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Refinement of the crystal structure of aquabis(2,2′-bipyridine)-bis(terephtalato)dicopper(II), $Cu_2(H_2O)(C_{10}H_8N_2)_2(C_8H_4O_4)_2$

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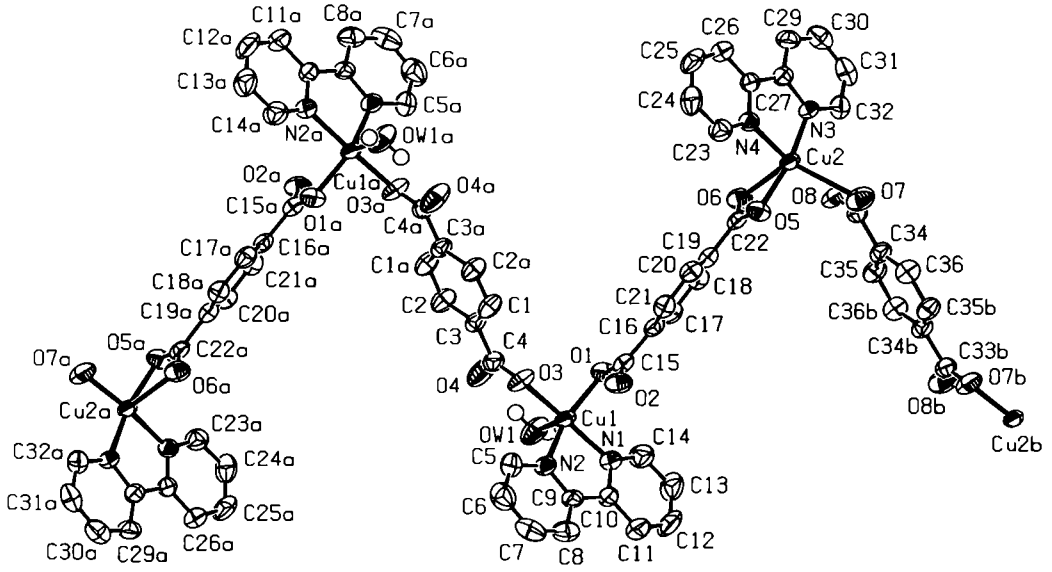

Abstract

$C_{36}H_{26}Cu_2N_4O_9$, monoclinic, $P12_1/c1$ (no. 14), a = 13.732(3) Å, b = 17.188(3) Å, c = 14.127(3) Å, β = 104.57(3)°, V = 3227.1 Å^3, Z = 4, $R_{gt}(F)$ = 0.032, $wR_{ref}(F^2)$ = 0.089, T = 293 K.

Source of material

Blue block-shaped crystals of the title compound were obtained by hydrothermal reaction of $CuSO_4 \cdot 5H_2O$ (1.00 mmol, 0.250 g), 2,2′-bipyridine (1.00 mmol, 0.156 g), 1,4-benzenedicarboxylic acid (1.00 mmol, 0.166 g), NaOH (1.5 mmol, 0.060 g) and water (15 mL) in a 23 mL Teflon-lined reaction vessel at 170 °C for 72 h (yield 83 % based on initial $CuSO_4 \cdot 5H_2O$ input).

Discussion

The crystal structure of the title complex was refined to obtain more accurate structural parameters than those received in the first analysis [1].

In the structure, there are two independent Cu^{2+} ions with different square-pyramidal environments which are similar for Co^{2+} ions in the isotypic $Co_2(H_2O)(bipy)_2(tp)_2$ structure [2]. The $Cu1^{2+}$ environment is completed by two nitrogen atoms from a bidentate chelating 2,2′-bipyridine (bipy) ligand, two oxygen atoms from two different bis-monodentate terephthalato (tp) ligands and one oxygen atom from a coordinated water molecule. The square plane of $Cu1^{2+}$ is formed by two nitrogen atoms and two carboxylato oxygen atoms with Cu1—N1, Cu1—N2, Cu1—O1 and Cu1—O3 bond distances of 2.012(2) Å, 2.000(2) Å, 1.988(2) Å and 1.955(2) Å, respectively, and N2–Cu1–O1, O1–Cu1–O3, O3–Cu1–N1 and N1–Cu1–N2 bond angles of 91.31(8)°, 92.07(8)°, 93.99(8)° and 80.46(8)°, respectively. The total amount of above-stated bond angles is about 357.83° showing a slightly distorted plane. The axial position of the pyramid is occupied by OW1 of the coordinated water ligand with the Cu1—OW1 bond distance of 2.211(2) Å. The square pyramidal environment of the $Cu2^{2+}$ being severely distorted is formed by two nitrogen atoms from a bidentate chelating bipy ligand, two oxygen atoms from one bidentate chelating end of a tp ligand, one oxygen atom from a bis-monodentate tp ligand. The basal plane is completed by N3, N4, O5 and O7 atoms. The bond distances of N3—Cu2, N4—Cu2, O5—Cu2 and O7—Cu2 are 1.983(2) Å, 1.993(2) Å, 1.988(2) Å and 1.936(2) Å, respectively, and the O7–Cu2–N3, N3–Cu2–N4, O5–Cu2–N4 and O7–Cu2–O5 bond angles are 95.39(8)°, 81.43(8)°, 92.32(8)° and 91.91(8)°, respectively. The total amount of the above bond angles is 361.05°, which also means that the plane is slightly distorted. The axial position of the square pyramid is occupied by the O6 atom with Cu2—O6 bond distance being 2.411(2) Å, which is much longer than other bond distances, and the O6–Cu2–O5 bond angle is only 59.58(7)°, resulting in a severely distorted square pyramid geometry of $Cu2^{2+}$. The O2 atoms of tp ligands are 2.619 Å away from the Cu center and hence, are deemed to be non-coordinated [3], although another literature [4] reported that weak interaction still exits even the bond distance of Cu—O is up to 2.8 Å. The O4 and O8 atoms are further away from Cu center (3.278 Å and 2.869 Å, respectively), so it is decidedly deemed to be non-coordinated. In the title compound, there are two coordination modes of the organic ligands, namely bis-monodentate-bridging

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(a) and monochelating-monobridging (b) tp ligands, which can also be found for $Co_2(bipy)_2(tp)_2(H_2O)$ [2] and $Ni(tp)(2,2'\text{-bipy})(H_2O)$ [5].

The $Cu1^{2+}$ and $Cu2^{2+}$ ions are bridged by mode (b)-tp, while the $Cu1^{2+}$ and $Cu1A^{2+}$ (A: $-x+1,-y+1,-z+2$) ions are bridged by mode (a)-tp ligands. A series of above-stated tp ligands bridge the Cu^{2+} ions to generate a zigzag chain, with neighboring bipy ligands *trans* to each other. The ring of N1-C5-C6-C7-C8-C9 and the ring of N2-C10-C11-C12-C13-C14 are not coplanar with a deviation angle of 6.2°. The coordinated water ligand is a double hydrogen bond donor toward oxygen atoms (O4 and O8) from the carboxylato groups, which belong to different tp ligands. One hydrogen bond (OW1–HW1B···O4) is intramolecular and the other (OW1–HW1A···O8) connects adjacent zigzag chains. Thus, the adjacent zigzag chains wrap together via strong π-π stacking interactions (mean interplanar distance: 3.32 Å) between one ring of tp ligands and hydrogen bonds to generate double chains with bipy ligands attached to both sides of the double chains. Furthermore, the double chains are linked to form 3D network via π-π stacking interactions and hydrogen bonds. The R values and the remaining electron difference density peak heights (0.374 eÅ^{-3}, –0.411 eÅ^{-3}) of the present analysis are significantly smaller than those values of the previous study ($R_{gt}(F)$ = 0.050, $wR_{ref}(F^2)$ = 0.101; 0.702 Å^{-3}, –0.489 Å^{-3} [1]).

Table 1. Data collection and handling.

Crystal:	blue block, size 0.11 × 0.12 × 0.37 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	13.83 cm^{-1}
Diffractometer, scan mode:	Rigaku R-AXIS RAPID IP, ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	25985, 5991
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4901
$N(param)_{refined}$:	564
Programs:	SHELXS-97 [6], SHELXL-97 [7]

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

Atom	Site	x	y	z	U_{iso}
HW(1A)	4e	0.234(3)	0.218(2)	0.738(2)	0.032(9)
HW(1B)	4e	0.256(2)	0.276(2)	0.807(2)	0.034(9)
H(1)	4e	0.580(2)	0.378(2)	1.034(2)	0.037(9)
H(2)	4e	0.331(2)	0.505(1)	0.909(2)	0.014(7)
H(5)	4e	0.390(2)	0.227(2)	1.089(2)	0.020(7)
H(6)	4e	0.376(2)	0.155(2)	1.222(2)	0.028(8)
H(7)	4e	0.371(2)	0.020(2)	1.216(2)	0.024(8)
H(8)	4e	0.373(2)	−0.042(2)	1.067(2)	0.030(8)
H(11)	4e	0.355(3)	−0.084(2)	0.908(2)	0.038(9)
H(12)	4e	0.347(3)	−0.118(2)	0.759(3)	0.05(1)
H(13)	4e	0.371(3)	−0.022(2)	0.647(3)	0.039(9)
H(14)	4e	0.400(2)	0.105(2)	0.697(2)	0.017(7)
H(17)	4e	0.573(2)	0.229(1)	0.651(2)	0.013(6)
H(18)	4e	0.696(2)	0.265(2)	0.573(2)	0.023(7)
H(20)	4e	0.898(2)	0.258(2)	0.834(2)	0.021(7)
H(21)	4e	0.778(2)	0.227(2)	0.912(2)	0.016(7)
H(23)	4e	1.075(2)	0.372(2)	0.792(2)	0.032(8)
H(24)	4e	1.121(2)	0.493(2)	0.869(2)	0.025(8)
H(25)	4e	1.162(2)	0.593(2)	0.782(2)	0.020(7)
H(26)	4e	1.162(2)	0.582(2)	0.616(2)	0.021(7)
H(29)	4e	1.151(3)	0.548(2)	0.460(2)	0.042(9)
H(30)	4e	1.140(2)	0.508(2)	0.302(2)	0.023(7)
H(31)	4e	1.099(2)	0.377(2)	0.263(2)	0.028(8)
H(32)	4e	1.076(2)	0.292(2)	0.383(2)	0.019(7)
H(35)	4e	0.902(2)	0.108(2)	0.432(2)	0.017(7)
H(36)	4e	1.158(2)	0.017(2)	0.607(2)	0.029(8)

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)	4e	0.40877(2)	0.19453(2)	0.88513(2)	0.0202(2)	0.0097(2)	0.0187(2)	−0.0037(1)	0.0058(1)	−0.0011(1)
Cu(2)	4e	1.05085(2)	0.30722(2)	0.58803(2)	0.0181(2)	0.0100(2)	0.0163(2)	−0.0023(1)	0.0048(1)	−0.0009(1)
OW(1)	4e	0.2574(2)	0.2277(1)	0.7973(2)	0.026(1)	0.020(1)	0.032(1)	−0.0015(9)	−0.0054(9)	−0.009(1)
O(1)	4e	0.4903(1)	0.2230(1)	0.7923(1)	0.018(1)	0.0198(9)	0.0209(9)	−0.0024(7)	0.0046(8)	0.0041(8)
O(2)	4e	0.6033(1)	0.1733(1)	0.9193(1)	0.025(1)	0.0193(9)	0.0184(9)	−0.0023(8)	0.0038(8)	0.0058(8)
O(3)	4e	0.4349(1)	0.29488(9)	0.9519(1)	0.028(1)	0.0108(8)	0.025(1)	−0.0024(7)	0.0001(8)	−0.0018(7)
O(4)	4e	0.3040(2)	0.3669(1)	0.8715(2)	0.027(1)	0.0183(9)	0.042(1)	−0.0001(8)	−0.007(1)	−0.0094(9)
O(5)	4e	0.9857(1)	0.2655(1)	0.6881(1)	0.0170(9)	0.0196(9)	0.0192(9)	−0.0010(7)	0.0050(8)	0.0041(8)
O(6)	4e	0.8722(1)	0.3218(1)	0.5681(1)	0.024(1)	0.0174(9)	0.0180(9)	−0.0008(8)	0.0044(8)	0.0051(7)
O(7)	4e	1.0249(2)	0.2121(1)	0.5125(1)	0.036(1)	0.0126(9)	0.0200(9)	−0.0029(8)	0.0065(9)	−0.0002(7)
O(8)	4e	1.1588(2)	0.1627(1)	0.6185(1)	0.031(1)	0.022(1)	0.023(1)	−0.0076(8)	0.0022(9)	−0.0053(8)
N(1)	4e	0.3828(2)	0.1393(1)	1.0019(2)	0.016(1)	0.014(1)	0.020(1)	−0.0034(8)	0.0033(9)	−0.0030(9)
N(2)	4e	0.3902(2)	0.0861(1)	0.8323(2)	0.018(1)	0.015(1)	0.021(1)	−0.0020(9)	0.0058(9)	−0.0013(9)
N(3)	4e	1.0928(2)	0.3683(1)	0.4860(2)	0.016(1)	0.012(1)	0.019(1)	−0.0032(8)	0.0049(9)	−0.0029(9)
N(4)	4e	1.0937(2)	0.4042(1)	0.6645(2)	0.013(1)	0.015(1)	0.017(1)	−0.0013(8)	0.0031(9)	−0.0009(9)
C(1)	4e	0.5461(2)	0.4281(2)	1.0208(2)	0.025(2)	0.013(1)	0.022(1)	0.004(1)	0.001(1)	0.001(1)
C(2)	4e	0.4010(2)	0.5045(1)	0.9460(2)	0.021(2)	0.015(1)	0.022(1)	0.002(1)	−0.001(1)	−0.000(1)
C(3)	4e	0.4473(2)	0.4315(1)	0.9661(2)	0.025(1)	0.011(1)	0.013(1)	0.000(1)	0.006(1)	0.001(1)
C(4)	4e	0.3892(2)	0.3592(1)	0.9264(2)	0.025(2)	0.016(1)	0.016(1)	−0.004(1)	0.008(1)	−0.003(1)
C(5)	4e	0.3823(2)	0.1722(2)	1.0877(2)	0.028(2)	0.022(1)	0.024(2)	−0.002(1)	0.011(1)	−0.006(1)
C(6)	4e	0.3783(2)	0.1287(2)	1.1689(2)	0.029(2)	0.035(2)	0.022(2)	−0.002(1)	0.010(1)	−0.004(1)
C(7)	4e	0.3739(2)	0.0488(2)	1.1615(2)	0.023(2)	0.036(2)	0.020(1)	−0.007(1)	0.006(1)	0.005(1)
C(8)	4e	0.3733(2)	0.0137(2)	1.0727(2)	0.018(1)	0.022(1)	0.026(2)	−0.004(1)	0.003(1)	0.002(1)
C(9)	4e	0.3782(2)	0.0606(1)	0.9941(2)	0.010(1)	0.015(1)	0.022(1)	−0.003(1)	0.003(1)	−0.002(1)
C(10)	4e	0.3765(2)	0.0310(1)	0.8956(2)	0.015(1)	0.013(1)	0.025(1)	−0.000(1)	0.006(1)	−0.002(1)
C(11)	4e	0.3627(2)	−0.0469(2)	0.8682(2)	0.026(2)	0.015(1)	0.034(2)	0.001(1)	0.011(1)	0.001(1)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(12)	4*e*	0.3600(2)	−0.0663(2)	0.7727(2)	0.037(2)	0.014(1)	0.035(2)	−0.002(1)	0.009(1)	−0.009(1)
C(13)	4*e*	0.3730(2)	−0.0100(2)	0.7078(2)	0.030(2)	0.026(2)	0.025(2)	−0.001(1)	0.007(1)	−0.010(1)
C(14)	4*e*	0.3872(2)	0.0662(2)	0.7400(2)	0.029(2)	0.021(1)	0.021(1)	−0.004(1)	0.007(1)	−0.003(1)
C(15)	4*e*	0.5806(2)	0.2047(1)	0.8376(2)	0.019(1)	0.011(1)	0.017(1)	−0.001(1)	0.003(1)	−0.002(1)
C(16)	4*e*	0.6616(2)	0.2237(1)	0.7868(2)	0.020(1)	0.010(1)	0.019(1)	0.001(1)	0.005(1)	0.001(1)
C(17)	4*e*	0.6405(2)	0.2345(1)	0.6859(2)	0.016(1)	0.015(1)	0.019(1)	−0.001(1)	0.000(1)	−0.003(1)
C(18)	4*e*	0.7152(2)	0.2539(1)	0.6406(2)	0.022(1)	0.015(1)	0.013(1)	0.002(1)	0.004(1)	0.001(1)
C(19)	4*e*	0.8141(2)	0.2629(1)	0.6963(2)	0.020(1)	0.011(1)	0.021(1)	0.001(1)	0.006(1)	−0.001(1)
C(20)	4*e*	0.8360(2)	0.2526(1)	0.7974(2)	0.016(1)	0.015(1)	0.016(1)	−0.001(1)	−0.001(1)	−0.001(1)
C(21)	4*e*	0.7605(2)	0.2323(1)	0.8422(2)	0.023(1)	0.016(1)	0.014(1)	0.003(1)	0.004(1)	0.001(1)
C(22)	4*e*	0.8952(2)	0.2852(1)	0.6470(2)	0.020(1)	0.010(1)	0.018(1)	−0.002(1)	0.004(1)	−0.003(1)
C(23)	4*e*	1.0959(2)	0.4162(2)	0.7590(2)	0.019(1)	0.019(1)	0.022(1)	−0.001(1)	0.004(1)	−0.001(1)
C(24)	4*e*	1.1207(2)	0.4876(2)	0.8042(2)	0.026(2)	0.028(2)	0.018(1)	0.002(1)	0.004(1)	−0.008(1)
C(25)	4*e*	1.1448(2)	0.5478(2)	0.7501(2)	0.022(2)	0.015(1)	0.033(2)	−0.002(1)	0.001(1)	−0.008(1)
C(26)	4*e*	1.1434(2)	0.5366(2)	0.6527(2)	0.023(2)	0.015(1)	0.028(2)	−0.004(1)	0.009(1)	−0.003(1)
C(27)	4*e*	1.1180(2)	0.4637(1)	0.6120(2)	0.012(1)	0.013(1)	0.022(1)	0.0010(9)	0.004(1)	0.000(1)
C(28)	4*e*	1.1138(2)	0.4444(1)	0.5094(2)	0.010(1)	0.014(1)	0.023(1)	−0.0006(9)	0.003(1)	−0.002(1)
C(29)	4*e*	1.1301(2)	0.4970(2)	0.4410(2)	0.015(1)	0.017(1)	0.028(2)	−0.003(1)	0.007(1)	0.002(1)
C(30)	4*e*	1.1224(2)	0.4721(2)	0.3459(2)	0.019(1)	0.028(1)	0.023(1)	0.004(1)	0.007(1)	0.009(1)
C(31)	4*e*	1.1028(2)	0.3950(2)	0.3230(2)	0.021(2)	0.033(2)	0.021(1)	0.006(1)	0.010(1)	0.001(1)
C(32)	4*e*	1.0878(2)	0.3445(2)	0.3940(2)	0.021(1)	0.020(1)	0.022(1)	0.000(1)	0.008(1)	−0.004(1)
C(33)	4*e*	1.0792(2)	0.1555(1)	0.5548(2)	0.030(2)	0.014(1)	0.014(1)	−0.004(1)	0.011(1)	−0.003(1)
C(34)	4*e*	1.0387(2)	0.0749(1)	0.5249(2)	0.026(2)	0.013(1)	0.014(1)	−0.001(1)	0.007(1)	−0.001(1)
C(35)	4*e*	0.9440(2)	0.0647(1)	0.4600(2)	0.023(2)	0.014(1)	0.018(1)	0.003(1)	0.002(1)	0.003(1)
C(36)	4*e*	1.0938(2)	0.0094(2)	0.5646(2)	0.022(2)	0.019(1)	0.018(1)	−0.000(1)	0.002(1)	0.000(1)

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