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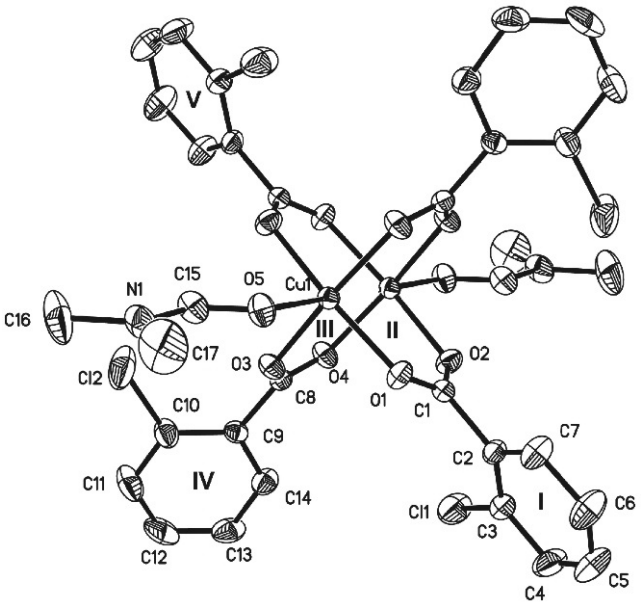
Crystal structure of tetrakis(μ-2-chlorobenzoato-*O*:*O'*)-bis(dimethylformamid)dicopper(II), $Cu_2(C_3H_7NO)_2(C_7H_4ClO_2)_4$

De-Zhong Niu*, Chang-Fu Shan, Xin Min and Fan Gao

College of Chemistry & Chemical Engineering, Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, Xuzhou Normal University, Xuzhou 221116, P. R. China

Received July 2, 2011, accepted and available on-line November 21, 2011; CCDC no. 1267/3612



Abstract

$C_{34}H_{30}Cl_4Cu_2N_2O_{10}$, monoclinic, $P12_1/n1$ (no. 14), a = 10.2037(8) Å, b = 10.933(1) Å, c = 17.192(2) Å, β = 91.703(1)°, V = 1917.1 Å^3, Z = 2, $R_{gt(F)}$ = 0.034, $wR_{ref(F^2)}$ = 0.095, T = 298 K.

Source of material

A mixture of 2-chlorobenzoic acid (Hcba) (0.156 g, 1.0 mmol) and $CuCl_2 \cdot 2H_2O$ (0.085 g, 0.5 mmol) was dissolved in 70 % alcohol (20 mL), and heated at 40-50 °C for 20 min and the pH adjusted to 7-8 with NaOH. The mixed solution was stirred for 2 h at 80 °C and cooled to room temperature to give brown microcrystals, which were collected by filtration, washed successively with H_2O and EtOH, and dried in vacuo. After about two weeks, brown polyhedral crystals suitable for X-ray analysis were obtained by recrystallization of the precipitate from *N*,*N*-dimethylformamide (DMF); m.p.: 259-261 °C.

Elemental analysis — found: C, 45.48 %; H, 3.42 %; N, 3.29; calculated for $C_{34}H_{30}Cl_4Cu_2N_2O_{10}$: C, 45.60 %; H, 3.38 %; N, 3.13 %. IR data are available in the CIF file.

Discussion

Since the first report of the crystal structure of copper(II) acetate monohydrate $[Cu_2(MeCO_2)_4(H_2O)_2]$[1], a large number of copper(II) carboxylates of this type, generally formulated as $[Cu_2(RCO_2)_4L_2]$ (L = denotes the axial ligand), have been structurally established [2-4] where the R represents a variety of small and bulky organic groups [1-8].

The title crystal structure consists of molecules with two Cu atoms linked by four cba groups in a fashion similar to that of $[Cu_2(Indo)_4(DMF)_2] \cdot 1.6DMF$ [3] and the dinuclear structure of $[Cu_2(CH_3COO)_4(H_2O)_2]$ [9-11]. A DMF molecule is bound *trans* to the Cu1—Cu1A vector on each of the Cu atoms, and a further two DMF molecules are loosely held in the lattice. These lattice DMF sites were highly mobile, and their sites were only partially occupied. During the data collection, some reductions in the intensities of the standard reflections were noted, and these are consistent with slow loss of these molecules of crystallization. The fused and conjugated five- and six-membered rings are close to being planar (deviations less than 0.008 Å), and the molecule makes no close contacts with other molecules in the lattice. In the molecular structure, there are five ring planes (I: C2,C3,C4,C5, C6,C7; II: Cu1,Cu1A,O1,O2,C1; III: Cu1,Cu1A,O3,O4,C8; IV: C9,C10,C11,C12,C13,C14 and V: C2A,C3A,C4A,C5A, C6A,C7A. The dihedral angles between planes I and II; II and III; III and IV; I and IV; I and V are 51.8(1)°, 89.88(5)°, 48.3(1)°, 58.4(1)° and 0.0(2)°, respectively.

The structure of the $[Cu_2(cba)_4(DMF)_2]$ complex is similar to that reported for $[Cu_2(Indo)_4(DMF)_2] \cdot 1.6DMF$, although the latter structure was of a lower precision. The individual Cu atoms have a Jahn-Teller-distorted octahedral coordination, with four short Cu—O_{obc} bond lengths (1.958(2) - 1.971(2) Å) and a long solvent Cu—O_{DMF} bond length (2.146(2) Å). The two copper atoms in each dimeric unit are separated by a distance of 2.6419(7) Å. This distance is similar to that found in $[Cu_2(Indo)_4(DMF)_2] \cdot 1.6DMF$ (2.630(1) Å) and other Cu carboxylate dimers [7,9] and slightly longer than that found in $[Cu_2(\mu\text{-}OAc)_4(PhNHpy)_2]$ complex (2.45-2.50 Å) [8].

Table 1. Data collection and handling.

Crystal:	brown square, size 0.32 × 0.46 × 0.49 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	14.44 cm^{-1}
Diffractometer, scan mode:	Bruker SMART, ω
$2\theta_{max}$:	50.02°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	9352, 3370
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2562
$N(param)_{refined}$:	235
Programs:	SHELXS-97, SHELXL-97 [12]

* Correspondence author (e-mail: xzsd_ndz@263.net)

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

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(4)	4*e*		0.6355	0.8411	0.8309	0.081
H(5)	4*e*		0.7049	0.6943	0.9179	0.092
H(6)	4*e*		0.7131	0.4927	0.8817	0.088
H(7)	4*e*		0.6582	0.4370	0.7551	0.068
H(11)	4*e*		0.8513	0.9257	0.2936	0.087
H(12)	4*e*		0.8216	1.0987	0.3650	0.085
H(13)	4*e*		0.6853	1.0968	0.4695	0.077
H(14)	4*e*		0.5843	0.9176	0.5035	0.061
H(15)	4*e*		0.8016	0.4162	0.3734	0.059
H(16A)	4*e*		1.0402	0.2919	0.2931	0.162
H(16B)	4*e*		1.1067	0.4120	0.3247	0.162
H(16C)	4*e*		0.9644	0.4165	0.2878	0.162
H(17A)	4*e*	0.50	1.1445	0.2993	0.4409	0.173
H(17B)	4*e*	0.50	1.0352	0.2015	0.4546	0.173
H(17C)	4*e*	0.50	1.0387	0.3225	0.5035	0.173
H(17D)	4*e*	0.50	1.0019	0.2487	0.4927	0.173
H(17E)	4*e*	0.50	1.1117	0.3468	0.4790	0.173
H(17F)	4*e*	0.50	1.1082	0.2254	0.4298	0.173

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)	4*e*	0.61312(3)	0.44230(3)	0.49468(2)	0.0267(2)	0.0292(2)	0.0321(2)	0.0011(2)	0.0016(1)	–0.0007(2)
Cl(1)	4*e*	0.5489(1)	0.8401(1)	0.67757(6)	0.127(1)	0.0464(6)	0.0588(6)	–0.0127(6)	–0.0079(6)	0.0041(5)
Cl(2)	4*e*	0.7593(2)	0.6889(1)	0.29860(7)	0.162(1)	0.0641(8)	0.0788(8)	0.0071(8)	0.0657(9)	–0.0071(6)
N(1)	4*e*	0.9712(3)	0.3461(3)	0.3954(2)	0.033(2)	0.061(2)	0.083(2)	0.003(2)	0.016(2)	–0.007(2)
O(1)	4*e*	0.6482(2)	0.4998(2)	0.6016(1)	0.042(1)	0.053(1)	0.032(1)	0.007(1)	–0.001(1)	–0.007(1)
O(2)	4*e*	0.4555(2)	0.5966(2)	0.6107(1)	0.036(1)	0.055(2)	0.038(1)	0.004(1)	–0.004(1)	–0.011(1)
O(3)	4*e*	0.6673(2)	0.6037(2)	0.4559(1)	0.037(1)	0.030(1)	0.052(1)	–0.002(1)	0.005(1)	0.007(1)
O(4)	4*e*	0.4757(2)	0.7019(2)	0.4646(1)	0.039(1)	0.034(1)	0.059(2)	–0.001(1)	0.009(1)	0.008(1)
O(5)	4*e*	0.8010(2)	0.3619(2)	0.4750(1)	0.036(1)	0.052(2)	0.054(2)	0.010(1)	0.009(1)	0.007(1)
C(1)	4*e*	0.5663(3)	0.5644(3)	0.6361(2)	0.036(2)	0.034(2)	0.032(2)	–0.007(2)	0.003(1)	–0.000(1)
C(2)	4*e*	0.6060(3)	0.6050(3)	0.7174(2)	0.036(2)	0.051(2)	0.031(2)	–0.003(2)	0.002(1)	–0.007(2)
C(3)	4*e*	0.6005(4)	0.7254(3)	0.7412(2)	0.056(2)	0.048(2)	0.038(2)	–0.008(2)	0.001(2)	–0.003(2)
C(4)	4*e*	0.6384(5)	0.7594(4)	0.8159(2)	0.092(3)	0.058(3)	0.052(2)	–0.007(2)	–0.009(2)	–0.018(2)
C(5)	4*e*	0.6801(5)	0.6719(5)	0.8674(2)	0.094(4)	0.093(4)	0.041(2)	0.008(3)	–0.020(2)	–0.016(2)
C(6)	4*e*	0.6859(5)	0.5518(4)	0.8458(2)	0.094(4)	0.083(3)	0.041(2)	0.025(3)	–0.017(2)	–0.002(2)
C(7)	4*e*	0.6511(4)	0.5183(4)	0.7703(2)	0.068(3)	0.061(2)	0.041(2)	0.015(2)	–0.006(2)	–0.006(2)
C(8)	4*e*	0.5945(3)	0.6956(3)	0.4483(2)	0.040(2)	0.032(2)	0.029(2)	–0.004(2)	–0.000(1)	–0.002(1)
C(9)	4*e*	0.6574(3)	0.8109(3)	0.4201(2)	0.036(2)	0.031(2)	0.039(2)	–0.002(1)	–0.002(1)	0.003(1)
C(10)	4*e*	0.7373(4)	0.8162(3)	0.3565(2)	0.059(2)	0.041(2)	0.059(2)	–0.003(2)	0.020(2)	0.003(2)
C(11)	4*e*	0.7976(5)	0.9237(4)	0.3364(3)	0.071(3)	0.063(3)	0.085(3)	–0.008(2)	0.033(2)	0.021(2)
C(12)	4*e*	0.7793(5)	1.0268(4)	0.3786(3)	0.072(3)	0.046(3)	0.094(3)	–0.024(2)	–0.007(3)	0.021(2)
C(13)	4*e*	0.6989(5)	1.0258(3)	0.4411(2)	0.096(3)	0.034(2)	0.062(3)	–0.012(2)	–0.014(2)	–0.001(2)
C(14)	4*e*	0.6389(4)	0.9183(3)	0.4611(2)	0.074(3)	0.035(2)	0.043(2)	–0.000(2)	0.003(2)	–0.000(2)
C(15)	4*e*	0.8520(3)	0.3780(3)	0.4123(2)	0.037(2)	0.046(2)	0.063(2)	0.008(2)	0.005(2)	0.006(2)
C(16)	4*e*	1.0253(5)	0.3685(6)	0.3186(3)	0.082(4)	0.127(5)	0.119(4)	0.008(3)	0.065(3)	0.014(4)
C(17)	4*e*	1.0543(5)	0.2875(6)	0.4535(3)	0.044(3)	0.169(6)	0.133(5)	0.036(3)	–0.008(3)	–0.002(4)

Acknowledgment. This work was sponsored by Qing Lan Project (grant no. 08QLT001).

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