Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

μ-Acetato-1:2κ^2*O*:*O*′-diacetato-1κ^2*O*,*O*′;2κ*O*-bis(di-2-pyridylamine)-1κ^2*N*,*N*′;2κ^2*N*,*N*′-isothiocyanato-2κ*N*-dicopper(II)

Sujittra Youngme,[a]* Thidarat Chotkhun[a] and Narongsak Chaichit[b]

[a]Department of Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand, and [b]Department of Physics, Faculty of Science and Technology, Thammasat University Rangsit, Pathumthani 12121, Thailand
Correspondence e-mail: sujittra@kku.ac.th

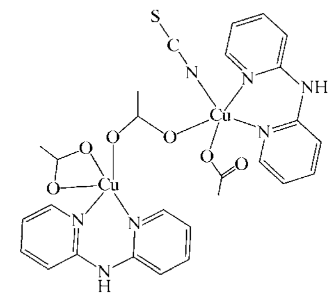
Received 19 November 2006
Accepted 13 December 2006
Online 23 January 2007

In the title dinuclear acetate-bridged complex, $[Cu_2(C_2H_3O_2)_3(NCS)(C_{10}H_9N_3)_2]$, the two Cu atoms are five-coordinated, with a basal plane consisting of two N atoms of a di-2-pyridylamine (dpyam) ligand and two O atoms of two different acetate ligands. The axial positions of these Cu atoms are coordinated to N and O atoms from thiocyanate and acetate molecules, respectively, leading to a distorted square-pyramidal geometry with τ values of 0.30 and 0.22. Both Cu^{II} ions are linked by an acetate group in the equatorial–equatorial positions and have *syn–anti* bridging configurations. Hydrogen-bond interactions between the amine H atom and the coordinated and uncoordinated O atoms of the acetate anions generate an infinite one-dimensional chain.

Comment

The coordination chemistry of copper(II) complexes with various carboxylates has been investigated for many years. Carboxylate chemistry is interesting for two reasons. Firstly, carboxylates play a vital role as ligands in biochemical systems involving mono-, di- or polymetallic active sites, and secondly, polynuclear carboxylates are very good probes for exchange-coupling interactions between adjacent metal ions. Carboxylate groups are known to assume different bridging conformations and the important types are *syn–syn*, *anti–anti* and *syn–anti* (Colacio *et al.*, 1993). It may be noted that structurally characterized examples of *syn–anti* configuration are far less numerous than those with the *syn–syn* configuration (Sen *et al.*, 1998). We report here the synthesis and crystal structure of a new acetate-bridged complex with a *syn–anti* configuration, $[Cu_2(\mu\text{-}O_2CCH_3)(O_2CCH_3)_2(NCS)(dpyam)_2]$ (dpyam is di-2-pyridylamine), (I).

The structure of (I) consists of a dinuclear $[Cu_2(\mu\text{-}O_2CCH_3)(O_2CCH_3)_2(NCS)(dpyam)_2]$ unit. The Cu atoms are bridged unsymmetrically by an acetate group in a *syn–anti* arrangement (Fig. 1). Atoms Cu1 and Cu2 are five-coordinated, with a basal plane consisting of two N atoms of the dpyam ligand and two O atoms of two different acetate ligands. The axial positions of Cu1 and Cu2 are coordinated by N and O atoms from thiocyanate and acetate ligands, respectively (Table 1), leading to a square-pyramidal geometry. The square bases of the copper chromophores are non-planar, with tetrahedral twists of 25.7 (1) and 43.7 (1)° for Cu1 and Cu2, respectively. The Cu atoms lie above the basal plane, at 0.280 (1) Å towards N7 for Cu1 and 0.112 (1) Å towards O6 for Cu2.



(I)

The distortion of a square pyramid can be best described by the structural parameter τ ($\tau = 0$ for a square pyramid and $\tau = 1$ for a trigonal bipyramid; Addison *et al.*, 1984), which in this case has values of 0.30 and 0.22 for Cu1 and Cu2, respectively. The copper chromophores can be described as having a distorted square-pyramidal geometry, with a high tetrahedral twist of the square bases. The Cu···Cu distance is 4.800 (3) Å. The dihedral angles between the pyridine rings of the dpyam ligands are 20.9 (1)° for Cu1 and 12.0 (1)° for Cu2. The molecular structure and bridging configuration of (I) are very

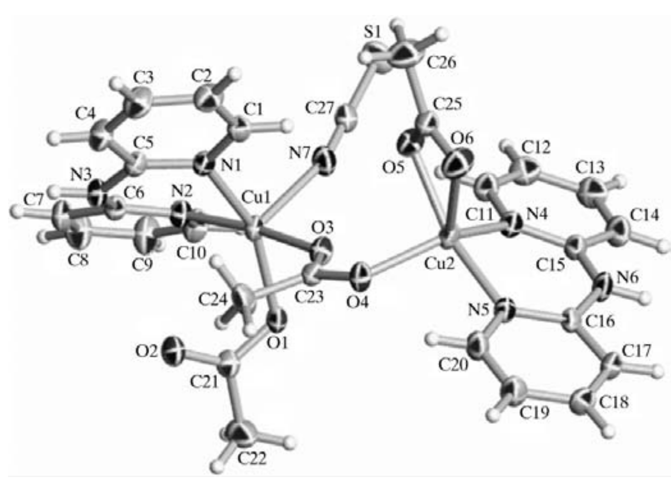


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are represented as spheres of arbitrary radii.

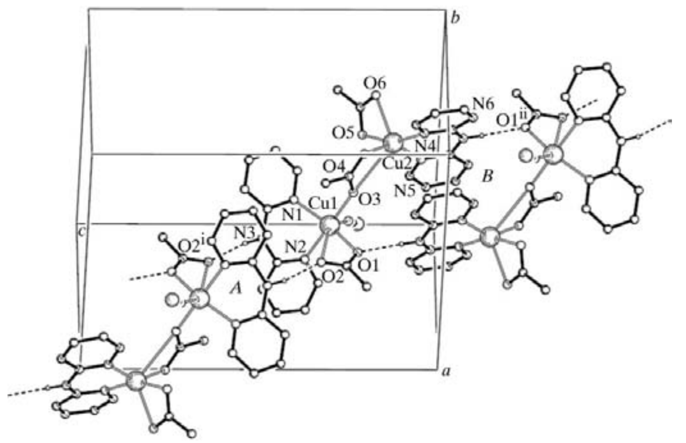


Figure 2
A view of the packing structure of (I), showing the hydrogen-bonding interactions (dashed lines). The hydrogen-bonded rings *A* and *B* are defined in the *Comment*. H atoms not involved in hydrogen bonding have been omitted for clarity. [Symmetry codes: (i) $2 - x, 1 - y, 1 - z$; (ii) $1 - x, 1 - y, -z$.]

similar to those of the closely related complexes [Cu(μ-O_2CH)(dpyam)(HO_2)]$_n$(NO_3)$_n$ (Youngme *et al.*, 2005) and {[Cu(μ-O_2CCH_3)(dpa)](ClO_4)·0.5THF}$_n$ [dpa is *N,N*-bis(2-pyridylmethyl)amine] with a single carboxylate bridge (Tanase *et al.*, 2005).

Analysis of the crystal packing of (I) shows hydrogen-bonding interactions between the NH group of the amide and the coordinated and uncoordinated O atoms of the acetate anions, with N—H···O contacts of 2.915 (3) and 2.862 (3) Å. A plot of the hydrogen-bond system forming a one-dimensional structure is given in Fig. 2 and details are given in Table 2. Classical N3—H5···O2^{i} [symmetry code: (i) $-x + 2, -y + 1, -z + 1$] and N6—H15···O1^{ii} [symmetry code: (ii) $-x + 1, -y + 1, -z$] intermolecular hydrogen bonds between adjacent dimeric units link them into a one-dimensional chain. The resulting motifs, *A* and *B*, in the formalism of graph-set analysis of hydrogen-bond patterns (Etter *et al.*, 1990), are characterized as $R_2^2(15)$ (N3, H5, O2^{i}, C21^{i}, O1^{i}, Cu1^{i}, N1^{i}, C5^{i}, N3^{i}, H5^{i}, O2, C21, Cu1, N1 and C5) and $R_2^2(20)$ (N6, H15, O1^{ii}, Cu1^{ii}, O3^{ii}, C23^{ii}, O4^{ii}, Cu2^{ii}, N4^{ii}, C15^{ii}, N6^{ii}, H15^{ii}, O1, Cu1, O3, C23, O4, Cu2, N4 and C15), respectively.

Experimental

The title complex was obtained as a by-product in the preparation of [Cu_3(μ-$OOCCH_3$)$_4$(μ-NCS)$_2$(dpyam)$_2$] by adding Cu(O_2CCH_3)$_2$·$n$$H_2O$ (1.5 mmol) to a warm solution of dpyam (1.0 mmol) in dimethylformamide (DMF) (10.0 ml). A solution of NaNCS (1.0 mmol) in DMF (5.0 ml) was then added and the resulting green solution was allowed to evaporate slowly at room temperature. After several days, green crystals of (I) were formed. The crystals were filtered off, washed with mother liquor and dried in air. IR data (KBr, ν, cm^{-1}): 2084 (*vs*), 1654 (*s*), 1589 (*s*), 1556 (*s*), 1486 (*vs*), 1424 (*s*), 1237 (*m*), 1160 (*m*), 1019 (*m*), 784 (*m*).

Crystal data

[$Cu_2(C_2H_3O_2)_3(NCS)(C_{10}H_9N_3)_2$]
M_r = 704.70
Triclinic, $P\bar{1}$
a = 9.6949 (2) Å
b = 10.4915 (2) Å
c = 16.9001 (2) Å
α = 97.6450 (10)°
β = 101.4580 (10)°
γ = 113.2150 (10)°
V = 1505.09 (4) Å^3
Z = 2
D_x = 1.555 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 1.54 mm^{-1}
T = 273 (2) K
Polygon, green
0.30 × 0.18 × 0.08 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000*a*)
T_{min} = 0.732, T_{max} = 0.891
8178 measured reflections
5440 independent reflections
4510 reflections with $I > 2\sigma(I)$
R_{int} = 0.021
θ_{max} = 25.4°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.099
S = 1.05
5440 reflections
399 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0423P)^2 + 1.2895P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.49 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O3	1.996 (2)	Cu2—N4	1.976 (3)
Cu1—N2	2.011 (3)	Cu2—N5	1.976 (3)
Cu1—O1	2.013 (2)	Cu2—O5	1.989 (2)
Cu1—N1	2.030 (3)	Cu2—O4	1.999 (2)
Cu1—N7	2.150 (3)	Cu2—O6	2.339 (3)
O3—Cu1—N2	173.03 (10)	N4—Cu2—N5	92.41 (11)
O3—Cu1—O1	86.58 (9)	N4—Cu2—O5	95.05 (11)
N2—Cu1—O1	90.75 (10)	N5—Cu2—O5	156.16 (11)
O3—Cu1—N1	91.91 (10)	N4—Cu2—O4	142.76 (10)
N2—Cu1—N1	87.77 (10)	N5—Cu2—O4	94.46 (10)
O1—Cu1—N1	154.89 (10)	O5—Cu2—O4	93.21 (10)
O3—Cu1—N7	93.57 (11)	N4—Cu2—O6	120.17 (11)
N2—Cu1—N7	93.31 (11)	N5—Cu2—O6	96.50 (10)
O1—Cu1—N7	103.31 (10)	O5—Cu2—O6	60.28 (9)
N1—Cu1—N7	101.80 (11)	O4—Cu2—O6	95.34 (10)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H5···O2^{i}	0.852 (18)	2.022 (18)	2.862 (3)	168.40
N6—H15···O1^{ii}	0.860 (18)	2.055 (18)	2.915 (3)	177.80

Symmetry codes: (i) $-x+2, -y+1, -z+1$; (ii) $-x+1, -y+1, -z$.

H atoms attached to atoms N3 and N6 were located in difference Fourier maps and refined with a DFIX (*SHELXTL*; Sheldrick, 2000*b*) restraint of N—H = 0.86 (1) Å. All H atoms attached to C atoms were fixed geometrically and treated as riding, with C—H = 0.93 (aromatic) or 0.96 Å (methyl), and with U_{iso}(H) = 1.2U_{eq}(aromatic C) or 1.5U_{eq}(methyl C).

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2000*b*); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* (Sheldrick 2000*b*) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL*.

The authors gratefully acknowledge the Thailand Research Fund (grant Nos. RTA 4880008 and BRG 4980007), Khon Kaen University, and the Higher Education Development Project: Postgraduate Education and Research Programme in Chemistry, Thailand, for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3030). 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.
Bruker (2000). *SMART* (Version 5.61) and *SAINT* (Version 6.02). Bruker AXS Inc., Madison, Wisconsin, USA.
Colacio, E., Dominguez-Vera, J. M., Kivekas, R., Moreno, J. M., Romerosa, A. & Ruiz, J. (1993). *Inorg. Chim. Acta*, **212**, 115–121.
Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* B**46**, 256–262.
Sen, S., Saha, M. K., Gupta, T., Karmakar, A. K., Kundu, P., Mitra, S., Hursthouse, M. B. & Malik, K. M. A. (1998). *J. Chem. Crystallogr.* **28**, 771–777.
Sheldrick, G. M. (2000*a*). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2000*b*). *SHELXTL*. Version 6.12. Bruker AXS Inc., Madison, Wisconsin, USA.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Tanase, S., van Albada, G. A., de Gelder, R., Bouwman, E. & Reedijk, J. (2005). *Polyhedron*, **24**, 979–983.
Youngme, S., Phuengphai, P., Chaichit, N., van Albada, G. A., Tanase, S. & Reedijk, J. (2005). *Inorg. Chim. Acta*, **358**, 3267–3271.