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## Key indicators

Single-crystal X-ray study  
 $T = 130\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$   
 $R$  factor = 0.070  
 $wR$  factor = 0.136  
Data-to-parameter ratio = 19.4For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.Tetrakis( $\mu$ - $\alpha$ -naphthylacetato- $\kappa^2\text{O}:\text{O}'$ )bis-  
[(dimethyl sulfoxide- $\kappa\text{O}$ )copper(II)]-  
 $\alpha$ -naphthylacetic acid–dimethyl sulfoxide (1/2/2)

The title complex,  $[\text{Cu}_2(\text{NAA})_4(\text{DMSO})_2] \cdot 2(\text{HNAA}) \cdot 2\text{DMSO}$  [NAA =  $\alpha$ -naphthylacetate ( $\text{C}_{12}\text{H}_9\text{O}_2$ ) and DMSO = dimethyl sulfoxide ( $\text{C}_2\text{H}_6\text{OS}$ )], consists of a centrosymmetric dinuclear cage unit, in which two  $\text{Cu}^{\text{II}}$  atoms are separated by 2.626 (1)  $\text{\AA}$  and bridged by four bidentate carboxylate groups of naphthylacetates, with an average Cu–O distance of 1.961 (2)  $\text{\AA}$ . Each  $\text{Cu}^{\text{II}}$  atom has a five-coordinate square-pyramidal environment with the dimethyl sulfoxide molecule at the apical position. The Cu–O bond length to the DMSO molecule is 2.160 (2)  $\text{\AA}$ .

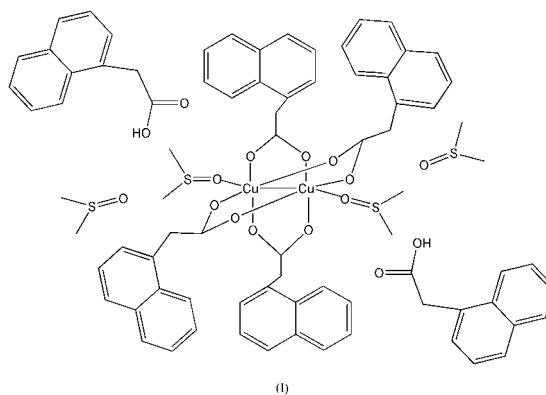
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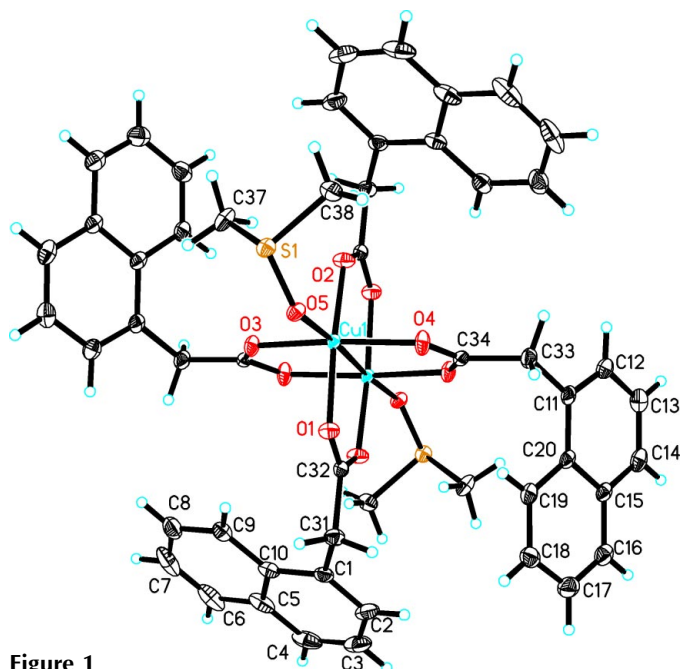
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## Comment

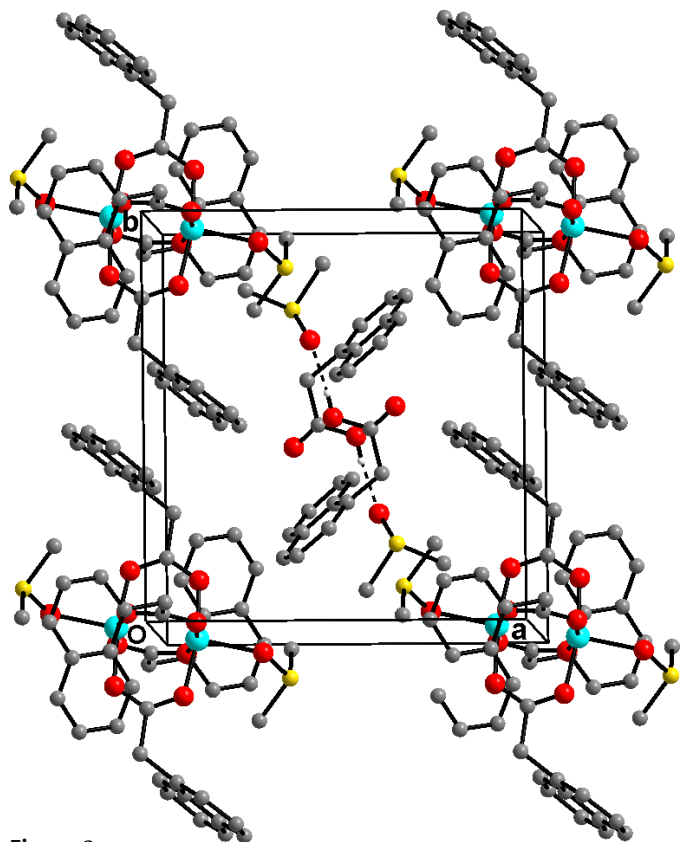
Metal–oxo clusters have been intensively studied due to their important functions and applications in magnetic materials and biological sciences (Aubin *et al.*, 2001; Weder *et al.*, 1999). A number of metal–oxo complexes with bridging carboxylate ligands bearing a benzene ring, such as benzoic acid (Speier & Fulop, 1989), 1,4-benzenedicarboxylic acid (Bakalbassis *et al.*, 1988), 1,3,5-benzenetricarboxylic acid (Cheng *et al.*, 2001) and 1,2,4,5-benzenetetracarboxylic acid (Cao *et al.*, 2002), have been studied because of their diverse coordination modes and structure types. In contrast, the studies of complexes involving transition metals with condensed aromatic rings have not been reported in any great numbers (Jiang & Yu, 1992). In view of various properties of carboxylate ligands with condensed benzene rings in molecular assemblies, *e.g.* coordination modes, flexibility, stereochemical effects and potential  $\pi$ – $\pi$  interactions, our interest in this area lies in the preparation of carboxylate-bridged metal complexes containing condensed aromatic rings which might exhibit unusual structural motifs and magnetic properties derived from the interactions of neighboring metal sites as well as aromatic rings.



We present here the synthesis and crystal structure of the title compound, (I) (Fig. 1). The crystal structure of (I) is composed of a neutral  $[\text{Cu}_2(\text{NAA})_4(\text{DMSO})_2]$  dinuclear unit



**Figure 1**  
View of (I), with 30% probability displacement ellipsoids. Free HNAA and DMSO molecules have been omitted for clarity.



**Figure 2**  
Packing diagram of (I), viewed along the *c* axis, showing the hydrogen-bonding interactions as dashed lines. H atoms have been omitted.

(NAA =  $\alpha$ -naphthylacetate anion and DMSO = dimethyl sulfoxide), two free HNAA molecules and two free DMSO molecules. The  $[\text{Cu}_2(\text{NAA})_4(\text{DMSO})_2]$  dinuclear unit has a centrosymmetric cage structure, with an inversion center that

is located at the mid-point of the Cu—Cu vector. Each  $\text{Cu}^{\text{II}}$  ion is in a five-coordinate square-pyramidal environment, with the basal plane being defined by the O atoms of four bridging bidentate carboxylate groups of naphthylacetate ligands, and the apical position occupied by the O atom of the terminal dimethyl sulfoxide molecule. The Cu—O(carboxylate) distances range from 1.950 (2) to 1.976 (2) Å, in good agreement with the values in other analogous  $\text{Cu}^{\text{II}}$  dimers (Battaglia *et al.*, 1981; Kani *et al.*, 1998). The Cu—O(DMSO) bond length of 2.160 Å, close to the values in a benzoate-bridged dinuclear unit with similar geometry (Melnik *et al.*, 1984), is slightly longer than the Cu—O(carboxylate) bonds. This might be attributed to the weak coordination ability of DMSO. In this typical cage structure, the Cu...Cu distance is 2.626 (1) Å, which is within the range of those observed for copper(II) acetate monohydrate and normal dimeric carboxylate complexes (Battaglia *et al.*, 1981). The four *cis*-angles between Cu—O(carboxylate) groups are all close to right angles. Atoms O1, O2, O3 and O4 constitute the basal plane of the Cu coordination, the mean deviation being 0.0614 Å. The  $\text{Cu}^{\text{I}} \cdots \text{Cu} - \text{O}(\text{DMSO})$  [Symmetry code: (i)  $-x, 1-y, -z$ ] angle is 175.9 (6)°, which deviates slightly from the value of 180° that is expected for a  $\text{Cu}_2(\text{O}_2\text{C})_4(\text{O})_2$  core of idealized  $D_{4h}$  symmetry.

The crystal packing of (I), demonstrating the hydrogen bonding between the free naphthylacetic acid molecules (hydroxyl O atoms) and DMSO molecules (Table 2), is shown in Fig. 2.

## Experimental

$\text{CuCl}_2 \cdot 4\text{H}_2\text{O}$  (2.0 mmol) was dissolved in DMSO/ $\text{H}_2\text{O}$  (1:4, 10 ml), then mixed with 4,4-bipyridine (0.5 mmol) in ethanol (5 ml). The mixture was heated to 333 K for 20 min with stirring. An ethanol (5 ml) solution of HNAA (1 mmol) was added dropwise to the above solution and the reaction temperature maintained for half an hour. The solution was filtered and the filtrate evaporated slowly at room temperature for a week. Finally, blue block-shaped crystals were obtained (yield 76%). Main IR features ( $\text{cm}^{-1}$ , KBr): 1706.5 (*m*), 1631.3 (*s*), 1596.2 (*m*), 1509.5 (*m*), 1422.7 (*m*), 1401.0 (*s*), 1234.2 (*m*), 1028 (*s*), 1008.9 (*s*), 952.2 (*m*), 793.7 (*s*), 783.6 (*s*), 711.9 (*m*), 640.2 (*m*), 546.7 (*m*).

### Crystal data

$[\text{Cu}_2(\text{C}_{12}\text{H}_9\text{O}_2)_4(\text{C}_2\text{H}_6\text{OS})_2] \cdot 2\text{C}_{12}\text{H}_{10}\text{O}_2 \cdot 2\text{C}_2\text{H}_6\text{OS}$   
 $M_r = 1552.76$   
 Monoclinic,  $P2_1/c$   
 $a = 12.367$  (4) Å  
 $b = 13.192$  (4) Å  
 $c = 22.682$  (7) Å  
 $\beta = 100.905$  (3)°  
 $V = 3634$  (2) Å<sup>3</sup>  
 $Z = 2$

$D_x = 1.419$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 8025 reflections  
 $\theta = 0.9$ –28.3°  
 $\mu = 0.77$  mm<sup>-1</sup>  
 T = 130.2 K  
 Cube, blue  
 0.30 × 0.20 × 0.10 mm

### Data collection

Rigaku MERCURY CCD diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (Blessing, 1995, 1997)  
 $T_{\text{min}} = 0.831$ ,  $T_{\text{max}} = 0.926$   
 29703 measured reflections

8999 independent reflections  
 7677 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.053$   
 $\theta_{\text{max}} = 28.3^\circ$   
 $h = -16 \rightarrow 16$   
 $k = -17 \rightarrow 15$   
 $l = -30 \rightarrow 28$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.070$   
 $wR(F^2) = 0.136$   
 $S = 1.18$   
 8999 reflections  
 463 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0375P)^2 + 5.2231P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.71 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.48 \text{ e } \text{\AA}^{-3}$

**Table 1**  
 Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Cu1—O4	1.950 (2)	Cu1—O1	1.976 (2)
Cu1—O2	1.958 (2)	Cu1—O5	2.160 (2)
Cu1—O3	1.960 (2)	Cu1...Cu1 <sup>i</sup>	2.6264 (11)
O4—Cu1—O2	89.19 (11)	O4—Cu1...Cu1 <sup>i</sup>	84.42 (7)
O4—Cu1—O3	168.76 (10)	O2—Cu1...Cu1 <sup>i</sup>	83.43 (7)
O2—Cu1—O3	90.18 (11)	O3—Cu1...Cu1 <sup>i</sup>	84.36 (7)
O4—Cu1—O1	89.19 (11)	O1—Cu1...Cu1 <sup>i</sup>	85.34 (7)
O2—Cu1—O1	168.76 (10)	O5—Cu1...Cu1 <sup>i</sup>	175.90 (7)
O3—Cu1—O1	89.24 (10)	C32—O1—Cu1	121.0 (2)
O4—Cu1—O5	99.56 (9)	C34—O4—Cu1	122.9 (2)
O2—Cu1—O5	97.58 (9)	C34 <sup>i</sup> —O3—Cu1	122.7 (2)
O3—Cu1—O5	91.65 (9)	C32 <sup>i</sup> —O2—Cu1	124.4 (2)
O1—Cu1—O5	93.66 (9)	S1—O5—Cu1	131.64 (14)

Symmetry code: (i)  $-x, 1 - y, -z$ .

**Table 2**  
 Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O6—H6B...O8 <sup>ii</sup>	0.80 (4)	1.84 (4)	2.635 (4)	172 (4)

Symmetry code: (ii)  $x, y - 1, z$ .

H atoms bonded to carbon were placed at calculated positions ( $C-H = 0.93-0.97 \text{ \AA}$ ) and refined using a riding model, with  $U(H) =$

1.2 or 1.5 (methyl) times  $U_{\text{eq}}$ (parent atom). H atoms associated with oxygen were located in a difference Fourier map and refined freely.

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL97*.

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