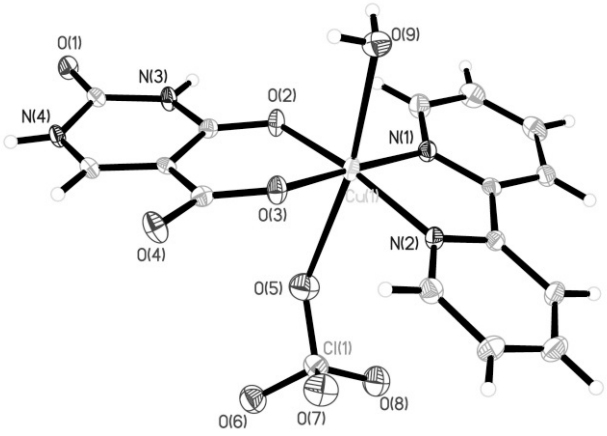
Crystal structure of aqua-[(2,2'-bipyridine)]-[(2,4-dihydroxypyrimidine-5-carboxylato)] perchloratocopper(II), $Cu(H_2O)(C_{10}H_8N_2)(C_5H_3N_2O_4)(ClO_4)$, $C_{15}H_{13}ClCuN_4O_9$

Qi Liu, Bo Xiao* and Min-Dong Chen

Jiangsu Key Laboratory of Agricultural Meteorology, Nanjing University of Information Science & Technology, Nanjing 210044, Jiangsu Province, P. R. China

Received January 22, 2012, accepted June 12, 2012, available online July 26, 2012, CCDC no. 1267/3799



Abstract

$C_{15}H_{13}ClCuN_4O_9$, monoclinic, $P2_1/n$ (no. 14), a = 8.1493(3) Å, b = 11.4761(4) Å, c = 19,3483(6) Å, β = 97.7438(3)°, V = 1793.05(11) Å^3, Z = 4, $R_{gt}(F)$ = 0.0459, $wR_{ref}(F^2)$ = 0.1149, T = 296 K

Table 1. Data collection and handling.

Crystal:	blue blocks, size 0.23×0.21×0.18 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	14.30 cm^{-1}
Diffractometer, scan mode:	Xcalibur Gemini, Eos CCD, φ and ω
$2\theta_{max}$:	52.6226°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7285, 3326
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2203
$N(param)_{refined}$:	273
Programs:	SHELXS-97 [13]

Source of material

A mixture of $Cu(ClO_4)_2$ (0.1 mmol), 2,4-dihydroxypyrimidine-5-carboxybic acid (0.1 mmol) and 2,2'-bipyridine (0.13 mmol) were dissolved in 15 ml of ethanol (95 %). The pH value of the resultant mixture was adjusted to about 4.8 by adding one drop of triethylamine solution and the reaction was kept under water-bath condition at 343 K for 20 h. Afterwards the mixture was filtrated, and the filtrate was cooled to room temperature slowly. Blue block-shaped single crystals of the title compound suitable for *X*-ray diffraction analysis were obtained after one week (yield 42 % based on Cu).

Experimental details

All of the hydrogen atoms were included in calculated positions and treated as riding with d(O–H) = 0.85Å, d(C–H) = 0.93Å and U_{iso}(H) = 1.2 U_{eq}(C,O).

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

Discussion

Inorganic-organic hybrid materials based upon the spontaneous self assembly of transition metal ions and multifunctional organic ligands constitute a dynamic, thriving field that has attracted increasing research interests during the last few decades. The remarkable progress in crystal engineering has provided a wide range of hybrid systems with potential applications and novel topologies [1-6]. However, controlling the unique orientation of organic ligands in hybrid systems and thus prediction of the resulting structure represent an appealing challenges. Some factors such as metal ions, the structural characteristics of polydentate organic ligands [7], pH value of the solution [8], the metal ligand ratio [9], the temperature [10] and different solvent systems, intensively influence the resulting structures. Furthermore, weak interactions also have a great influence that can help to direct and stabilize the architectures [11]. Copper is biologically active and an essential trace element in biology as a component of a wide variety of metallo- proteins and a wealth of enzyme families. Organic ligands with carboxylic groups have been investigated extensively because they usually display various coordination modes and result in a variety of multidimensional frameworks [12]. Continuing our interests in the structures and properties of an extensive series of coordination architectures and oligomers consisting of 2,4-di- hydroxypyrimidine-5-carboxybic acid (Hdpca) and Cu(II) building blocks, the title compound is synthesized. The crystal structure consists of asymmetric units containing one Cu complex, $[Cu(H_2O)(C_{10}H_8N_2)(C_5H_3N_2O_4)(ClO_4)]$. The central copper atom has a slightly distorted octahedral geometry (CuN_2O_4), provided by four oxygen donors from one deprotonated $dpca^-$ ligand, one coordinated water molecule, one ClO_4^- ion and two N atoms from one bipy ligand. The bond lengths and angles around the Cu(II) ion are in the ranges of 1.924 (3) - 2.620 (4) Å and 81.54 (15)° - 175.30 (15)°, respectively, which is in the normal bond range for an octahedral Cu complex. Both bipy and $dpca^-$ act as chelating ligands terminating the coordination of the Cu(II) center. The pyrimidine ring (C11/N4/C12/C13/C14 /N3) and the chelate ring (O2/Cu/O3/C15/C13/C14) are nearly coplanar with a dihedral angle of 7.3°. This can also be indicated by the torsion angle of C11–N3–C14–O2 of -178.4(4)°. The pyridyl ring (N1/C1/C2/ C3/C4/C5) and another chelate ring (Cu/N1/C5/C6/N2) have a dihedral angle of 4.2°. Hydrogen bonding interactions are usually important in the supramolecular architectures. There are persistent O–H···O and N–H···O intermolecular hydrogen-bonding interactions between the pyrimidine group, the perchlorate ion and the coordinated water molecule with the distances in the range of 2.65 - 3.072 Å, which further consolidate the two-dimensional supramolecular network running parallel to the *a* axis.

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	4*e*	–0.2065	0.1512	–0.0690	0.039
H(1W)	4*e*	–0.4109	0.3026	0.0287	0.058
H(2)	4*e*	–0.1565	0.2125	–0.1776	0.046
H(2W)	4*e*	–0.3976	0.3019	0.0976	0.058
H(3)	4*e*	0.0340	0.3606	–0.1859	0.043
H(3D)	4*e*	–0.3401	–0.0981	0.0161	0.029
H(4)	4*e*	0.1742	0.4405	–0.0852	0.036
H(4D)	4*e*	–0.3536	–0.2495	0.1889	0.028
H(7)	4*e*	0.3198	0.4889	0.0182	0.038
H(8)	4*e*	0.4319	0.5468	0.1296	0.046
H(9A)	4*e*	0.3154	0.4786	0.2243	0.041
H(10)	4*e*	0.0932	0.3551	0.2065	0.036
H(12)	4*e*	–0.2447	-0.0973	0.2473	0.025

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*		–0.09543(7)	0.22277(5)	0.08203(3)	0.0299(3)	0.0208(3)	0.0216(3)	–0.0073(3)	0.0052(2)	-0.0005(3)
Cl(1)	4*e*		0.32529(16)	0.08753(12)	0.14147(6)	0.0393(6)	0.0371(6)	0.0319(5)	0.0060(5)	0.0068(5)	0.0018(5)
C(1)	4*e*		–0.1300(6)	0.2103(5)	–0.0725(2)	0.040(3)	0.030(3)	0.027(3)	–0.004(3)	0.002(2)	0.000(2)
C(2)	4*e*		–0.1005(7)	0.2466(5)	–0.1376(2)	0.047(3)	0.047(4)	0.022(2)	0.002(3)	0.002(2)	-0.002(3)
C(3)	4*e*		0.0134(7)	0.3342(5)	–0.1425(2)	0.041(3)	0.047(4)	0.023(3)	0.012(3)	0.012(2)	0.009(3)
C(4)	4*e*		0.0959(6)	0.3822(4)	–0.0827(2)	0.027(3)	0.026(3)	0.038(3)	0.003(2)	0.008(2)	0.009(2)
C(5)	4*e*		0.0616(5)	0.3431(4)	–0.0190(2)	0.018(2)	0.021(3)	0.028(2)	0.007(2)	0.0051(19)	0.004(2)
C(6)	4*e*		0.1400(5)	0.3871(4)	0.0490(2)	0.020(2)	0.016(2)	0.034(3)	0.003(2)	0.005(2)	0.001(2)
C(7)	4*e*		0.2748(6)	0.4622(4)	0.0570(3)	0.025(3)	0.023(3)	0.046(3)	–0.004(2)	0.005(2)	0.003(2)
C(8)	4*e*		0.3414(7)	0.4967(5)	0.1232(3)	0.028(3)	0.030(3)	0.056(4)	–0.006(2)	0.001(3)	-0.004(3)
C(9)	4*e*		0.2726(6)	0.4562(5)	0.1793(3)	0.034(3)	0.033(3)	0.034(3)	–0.008(3)	–0.002(2)	-0.007(3)
C(10)	4*e*		0.1396(6)	0.3821(4)	0.1682(2)	0.035(3)	0.028(3)	0.028(3)	–0.001(2)	0.003(2)	0.000(2)
C(11)	4*e*		–0.3778(6)	–0.1911(4)	0.0943(2)	0.025(3)	0.022(3)	0.025(3)	0.004(2)	0.001(2)	0.006(2)
C(12)	4*e*		–0.2646(5)	–0.0953(4)	0.1988(2)	0.026(3)	0.019(3)	0.017(2)	0.003(2)	0.0022(19)	0.001(2)
C(13)	4*e*		–0.2215(5)	0.0018(4)	0.1658(2)	0.017(2)	0.018(2)	0.018(2)	0.004(2)	0.0000(18)	0.000(2)
C(14)	4*e*		–0.2511(6)	0.0017(4)	0.0912(2)	0.021(3)	0.018(3)	0.023(2)	–0.001(2)	0.001(2)	-0.003(2)
C(15)	4*e*		–0.1647(5)	0.1074(4)	0.2076(2)	0.021(2)	0.019(3)	0.026(3)	0.002(2)	0.0029(19)	-0.003(2)
N(1)	4*e*		–0.0513(5)	0.2582(3)	–0.01397(18)	0.027(2)	0.023(2)	0.021(2)	–0.0034(18)	0.0034(16)	0.002(2)
N(2)	4*e*		0.0741(5)	0.3474(3)	0.10488(18)	0.026(2)	0.019(2)	0.028(2)	–0.0018(18)	0.0044(17)	0.004(2)
N(3)	4*e*		–0.3252(5)	–0.0962(3)	0.06097(18)	0.037(2)	0.021(2)	0.0158(18)	–0.0068(19)	0.0035(17)	0.001(2)
N(4)	4*e*		–0.3349(5)	–0.1888(3)	0.16510(19)	0.031(2)	0.017(2)	0.0225(19)	–0.0004(18)	0.0021(17)	0.007(2)
O(1)	4*e*		–0.4522(4)	–0.2720(3)	0.06387(16)	0.039(2)	0.0217(18)	0.0291(17)	–0.0122(17)	–0.0049(15)	-0.001(2)
O(2)	4*e*		–0.2155(4)	0.0803(3)	0.05130(15)	0.044(2)	0.0239(19)	0.0185(16)	–0.0138(16)	0.0036(15)	0.001(2)
O(3)	4*e*		–0.1336(4)	0.2014(3)	0.17719(15)	0.040(2)	0.0188(19)	0.0219(16)	–0.0068(16)	0.0059(14)	-0.003(1)
O(4)	4*e*		–0.1544(4)	0.0999(3)	0.27216(15)	0.053(2)	0.0228(19)	0.0171(16)	0.0027(17)	0.0020(15)	-0.002(2)
O(5)	4*e*	0.715	0.1541(4)	0.0777(4)	0.1052(3)	0.0445(9)	0.0493(13)	0.0509(13)	0.0035(9)	0.0024(8)	-0.001(1)
O(5')	4*e*	0.285	0.1648(13)	0.0927(11)	0.1463(7)	0.0445(9)	0.0493(13)	0.0509(13)	0.0035(9)	0.0024(8)	-0.001(1)
O(6)	4*e*	0.715	0.3727(6)	–0.0290(3)	0.1660(2)	0.0470(13)	0.0431(9)	0.0491(13)	0.0034(9)	0.0069(10)	0.0057(8)
O(6')	4*e*	0.285	0.3970(15)	–0.0171(10)	0.1447(7)	0.0470(13)	0.0431(9)	0.0491(13)	0.0034(9)	0.0069(10)	0.0057(8)
O(7)	4*e*	0.715	0.3235(7)	0.1599(4)	0.19825(18)	0.0581(14)	0.0531(12)	0.0501(11)	0.003(1)	0.0062(9)	-0.0099(9)
O(7')	4*e*	0.285	0.4188(16)	0.1677(11)	0.1894(6)	0.0581(14)	0.0531(12)	0.0501(11)	0.003(1)	0.0062(9)	-0.0099(9)
O(8)	4*e*	0.715	0.4256(5)	0.1234(4)	0.0918(2)	0.0520(13)	0.0570(14)	0.0493(12)	–0.003(1)	0.0116(10)	0.0080(9)
O(8')	4*e*	0.285	0.3505(16)	0.1419(11)	0.0745(5)	0.0520(13)	0.0570(14)	0.0493(12)	–0.003(1)	0.0116(10)	0.0080(9)
O(9)	4*e*		–0.3502(4)	0.3288(3)	0.06446(17)	0.033(2)	0.044(2)	0.0375(19)	–0.0004(18)	0.0019(16)	-0.001(2)

Acknowledgments. This work was supported by A Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

References

1. Schubert, U.: Cluster-based inorganic--organic hybrid materials. Chem. Soc. Rev. **40** (2011) 575-582.
2. Khan, M. I.; Nome, R. C.; Deb, S.; McNeely, J. H.; Cage, B.; Doedens, R. J.: Inorganic-Organic Hybrid Materials with Novel Framework Structures: Synthesis, Structure, and Magnetic Properties of $[Ni(py)_4]_2V_{10}O_{29}$ and $[Ni_2(py)_5(H_2O)_3]V_4O_{12}$. Cryst. Growth Des. **9** (2009) 2848-2852.
3. Murray, L. J.; Dinca, M.; Long, J. R.: Hydrogenstorage in metal-organic frameworks. Chem. Soc. Rev. **38** (2009) 1294-1314.
4. Düren, T.; Bae, Y. S.; Snurr, R. Q.: Using molecular simulation to characterise metal-organic frameworks for adsorption applications. Chem. Soc. Rev. **38** (2009) 1237-1247.
5. Kuppler, R. J.; Timmons, D. J.; Fang, Q. R.; Li, J. R.; Makal, T. A.; Young, M. D.; Yuan, D. Q.; Zhao, D.; Zhuang, W. J.; Zhou, H. C.: Potential applications of metal-organic frameworks. Coord. Chem. Rev. **253** (2009) 3042-3066.
6. Alkordi, M. H.; Liu, Y. L.; Larsen, R. W.; Eubank, J. F.; Eddaoudi, M.: Zeolite-like Metal-Organic Frameworks as Platforms for Applications: On Metalloporphyrin-Based Catalysts. J. Am. Chem. Soc. **130** (2008) 12639-12641.
7. Chiang, L. M.; Yeh, C. W.; Chan, Z. K.; Wang, K. M.; Chou, Y. C.; Chen, J. D.; Wang, J. C.; Lai, J. Y.: Ag(I) Complexes Containing *N*-Phenyl-*N*'-cyano-formamidine: Syntheses, Structures, and Ligand Conformations. Cryst. Growth Des. **8** (2008) 470-477.
8. Yin, P. X.; Zhang, J.; Li, Z. J.; Qin, Y. Y.; Cheng, J. K.; Zhang, L.; Lin, Q. P.; Yao, Y. G.: Supramolecular Isomerism and Various Chain/Layer Substructures in Silver(I) Compounds: Syntheses, Structures, and Luminescent Properties. Cryst. Growth Des. **9** (2009). 4884-4896.
9. Wang, Y. H.; Chu, K. L.; Chen, H. C.; Yeh, C. W.; Chan, Z. K.; Suen, M. C.; Chen, J. D.; Wang, J. C.: Adjusting the frameworks of polymeric silver(I) complexes with 2-aminopyrimidyl ligands by changing the counterions. CrystEngComm. **8** (2006) 84-93.
10. Forster, P. M.; Burbank, A. R.; Livage, C.; F\'erey, G.; Cheetham, A. K.: The role of temperature in the synthesis of hybrid inorganic-organic materials: the example of cobalt succinates. Chem. Commun. (2004) 368-369.
11. Domasevitch, K. V.; Solntsev, P. V.; Guraiskiy, I. A.; Krautscheid, H.; Rusanov, E. B.; Chernega, A. N.; Howard, J. A. K.: Silver(I) ions bridged by pyridazine: doubling the ligand functionality for the design of unusual 3D coordination frameworks. Dalton Trans. (2007) 3893-3905.
12. Fang, Q. R.; Zhu, G. S.; Xue, M.; Sun, J. Y.; Sun, F. X.; Qiu, S. L.: Structure, Luminescence, and Adsorption Properties of Two Chiral Microporous Metal-Organic Frameworks. Inorg. Chem. **45** (2006) 3582-3587.
13. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.