediamine, were reported by Fukuhara *et al.* (1990). Only the structure of $[ZnCu_2(SALPD)_2(CH_3CO_2)_2]$ in this group of compounds has been determined by X-ray diffraction (Fukuhara *et al.*, 1990). Similar trinuclear structures formulated as $[M_3\{(SALPN)(CH_3CO_2)[(CH_3)_2NCHO]\}_2]$ [$M = Co^{2+}, Fe^{2+}$; SALPN = *N,N'*-bis(salicylidene)-2,2-dimethylpropylenediamine] (Gerli *et al.*, 1991), $[Ni_3\{(SALPD)(CH_3CO_2)[(CH_3)_2SO]\}_2]$ (Ülkü, Ercan *et al.*, 1997), $[Cd\{Ni(SALPD)(CH_3CO_2)[(CH_3)_2NCHO]\}_2]$ (Ülkü, Tahir *et al.*, 1997), $[Mn\{Ni(SALPD)(CH_3CO_2)[(CH_3)_2NCHO]\}_2]$ (Ercan & Atakol, 1998) and $[Cd\{Cu(SALPD)(CH_3CO_2)\}_2]\cdot C_4H_8O_2$ (Ercan *et al.*, 1998) have also been described. We report here a new linear homometal trinuclear complex, $[Cu_3\{(SALPD)(CH_3CO_2)\}_2]\cdot C_4H_8O_2$, (V).



(V)

The molecular structures of the trinuclear compounds cited above and the structure of the title compound are extremely similar, especially with respect to the coordination geometry around the metal ions. The triclinic unit cell of (V) contains a centrosymmetric trinuclear molecule whose central Cu^{II} ion is located at the inversion centre on the origin. The two inversion-related terminal Cu^{II} ions each have an irregular square-pyramidal coordination polyhedron, with the four equatorial positions occupied by the two N and two O atoms of the $SALPD^{2-}$ ligand. The axial position is occupied by an O atom from the bridging acetate group.

The coordination around the central Cu^{II} metal ion is an irregular octahedron involving four bridging O atoms from two $SALPD^{2-}$ ligands in the equatorial plane, with the apical positions occupied by an O atom from each of the two bridging acetate groups. Within the coordination sphere, the Cu1—O($SALPD^{2-}$) bond lengths [2.026 (3)–2.356 (3) Å] are longer than the Cu1—O(acetate) distance [1.951 (2) Å]. The range of O···Cu1···O angles in the irregular octahedron is 73.6 (1)–92.3 (1)°.

The Cu1···Cu2 distance is 3.1242 (7) Å. The Cu—O distances in the equatorial positions of the irregular square-pyramidal coordination around the terminal Cu^{II} ions [1.922 (3)–2.008 (3) Å] are shorter than the axial Cu2—O4 bond distance of 2.265 (3) Å.

Dioxane molecules bridge trinuclear complexes in neighbouring unit cells through Cu2···O5 contacts of 2.649 (3) Å. Taking this long-range interaction into account, each terminal Cu^{II} ion possesses irregular octahedral coordination. The dioxane molecules are located on inversion centres and have a chair conformation

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[†] Alternative name: bis(μ-acetato)-1:2κ^2*O*:*O'*;1:3κ^2*O*:*O'*-bis{μ-2,2'-[1,3-propanediylbis(nitrilomethylidyne)]diphenolato}-1κ^2*O*,*O'*:2κ^4-*N*,*N'*,*O*,*O'*:1κ^2*O*,*O'*:3κ^4*N*,*N'*,*O*,*O'*-tricopper(II) dioxane solvate.

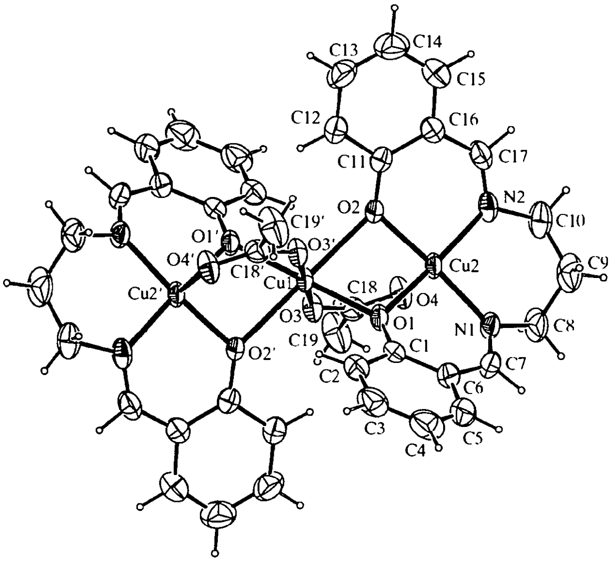

Fig. 1. *PLATON* (Spek, 1998) drawing of (V) with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radii. Dioxane molecules bridging neighbouring complexes have not been shown for clarity. [Symmetry code: (i) $-x, -y, -z$.]

with the *para*-positioned chair atoms, O5 and O5^{i}, lying ±0.6530 (3) Å from the best plane of the four C atoms.

The dihedral angle between the equatorial planes of the neighbouring polyhedra (O1, O2, N1, N2 and O1, O2, O1^{i}, O2^{i}) is 21.64 (9)° [symmetry code: (i) $-x$, $-y$, $-z$]. The terminal Cu^{II} ion is 0.1362 (4) Å out of the equatorial plane. The six-membered chelate ring (Cu2, N1, C8, C9, C10, N2) has a chair conformation and the two *para*-positioned chair atoms, Cu2 and C9, are displaced from their respective planes by 0.0993 (5) and −0.267 (5) Å. A comparison of the dihedral angle between the two equatorial planes of the neighbouring polyhedra (φ), and between the $M(Ni^{2+}, Cu^{2+})$—O—$M(Mn^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+})$—O bridging plane and the coordination plane around the central atom (κ), along with the related distance ranges and bridging angles, are given in Table 1 for the five trinuclear complexes studied recently in this laboratory. From this Table, the remarkable similarity of the five structures is obvious.

Experimental

N,N'-Bis(salicylidene)-1,3-propanediamine (0.565 g, 2 mmol) was dissolved in hot dioxane (100 ml). A solution of $Cu(CH_3CO_2)_2\cdot H_2O$ (0.600 g, 3 mmol) in a hot methanol/dimethylformamide mixture (50 ml, 4:1) was then added slowly. The resulting mixture was set aside for 2 d and the green crystals which formed were filtered off and dried in air.

Crystal data

$[Cu_3(C_2H_3O_2)_2(C_{17}H_{16}N_2O_2)_2]\cdot C_4H_8O_2$
$M_r = 957.476$
Triclinic
$P\bar{1}$
$a = 10.0761\ (12)$ Å
$b = 10.6819\ (13)$ Å
$c = 10.9819\ (12)$ Å
$\alpha = 63.847\ (2)°$
$\beta = 72.015\ (3)°$
$\gamma = 79.359\ (2)°$
$V = 1007.5\ (2)$ Å^3
$Z = 1$
$D_x = 1.578$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 8.77–18.07°$
$\mu = 1.635$ mm^{-1}
$T = 295$ K
Pinacoid
0.40 × 0.30 × 0.20 mm
Green

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (Fair, 1990)
$T_{min} = 0.935$, $T_{max} = 0.999$
4120 measured reflections
3926 independent reflections

2733 reflections with $I > 1\sigma(I)$
$R_{int} = 0.014$
$\theta_{max} = 26.42°$
$h = -12 \rightarrow 0$
$k = -13 \rightarrow 12$
$l = -13 \rightarrow 13$
3 standard reflections frequency: 120 min intensity decay: 1.26%

Refinement

Refinement on F
$R = 0.044$
$wR = 0.046$
$S = 0.96$
2733 reflections
268 parameters
H atoms: see below
$w = 1/[\sigma F^2 + (0.02F)^2 + 0.2]$ if $F^2 > \sigma F^2$; $w = 0$ if $F^2 < \sigma F^2$

$(\Delta/\sigma)_{max} = 0.00031$
$\Delta\rho_{max} = 0.970$ e Å^{-3}
$\Delta\rho_{min} = -0.139$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Structural data, bridging angles and dihedral angles (φ and κ) for five homo- or hetero-trinuclear complexes*

$M_{terminal}$ atoms are Ni^{2+} and Cu^{2+}, and $M_{central}$ atoms are Ni^{2+}, Cu^{2+}, Cd^{2+} and Mn^{2+}.

Complex	$M_{terminal}$—O (Å)	$M_{central}$—O (Å)	M—M (Å)	O—$M_{central}$—O (°)	O—$M_{terminal}$—N (°)	φ (°)	κ (°)
(I)	2.010 (3)–2.254 (3)	2.024 (3)–2.098 (3)	3.043 (2)	79.4 (1)	89.8 (2)–90.6 (2)	21.9 (1)	33.1 (1)–35.06 (7)
(II)	2.012 (1)–2.190 (2)	2.260 (1)–2.293 (2)	3.227 (5)	73.66 (5)	88.09 (7)–89.76 (6)	23.10 (7)	26.38 (6)–32.80 (7)
(III)	2.017 (2)–2.184 (2)	2.163 (1)–2.194 (2)	3.133 (2)	76.66 (6)	88.93 (8)–90.38 (7)	23.68 (8)	26.91 (7)–32.36 (9)
(IV)	1.953 (3)–2.324 (2)	2.280 (3)–2.310 (3)	3.244 (3)	70.06 (9)	89.5 (1)–90.8 (1)	21.51 (8)	31.24 (10)–37.24 (6)
(V)	1.922 (3)–2.265 (3)	2.026 (3)–2.356 (3)	3.1247 (7)	73.61 (1)	89.6 (1)–91.4 (2)	21.64 (9)	32.16 (12)–38.23 (7)

Notes: (I) is $[Ni_3\{(CH_3CO_2)(SALPD)[(CH_3)_2SO]\}_2]$ (Ülkü, Ercan *et al.*, 1997), (II) is $[CdNi_2\{(CH_3CO_2)(SALPD)[(CH_3)NCHO]\}_2]$ (Ülkü, Tahir *et al.*, 1997), (III) is $[MnNi_2\{(CH_3CO_2)(SALPD)[(CH_3)NCHO]\}_2]$ (Ercan & Atakol, 1998), (IV) is $[CdCu_2\{(CH_3CO_2)(SALPD)\}_2]\cdot C_4H_8O_2$ (Ercan *et al.*, 1998) and (V) is $[Cu_3\{(CH_3CO_2)(SALPD)\}_2]\cdot C_4H_8O_2$ (title compound).

Table 2. *Selected geometric parameters (Å, °)*

Cu1—Cu2	3.1242 (7)	Cu2—N1	1.957 (4)
Cu1—O1	2.026 (3)	Cu2—N2	1.997 (4)
Cu1—O2	2.356 (3)	O1—C1	1.319 (5)
Cu1—O3	1.951 (2)	O2—C11	1.303 (5)
Cu2—O1	2.008 (3)	O3—C18	1.265 (6)
Cu2—O2	1.922 (3)	O4—C18	1.236 (7)
Cu2—O4	2.265 (3)		
O1—Cu1—O2	73.6 (1)	N1—Cu2—N2	94.0 (2)
O1—Cu1—O3	89.2 (1)	Cu1—O1—Cu2	101.5 (1)
O2—Cu1—O3	92.3 (1)	Cu2—O1—C1	122.8 (3)
O1—Cu2—O2	84.3 (1)	Cu2—O2—C11	124.4 (3)
O1—Cu2—O4	90.7 (1)	Cu1—O3—C18	134.1 (3)
O1—Cu2—N1	89.6 (1)	Cu2—O4—C18	122.4 (2)
O1—Cu2—N2	167.7 (1)	Cu2—N1—C7	123.2 (4)
O2—Cu2—O4	90.4 (1)	Cu2—N1—C8	119.4 (3)
O2—Cu2—N1	173.0 (1)	Cu2—N2—C10	122.3 (3)
O2—Cu2—N2	91.4 (2)	Cu2—N2—C17	121.3 (4)
O4—Cu2—N1	93.1 (1)	O3—C18—O4	127.4 (3)
O4—Cu2—N2	100.9 (1)		

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O3$^{\rm i}$	0.950	2.522	3.125 (6)	121.4 (3)
C21—H211···O3$^{\rm i}$	0.906	2.542	3.408 (6)	160.3 (4)

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

All non-H atoms were refined with anisotropic displacement parameters. The H7, H17, H81, H82, H91, H92, H101, H102, H191, H192, H193, H201, H202, H211 and H212 atoms were taken from difference maps, while other H atoms were placed geometrically 0.95 Å from their parent C atoms and then a riding model was used for all H atoms with $U_{\rm iso}({\rm H}) = 1.3U_{\rm eq}({\rm C})$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1994). Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MolEN*. Program(s) used to refine structure: *MolEN*. Molecular graphics: *PLATON* (Spek, 1998). Software used to prepare material for publication: *MolEN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1276). Services for accessing these data are described at the back of the journal.

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Copper(II) 2-thiopheneglyoxylate adducts with pyridine derivatives

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Abstract

In the crystals of *trans*-bis(pyridine-*N*)bis(2-thiopheneglyoxylato-O^1,O^2)copper(II), $[{\rm Cu}({\rm C_6H_3O_3S})_2({\rm C_5H_5N})_2]$, there is a mononuclear Cu$^{\rm II}$ complex molecule. In the crystal of *catena*-poly[[[bis(2-thiopheneglyoxylato-O^1,O^2)copper(II)]-μ-(2-thiopheneglyoxylato-O^1:$O^{1'}$,O^2)-[bis(3-methylpyridine-*N*)copper(II)]-μ-(2-thiopheneglyoxylato-O^1,O^2:$O^{1'}$)] monohydrate], $\{[{\rm Cu_2}({\rm C_6H_3O_3S})_4({\rm C_6H_7N})_2]\cdot{\rm H_2O}\}_n$, there is a zigzag polymer chain where the Cu$^{\rm II}$ atoms are bridged by the thiopheneglyoxylate ions. In the crystal of *cis*-bis(4-methylpyridine-*N*)bis(2-thiopheneglyoxylato-O^1,O^2)copper(II), $[{\rm Cu}({\rm C_6H_3O_3S})_2({\rm C_6H_7N})_2]$, there is a mononuclear Cu$^{\rm II}$ complex. The coordination geometry around the Cu atoms is distorted octahedral. Each thiopheneglyoxylate ion adopts a flattened structure and forms a five-membered chelate ring with the Cu atom.

Comment

Dimeric copper(II) benzoylformates adopt a cage structure and show an abnormally large antiferromagnetic spin-exchange interaction between the Cu atoms (Harada *et al.*, 1997). In the present study, 2-thiopheneglyoxylic acid was selected as another α-keto acid to prepare a binuclear copper(II) complex with pyridine derivatives as axial ligands. However, the compounds