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Crystal structure of (2,2′-bipyridine-κ^2:*N*1:*N*2)-bis(4-acetamidobenzoato-κ^2:*O*:*O*2)copper(II) hydrate, $Cu(C_{10}H_8N_2)(C_9H_8NO_3)_2 \cdot 2.43H_2O$

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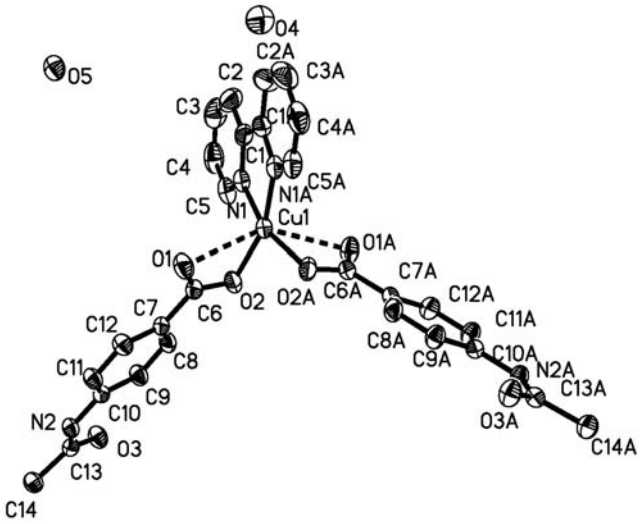

Abstract

$C_{28}H_{28.42}CuN_4O_{8.43}$, orthorhombic, *Pccn* (no. 56), $a = 25.361(4)$ Å, $b = 6.604(1)$ Å, $c = 16.771(3)$ Å, $V = 2808.8$ Å^3, $Z = 4$, $R_{gt}(F) = 0.036$, $wR_{ref}(F^2) = 0.112$, $T = 296$ K.

Source of material

A mixture of 4-acetamidobenzoic acid (0.072 g, 0.4 mmol), copper chloride (0.034 g, 0.2 mmol) and 2,2′-bipyridine (2,2′-bipy, 0.031 g, 0.2 mmol) was dissolved in 15 ml of 95 % ethanol. The pH value of the resultant mixture was adjusted to about 6.5 by adding three drops of triethylamine solution and the reaction was kept under water-bath condition at 343 K for 20 h. Afterwards, the system was filtrated, and the filtrate was cooled to room temperature slowly. Deep blue single crystals suitable for X-ray diffraction analysis were obtained after three weeks.

Experimental details

Hydrogen atoms bound to carbon atoms were placed in calculated positions and treated as riding on their parent atoms with d(C—H) = 0.93 Å, U_{iso}(H) = 1.2 U_{eq}(C) (aromtic); and d(C—H) = 0.96 Å, U_{iso}(H) = 1.5 U_{eq}(C) (methyl). Hydrogen atoms attached to O atoms of water molecule and N atom were restrained with d(O—H) = 0.85 Å, d(N—H) = 0.86 Å and U_{iso}(H) = 1.2 U_{eq}(O,N) in the refinement.

Discussion

Inorganic-organic hybrid materials are of great interest because of their intriguing structural features and potential in various applications, such as electrical conductivity, photochemistry, ion exchange, catalysis, biochemistry, and nonlinear optical behavior [1-3]. A large variety of ligands containing bridging functionalities such as carboxylates, phosphonates, 4,4′-bipy, and 2,2′-bipy have been exploited to prepare new inorganic-organic hybrid materials [4]. The metal-halide-bipy (bipy: 2,2′-bipy or 4,4′-bipy) systems have attracted more and more attention in recent years not only for their intrinsic aesthetic appeals but also for their various potential applications, as well as the special coordination modes of bipy [5-7].

The crystal structure of the title complex contains a [Cu(2,2′-bipy)$(C_9H_8NO_3)_2$] complex and lattice water molecules. The Cu(II) ion is coordinated by two nitrogen atoms from one 2,2′-bipyridine molecule and four oxygen atoms from two 4-acetamidobenzoate anions in a distorted octahedral manner, in which O1 and O1A occupy the axial positions, while O2, O2A, N1 and N1A are located at the equatorial plane. The bond angle of O1–Cu1–O1A is 142.13(8)°, and at the equatorial plane, the bond angles of N1–Cu1–N1A, N1A–Cu1–O2A, O2A–Cu1–O2 and O2–Cu1–N1 are 81.4(1)°, 94.06(9)°, 95.5(1)° and 94.06(9)°, respectively, with the sum of 365.02° close to 360°. The bond length Cu1—O1 (or Cu1—O1A) is 2.552 Å, indicating a weak coordination bonding between the carbonyl oxygen atoms of 4-carboxylaminobenzoate and the copper ion [8].

In the complex, there exist hydrogen bonding interactions. The uncoordinated and coordinated carbonyl oxygen atoms of 4-acetamidobenzoate ligands and the free water molecules are linked by strong hydrogen bonds: N2–H2A···O5 (d(N2–H2A···O5) = 2.907(3) Å, ∠N2–H2A···O5 = 176°), O5–H5A···O1 (d(O5–H5A···O1) = 2.860(3) Å, ∠O5–H5A···O1 = 174°) and O5–H5B···O3 (d(O5–H5B···O3) = 2.848(3) Å, ∠O5–H5B···O3 = 175°).

Table 1. Data collection and handling.

Crystal:	blue block, size 0.20 × 0.20 × 0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	8.39 cm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX-II, φ/ω
$2\theta_{max}$:	52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	12166, 2761
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2054
$N(param)_{refined}$:	191
Programs:	SHELXS-97, SHELXL-97 [8]

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

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(2)	8*e*		0.2721	0.6003	0.4337	0.103
H(3)	8*e*		0.3190	0.3063	0.4204	0.123
H(4)	8*e*		0.3398	0.1847	0.2956	0.110
H(5)	8*e*		0.3121	0.3609	0.1854	0.085
H(8)	8*e*		0.3637	0.4057	0.0062	0.066
H(9)	8*e*		0.4325	0.3174	–0.0766	0.065
H(11)	8*e*		0.4807	0.8951	–0.0753	0.064
H(12)	8*e*		0.4118	0.9806	0.0066	0.064
H(14A)	8*e*		0.6012	0.4107	–0.1909	0.081
H(14B)	8*e*		0.5669	0.5282	–0.2535	0.081
H(14C)	8*e*		0.5716	0.2918	–0.2584	0.081
H(2A)	8*e*		0.5255	0.6641	–0.1476	0.055
H(5A)	8*e*		0.6032	0.9450	0.8460	0.088
H(5B)	8*e*		0.5515	0.9905	0.8285	0.088
H(4A)	8*e*	0.43	0.2618	0.1556	0.5651	0.144

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*d*		¼	¾	0.15235(3)	0.0342(2)	0.0637(3)	0.0567(3)	–0.0030(2)	0	0
C(1)	8*e*		0.2651(1)	0.6553(4)	0.3154(2)	0.049(1)	0.072(2)	0.060(2)	–0.013(1)	–0.006(1)	0.008(1)
C(2)	8*e*		0.2806(1)	0.5512(6)	0.3833(2)	0.084(2)	0.104(3)	0.070(2)	–0.015(2)	–0.020(2)	0.012(2)
C(3)	8*e*		0.3083(2)	0.3769(7)	0.3752(3)	0.084(3)	0.105(3)	0.117(3)	–0.004(2)	–0.033(2)	0.044(3)
C(4)	8*e*		0.3207(1)	0.3039(5)	0.3013(3)	0.053(2)	0.080(2)	0.142(4)	0.003(2)	–0.012(2)	0.033(2)
C(5)	8*e*		0.3042(1)	0.4104(4)	0.2360(2)	0.042(1)	0.068(2)	0.104(2)	0.001(1)	0.006(2)	0.010(2)
C(6)	8*e*		0.33479(9)	0.7578(4)	0.0673(2)	0.035(1)	0.065(2)	0.050(1)	0.003(1)	–0.004(1)	0.003(1)
C(7)	8*e*		0.37983(8)	0.7021(4)	0.0146(1)	0.034(1)	0.058(1)	0.045(1)	–0.0034(9)	–0.003(1)	0.003(1)
C(8)	8*e*		0.38720(9)	0.5051(4)	–0.0107(2)	0.045(1)	0.056(1)	0.063(2)	–0.017(1)	0.006(1)	–0.001(1)
C(9)	8*e*		0.42849(9)	0.4511(4)	–0.0603(2)	0.050(1)	0.048(1)	0.064(2)	–0.011(1)	0.010(1)	–0.005(1)
C(10)	8*e*		0.46384(8)	0.5982(3)	–0.0853(1)	0.038(1)	0.048(1)	0.042(1)	–0.0027(9)	–0.001(1)	0.0017(9)
C(11)	8*e*		0.4570(1)	0.7957(3)	–0.0593(2)	0.052(1)	0.045(1)	0.062(2)	–0.010(1)	0.012(1)	0.001(1)
C(12)	8*e*		0.41570(9)	0.8472(3)	–0.0101(2)	0.054(2)	0.044(1)	0.062(2)	–0.003(1)	0.008(1)	–0.001(1)
C(13)	8*e*		0.52241(9)	0.3850(3)	–0.1698(1)	0.041(1)	0.045(1)	0.047(1)	–0.000(1)	–0.005(1)	0.001(1)
C(14)	8*e*		0.56981(9)	0.4058(4)	–0.2230(2)	0.052(1)	0.050(1)	0.060(2)	0.002(1)	0.007(1)	–0.001(1)
N(1)	8*e*		0.27721(7)	0.5833(3)	0.2424(1)	0.035(1)	0.061(1)	0.071(2)	–0.0039(9)	0.001(1)	0.004(1)
N(2)	8*e*		0.50654(7)	0.5601(3)	–0.1362(1)	0.042(1)	0.042(1)	0.055(1)	–0.0079(8)	0.0066(9)	–0.0007(8)
O(1)	8*e*		0.33394(7)	0.9221(3)	0.1028(1)	0.047(1)	0.067(1)	0.089(1)	0.0021(9)	0.014(1)	–0.011(1)
O(2)	8*e*		0.29755(7)	0.6295(3)	0.0741(1)	0.0416(9)	0.083(1)	0.067(1)	–0.0131(9)	0.0096(8)	–0.011(1)
O(3)	8*e*		0.50115(8)	0.2215(2)	–0.1586(1)	0.059(1)	0.0455(9)	0.078(1)	–0.0085(7)	0.0126(9)	–0.0060(8)
O(5)	8*e*		0.57500(8)	0.8993(3)	0.8254(1)	0.071(1)	0.0473(9)	0.102(2)	–0.0114(8)	0.013(1)	–0.013(1)
O(4)	4*c*	0.43(1)	¼	¼	0.5357(1)	0.121(5)	0.119(5)	0.120(5)	0.001(1)	0	0

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References

1. Chen, W.-T.; Wang, M.-S.; Liu, X.; Guo, G.-C.; Huang, J.-S.: Investigations of Group 12 (IIB) Metal Halide/Pseudohalide - BipySystems: Syntheses, Structures, Properties, and TDDFT Calculations (Bipy: 2,2′-bipyridine or 4,4′-bipyridine). Cryst. Growth Des. **10** (2006) 2289-2300.
2. Jung, M. C; Munro, N.; Shi, G.; Michael, A. C.; Weber, S. G.: Use of Tris(2,2′-bipyridine)osmium as a Photoluminescence - Following Electron Transfer Reagent for Postcolumn Detection in Capillary High-Performance Liquid Chromatography. Anal. Chem. **78** (2006) 1761-1768.
3. Fojta, M.; Billova, S.; Havran, L.; Pivonkova, H.; Cernocka, H.; Horakova, P.; Palecek, E.: Osmium Tetroxide, 2,2′-Bipyridine: Electroactive Marker for Probing Accessibility of Tryptophan Residues in Proteins. Anal. Chem. **80** (2008) 4598-4605.
4. Hulvey, Z.; Ayala, E.; Furman, J. D.; Forster, P. M.; Cheetham, A. K.: Structural Diversity in Coordination Polymers Composed of Divalent Transition Metals, 2,2′-Bipyridine, and Perfluorinated Dicarboxylates. Cryst. Growth Des. **9** (2009) 4759-4765
5. Nozaki, K.; Takamori, K.; Nakatsugawa, Y.; Ohno, T.: Theoretical Studies of Phosphorescence Spectra of Tris(2,2′-bipyridine) Transition Metal Compounds. Inorg. Chem. **45** (2006) 6161-6178.
6. Adugna, S.; Revunova, K.; Djukic, B.; Gorelsky, S. I.; Jenkins, H. A.; Lemaire, M. T.: Persistent Metal Bis(Hexafluoroacetylacetonato) Complexes Featuring a 2,2′-Bipyridine Substituted Triarylamminium Radical Cation. Inorg. Chem. **49** (2010) 10183-10190.
7. Li, W.; Li, C.-H.; Yang, Y.-Q.; Kang, Y.-F.: Hydrothermal Synthesis, Crystal Structure and Electrochemical Properties of the Complex Cu(α-Furacrylic acid)$_2$(phen). Chin. J. Struct. Chem. **26** (2007) 1228-1232.
8. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.