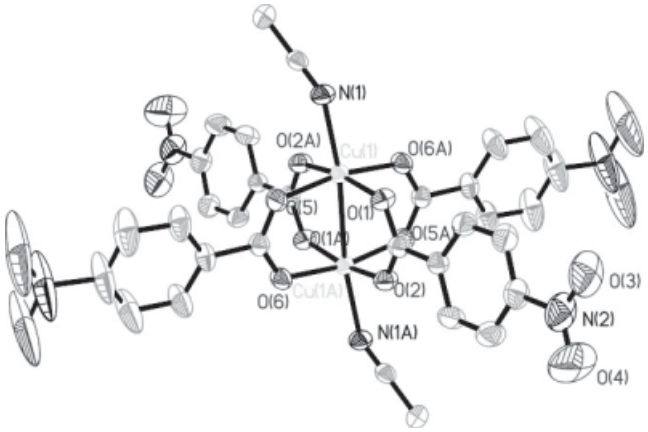
Crystal structure of bis(acetonitrile-κ*N*)-tetrakis-μ-(*p*-nitrobenzoato-κ^2*O:O′*)copper(II) – (Cu–Cu), $Cu_2(p\text{-}NO_2C_6H_4COO)_4(CH_3CN)_2$, $C_{16}H_{11}CuN_3O_8$

Shu-Tao Song, Jun-Yan Cui, Zhen Li and Feng-Mei Nie*

Department of Chemistry, Capital Normal University, Beijing 100048, P. R. China

Received October 17, 2012, accepted December 03, 2012, available online April 19, 2013, CCDC no. 1267/3942



Abstract

$C_{16}H_{11}CuN_3O_8$, tetragonal, $I4_1/a$ (no. 88), a = 17.1139(2) Å, c = 25.5803(5) Å, V = 7492.1 Å^3, Z = 16, $R_{gt}(F)$ = 0.0409, $wR_{ref}(F^2)$ = 0.1261, T = 296 K.

Table 1. Data collection and handling.

Crystal:	blue blocks, size 0.25×0.30×0.31 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	12.15 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω
$2\theta_{max}$:	56.2°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	49083, 4547
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2849
$N(param)_{refined}$:	254
Programs:	SHELX [7]

Source of material

To a stirred acetonitrile solution (30 mL) of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.19 g, 0.5 mmol), sodium *p*-nitrobenzoate (0.19 g, 1.0 mmol) in 15 mL acetonitrile was added dropwise. After stirring for 3 hours at room temperature, the solution was filtered and allowed to stand at room temperature for slow evaporation. Blue crystals suitable for X-ray structure determination were formed.

Discussion

The chemistry of copper(II) dinuclear compound has been of interest for many years. These complexes are very important in biology and also in material science. A number of compounds with the basic structure of $[Cu_2(\mu\text{-}OAc)_4]$ have been synthesized and studied [1-6]. To the best of our knowledge, the structure of copper complex containing *p*-nitrobenzoate has not been reported yet. The title complex is a centrosymmetric dinuclear compound with four carboxylate bridges. The copper(II) atoms are bridged by four anions of *p*-nitrobenzoate to form a typical paddle-wheel complex with two acetonitrile molecules at the axial postions. Each copper(II) atom is coordinated by four carboxylate O atoms of *p*-nitrobenzoate and one N atom of acetonitrile. The Cu–O distances range from 1.956(2) Å to 1.976(2) Å. These bond lengths are comparable to those of other acetate copper complexes [5]. The Cu–N distance is slightly longer (2.182(3) Å). The N1–Cu1–O2A, N1–Cu1–O5, N1–Cu1–O6A, N1–Cu1–O1, O5–Cu1–O6A and O1–Cu1–O2A angles are 89.65(10)°, 91.75(10)°, 99.87(10)°, 101.71(10)°, 168.36(9)° and 168.63(8)°, respectively. The geometric parameter of the title complex exhibits a distorted square pyramidal environment, in which four *p*-$NO_2C_6H_4COO^-$ anions coordinate to the copper atoms to form a paddle-wheel structure with the summit being occupied by the N1 atom of the acetonitrile molecule. The basal plane being formed by O1, O2, O5, and O6, while Cu1 is shifted by 0.201 Å out of the plane toward N1 of acetonitrile. The Cu–Cu separation is 2.6238(6) Å in the dinuclear complex, which is shorter than the van der Waals distance for two copper atoms (2.86 Å) and slightly longer than the Cu–Cu single bond distance (2.55 Å) [6].

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

Atom	Site	x	y	z	U_{iso}
H(1)	16*f*	–0.1625	0.0443	0.1448	0.079
H(5)	16*f*	–0.2521	–0.0976	0.0363	0.088
H(2)	16*f*	–0.2695	0.0226	0.1977	0.091
H(4)	16*f*	–0.3609	–0.1175	0.0885	0.105
H(16A)	16*f*	0.1350	0.3260	0.0630	0.116
H(16B)	16*f*	0.1916	0.2722	0.0309	0.116
H(16C)	16*f*	0.1971	0.2745	0.0921	0.116
H(8)	16*f*	–0.0872	0.2445	–0.0601	0.110
H(12)	16*f*	–0.1022	0.0707	–0.1631	0.121
H(9)	16*f*	–0.1165	0.3339	–0.1255	0.166
H(11)	16*f*	–0.1374	0.1586	–0.2269	0.185

* Correspondence author (e-mail: niefm@mail.cnu.edu.cn)

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

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	16*f*	0.02000(2)	0.05906(2)	0.02983(1)	0.0519(2)	0.0401(2)	0.0493(2)	–0.0015(1)	–0.0058(2)	–0.0020(2)
O(6)	16*f*	–0.0634(1)	0.0210(1)	–0.07605(8)	0.074(2)	0.050(1)	0.056(1)	0.007(1)	–0.016(1)	0.000(1)
O(1)	16*f*	–0.0795(1)	0.0427(1)	0.06583(8)	0.056(1)	0.054(1)	0.066(1)	–0.006(1)	0.004(1)	–0.008(1)
O(5)	16*f*	–0.0332(1)	0.1214(1)	–0.02393(9)	0.081(2)	0.046(1)	0.062(1)	0.002(1)	–0.013(1)	0.003(1)
O(2)	16*f*	–0.1149(1)	–0.0566(1)	0.01417(8)	0.063(1)	0.065(1)	0.060(1)	–0.012(1)	0.004(1)	–0.013(1)
C(6)	16*f*	–0.1964(2)	–0.0238(2)	0.0850(1)	0.055(2)	0.051(2)	0.052(2)	0.001(1)	–0.003(1)	0.001(1)
N(1)	16*f*	0.0638(2)	0.1639(2)	0.0685(1)	0.075(2)	0.049(2)	0.066(2)	–0.006(1)	–0.009(1)	–0.010(1)
C(7)	16*f*	–0.1252(2)	–0.0116(2)	0.0523(1)	0.053(2)	0.047(2)	0.053(2)	0.005(1)	–0.004(1)	0.003(1)
C(1)	16*f*	–0.2024(2)	0.0116(2)	0.1334(1)	0.080(2)	0.057(2)	0.062(2)	–0.009(2)	0.005(2)	–0.010(2)
C(5)	16*f*	–0.2559(2)	–0.0727(2)	0.0685(1)	0.059(2)	0.104(3)	0.057(2)	–0.016(2)	0.002(2)	–0.015(2)
O(3)	16*f*	–0.3975(3)	–0.0247(2)	0.2213(2)	0.167(4)	0.141(3)	0.116(3)	0.003(3)	0.077(3)	–0.009(2)
C(2)	16*f*	–0.2662(2)	–0.0005(2)	0.1649(2)	0.102(3)	0.064(2)	0.062(2)	–0.001(2)	0.015(2)	–0.009(2)
C(4)	16*f*	–0.3207(2)	–0.0848(3)	0.0994(2)	0.068(2)	0.117(3)	0.078(3)	–0.027(2)	0.005(2)	–0.010(2)
C(3)	16*f*	–0.3243(2)	–0.0473(2)	0.1466(2)	0.077(2)	0.084(3)	0.069(2)	–0.001(2)	0.021(2)	0.005(2)
N(2)	16*f*	–0.3956(3)	–0.0574(3)	0.1793(2)	0.111(3)	0.125(4)	0.103(3)	–0.011(3)	0.048(3)	–0.001(3)
C(15)	16*f*	0.1061(2)	0.2136(2)	0.0660(1)	0.067(2)	0.048(2)	0.043(2)	0.005(2)	–0.009(1)	–0.007(1)
C(14)	16*f*	–0.0598(2)	0.0931(2)	–0.0653(1)	0.053(2)	0.052(2)	0.056(2)	0.006(1)	–0.003(1)	0.007(1)
C(16)	16*f*	0.1622(2)	0.2770(2)	0.0627(2)	0.086(3)	0.072(2)	0.074(2)	–0.023(2)	–0.004(2)	0.013(2)
C(13)	16*f*	–0.0882(2)	0.1492(2)	–0.1057(1)	0.075(2)	0.064(2)	0.057(2)	0.017(2)	0.003(2)	0.015(2)
C(8)	16*f*	–0.0953(3)	0.2274(2)	–0.0941(2)	0.140(4)	0.065(2)	0.071(2)	0.039(2)	0.016(2)	0.015(2)
C(12)	16*f*	–0.1051(3)	0.1237(3)	–0.1553(2)	0.158(4)	0.083(3)	0.063(2)	0.043(3)	–0.021(3)	0.008(2)
C(9)	16*f*	–0.1144(4)	0.2805(3)	–0.1324(2)	0.226(7)	0.091(3)	0.098(4)	0.090(4)	0.043(4)	0.029(3)
C(10)	16*f*	–0.1301(5)	0.2512(4)	–0.1812(2)	0.254(8)	0.137(5)	0.078(4)	0.120(5)	0.021(4)	0.046(3)
O(4)	16*f*	–0.4457(3)	–0.0994(4)	0.1637(2)	0.126(3)	0.302(7)	0.183(5)	–0.096(4)	0.079(3)	–0.062(5)
C(11)	16*f*	–0.1261(4)	0.1757(4)	–0.1932(2)	0.264(8)	0.130(5)	0.068(3)	0.087(5)	–0.027(4)	0.016(3)
O(8)	16*f*	–0.1629(7)	0.2812(5)	–0.2669(3)	0.68(2)	0.285(9)	0.118(5)	0.24(1)	–0.016(8)	0.095(5)
O(7)	16*f*	–0.1437(7)	0.3761(4)	–0.2137(2)	0.82(2)	0.200(6)	0.137(4)	0.32(1)	0.098(7)	0.086(4)
N(3)	16*f*	–0.1469(7)	0.3104(5)	–0.2231(3)	0.53(2)	0.193(7)	0.097(5)	0.22(1)	0.047(7)	0.069(5)

Acknowledgments. This study was supported by Beijing Natural Science Foundation (Grant No. 2092010), Beijing Municipal Education Commission research program (Grant No. KM200810028009) and the Scientific Research Foundation for Returned Overseas Chinese Scholars, Beijing Municipal Government.

References

1. Ali, M. E.; Datta, S. N.: Theoretical investigation of magnetic properties of a dinuclear copper complex $[Cu_2(\mu\text{-}OAC)_4(MeNHpy)_2]$. J. Mol. Struct. Theochem. **775** (2006) 19-27.
2 Sarma, R.; Baruah, J. B.: A mixed carboxylate polymer as an intermediate during synthesis of mononuclear bis-3,5-dimethylpyrazole copper(II) benzoates. J. Coord. Chem. **61** (2008) 3329-3335.
3. Baruah, J. B.: Perspectives of study on low nuclearity carboxylate complexes. Comments on Inorg. Chem. **30** (2009) 67-88.
4. Bie, H. Y.; Yu, J. H.; Zhao, K.; Lu, J.; Duan, L. M.; Xu, J. Q.: Syntheses, characterization and fluorescent properties of two square pyramidal Cu(II) inorganic-organic hybrid polymers. J. Mol. Struct. **741** (2005) 77-84.
5. Van Niekerk, J. N.; Schoening, F. R. L.: A new type of copper complex as found in the crystal structure of cupric acetate, $Cu_2(CH_3COO)_4{\cdot}2H_2O$. Acta Crystallogr. **6** (1953) 227-232.
6. Xu, R. B.; Xu, X. Y.; Wang, M. Y.; Yang, X. J.: Hydrothermal synthesis, crystal structure and electrochemical properties of a new dinuclear copper complex $[C_2H_6ON]_2[Cu_2Cl_2(\mu\text{-}CH_3COO)_4]$. Jiegou huaxue. **28** (2009) 703-707.
7. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.