

Bis[μ -[6-(hydroxymethyl)-2-pyridyl]-methanolato- $\kappa^3 N, O: O$]bis[[2,6-bis-(hydroxymethyl)pyridine- $\kappa^3 O, N, O'$]-copper(II)] diacetate

Akhilesh Kumar Gupta and Jinkwon Kim*

Department of Chemistry, Kongju National University, 182 Shinkwan, Kongju, Chungnam 314-701, South Korea

Correspondence e-mail: jkim@kongju.ac.kr

Received 9 April 2003

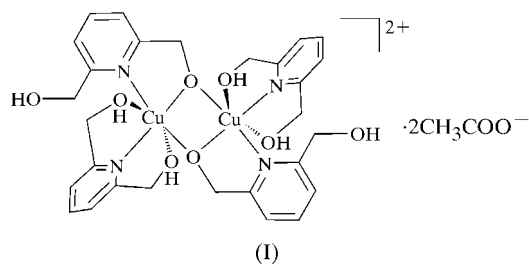
Accepted 28 April 2003

Online 11 June 2003

The title dinuclear Cu^{II} complex, $[\text{Cu}_2(\text{C}_7\text{H}_8\text{NO}_2)_2(\text{C}_7\text{H}_9\text{NO}_2)_2](\text{CH}_3\text{COO})_2$, has been synthesized by the reaction of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ with pdmH_2 (pdmH_2 is pyridine-2,6-diylidimethanol) in the presence of tetrabutylammonium hydroxide. The title complex contains a centrosymmetric Cu_2O_2 core and each Cu^{II} atom has distorted octahedral geometry. Molecular $[\text{Cu}_2(\text{pdmH})_2(\text{pdmH}_2)]^{2+}$ cations are connected by hydrogen bonds involving the CH_3COO^- anions, forming one-dimensional chains along the a axis.

Comment

The pyridine-2,6-diylidimethanolate ligand functions as a bridge through its two O atoms to afford polynuclear metal complexes (Boskovic *et al.*, 2002; Yoo *et al.*, 2000). Our main strategy is to synthesize polynuclear copper complexes using N,O-donor hydroxyalkylpyridyl ligands, because these cluster complexes act as model complexes for the active centers of many metalloenzymes (Agnus, 1983) and as supramolecular building blocks for promising magnetic materials (Del Sesto *et al.*, 2000). Little attention has been paid to copper complexes



based on N,O-donor hydroxyalkylpyridyl ligands, although a few mononuclear (Andac *et al.*, 2002; Koman *et al.*, 2000) and dinuclear complexes (Cheng & Wei, 2002) have been reported. We report here the synthesis and X-ray structure of

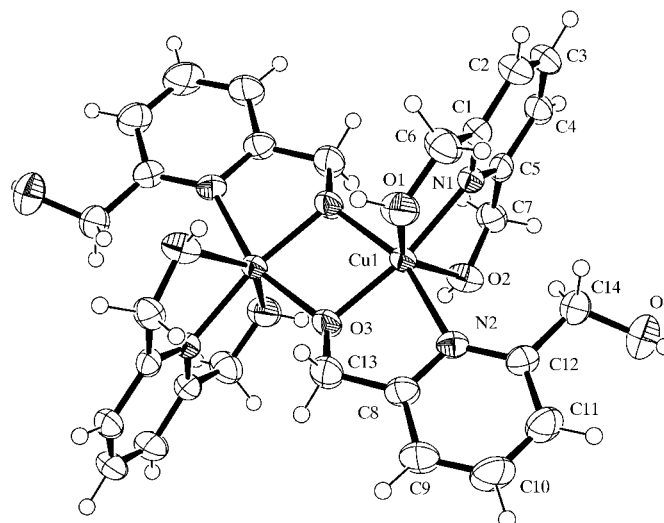


Figure 1
An ORTEP-3 (Farrugia, 1997) diagram of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

a new dinuclear Cu^{II} complex, *viz.* the title complex, (I), which has been obtained from the reaction of $\text{Cu}(\text{acetate})_2 \cdot \text{H}_2\text{O}$ and pdmH_2 (pdmH_2 is pyridine-2,6-diylidimethanol) in the presence of tetrabutylammonium hydroxide.

The complex cation of (I) comprises a $\text{Cu}_2^{\text{II}}(\mu\text{-O})_2$ core, in which the two $\mu\text{-O}$ atoms belong to the bridging pdmH^- ligand. As shown in Fig. 1, each Cu^{II} atom is coordinated by neutral pdmH_2 as a terminal tridentate ligand and anionic pdmH^- as a bridging bidentate ligand. The crystallographic inversion center is located in the middle of the Cu_2O_2 rhombus. In the planar Cu_2O_2 unit, the $\text{Cu}\cdots\text{Cu}$ separation and $\text{Cu}-\text{O}-\text{Cu}$ angle are comparable to those of other alkoxo-bridged Cu_2O_2 complexes (Berti *et al.*, 2003; Cheng & Wei, 2002; Graham *et al.*, 2001). Each Cu atom has a highly distorted octahedral geometry (see Table 1), with acute $\mu\text{-O}-\text{Cu}-\mu\text{-O}$ and $\text{N}-\text{Cu}-\text{O}$ angles that are similar to those found in other distorted-octahedral Cu_4N_2 cores containing the pdmH_2 ligand (Andac *et al.*, 2002; Koman *et al.*, 2000). The axial $\text{Cu}1-\text{O}1$ [2.358 (2) Å] and $\text{Cu}1-\text{O}2$ [2.360 (2) Å] distances are substantially longer than the equatorial $\text{Cu}-\text{O}$ and $\text{Cu}-\text{N}$ distances [1.909 (2)–2.094 (2) Å], which indicates severe Jahn–Teller distortion, despite the restraining effects of the chelate rings. The equatorial distances are similar to the corresponding distances in the tetragonally elongated octahedral $[\text{Cu}(\text{C}_5\text{H}_5\text{NO})_6](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ complex (Wood *et al.*, 1984), while the axial $\text{Cu}-\text{O}$ bond distances are shorter than the bond length of 2.478 (2) Å found in $[\text{Cu}(\text{C}_5\text{H}_5\text{NO})_6](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and that of 2.548 Å found in $[\text{Cu}(3,2,3\text{-tet})\text{-(ClO}_4)_n]$ [3,2,3-tet is N,N' -bis(3-aminopropyl)ethylenediamine; Kwak *et al.*, 2001], in which axial coordination ligands have no geometric constraints. The $\text{O}1-\text{Cu}1-\text{O}2$ angle [147.54 (8)°] is significantly smaller than 180°.

It is difficult to estimate quantitatively the elongation of the axial $\text{Cu}-\text{O}$ bond that results from the Jahn–Teller effect and from the geometric restraints of the chelate ring. However, it

is certain that there is conflict between stabilization from the Jahn–Teller effect and the geometric requirements, because the nature of the chelate ring tends to restrict the distortion of a complex (Huheey, 1983). The bond parameters of (I) do not differ from those of various CuL_2 compounds having the CuO_4N_2 chromophore (L = chelate ligand; Koman *et al.*, 2000) and Cu^{II} compounds containing the pdmH fragment (Atkinson *et al.*, 2000), whereas $[\text{Cu}(\text{pdmH}_2)_2]^{2+}$ exhibits a Jahn–Teller contraction effect (Andac *et al.*, 2002).

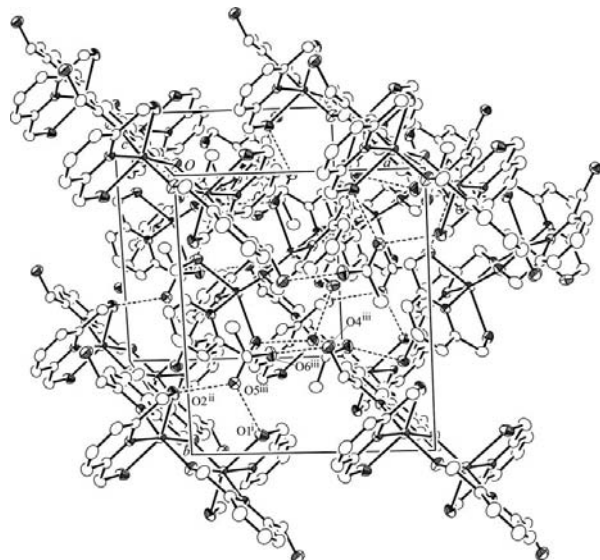


Figure 2
The crystal packing of (I), viewed approximately down the c axis, showing the linear chain structure formed *via* hydrogen bonds (dashed lines). Ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i) $x, 1 + y, z$; (ii) $-x, 1 - y, -z$; (iii) $1 - x, 1 - y, -z$.]

Adjacent dinuclear copper complex units are associated *via* hydrogen bonds between the hydroxide groups of the pdmH₂ ligands and the acetate anions, as illustrated in Fig. 2 and Table 2. There is one carboxylate anion in the asymmetric unit. Carboxylate atom O5 interacts with two hydroxide H atoms of adjacent pdmH₂ ligands, while carboxylate atom O6 interacts with the H atom on hydroxide atom O4 of a pdmH[−] group, resulting in one-dimensional linear chains running parallel to the a axis.

Experimental

To a green solution of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (0.3254 g, 1.63 mmol) in acetonitrile (30 ml) was added pdmH₂ (0.56 g, 4 mmol). The reaction mixture was stirred continuously, and then a solution of $n\text{-Bu}_4\text{NOH}$ (0.4 ml, 1.0 M) in methanol was added dropwise, causing the color of the reaction mixture to change to bright blue. The solution was stirred for 4 h, then filtered and concentrated under reduced pressure. The resulting green solution was treated with hexane to afford a crystalline solid. Recrystallization from a dichloromethane–hexane solution gave single crystals suitable for X-ray analysis. Analysis found: C 48.7, H 5.09, N 7.14%; $\text{C}_{32}\text{H}_{40}\text{Cu}_2\text{N}_4\text{O}_{12}$ requires: C 48.1, H 5.04, N 7.00%.

Crystal data

$[\text{Cu}_2(\text{C}_7\text{H}_8\text{NO}_2)_2(\text{C}_7\text{H}_9\text{NO}_2)_2] \cdot (\text{C}_2\text{H}_3\text{O}_2)_2$
 $M_r = 799.76$
Monoclinic, $P2_1/n$
 $a = 10.252$ (1) Å
 $b = 12.1310$ (7) Å
 $c = 14.2226$ (8) Å
 $\beta = 109.150$ (5)°
 $V = 1671.0$ (2) Å³
 $Z = 2$

$D_x = 1.590$ Mg m^{−3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
 $\theta = 19.9\text{--}31.3^\circ$
 $\mu = 1.34$ mm^{−1}
 $T = 296$ (2) K
Plate, green
 $0.25 \times 0.20 \times 0.11$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\theta/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.761$, $T_{\max} = 0.883$
3061 measured reflections
2938 independent reflections
2427 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.045$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -12 \rightarrow 11$
 $k = 0 \rightarrow 14$
 $l = 0 \rightarrow 16$
3 standard reflections every 200 reflections
intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.096$
 $S = 1.07$
2938 reflections
227 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0497P)^2 + 1.3695P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.34$ e Å^{−3}
 $\Delta\rho_{\text{min}} = -0.39$ e Å^{−3}

Table 1

Selected geometric parameters (Å, °).

Cu1—O3	1.909 (2)	Cu1—O1	2.358 (2)
Cu1—O3 ⁱ	1.983 (2)	Cu1—O2	2.360 (2)
Cu1—N1	2.018 (2)	Cu1 ⁱ —Cu1 ⁱ	3.0298 (7)
Cu1—N2	2.094 (2)		
O3—Cu1—O3 ⁱ	77.79 (9)	N1—Cu1—O1	76.39 (9)
O3—Cu1—N1	169.80 (9)	N2—Cu1—O1	82.91 (9)
O3 ⁱ —Cu1—N1	92.23 (9)	O3—Cu1—O2	108.24 (9)
O3—Cu1—N2	81.17 (9)	O3 ⁱ —Cu1—O2	97.08 (9)
O3 ⁱ —Cu1—N2	158.71 (9)	N1—Cu1—O2	74.75 (9)
N1—Cu1—N2	108.7 (1)	N2—Cu1—O2	92.48 (9)
O3—Cu1—O1	102.8 (1)	O1—Cu1—O2	147.54 (8)
O3 ⁱ —Cu1—O1	98.6 (1)	Cu1—O3—Cu1 ⁱ	102.21 (9)

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

Table 2

Hydrogen-bonding geometry (Å, °).

$D\text{—}H \cdots A$	$D\text{—}H$	$H \cdots A$	$D \cdots A$	$D\text{—}H \cdots A$
O1—H51 ⁱ ⋯O5 ⁱⁱ	0.82	1.82	2.636 (4)	173
O2—H52 ⁱ ⋯O5 ⁱⁱⁱ	0.82	1.80	2.596 (4)	165
O4—H54 ⁱ ⋯O6	0.82	1.88	2.689 (4)	167

Symmetry codes: (ii) $1 - x, -y, -z$; (iii) $x - 1, y, z$.

All H atoms were introduced at calculated positions as riding atoms, with bond lengths of 0.93 (CH), 0.96 (CH₃) and 0.82 Å (OH), and displacement parameters equal to 1.2 (CH and OH) or 1.5 (CH₃) times those of the parent atoms.

Data collection: MACH3 (Nonius, 1996); cell refinement: CELDIM (Nonius, 1996); data reduction: XCAD4 (Harms &

Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

This work was supported by the NRL program of the Ministry of Science and Technology, South Korea.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA1016). Services for accessing these data are described at the back of the journal.

References

- Agnus, Y. L. (1983). *Copper Coordination Chemistry: Biochemical and Inorganic Perspective*. Guilderland, New York: Adenine Press.
- Andac, O., Guney, S., Topcu, Y., Yilmaz, V. T. & Harrison, W. T. A. (2002). *Acta Cryst.* **C58**, m17–m20.
- Atkinson, I. M., Chartres, J. D., Everett, G. W., Ji, X.-K., Lindoy, L. F., Matthews, O. A., Meehan, G. V., Skelton, B. W., Wei, G. & White, A. H. (2000). *J. Chem. Soc. Dalton Trans.* pp. 1191–1198.
- Berti, E., Caneschi, A., Daiguebonne, C., Dapporto, P., Formica, M., Fusi, V., Giorgi, L., Guerri, A., Micheloni, M., Paoli, P., Pontellini, R. & Rossi, P. (2003). *Inorg. Chem.* **42**, 348–357.
- Boskovic, C., Wernsdorfer, W., Folting, K., Huffman, J. C., Hendrickson, D. N. & Christou, G. (2002). *Inorg. Chem.* **41**, 5107–5118.
- Cheng, S.-C. & Wei, H.-H. (2002). *Inorg. Chim. Acta*, **340**, 105–113.
- Del Sesto, R. E., Arif, A. M. & Miller, J. S. (2000). *Inorg. Chem.* **39**, 4894–4902.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Graham, B., Hearn, M. T. W., Junk, P. C., Kepert, C. M., Mabbs, F. E., Moubaraki, B., Murray, K. S. & Spiccia, L. (2001). *Inorg. Chem.* **40**, 1536–1543.
- Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
- Huheey, J. E. (1983). *Inorganic Chemistry*, 3rd ed., pp. 396–409. New York: Harper and Row.
- Koman, M., Melnik, M. & Moncol, J. (2000). *Inorg. Chem. Commun.* **3**, 262–266.
- Kwak, C.-H., Jeong, J. & Kim, J. (2001). *Inorg. Chem. Commun.* **4**, 264–268.
- Nonius (1996). *CELDIM* and *MACH3* (Version 2.0). Nonius BV, Delft, The Netherlands.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
- Wood, J. S., Keijaers, C. P. & Day, R. O. (1984). *Acta Cryst.* **C40**, 404–406.
- Yoo, J., Brechin, E. K., Yamaguchi, A., Nakano, M., Huffman, J. C., Maniero, A. L., Brunel, L.-C., Awaga, K., Ishimoto, H., Christou, G. & Hendrickson, D. N. (2000). *Inorg. Chem.* **39**, 3615–3623.