Crystal structure of aqua-(1,10-phenanthroline)-(2-(1,2,4-triazol-1-yl)-acetate)copper(II)nitrate, $C_{16}H_{14}CuN_6O_6$

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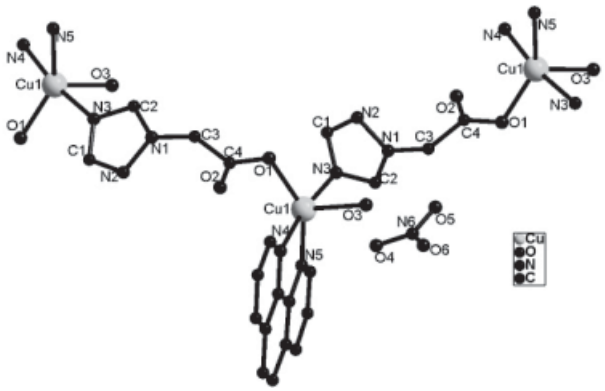

Abstract

$C_{16}H_{14}CuN_6O_6$, monoclinic, $P2_1/c$ (no. 14), a = 12.831(4) Å, b = 14.525(4) Å, c = 9.539(3) Å, β = 103.701(8)°, V = 1727.2 Å^3, Z = 4, $R_{gt}(F)$ = 0.0493, $wR_{ref}(F^2)$ = 0.1137, T = 293 K.

Table 1. Data collection and handling.

Crystal:	blue blocks, size 0.12×0.25×0.45 mm
Wavelength:	Mo K_α radiation (0.71070 Å)
μ:	13.17 cm^{-1}
Diffractometer, scan mode:	Rigaku Mercury CCD, ω
$2\theta_{max}$:	50.68°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	16513, 3157
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2799
$N(param)_{refined}$:	270
Programs:	SHELX [12]

Source of material

A solution of 2-(1,2,4-triazol-1-yl)acetate (0.064 g, 0.5 mmol) in 10 mL H_2O was adjusted to approximately pH 6 with 1 mol·L^{-1} NaOH solution. Then $Cu(NO_3)_2{\cdot}3H_2O$ (0.121 g, 0.5 mmol) in 10 mL aqueous solution was added with stirring. A methanolic solution (7 mL) of 1,10-phenanthroline (0.100 g, 0.5 mmol) was added to the above mixture with continuous stirring and the result solutions were filtered. Blue block-shaped single crystals of the title compound suitable for X-ray diffraction analysis were obtained after one week (yield 51 % based on Cu).

Discussion

Studies on metal-organic frameworks (MOFs) have rapidly increased because of their intriguing variety of topologies and potential applications as functional materials [1-4]. The ligands and metal centers both are the key to the design and construction of metal-organic frameworks with fascinating topology and physicochemical properties. A large number of mononuclear, oligonuclear, and polynuclear transition metal complexes of 1- and 4-substituted 1,2,4-triazole derivatives have been synthesized and characterized due to their interesting properties and novel topologies [5-8]. On the other hand, because of the diversity of the coordination modes and high structural stability, carboxylate ligands are frequently used for the construction of MOFs [9-11]. In this paper, we selected 2-(1,2,4-triazol-1-yl)acetate (*tza*) and 1,10-Phenanthroline (*phen*) to react with Cu(II) ions to obtain a new MOF. The X-ray structural analysis shows that the title complex crystallizes monoclinic, space group $P2_1/c$. The asymmetric unit of the title structure consists of a Cu^{2+} ion, a 1,10-phenanthroline ligand (*phen*), a 2-(1,2,4-triazol-1-yl)acetate (*tza*) ligand, one coordinated water molecule and one NO_3^- counter anion. The central copper atom is distorted trigonal bipyramidal coordinated by two oxygen donors from one deprotonated tza^- ligand, one coordinated water molecule, and three N atoms from one *phen* ligand and one triazole nitrogen atom from another tza^- ligand. The bond lengths around the Cu(II) are in the ranges of 1.969(3)-2.222(3) Å, which is in the normal bond range for an trigonal bipyramidal Cu complex. The carboxylate group of the tza^- ligand shows a monodentate coordination mode. The triazolyl group links to the next Cu metal center and exhibits a monodentate coordination mode. In conclusion each *tza* acts as a bidentate node and bridges two neighbouring Cu (II) atoms to yield a 1D chain, with the bridged Cu···Cu distance of 8.6079(19) Å. Hydrogen bonding interactions are important in the supramolecular architectures. The nitrate counter anion forms one medium strong hydrogen bond to the coordinated water molecule. Furthermore, there are inter-chain hydrogen bonding interactions between the coordinaton water molecules and the uncoordinated oxygen atoms from carboxylate groups forming 2D layers.

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

Atom	Site	x	y	z	U_{iso}
H(1A)	4*e*	0.5658	0.4498	0.8158	0.038
H(2A)	4*e*	0.3367	0.6293	0.7482	0.039
H(3A)	4*e*	0.5192	0.7069	1.0650	0.040
H(3B)	4*e*	0.4138	0.7398	0.9570	0.040
H(5A)	4*e*	0.3158	0.3632	0.2827	0.047
H(6A)	4*e*	0.1777	0.3119	0.0971	0.057
H(7A)	4*e*	0.0056	0.3043	0.1282	0.058
H(12A)	4*e*	–0.0568	0.4222	0.7807	0.056
H(13A)	4*e*	0.0953	0.4707	0.9446	0.056
H(14A)	4*e*	0.2559	0.4805	0.8766	0.047
H(15A)	4*e*	–0.1202	0.3213	0.3034	0.057
H(16A)	4*e*	–0.1412	0.3619	0.5242	0.058
H(2W)	4*e*	0.303(5)	0.570(4)	0.370(6)	0.08(2)
H(1W)	4*e*	0.395(4)	0.581(3)	0.464(5)	0.06(2)

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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*	0.33482(3)	0.44255(3)	0.58752(4)	0.0244(2)	0.0298(3)	0.0308(3)	–0.0014(2)	0.0039(2)	–0.0058(2)
O(1)	4*e*	0.5433(2)	0.8712(2)	0.9605(3)	0.030(1)	0.024(1)	0.039(1)	–0.002(1)	0.011(1)	–0.002(1)
O(2)	4*e*	0.6025(2)	0.7731(2)	0.8191(3)	0.053(2)	0.040(2)	0.046(2)	–0.006(1)	0.027(1)	–0.006(1)
O(3)	4*e*	0.3343(3)	0.5668(2)	0.4514(3)	0.037(2)	0.042(2)	0.038(2)	–0.006(1)	0.005(1)	0.007(1)
O(4)	4*e*	0.2230(3)	0.5755(2)	0.1555(4)	0.056(2)	0.067(2)	0.069(2)	–0.016(2)	0.011(2)	0.006(2)
O(5)	4*e*	0.3106(3)	0.7009(3)	0.1776(4)	0.096(3)	0.074(3)	0.063(2)	–0.030(2)	–0.004(2)	0.000(2)
O(6)	4*e*	0.2117(3)	0.6668(3)	–0.0267(4)	0.107(3)	0.091(3)	0.041(2)	0.008(2)	–0.012(2)	0.006(2)
N(1)	4*e*	0.4809(2)	0.6310(2)	0.8863(3)	0.035(2)	0.026(2)	0.029(2)	–0.004(1)	0.008(1)	–0.003(1)
N(2)	4*e*	0.5634(2)	0.5696(2)	0.9121(3)	0.031(2)	0.036(2)	0.033(2)	–0.000(1)	0.001(1)	–0.002(1)
N(3)	4*e*	0.4261(2)	0.5169(2)	0.7413(3)	0.029(2)	0.025(2)	0.032(2)	–0.000(1)	0.002(1)	–0.004(1)
N(4)	4*e*	0.2295(2)	0.3858(2)	0.4225(3)	0.031(2)	0.028(2)	0.029(2)	–0.002(1)	0.004(1)	–0.003(1)
N(5)	4*e*	0.2047(2)	0.4389(2)	0.6775(3)	0.029(2)	0.028(2)	0.030(2)	0.001(1)	0.005(1)	–0.002(1)
N(6)	4*e*	0.2461(3)	0.6493(2)	0.1017(4)	0.033(2)	0.051(2)	0.042(2)	0.001(2)	0.007(2)	–0.004(2)
C(1)	4*e*	0.5264(3)	0.5027(3)	0.8228(4)	0.031(2)	0.030(2)	0.033(2)	0.000(2)	0.005(2)	0.002(2)
C(2)	4*e*	0.4012(3)	0.5988(3)	0.7845(4)	0.028(2)	0.033(2)	0.034(2)	0.001(2)	0.001(2)	–0.001(2)
C(3)	4*e*	0.4861(3)	0.7175(2)	0.9638(4)	0.040(2)	0.028(2)	0.033(2)	–0.007(2)	0.012(2)	–0.005(2)
C(4)	4*e*	0.5492(3)	0.7908(2)	0.9066(4)	0.030(2)	0.028(2)	0.028(2)	–0.002(2)	0.004(2)	0.001(2)
C(5)	4*e*	0.2466(3)	0.3603(3)	0.2967(4)	0.042(2)	0.036(2)	0.038(2)	–0.002(2)	0.008(2)	–0.005(2)
C(6)	4*e*	0.1636(4)	0.3291(3)	0.1846(4)	0.062(3)	0.044(2)	0.032(2)	–0.001(2)	0.002(2)	–0.013(2)
C(7)	4*e*	0.0615(4)	0.3239(3)	0.2034(5)	0.055(3)	0.036(2)	0.045(2)	–0.004(2)	–0.009(2)	–0.007(2)
C(8)	4*e*	0.0412(3)	0.3481(2)	0.3369(4)	0.035(2)	0.025(2)	0.045(2)	–0.001(2)	–0.005(2)	–0.001(2)
C(9)	4*e*	0.1287(3)	0.3801(2)	0.4441(4)	0.027(2)	0.023(2)	0.036(2)	–0.000(1)	0.004(2)	0.003(1)
C(10)	4*e*	0.1156(3)	0.4076(2)	0.5820(4)	0.027(2)	0.022(2)	0.037(2)	0.002(2)	0.006(2)	0.003(2)
C(11)	4*e*	0.0153(3)	0.4000(3)	0.6152(4)	0.029(2)	0.030(2)	0.052(2)	0.003(2)	0.010(2)	0.009(2)
C(12)	4*e*	0.0085(3)	0.4254(3)	0.7544(5)	0.039(2)	0.046(2)	0.061(3)	0.004(2)	0.026(2)	0.007(2)
C(13)	4*e*	0.0985(4)	0.4547(3)	0.8513(5)	0.051(3)	0.051(3)	0.042(2)	0.004(2)	0.020(2)	0.004(2)
C(14)	4*e*	0.1952(3)	0.4605(3)	0.8093(4)	0.045(2)	0.042(2)	0.031(2)	0.003(2)	0.009(2)	0.001(2)
C(15)	4*e*	–0.0612(3)	0.3423(3)	0.3725(5)	0.029(2)	0.037(2)	0.068(3)	–0.003(2)	–0.007(2)	0.004(2)
C(16)	4*e*	–0.0738(3)	0.3667(3)	0.5045(5)	0.028(2)	0.039(2)	0.074(3)	–0.002(2)	0.009(2)	0.009(2)

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