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Key indicators

Single-crystal X-ray study
 $T = 273$ K
Mean $\sigma(\text{C}-\text{C}) = 0.006$ Å
Disorder in main residue
 R factor = 0.049
 wR factor = 0.140
Data-to-parameter ratio = 16.0For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Tetrakis(μ -4-tolylsulfanylacetato- $\kappa^2\text{O}:\text{O}'$)-
bis[$(N,N'$ -dimethylformamide- κO)copper(II)]Molecules of the title dinuclear complex, $[\text{Cu}_2(\text{C}_9\text{H}_9\text{O}_2\text{S})_4(\text{C}_3\text{H}_7\text{NO})_2]$, lie on centers of inversion located midway between the Cu atoms. Four carboxylate anions function as bridges to the two Cu atoms and each Cu atom is coordinated by an N,N' -dimethylformamide molecule.

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Comment

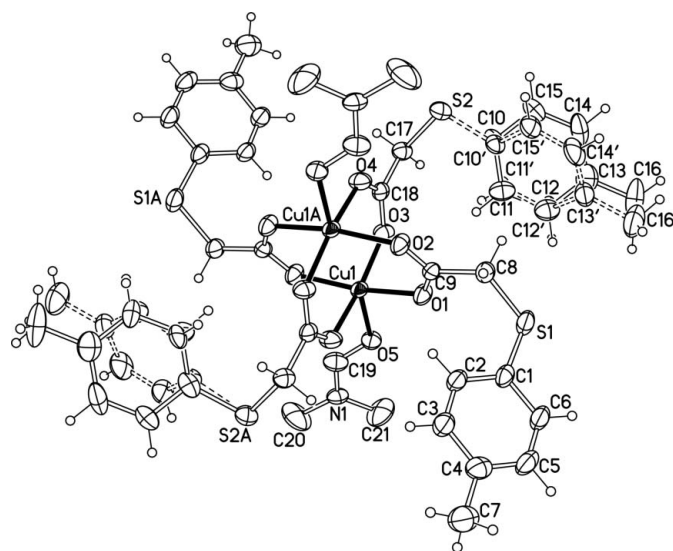
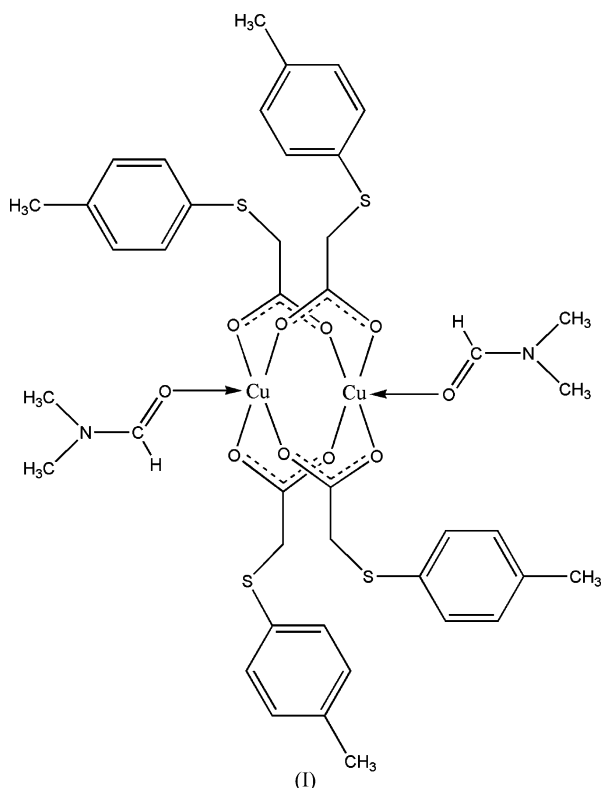
Interest in the structural characterization of tetracarboxylate-bridged dimeric copper(II) complexes has been increased since the crystal structure of copper acetate monohydrate was reported by van Niekerk & Schoening (1953). In general, a large number of copper(II) carboxylates can be formulated as $[\text{Cu}_2(\text{RCO}_2)_4L_2]$, where L denotes an axial oxygen- or nitrogen-donor ligand (Tong *et al.*, 2002; Morgan *et al.*, 2001; Tian *et al.*, 2002; Calderazzo *et al.*, 2003; Ponikiewski & Rothenberger, 2005). Among these dinuclear copper tetracarboxylate adducts are several having a mercapto entity in the acetate residue, such as, for example, the adducts phenylthioacetate pyridine (O'Reilly *et al.*, 1984), isopropylthioacetate quinoline (Ouchi *et al.*, 1983), 2,4-dichloro-5-methylphenylthioacetate acetone (Kennard *et al.*, 1985), 2-(2-chlorophenylthio)-2-methylpropionate water (Chan, Mak, Yip, Kennard *et al.*, 1987), 2,4-dichloro-5-methylphenylthioacetate acetone (Smith *et al.*, 1985) and 2-methyl-2-(phenylthio)propionate ethanol (Chan, Mak, Yip, Smith *et al.*, 1987). In order to explore

Figure 1

The structure of (I). Displacement ellipsoids are drawn at the 30% probability level. Unlabeled atoms and atoms labeled with the suffix A are generated by the symmetry operation $(1 - x, 1 - y, -z)$. Both the major and the minor components of the disordered 4-tolyl group are shown.

further the coordination behavior of the dinuclear copper(II) complexes with tetracarboxylate which have a mercapto entity, we synthesized a new dinuclear copper(II) complex, $[\text{Cu}_2(4\text{-MPTA})_4(\text{DMF})_2]$ (where 4-MPTA is the 4-methylphenylthioacetate anion and DMF is *N,N'*-dimethylformamide), (I).



Molecules of (I) lie on centers of inversion. As illustrated in Fig. 1, the two Cu^{II} atoms are bridged by four carboxylate groups of four 4-MPTA anions forming a dinuclear structure, the $\text{Cu}\cdots\text{Cu}$ distance being 2.6409 (15) Å. Each Cu atom is also coordinated by an *N,N'*-dimethylformamide molecule. Each Cu^{II} atom displays an approximate square-pyramidal geometry with four carboxylate O atoms from four 4-MPTA anions in the basal plane [$\text{Cu}-\text{O}_{\text{carboxyl}} = 1.961(2)$ – $1.974(2)$ Å], and the O atom of the *N,N'*-dimethylformamide molecule in the apical position [$\text{Cu}-\text{O} = 2.149(2)$ Å]. The C–O bond distances of the carboxyl groups are nearly identical (Table 1), suggesting delocalization of electrons in these groups. No significant hydrogen-bonding interaction is observed in the crystal structure.

Experimental

Blue vitriol (0.25 g, 1 mmol) and 4-methylphenylthioacetic acid (0.36 g, 2 mmol) were dissolved separately in a water–DMF (1:1) solution, and the two solutions were mixed slowly with stirring at room temperature. The pH was adjusted to 6 with triethylamine. Green crystals were obtained from the filtrate at room temperature over a period of several days. Analysis calculated for

$\text{C}_{42}\text{H}_{50}\text{Cu}_2\text{N}_2\text{O}_{10}\text{S}_4$: C 50.54, H 5.05, N 2.81%; found: C 50.64, H 5.15, N 2.71%.

Crystal data

$[\text{Cu}_2(\text{C}_9\text{H}_9\text{O}_2\text{S})_4(\text{C}_3\text{H}_7\text{NO})_2]$
 $M_r = 984.11$
 Monoclinic, $P2_1/n$
 $a = 10.997(7)$ Å
 $b = 7.808(5)$ Å
 $c = 27.066(17)$ Å
 $\beta = 97.49(1)^\circ$
 $V = 2304(3)$ Å³

$Z = 2$
 $D_x = 1.418$ Mg m^{−3}
 Mo $K\alpha$ radiation
 $\mu = 1.16$ mm^{−1}
 $T = 273(2)$ K
 Prism, green
 $0.30 \times 0.20 \times 0.18$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\text{min}} = 0.757$, $T_{\text{max}} = 0.812$

14547 measured reflections
 5397 independent reflections
 3383 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.043$
 $\theta_{\text{max}} = 27.8^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.140$
 $S = 1.09$
 5397 reflections
 338 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0643P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.89$ e Å^{−3}
 $\Delta\rho_{\text{min}} = -0.47$ e Å^{−3}

Table 1

Selected geometric parameters (Å, °).

Cu1–O1	1.961 (2)	O1–C9	1.245 (4)
Cu1–O3	1.962 (3)	O2–C9	1.253 (4)
Cu1–O4 ⁱ	1.965 (3)	O3–C18	1.263 (4)
Cu1–O2 ⁱ	1.974 (2)	O4–C18	1.250 (4)
Cu1–O5	2.149 (2)	O5–C19	1.263 (4)
Cu1–Cu1 ⁱ	2.6409 (15)		
O1–Cu1–O3	87.68 (10)	O4 ⁱ –Cu1–O2 ⁱ	89.07 (11)
O1–Cu1–O4 ⁱ	90.54 (11)	O1–Cu1–O5	98.89 (9)
O3–Cu1–O4 ⁱ	167.97 (9)	O3–Cu1–O5	99.79 (10)
O1–Cu1–O2 ⁱ	167.81 (9)	O4 ⁱ –Cu1–O5	92.23 (10)
O3–Cu1–O2 ⁱ	90.18 (10)	O2 ⁱ –Cu1–O5	93.30 (9)

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

One of the 4-tolyl groups was found to be disordered over two orientations. The occupancy factors for the disordered atoms C10–C16/C10ⁱ–C16ⁱ refined to 0.485 (4)/0.515 (4). The C–C bond lengths involving the disordered atoms were restrained to be equal. In addition, atoms in each disordered group were restrained to be coplanar. H atoms were placed in idealized positions and allowed to ride on their parent atoms, with C–H = 0.93–0.97 Å and $U_{\text{iso}}(\text{H}) = 1.2$ – $1.5U_{\text{eq}}(\text{C})$. A rotating group model was used for the methyl groups. Large U_{eq} values for the methyl C atoms of the DMF molecule suggest disorder, but no suitable disorder model was found.

Data collection: SMART (Bruker, 2002); cell refinement: SAINT (Bruker, 2002); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 2002); software used to prepare material for publication: SHELXL97.

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References

- Bruker (2002). *SMART, SAINT and SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Calderazzo, F., Donati, N., Englert, U., Marchetti, F., Pampaloni, G. & Passarelli, V. (2003). *Inorg. Chim. Acta*, **346**, 100–110.
- Chan, W.-H., Mak, T. C. W., Yip, W. H., Kennard, C. H. L., Smith, G. & O'Reilly, E. J. (1987). *Aust. J. Chem.* **40**, 1161–1168.
- Chan, W.-H., Mak, T. C. W., Yip, W.-H., Smith, G., O'Reilly, E. J. & Kennard, C. H. L. (1987). *Polyhedron*, **6**, 881–889.
- Kennard, C. H. L., Smith, G., O'Reilly, E. J., Mak, T. C. W. & Yip, W. H. (1985). *Inorg. Chim. Acta*, **98**, L31–L34.
- Morgan, Y. R., Turner, P., Kennedy, B. J., Hambley, T. W., Lay, P. A., Biffin, J. R., Regtop, H. L. & Warwick, B. (2001). *Inorg. Chim. Acta*, **324**, 150–161.
- Niekerk, J. N. van & Schoening, F. R. L. (1953). *Acta Cryst.* **6**, 227–232.
- O'Reilly, E. J., Smith, G., Kennard, C. H. L., Mak, T. C. W. & Yip, W. H. (1984). *Inorg. Chim. Acta*, **83**, L63–L66.
- Ouchi, A., Sato, Y., Yukawa, Y. & Takeuchi, T. (1983). *Bull. Chem. Soc. Jpn*, **56**, 2241–2241.
- Ponikiewski, L. & Rothenberger, A. (2005). *Inorg. Chim. Acta*, pp. 1322–1326.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXS97 and SHELXL97*. University of Göttingen, Germany.
- Smith, G., O'Reilly, E. J., Kennard, C. H. L., Mak, T. C. W. & Yip, W. H. (1985). *Polyhedron*, **4**, 451–455.
- Tian, Y.-P., Zhang, X.-J., Wu, J.-Y., Fun, H.-K., Jiang, M.-H., Xu, Z.-Q., Usman, A., Chantrapomma, S. & Thompson, L. K. (2002). *New J. Chem.* **26**, 1468–1473.
- Tong, M.-L., Li, W., Chen, X.-M., Zheng, S.-L. & Ng, S. W. (2002). *Acta Cryst. C* **58**, m232–m234.