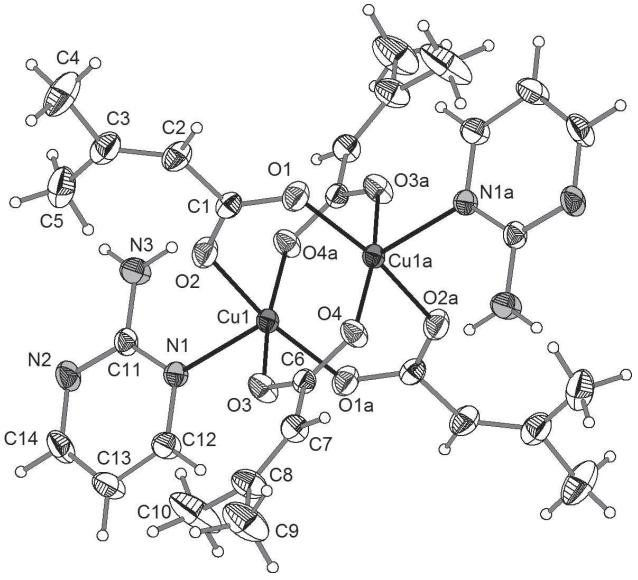
Open Access

Jaeun Kang, Minji Kim, Kang Min Ok and Junghwan Do*

Crystal structure of tetrakis(μ_2-3,3-dimethylacrylato-κ^2O,O')-bis(2-aminopyrimidine-κN) dicopper(II), $C_{28}H_{38}Cu_2N_6O_8$



DOI 10.1515/ncrs-2016-0337
Received October 27, 2016; accepted March 29, 2017; available online April 7, 2017

Abstract

$C_{28}H_{38}Cu_2N_6O_8$, monoclinic, $P2_1/c$ (no. 14), $a = 10.6191(1)$ Å, $b = 14.6736(2)$ Å, $c = 11.6519(2)$ Å, $\beta = 111.056(1)°$, $V = 1694.38(4)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0298$, $wR_{ref}(F^2) = 0.0871$, $T = 296$ K.

CCDC no.: 1541000

The crystal structure of the dinuclear title complex is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

***Corresponding author: Junghwan Do,** Department of Chemistry, Konkuk University, Seoul 147-701, Republic of Korea, e-mail: junghwan@konkuk.ac.kr
Jaeun Kang and Minji Kim: Department of Chemistry, Konkuk University, Seoul 147-701, Republic of Korea
Kang Min Ok: Department of Chemistry, Chung-Ang University, Seoul 156-756, Republic of Korea

Table 1: Data collection and handling.

Crystal:	Green Polyhedron
Size:	0.28 × 0.25 × 0.19 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	13.1 cm^{-1}
Diffractometer, scan mode:	Bruker P4, ω-scans
$2\theta_{max}$, completeness:	56.6°, >98%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	15966, 4157, 0.044
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3380
$N(param)_{refined}$:	203
Programs:	SHELX [1], DIAMOND [2]

Source of material

The mixture of $CuCl_2$ (0.030 g, 0.3 mmol), 3,3–dimethylacrylic acid (0.031 g, 0.3 mmol), 2–aminopyrimidine (0.0860 g, 0.9 mmol) and ethanol (1.0 mL) was sealed under vacuum in a Pyrex tube and heated to 70 °C for 68 h, then cooled to room temperature at 20 °C/h. The pH before and after the reaction was 6̃. The solid products were recovered by vacuum filtration and washed with distilled water. Green polyhedral crystals were obtained together with unidentified green powder. The product is stable in air. The yield of the compound was about 30% based on copper.

Experimental details

H atoms were placed in calculated positions and refined as riding model. The U_{iso} value of the methyl group was set to $1.5U_{eq}$(C) and the U_{iso} values of other H atoms were set to $1.2U_{eq}$(C, N).

Discussion

Metal carboxylate complexes are one of the most important classes in coordination chemistry [3–5]. Especially, Cu(II) carboxylates with nitrogen donor ligands have been extensively studied due to their importance in biology and magnetism [6–9]. In this study we report a new copper(II) complex containing 3,3–dimethylacrylate and 2–aminopyrimidine.

The crystal structure of the title compound comprises classical dimetallic Cu(II) paddle-wheel moiety. The dinuclear

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
Cu1	−0.065298(18)	0.471150(12)	0.887801(17)	0.03058(8)
O1	0.09233(14)	0.51463(10)	0.85447(13)	0.0481(3)
O2	−0.20228(13)	0.43497(11)	0.95527(13)	0.0504(3)
C1	0.19185(18)	0.55255(12)	0.93482(18)	0.0383(4)
C2	0.3001(2)	0.58318(14)	0.8926(2)	0.0508(5)
H2	0.2812	0.5802	0.8084	0.061*
C3	0.4217(2)	0.61461(16)	0.9604(2)	0.0594(6)
C4	0.5192(3)	0.6419(3)	0.8986(3)	0.0999(11)
H4A	0.4869	0.6197	0.8155	0.150*
H4B	0.6063	0.6162	0.9428	0.150*
H4C	0.5261	0.7071	0.8982	0.150*
C5	0.4751(2)	0.6254(2)	1.0956(3)	0.0768(8)
H5A	0.4020	0.6235	1.1255	0.115*
H5B	0.5209	0.6829	1.1168	0.115*
H5C	0.5372	0.5769	1.1322	0.115*
O3	0.02746(13)	0.35399(8)	0.94601(11)	0.0458(3)
O4	−0.13974(13)	0.59578(8)	0.86499(12)	0.0431(3)
C6	0.10646(16)	0.34227(11)	1.05433(16)	0.0331(4)
C7	0.16402(18)	0.25139(12)	1.09685(17)	0.0409(4)
H7	0.2165	0.2473	1.1800	0.049*
C8	0.1516(2)	0.17537(13)	1.03376(19)	0.0539(5)
C9	0.2132(4)	0.08883(16)	1.0978(3)	0.0928(10)
H9A	0.2336	0.0953	1.1846	0.139*
H9B	0.2947	0.0763	1.0829	0.139*
H9C	0.1508	0.0395	1.0669	0.139*
C10	0.0742(4)	0.16423(19)	0.8992(2)	0.1074(12)
H10A	0.0026	0.2082	0.8731	0.161*
H10B	0.0368	0.1039	0.8836	0.161*
H10C	0.1335	0.1733	0.8545	0.161*
N1	−0.17866(14)	0.42116(10)	0.69979(13)	0.0361(3)
N2	−0.37187(16)	0.40935(11)	0.51569(15)	0.0472(4)
N3	−0.36348(17)	0.51460(12)	0.66252(17)	0.0582(5)
H3A	−0.4426	0.5326	0.6164	0.070*
H3B	−0.3230	0.5404	0.7324	0.070*
C11	−0.30337(18)	0.44661(12)	0.62551(16)	0.0376(4)
C12	−0.12041(19)	0.35552(13)	0.65810(17)	0.0463(5)
H12	−0.0335	0.3375	0.7065	0.056*
C13	−0.1820(2)	0.31283(14)	0.54706(19)	0.0567(6)
H13	−0.1402	0.2666	0.5193	0.068*
C14	−0.3097(2)	0.34315(14)	0.47980(19)	0.0563(6)
H14	−0.3553	0.3155	0.4044	0.068*

Cu(II) complex is positioned around a center of inversion. The two Cu(II) [d(Cu—Cu) = 2.6213(4) Å] are bridged by four 3,3–dimethylacrylato ligands. The four oxygen atoms around each Cu(II) form a distorted square planar geometry with the distance of 1.956(1)–1.976(1) Å. An additional nitrogen atom of the 2–aminopyrimidine [d(Cu—N) = 2.212(1) Å] completes the square pyramidal environment of Cu(II). The bond valence sum (BVS) calculation for Cu gives a value of + 2.04 [10]. The NH_2 group forms a hydrogen bond with a neighbouring oxygen atom of a carboxylate group with the distance of 2.933(2) Å. In addition, each 2-aminopyrimidine forms weak NH···N (d = 3.043(2) Å) hydrogen bonds to the proton donating NH_2–group and also to proton accepting N atom of the 2–minopyrimidine in an adjacent complex to complete one–dimensional chains. The interchain distance between the carbon atoms is > 3.61 Å, suggesting that van der Waals interactions predominate along the chain direction. The weakness of the interactions between the chains are reflected in the high thermal displacement parameters of the terminal carbon atoms of the 3,3–dimethylacrylate.

Acknowledgements: This paper was written as part of Konkuk University's research support program for its faculty on sabbatical leave in 2016.

References

1. Sheldrick, G. M.: A short history of *SHELX*. Acta Crystallogr. **A64** (2008) 112–122.
2. Brandenburg, K.: DIAMOND. Visual crystal structure information system. Version 4.2.2. Crystal Impact, Bonn, Germany, (2016).
3. Eddaoudi, M.; Moler, D.; Li, H.; Chen, B.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M.: Modular chemistry: Secondary building units as a basis for the design of highly porous and robust metal-organic carboxylate frameworks. Acc. Chem. Res. **34** (2001) 319–330.
4. Eddaoudi, M.; Li, H.; Yaghi, O. M.: Design, synthesis, structure, and gas (N_2, Ar, CO_2, CH_4, and H_2) sorption properties of porous metal-organic tetrahedral and heterocuboidal polyhedra. J. Am. Chem. Soc. **127** (2005) 7110–7118.
5. Wang, Z.; Kravtsov, V. C.; Zaworotko, M. J.: Ternary nets formed by self-assembly of triangles, squares, and tetrahedra. Angew. Chem. Int. Ed. **44** (2005) 2877–2880.
6. Kato, M.; Muto, Y.: Factors affecting the magnetic properties of dimeric copper(II) complexes. Coord. Chem. Rev. **92** (1988) 45–83.
7. Ferrer, S.; Lioret, F.; Beertmenu, I.; Alzuet, G.; Borras, J.; Garcia-Granda, S.; Liu-Gonzales, M.; Hassnoot, J. G.: Cyclic trinuclear and chain of cyclic trinuclear copper(II) complexes containing a pyramidal $Cu_3O(H)$ core. Crystal structures and magnetic properties of $[Cu_3(\mu_3\text{-}OH)(aaat)_3(H_2O)_3](NO_3)_2\cdot H_2O$ [aaat = 3-acetylamino-5-amino-1,2,4-triazolate] and $\{[Cu_3(\mu_3\text{-}OH)(aat)_3(\mu_3\text{-}SO_4)]\cdot 6H_2O\}_n$ [aat = 3-acetylamino-1,2,4-triazolate]: New cases of spin-frustrated systems. Inorg. Chem. **41** (2002) 5821–5830.
8. Christou, G.; Perlepes, S. P.; Libby, E.; Folting, K.; Huffman, J. C.; Webb, R. J.; Hendrickson, D. N.: Preparation and properties of the triply bridged, ferromagnetically coupled dinuclear copper(II) complexes $[Cu_2(OAc)_3(bpy)_2](ClO_4)$ and $[Cu_2(OH)(H_2O)(OAc)(bpy)_2](ClO_4)_2$. Inorg. Chem. **29** (1990) 3657–3666.
9. Holm, R. H.; Kennepohl, P.; Solomon, E. I.: Structural and functional aspects of metal sites in biology. Chem. Rev. **96** (1996) 2239–2314.
10. Brese, N. E.; O'Keeffe, M.: Bond-valence parameters for solids. Acta Crystallogr. **B47** (1991) 192–197.