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Crystal structure of bis(biimidazole-κ^2N,N')bis(perchlorato-κO)copper(II) — *N*,*N*-dimethylformamide (1:1), $Cu(C_6H_6N_4)_2(ClO_4)_2 \cdot C_3H_7NO$

Yuan-Yuan Zhang[I], Wei Yang[I], Qiong-Hua Jin[*,I], Hao Liu[I] and Cun-Lin Zhang[II]

[I] Capital Normal University, Department of Chemistry, Beijing 100048, P. R. China
[II] Key Laboratory of Terahertz Optoelectronics, Ministry of Education, Capital Normal University, Beijing 100048, P. R. China

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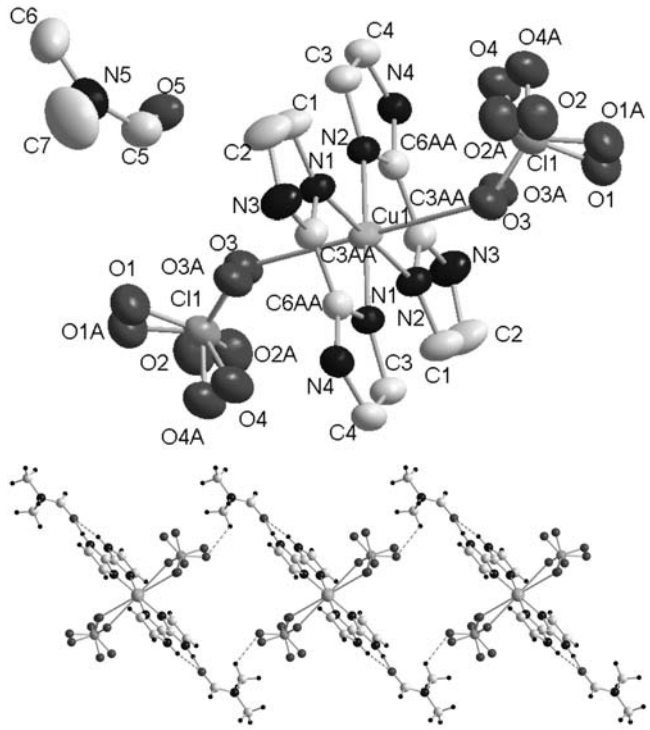

Abstract

$C_{18}H_{26}Cl_2CuN_{10}O_{10}$, monoclinic, $P12_1/n1$ (no. 14), a = 8.1744(4) Å, b = 15.4829(8) Å, c = 10.9577(6) Å, β = 93.683(3)°, V = 1384.0 Å^3, Z = 2, $R_{gt}(F)$ = 0.049, $wR_{ref}(F^2)$ = 0.155, T = 296 K.

Source of material

An aqueous solution (5 ml) of copper perchlorate (0.5 mmol, 0.1853 g) was poured slowly dropwise into hot aqueous solution of biimidazole (1 mmol, 0.134 g). The mixture was stirred for 6 h, then DMF (1 mmol) was added. The resultant mixture was refluxed for 30 min and then allowed to cool to ambient temperature. The insoluble residues were removed by fitration, and the filtrate was evaporated slowly at room temperature for about one week to yield green crystalline product. Plate-like crystals suitable for single crystal X-ray diffraction analysis were selected directly from the product.

Discussion

Supramolecular polymers have received much attention due to their structural diversities and potential applications as new materials. The assembly of supramolecular complexes depends on many factors such as the nature of the metal, ligand, counter ion and solvent. The consideration and utilization of the coordination bonds of a transition metal ion, intermolecular hydrogen bonds and π-π packing interactions also help to control the molecular arrangement [1-4]. 2,2′-Biimidazole (H_2biim) is an excellent candidate for building supramolecular structures involving directed hydrogen bonding interactions. H_2biim exists in the reported compounds in different forms, such as neutral ligand H_2biim, anion ligand $Hbiim^-$, $biim^{2-}$, or cations H_3biim^+ and H_4biim^{2+}. The uncoordinated N–H groups in H_2biim and its ions participate in various hydrogen bonds with counter anions or other acceptors. The hydrogen bonding is regarded as robust power in the construction of supramolecular polymers. It also provides useful information to understand the complicated processes in biological systems [5-7]. The complexes $[Cu(C_6H_6N_4)_2](ClO_4)_2 \cdot 2DMSO$ and $[Cu(H_2biim)_2]Cl_2$ [8] similar to the the title one will be compared here.

The asymmetric unit of the title crystal structure consists of one $[Cu(C_6H_6N_4)_2]^{2+}$ cation, two ClO_4^- anions and a DMF molecule (figure, top). The coordination environment of Cu^{2+} can be described as a distorted octahedron with four nitrogen atoms from two H_2biim ligands in equatorial positions and two oxygen donor atoms from perchlorates in apical sites. The Cu—N bond lengths range from 2.009(3) to 2.020(3) Å, being shorter than the Cu—O bond length 2.610 Å. The Cu—N bond lengths are similar to those in the compound of $[Cu(H_2biim)_2]Cl_2$ [d(Cu—N1) = 2.010(2) Å, d(Cu—N3) = 2.036(2) Å] [9]. Such bond lengths are observed for H_2biim-Cu complexes retrieved from the CSD [10]. The N–Cu–N angle of 82.4° generated by chelating H_2biim is in the upper limit of the range registered in the CSD so far (range of ∠N–Cu–N = 78.6° - 81.6°.

Molecule packing is controlled to a great extent by the ability of coordinated H_2biim to form hydrogen bonds with counter ions and solvent molecules. The units $[Cu(H_2biim)_2]^{2+}$ form an infinite step-like chain along [010]. The hydrogen bonds are formed between the N–H donors of H_2biim and the oxygen atoms from DMF or ClO_4^- (figure, bottom). All O atoms of the perchlorate anion are disordered, and O4 acts as acceptor for one of the N–H groups of a H_2biim ligand with d(N3···O4) = 3.044 Å and ∠N3–H3···O4 = 109.24°. The other hydrogen bonds involve the oxygen of DMF molecule with the N–H groups: d(N3···O5) = 2.718 Å, d(N4···O5) = 2.784 Å. These chains are further assembled into a 3D framework by hydrogen bonds and π-π interactions between H_2biim ligands.

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

Table 1. Data collection and handling.

Crystal:	green block, size 0.28 × 0.32 × 0.38 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	10.52 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ/ω
$2\theta_{max}$:	55°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	9230, 3139
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2618
$N(param)_{refined}$:	205
Programs:	SHELXS-97, SHELXL-97 [11]

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

Atom	Site	x	y	z	U_{iso}
H(4)	4*e*	–0.0134	0.5402	0.6727	0.063
H(3)	4*e*	0.2124	0.6690	0.4290	0.064
H(3A)	4*e*	0.1258	0.3860	0.7722	0.077
H(4A)	4*e*	–0.0374	0.6667	0.5408	0.068
H(1)	4*e*	0.5579	0.3121	0.6825	0.079
H(5)	4*e*	0.7116	0.4688	0.8317	0.084
H(2)	4*e*	0.3332	0.2746	0.8088	0.094
H(6A)	4*e*	0.9650	0.3074	0.9983	0.162
H(6C)	4*e*	0.9655	0.3721	1.1084	0.162
H(6B)	4*e*	1.0545	0.3967	0.9906	0.162
H(7C)	4*e*	0.6749	0.4232	1.1090	0.210
H(7B)	4*e*	0.6467	0.3336	1.0442	0.210
H(7A)	4*e*	0.5732	0.4178	0.9829	0.210

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)	2*a*		½	½	½	0.0396(3)	0.0363(3)	0.0598(4)	–0.0006(2)	0.0018(3)	0.0089(2)
Cl(1)	4*e*		0.3646(1)	0.32909(6)	0.2731(1)	0.0478(5)	0.0528(5)	0.0726(6)	–0.0005(4)	0.0052(4)	–0.0115(4)
N(2)	4*e*		0.2822(3)	0.5574(2)	0.5227(3)	0.043(2)	0.037(1)	0.056(2)	–0.001(1)	–0.000(1)	0.003(1)
N(1)	4*e*		0.4204(4)	0.4181(2)	0.6254(3)	0.045(2)	0.041(2)	0.063(2)	–0.002(1)	0.001(1)	0.011(1)
N(4)	4*e*		0.0580(4)	0.5562(2)	0.6230(3)	0.049(2)	0.052(2)	0.056(2)	0.003(1)	0.008(1)	–0.003(1)
C(3)	4*e*		0.1861(5)	0.6279(2)	0.4864(4)	0.053(2)	0.039(2)	0.067(2)	0.003(2)	–0.002(2)	0.005(2)
C(3AA)	4*e*		0.2728(5)	0.4405(2)	0.6586(3)	0.049(2)	0.044(2)	0.053(2)	–0.002(2)	0.001(2)	0.007(2)
N(3)	4*e*		0.2180(4)	0.3839(2)	0.7388(3)	0.056(2)	0.066(2)	0.074(2)	0.001(2)	0.015(2)	0.022(2)
C(4)	4*e*		0.0480(5)	0.6270(3)	0.5480(4)	0.055(2)	0.047(2)	0.068(2)	0.010(2)	–0.003(2)	–0.005(2)
C(6AA)	4*e*		0.1993(4)	0.5169(2)	0.6048(3)	0.045(2)	0.042(2)	0.049(2)	–0.002(1)	–0.001(1)	–0.002(1)
C(1)	4*e*		0.4612(5)	0.3431(3)	0.6876(5)	0.057(2)	0.051(2)	0.089(3)	0.004(2)	0.005(2)	0.023(2)
N(5)	4*e*		0.8121(6)	0.4060(3)	0.9687(4)	0.099(3)	0.068(2)	0.066(2)	–0.013(2)	0.023(2)	–0.005(2)
C(5)	4*e*		0.8103(6)	0.4453(3)	0.8628(4)	0.073(3)	0.065(3)	0.074(3)	0.005(2)	0.015(2)	0.006(2)
C(2)	4*e*		0.3366(6)	0.3222(3)	0.7574(5)	0.071(3)	0.065(3)	0.099(4)	0.002(2)	0.007(3)	0.041(3)
O(5)	4*e*		0.9298(4)	0.4531(2)	0.8019(3)	0.076(2)	0.079(2)	0.082(2)	0.012(2)	0.028(2)	0.019(2)
C(6)	4*e*		0.962(1)	0.3673(5)	1.0209(6)	0.157(7)	0.086(4)	0.077(4)	–0.002(4)	–0.015(4)	0.009(3)
C(7)	4*e*		0.665(1)	0.3941(6)	1.0314(7)	0.160(8)	0.154(7)	0.114(5)	–0.043(6)	0.072(5)	–0.006(5)
O(4)	4*e*	0.70(1)	0.5276(7)	0.3014(5)	0.3036(7)	0.058(2)	0.076(2)	0.106(2)	0.007(2)	–0.006(2)	–0.023(2)
O(1)	4*e*	0.42(1)	0.343(2)	0.3580(9)	0.139(1)	0.106(2)	0.069(3)	0.085(2)	–0.009(2)	–0.005(2)	–0.009(2)
O(2)	4*e*	0.59(1)	0.2424(9)	0.2692(5)	0.298(1)	0.073(2)	0.087(2)	0.092(3)	–0.019(2)	0.004(2)	–0.011(3)
O(3)	4*e*	0.71(1)	0.3350(7)	0.4100(3)	0.3325(5)	0.064(2)	0.059(2)	0.083(2)	0.003(2)	–0.001(2)	–0.016(2)
O(3A)	4*e*	0.29	0.414(2)	0.4134(8)	0.298(1)	0.064(2)	0.059(2)	0.083(2)	0.003(2)	–0.001(2)	–0.016(2)
O(2A)	4*e*	0.41	0.265(1)	0.2778(7)	0.360(1)	0.073(2)	0.087(2)	0.092(3)	–0.019(2)	0.004(2)	–0.011(3)
O(1A)	4*e*	0.58	0.314(1)	0.3199(7)	0.1494(7)	0.106(2)	0.069(3)	0.085(2)	–0.009(2)	–0.005(2)	–0.009(2)
O(4A)	4*e*	0.30	0.493(2)	0.270(1)	0.268(2)	0.058(2)	0.076(2)	0.106(2)	0.007(2)	–0.006(2)	–0.023(2)

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