

***catena*-Poly[[tetrakis(μ -propionato- κ^2 O:O')dicopper(II)]- μ -3-pyridylmethanol- κ^2 N:O-[bis(propionato- κ O)-bis(3-pyridylmethanol- κ N)copper(II)]- μ -3-pyridylmethanol- κ O:N]**

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Received 16 December 2006

Accepted 26 January 2007

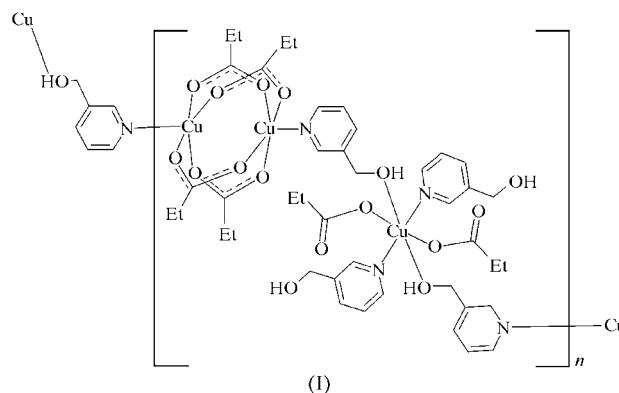
Online 17 February 2007

The title compound, $[\text{Cu}_3(\text{C}_3\text{H}_5\text{O}_2)_6(\text{C}_6\text{H}_7\text{NO})_4]_n$, is composed of polymeric chains formed by alternating centrosymmetric $\text{Cu}_2(\mu\text{-CH}_3\text{CH}_2\text{CO}_2)_4$ and $\text{Cu}(\text{C}_3\text{H}_5\text{O}_2)_2(\text{C}_6\text{H}_7\text{NO})_2$ units. These elemental units are linked by two bridging 3-pyridylmethanol (3PM) ligands. The $\text{Cu}_2(\mu\text{-CH}_3\text{CH}_2\text{CO}_2)_4$ group presents a centrosymmetric tetrabridged structure with four *syn-syn* bridging propionate ligands to which two 3PM molecules are bonded (through N), occupying the apical positions of each square-pyramidal polyhedron around the Cu^{II} ions. The remaining mononuclear group is centred around a third Cu^{II} ion, which lies on a symmetry centre and is bound to two monodentate propionate groups (through O), two monodentate 3PM molecules (through N) and two bridging 3PM molecules (through O), thus completing a square-bipyramidal $\text{CuO}_2\text{N}_2\text{O}_2$ coordination.

Comment

3-Pyridylmethanol (3PM) is a non-steroidal anti-inflammatory agent in current use. It can act as an effective ligand in coordination compounds, where it presents a variety of binding modes. In the monomeric structures $[\text{CuCl}_2(3\text{PM})_4]$, (II) (Moncol *et al.*, 2004), and $[\text{Cu}(2\text{-nitrobenzoato})_2(3\text{PM})_2(\text{H}_2\text{O})_2]$, (III) (Stachová *et al.*, 2006), 3PM behaves as a terminal ligand, coordinating through the N atom of its pyridine ring. An analogous binding mode is found in dimeric $[\text{Cu}_2(\mu\text{-CH}_3\text{CO}_2)_4(3\text{PM})_2]\cdot\text{CH}_2\text{Cl}_2$, (IV) (Melník *et al.*, 1985), where the Cu^{II} atoms are bridged into pairs by four acetate groups to form two crystallographically independent binuclear molecules, with the N atoms of the 3PM ligands situated at the vertices of a slightly deformed square pyramid around the cations. More complex intermolecular interactions are achieved in complexes of general formula $[\text{Cu}(\text{RCO}_2)_2(\mu\text{-}$

$3\text{PM})_2]_n$. For $\text{RCO}_2 = \text{salicylate}$, (V) (Hoang *et al.*, 1992; Maroszová, Moncol *et al.*, 2006), 4-chlorosalicylate, (VI) (Maroszová, Martiška *et al.*, 2006), flufenamate, (VII) (Lörinc *et al.*, 2004), clofibrate, (VIII) (Moncol *et al.*, 2001), or 2-chlorobenzoate, (IX) (Moncol *et al.*, 2006), a two-dimensional sheet is built up with Cu^{II} ions linked by bridging 3PM ligands. When $\text{RCO}_2 = \text{trichloroacetate}$, (X) (Múdra *et al.*, 2003), dichloroacetate, (XI) (Múdra *et al.*, 2003), 3-nitrobenzoate, (XII) (Stachová *et al.*, 2005), 3,5-dinitrobenzoate, (XIII) (Stachová *et al.*, 2006), niflumate, (XIV) (Valach *et al.*, 1997), or 2-methylthionicotinate, (XV) (Moncol *et al.*, 2006), the result is a one-dimensional coordination polymer. Finally, the crystal structure of $[\text{Cu}_3(2\text{-chloronicotinate})_6(\mu\text{-}3\text{PM})_4(3\text{PM})_2]_n$, (XVI) (Moncol *et al.*, 2006), consists of one-dimensional ‘accordion chain’ coordination polymers with different coordination environments around the Cu^{II} ions (square bipyramidal and square pyramidal).



The crystal structure of (I) consists of zigzag chains (Fig. 1) that are formed by alternating dinuclear $\text{Cu}_2(\mu\text{-CH}_3\text{CH}_2\text{CO}_2)_4$ and mononuclear $\text{Cu}(\text{CH}_3\text{CH}_2\text{CO}_2)_2(3\text{PM})_2$ units linked by bridging 3PM molecules. The dimeric unit is formed around a symmetry centre and presents a tetrabridged paddle-wheel structure with four *syn-syn* bridging propionate ligands. The $\text{Cu}_2 \cdots \text{Cu}_2^{\text{II}}$ [symmetry code: (i) $-x, 1-y, 1-z$] distance is 2.6367 (12) Å, very similar to the values found in other dimeric copper(II) propionate complexes (range 2.569–2.655 Å; Melník *et al.*, 1998). The τ value (Addison *et al.*, 1984) is 0.005 for atom Cu2, which is typical for a square-pyramidal geometry. The basal plane consists of four O atoms [O4, O5ⁱ, O6 and O7ⁱ; symmetry code: (i) $-x, -y+1, -z+1$], at distances in the range 1.958 (3)–1.964 (3) Å. The apical site is occupied by the N atom of the 3PM pyridine ring [Cu2–N2 = 2.176 (3) Å]. Atom Cu2 is displaced from the least-squares plane defined by the basal atoms by 0.207 (1) Å towards the apical N atom. The $\text{Cu}(\text{CH}_3\text{CH}_2\text{CO}_2)_2(3\text{PM})_2$ unit also has a centrosymmetric structure, with a $\text{CuO}_2\text{N}_2\text{O}_2$ square-bipyramidal coordination around atom Cu1, which lies at the symmetry centre. The environment is defined by two O atoms from two monodentate propionate groups, two N atoms from two monodentate 3PM molecules and two O atoms from two bridging 3PM molecules. The basal plane is built up by a pair of carboxylate O atoms [Cu1–O1 = 1.954 (2) Å] and a pair of N atoms [Cu1–N1 = 2.003 (2) Å] from the pyridine rings in the terminal neutral 3-pyridylmethanol molecules. The axial

positions are occupied by two hydroxyl O atoms [Cu1—O8 = 2.502 (3) Å] from the bridging 3PM ligands.

Intramolecular hydrogen bonds [O8...O2 = 2.625 (5) Å] create a six-membered metalocycle and stabilize the molecular structure of the chain building units. The crystal structure of (I) consists of zigzag one-dimensional chains (Fig. 2), which are connected by intermolecular hydrogen bonds [O3...O2ⁱⁱⁱ = 2.768 (5) Å; symmetry code: (iii) $x + 1, y, z$] to form two-dimensional sheets.

The structure of (I) can be compared with the dimeric structure of (IV) mentioned above and the polymeric structures (V)–(XV). The Cu2...Cu2ⁱ distance and the average Cu2—O_{COO} and Cu2—N2 bond distances of the Cu₂(μ-CH₃CH₂CO₂)₄ unit are very similar to the bond distances in (IV), where the molecular structure consists of two crystallographically independent molecules of Cu₂(CH₃CO₂)₄(3PM)₂. The Cu...Cu distance, and average Cu—O_{COO} (acetate anions) and Cu—N_{ax} (N atom of the pyridine ring of 3PM) bond lengths in the two independent dimers of (IV) are 2.654 (1), 1.963 (4) and 2.197 (5) Å, and 2.634 (1), 1.969 (4) and 2.152 (5) Å, respectively. The geometry of the Cu(CH₃CH₂CO₂)₂(3PM)₂ unit and the bond distances are

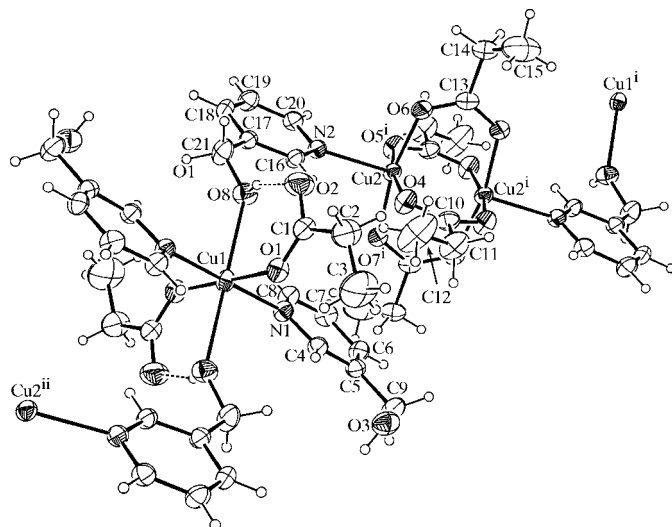


Figure 1

A perspective view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i) $-x, 1 - y, 1 - z$; (ii) $-x, -y, -z$.]

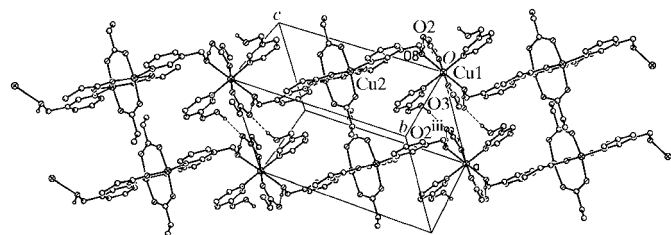


Figure 2

The O—H...O hydrogen bonding in the crystal structure of (I). [Symmetry code: (iii) $x + 1, y, z$.]

very similar to the molecular structure of complexes with the formula [Cu(RCO₂)₂(μ-3PM)₂]_n, viz. (V)–(XV). The present crystal structure can be considered as the connecting link between two types of structures of copper(II) carboxylate adducts with 3PM (dimeric and polymeric).

Experimental

Cu(CH₃CH₂CO₂)₂·H₂O was prepared as described by Battaglia & Corradi (1986). Compound (I) was prepared by treating 3-pyridylmethanol with Cu(CH₃CH₂CO₂)₂·H₂O in a 2:3 molar ratio in hot methanol. The resulting solution was filtered and the filtrate left to stand at room temperature, allowing fine green crystals to precipitate out. These crystals were filtered off, washed with cold methanol and dried at room temperature. Crystals of (I) suitable for structural determination were obtained by recrystallizing the crude product from methanol with a small amount of acetone (yield 70%). Analysis found: C 47.56, H 5.68, N 5.30, Cu 17.82%; C₄₂H₅₈Cu₃N₄O₁₆ requires: C 47.34, H 5.49, N 5.26, Cu 17.89%.

Crystal data

[Cu₃(C₃H₅O₂)₆(C₆H₇NO)₄]
M_r = 1065.54
 Triclinic, *P* $\bar{1}$
a = 8.194 (2) Å
b = 9.959 (2) Å
c = 15.358 (3) Å
 α = 104.27 (3)°
 β = 103.99 (3)°
 γ = 91.10 (3)°
V = 1174.4 (4) Å³

Z = 1
D_x = 1.507 Mg m⁻³
D_m = 1.50 Mg m⁻³
D_m measured by flotation in a mixture of CHCl₃ and CHBr₃
 Mo *K*α radiation
 μ = 1.42 mm⁻¹
T = 293 (2) K
 Rectangular prism, green
 0.45 × 0.40 × 0.30 mm

Data collection

Syntax *P2*₁ diffractometer
 $\theta/2\theta$ scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
*T*_{min} = 0.576, *T*_{max} = 0.654
 5808 measured reflections
 5428 independent reflections

3645 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.035
 θ _{max} = 27.6°
 2 standard reflections
 every 100 reflections
 intensity decay: 15%

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.053
wR(*F*²) = 0.153
S = 1.01
 5428 reflections
 300 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.103P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.76 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.70 \text{ e } \text{Å}^{-3}$

Table 1

Selected interatomic distances (Å).

Cu1—O1	1.954 (2)	Cu2—O6	1.964 (3)
Cu1—N1	2.003 (3)	Cu2—O7 ⁱ	1.963 (3)
Cu1—O8	2.502 (3)	Cu2—N2	2.176 (3)
Cu2—O4	1.960 (3)	Cu2...Cu2 ⁱ	2.6367 (12)
Cu2—O5 ⁱ	1.958 (3)		

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

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O3—H3O...O2 ⁱⁱ	0.82	1.95	2.768 (5)	174
O8—H8O...O2	0.82	1.84	2.625 (5)	160

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

All H atoms attached to C atoms were placed in calculated positions, with C—H = 0.93, 0.97 and 0.96 Å for aromatic, methylene and methyl groups, respectively. The hydroxyl H atom was positioned using the AFIX 147 facility in *SHELXL97* (Sheldrick, 1997) (O—H = 0.82 Å). In all cases, $U_{\text{iso}}(\text{H}) = xU_{\text{iso}}(\text{C}, \text{O})$, where $x = 1.2$ for aromatic and methylene, and $x = 1.5$ for methyl and hydroxyl H atoms.

Data collection: *P2₁ Software* (Syntex, 1973); cell refinement: *P2₁ Software*; data reduction: *XP21* (Pavelčík, 1993); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *XP* in *SHELXTL* (Sheldrick, 1998); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

The authors thank the Scientific Grant Agency of the Ministry of Education of the Slovak Republic and the Slovak Academy of Sciences for financial support through grant No. 1/2452/05, and the Research and Development Support Agency for financial support through grant No. APVT-20-005504.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3026). Services for accessing these data are described at the back of the journal.

References

- Addison, A. W., Rao, T. N., Reedijk, J., van Rijn, J. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.
- Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). *J. Appl. Cryst.* **37**, 335–338.
- Battaglia, L. P. & Corradi, A. B. (1986). *J. Chem. Soc. Dalton Trans.* pp. 1653–1657.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Hoang, N. N., Valach, F., Macášková, L. & Melník, M. (1992). *Acta Cryst.* **C48**, 1933–1936.
- Lörinc, S., Koman, M., Melník, M., Moncol, J. & Ondrušová, D. (2004). *Acta Cryst.* **E60**, m590–m592.
- Maroszová, J., Martiška, L., Valigura, D., Koman, M. & Głowiak, T. (2006). *Acta Cryst.* **E62**, m1164–m1166.
- Maroszová, J., Moncol, J., Koman, M., Melník, M. & Głowiak, T. (2006). *Acta Cryst.* **E62**, m3385–m3387.
- Melník, M., Kabešová, M., Koman, M., Macášková, Ľ., Garaj, J., Holloway, C. & Valent, A. (1998). *J. Coord. Chem.* **45**, 147–359.
- Melník, M., Smolander, K. & Sharrock, P. (1985). *Inorg. Chim. Acta*, **103**, 187–194.
- Moncol, J., Koman, M., Melník, M. & Głowiak, T. (2001). *CrystEngComm*, **3**, 262–264.
- Moncol, J., Múdra, M., Lönnecke, P., Koman, M. & Melník, M. (2004). *J. Chem. Crystallogr.* **34**, 423–431.
- Moncol, J., Segla, P., Mikloš, D., Mazúr, M., Melník, M., Głowiak, T., Valko, M. & Koman, M. (2006). *Polyhedron*, **25**, 1561–1566.
- Múdra, M., Moncol, J., Švorec, J., Melník, M., Lönnecke, P., Głowiak, T. & Kirmse, R. (2003). *Inorg. Chem. Commun.* **6**, 1259–1265.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Pavelčík, F. (1993). *XP21*. Comenius University, Bratislava, Slovakia.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Sheldrick, G. M. (1998). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Stachová, P., Korabik, M., Koman, M., Melník, M., Mrozinski, J., Głowiak, T., Mazúr, M. & Valigura, D. (2006). *Inorg. Chim. Acta*, **359**, 1275–1281.
- Stachová, P., Valigura, D., Koman, M. & Głowiak, T. (2005). *Acta Cryst.* **E61**, m994–m996.
- Syntex (1973). *P2₁ Software*. Syntex Analytical Instruments, Cupertino, California, USA.
- Valach, F., Tokarčík, M., Kubinec, P., Melník, M. & Macášková, L. (1997). *Polyhedron*, **16**, 1461–1464.