Crystal structure of tetrakis(6-methylpyridin-2-yl)methanolato-$\kappa^3O,N:O'$ dicopper(II), $C_{28}H_{34}Cu_2N_6O_{10}$

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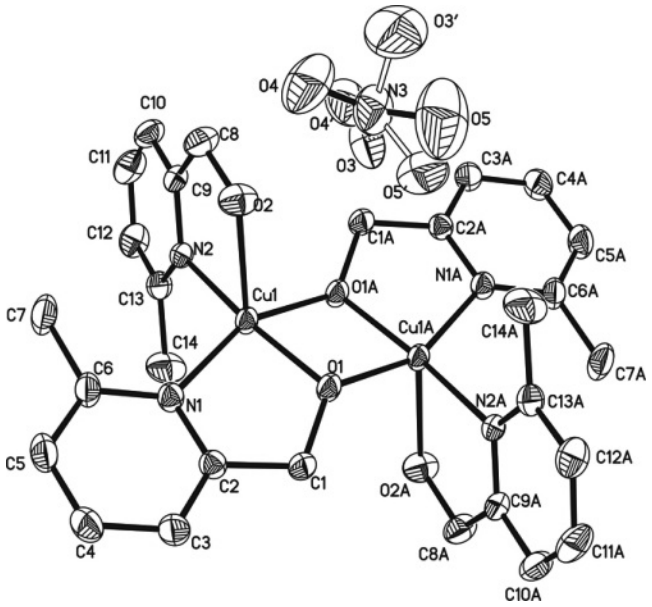
Received May 28, 2014, accepted September 30, 2014, available online October 30, 2014, CCDC no. 1267/4188



Abstract

$C_{28}H_{34}Cu_2N_6O_{10}$, monoclinic, $P2_1/c$ (no. 14), a = 10.009(2) Å, b = 11.787(2) Å, c = 13.928(3) Å, β = 106.846(2)°, V = 1572.6 Å^3, Z = 2, $R_{gt}(F)$ = 0.0409, $wR_{ref}(F^2)$ = 0.1241, T = 298 K.

Table 1. Data collection and handling.

Crystal:	green blocks, size 0.23×0.46×0.50 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	14.17 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7731, 2777
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2149
$N(param)_{refined}$:	238
Programs:	SHELX [12]

Source of material

A 6 mL MeOH solution of $Cu(NO_3)_2{\cdot}3H_2O$ (242 mg, 1 mmol) was added into a stirred solution of 6-methyl-2-pyridinemethanol ligand (630 mg, 5 mmol) in CH_2Cl_2 (12 mL) in the presence of 20 % Et_4NOH solution (368 mg, 0.5 mmol). The mixture was stirred for 2 h, then filtered. The filtrate was left to stand at the room temperature. After two weeks, the resulting green crystals were obtained. Yield: 23.2%. **Elemental analysis**: Found: C, 30.33; H, 3.14; N, 7.56. Calcd. For $Cu_2C_{28}H_{34}N_6O_{10}$: C, 30.02; H, 3.04; N. 7.50%. **IR** (cm^{-1}): 2989s, 2255s, 1490s, 1446m, 1386s, 1328s, 1228w, 1130m, 768w, 626m, 564m, 520s.

Experimental details

The methyl and aromatic H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C–H = 0.95 Å and 0.98 Å and U_{iso}(H) = 1.5U_{eq}(C) and 1.2U_{eq}(C), respectively [12].

Discussion

An interesting area in coordination chemistry is related to the syntheses and the different architectures of the complexes. To richly study the domain, the use of simple ligands for the construction of larger architectures also receives consideration attention [1–3]. For example, pyridine-based alkoxide ligands have been investigated to prepare polynuclear transition-metal complexes. These simple pyridine alcohols are of particular interest. Not only they can form various structural topologies through a versatile N,O-chelating and -bridging group, but also their alkoxide arm usually supports ferromagnetic coupling between the metal atoms it bridges and may result in a large S value, which is one of the necessary requirements for molecules presenting the behavior of single-molecule magnetism [4–10]. In this paper, we report a novel dimer Cu(II) complex. The symmetrical coordination of this complex consists of two Cu(II) centers surrounded by four 6-Me-hmp ligands and isolated NO_3^- anions. Two ligands are located in neutral form and the remaining two display deprotonated form. Each Cu(II) adopts a tetragonal pyramidal coordination geometry and is coordinated by two 6-Me-hmp ligands in a chelating manner with the Cu–N distance of 2.044(3) and 1.991(3) Å and Cu–O distance of 1.905(2) and 2.261(3) Å for two cystallographically independent ligands, respectively. The fifth coordinating atom is afforded by the alkoxo group connecting the Cu metal centers with the distances of 1.905(2) and 1.963(3) Å. Thus, two Cu(II) ions are linked by two alkoxo bridging groups with the Cu1···Cu1A distance of 3.0009(9) Å and Cu1–O1–Cu1A angle of 101.76°, which are smaller than the similar bond length and bond angle in [Cu_2(*pdm*)(OAc)] (*pdm* = 2,6-pyridinedimethanol) complex [11]. Upon further investigation of the structure, the dinuclear complex could assemble into a one-dimensional network via two kinds of C–H···O interaction with the distance of 3.270 and 3.301 Å.

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(2)	4*e*	0.4328	0.7771	0.5213	0.083
H(1A)	4*e*	0.6302	0.5003	0.3198	0.050
H(1B)	4*e*	0.6911	0.4143	0.4077	0.050
H(3)	4*e*	0.8797	0.5514	0.3299	0.055
H(4)	4*e*	1.0590	0.6757	0.4022	0.065
H(5)	4*e*	1.0606	0.7669	0.5486	0.067
H(7A)	4*e*	0.7897	0.7905	0.6476	0.101
H(7B)	4*e*	0.9488	0.8189	0.6699	0.101
H(7C)	4*e*	0.9023	0.7073	0.7124	0.101
H(8A)	4*e*	0.4014	0.7854	0.6611	0.062
H(8B)	4*e*	0.5395	0.8547	0.6749	0.062
H(10)	4*e*	0.5226	0.7643	0.8549	0.060
H(11)	4*e*	0.6414	0.6333	0.9706	0.070
H(12)	4*e*	0.7661	0.4929	0.9222	0.066
H(14A)	4*e*	0.7378	0.4192	0.6762	0.101
H(14B)	4*e*	0.8174	0.3862	0.7871	0.101
H(14C)	4*e*	0.8795	0.4786	0.7312	0.101

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	4*e*		0.60694(5)	0.57975(4)	0.56278(3)	0.0314(3)	0.0420(3)	0.0235(3)	–0.0062(2)	0.0062(2)	–0.0061(2)
N(1)	4*e*		0.7804(3)	0.6226(3)	0.5215(2)	0.034(2)	0.043(2)	0.029(2)	–0.004(1)	0.008(1)	–0.002(1)
N(2)	4*e*		0.6444(3)	0.6132(3)	0.7083(2)	0.031(2)	0.040(2)	0.025(2)	–0.001(1)	0.004(1)	–0.005(1)
N(3)	4*e*		0.2429(6)	0.8808(5)	0.3676(4)	0.080(4)	0.077(4)	0.053(3)	0.004(3)	–0.009(3)	0.009(3)
O(1)	4*e*		0.5507(3)	0.5164(2)	0.4314(2)	0.037(2)	0.053(2)	0.029(1)	–0.012(1)	0.012(1)	–0.013(1)
O(2)	4*e*		0.4994(3)	0.7484(3)	0.5631(2)	0.066(2)	0.055(2)	0.043(2)	0.020(2)	0.013(2)	0.008(1)
O(3)	4*e*	0.637	0.272(1)	0.795(1)	0.423(1)	0.056(5)	0.074(7)	0.085(8)	–0.013(5)	–0.004(5)	0.026(5)
O(4)	4*e*	0.637	0.308(1)	0.9687(7)	0.3849(7)	0.15(1)	0.064(5)	0.132(8)	–0.028(5)	0.029(7)	–0.018(5)
O(5)	4*e*	0.637	0.169(2)	0.870(2)	0.287(1)	0.16(2)	0.15(2)	0.13(1)	–0.02(1)	–0.04(1)	0.03(1)
O(3')	4*e*	0.363	0.151(2)	0.955(2)	0.357(2)	0.15(2)	0.10(1)	0.13(2)	0.06(1)	0.00(1)	0.01(1)
O(4')	4*e*	0.363	0.264(3)	0.842(2)	0.450(2)	0.073(9)	0.10(2)	0.06(1)	0.02(1)	0.000(7)	0.02(1)
O(5')	4*e*	0.363	0.236(2)	0.828(2)	0.288(2)	0.10(2)	0.12(2)	0.09(1)	0.02(1)	0.03(1)	–0.03(1)
C(1)	4*e*		0.6611(4)	0.4921(4)	0.3922(3)	0.040(2)	0.054(3)	0.035(2)	–0.007(2)	0.015(2)	–0.013(2)
C(2)	4*e*		0.7799(4)	0.5700(3)	0.4352(3)	0.033(2)	0.039(2)	0.032(2)	–0.001(2)	0.009(2)	0.000(2)
C(3)	4*e*		0.8824(4)	0.5886(4)	0.3893(3)	0.042(2)	0.059(3)	0.038(2)	–0.005(2)	0.016(2)	–0.005(2)
C(4)	4*e*		0.9884(5)	0.6624(4)	0.4319(4)	0.042(2)	0.070(3)	0.058(3)	–0.013(2)	0.024(2)	–0.006(2)
C(5)	4*e*		0.9890(5)	0.7165(4)	0.5191(4)	0.040(2)	0.067(3)	0.060(3)	–0.021(2)	0.013(2)	–0.011(2)
C(6)	4*e*		0.8842(4)	0.6969(4)	0.5638(3)	0.037(2)	0.055(3)	0.040(2)	–0.012(2)	0.006(2)	–0.008(2)
C(7)	4*e*		0.8810(5)	0.7590(5)	0.6567(4)	0.059(3)	0.087(4)	0.058(3)	–0.037(3)	0.020(2)	–0.034(3)
C(8)	4*e*		0.4973(5)	0.7803(4)	0.6593(3)	0.064(3)	0.043(2)	0.045(2)	0.009(2)	0.012(2)	–0.006(2)
C(9)	4*e*		0.5745(4)	0.6972(3)	0.7367(3)	0.038(2)	0.037(2)	0.035(2)	–0.005(2)	0.008(2)	–0.010(2)
C(10)	4*e*		0.5722(5)	0.7061(4)	0.8357(3)	0.059(3)	0.050(3)	0.043(2)	–0.005(2)	0.021(2)	–0.015(2)
C(11)	4*e*		0.6431(6)	0.6288(4)	0.9043(3)	0.082(4)	0.067(3)	0.029(2)	–0.011(3)	0.019(2)	–0.008(2)
C(12)	4*e*		0.7163(5)	0.5452(4)	0.8754(3)	0.062(3)	0.062(3)	0.034(2)	–0.001(2)	0.003(2)	0.004(2)
C(13)	4*e*		0.7173(4)	0.5374(4)	0.7769(3)	0.037(2)	0.048(2)	0.033(2)	0.003(2)	0.002(2)	–0.001(2)
C(14)	4*e*		0.7950(6)	0.4473(5)	0.7395(4)	0.068(3)	0.069(3)	0.061(3)	0.033(3)	0.012(3)	0.015(3)

Acknowledgments. We are grateful for financial support of this work from science and technology project in Colleges and universities in Shandong Province (J10LB61).

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