Crystal structure of *catena*-(dimethylammonium) tris(μ_2 -formato)copper(II), $[\text{C}_2\text{H}_8\text{N}][\text{Cu}(\text{CHO}_2)_3]$

Shu-Qing Xu and Jia-Ming Li*

Qinzhou University, Department of Chemistry and Biology, Laboratory of Beibu Gulf Marine Protection and Exploitation, Qinzhou, Guangxi 535000, P. R. China

Received January 21, 2009; accepted and available on-line May 6, 2009; CCDC no. 1267/2545

Abstract

$\text{C}_5\text{H}_{11}\text{CuNO}_6$, trigonal, $R\bar{3}c$ (no. 167), $a = 8.1929(3)$ Å, $c = 22.240(2)$ Å, $V = 1292.8$ Å³, $Z = 6$, $R_{\text{int}}(F) = 0.029$, $wR_{\text{ref}}(F^2) = 0.123$, $T = 293$ K.

Source of material

Reagents and solvents used were of commercially available quality. The title complex was synthesized according to the method of [1]. A mixture of $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.5 mmol), formic acid (1.7 mmol), dimethylamine (0.6 mmol) in 20 ml distilled water was refluxed for 2 h, and then the resulted solution was kept still and allowed to evaporate at room temperature. A few days later, blue single crystals suitable for X-ray diffraction study were obtained by slow evaporation of the resulted solution in yield of about 30 %.

Experimental details

All H atoms were placed in idealized positions ($d(\text{C}—\text{H}) = 0.93$ – 0.96 Å, $d(\text{N}—\text{H}) = 0.90$ Å) and refined as riding atoms with

$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$. The nitrogen atom of dimethylammonium was disordered over three positions with equal site-occupancy of 1/3.

Discussion

The design and synthesis of porous metal-organic frameworks (MOFs) is currently an active research area due to their intriguing structural architectures as well as potential applications in catalysis, gas adsorption and separation [2–5]. In order to achieve such functionalities, the common strategy for the construction of porous metal-organic networks is based primarily on the proper selection of inorganic building blocks as nodes and long rigid organic polycarboxylate ligands as linkers [6] to form a 3D robust framework [7,8]. However, formate anions, HCOO^- , which is the simplest carboxylate, has been used very seldom as a building block, although simple metal-formate hydrates have long been known. Even now, example of formate coordination polymers with porous structure is still scarce [1].

Two crystal structures of the title complex's polymorphs have been studied [9,10]. These polymorphs have significant different unit cell parameters, which crystallize in the space groups $I2/c$ [9] and $C2/c$ [10], respectively. The central Cu atom is coordinated by six O of formate anions completing its octahedral coordination sphere (figure, top). The mean Cu—O distance is $2.110(2)$ Å and the bond angles around Cu sites are $88.71(6)^\circ$ – $91.29(6)^\circ$ for *cis* O—Cu—O angles and 180.0° for *trans* O—Cu—O angles, characterizing the distortion of the CuO_6 octahedra. Every formate anion connects two metal atoms in μ_2 -bridging coordination mode *anti-anti*. The neighbouring Cu...Cu separation is $6.009(6)$ Å, which is much longer than that in $\text{Co}_3(\text{HCOO})_6$ in literature [5]. The μ_2 -bridging formate ligands link the metal atoms into a 3D network. The free dimethylammonium cations occupy the structural cavities (figure, bottom) and nitrogen atom of dimethylammonium was disordered over three symmetry positions with occupancy of 1/3.

Table 1. Data collection and handling.

Crystal:	blue prism, size $0.14 \times 0.16 \times 0.18$ mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	25.34 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{\text{max}}$:	56.3°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	2503, 355
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 343
$N(\text{param})_{\text{refined}}$:	25
Programs:	SHELXS-97 [11], SHELXL-97 [12], SHELXTL [13]

* Correspondence author (e-mail: ljmmarise@163.com)

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	U _{iso}
H(2)	18e		0.4290	0.4290	¼	0.022
H(1A)	36f	0.167	0.0987	0.1997	0.2500	0.033
H(1B)	36f	0.167	0.2006	0.0978	0.2500	0.033

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U _{iso}
H(2A)	36f	0.333	0.0767	0.0767	0.1633	0.073
H(2B)	36f	0.333	-0.1226	-0.0121	0.1935	0.073
H(2C)	36f	0.333	-0.0121	-0.1226	0.1935	0.073

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Cu(1)	6b		⅓	⅓	⅓	0.0172(4)	U ₁₁	0.0169(5)	½U ₁₁	0	0
O(1)	36f		0.6745(2)	0.5498(2)	0.27980(7)	0.0223(9)	0.0213(8)	0.0262(9)	0.0106(6)	-0.0045(6)	0.0058(6)
C(1)	18e		0.5425(4)	x	¼	0.017(1)	U ₁₁	0.022(1)	0.008(1)	-0.0003(5)	-U ₁₃
N(1)	18e	0.333	0.084(1)	x	¼	0.025(3)	U ₁₁	0.039(5)	0.017(5)	-0.001(2)	-U ₁₃
C(2)	12c		0	0	0.1959(4)	0.058(3)	U ₁₁	0.030(3)	½U ₁₁	0	0

Acknowledgments. This work was supported by grants from Foundation and the Young Key Teacher's Plan of Qinzhou University Guangxi Zhuang Autonomous Region of the P. R. China (grant nos. 2008XJKY-10B and 2008(30)).

References

- Wang, Y.-Q.; Cao, R.; Bi, W.-H.; Li, X.; Yuan, D.-Q.; Sun, D.-F.: Four novel porous frameworks constructed by formate ligand. *Microporous Mesoporous Mater.* **91** (2006) 215-220.
- He, J.-H.; Zhang, Y.-T.; Pan, Q.-H.; Yu, J.-H.; Hong, D.; Xu, R.-R.: Three metal-organic frameworks prepared from mixed solvents of DMF and HAc. *Microporous Mesoporous Mater.* **90** (2006) 145-152.
- Wang, Z.-M.; Zhang, X.-Y.; Batten, S. R.: [CH₃NH₂(CH₂)₂NH₂CH₃][M₂(HCOO)₆] (M = Mn^{II} and Co^{II}): Weak Ferromagnetic Metal Formate Frameworks of Unique Binodal 6-Connected (4¹²·6³)(4⁹·6⁶) Topology, Templated by a Diammonium Cation. *Inorg. Chem.* **46** (2007) 8439-8441.
- Baggio, R.; Stoilova, D.; Polla, G.; Leyva, G.; Garland, M. T.: Double formates Ba₂M(HCOO)₆(H₂O)₄ (M = Co, Ni, Cu, Zn): crystal structures and hydrogen bonding systems. *J. Mol. Struct.* **697** (2004) 173-180.
- Wang, Z.-M.; Zhang, B.; Kurmoo, M.; Green, M. A.; Fujiwara, H.; Otsuka, T.; Kobayashi, H.: Synthesis and Characterization of a Porous Magnetic Diamond Framework, Co₃(HCOO)₆, and Its N₂ Sorption Characteristic. *Inorg. Chem.* **44** (2005) 1230-1237.
- Janiak, C.: Engineering coordination polymers towards applications. *Dalton Trans.* (2003) 2781-2804.
- Yigit, M. V.; Biyikli, K.; Moulton, Brian.; MacDonald, J. C.: Bis(imidazolium 2,4,6-tricarboxypyridine) Metal(II) Complexes: Molecular Building Blocks that Generate Isomorphous Hydrogen-Bonded Frameworks. *Cryst. Growth Design* **6** (2006) 63-69.
- Maji, T. K.; Kaneko, W.; Ohba, M.; Kitagawa, S.: Diversity in magnetic properties of 3D isomorphous networks of Co(II) and Mn(II) constructed by naphthalene-1,4-dicarboxylate. *Chem. Commun.* (2005) 4613-4615.
- Sletten, E.; Jensen L.H.: The Crystal Structure of Dimethylammonium Copper(II) Formate, NH₂(CH₃)₂[Cu(OOCH)₃]. *Acta Crystallogr. B* **29** (1973) 1752-1756.
- Kong, D.-Y.; Zou, J.; McBee, J.; Clearfield, A.: Rational Design and Synthesis of Porous Organic-Inorganic Hybrid Frameworks Constructed by 1,3,5-Benzenetriphosphonic Acid and Pyridine Synthons. *Inorg. Chem.* **45** (2006) 977-986.
- Sheldrick, G. M.: SHELXS-97. Program for the Solution of Crystal Structures. University of Göttingen, Germany 1997.
- Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.
- Sheldrick, G. M.: SHELXTL. Structure Determination Software Suite. Version 6.14. Bruker AXS, Madison, Wisconsin, USA 2000.