Crystal structure of bis(diaqua-μ-(4,4′-bipyridine-κN)bis(pyridine-2,6-dicarboxylato-$\kappa^3 O,N,O$)dicopper(II)) monoaqua-μ-(4,4′-bipyridine-κN)-bis(pyridine-2,6-dicarboxylato-$\kappa^3 O,N,O$)dicopper(II) hexahydrate, $2Cu_2(H_2O)_2(C_{10}H_8N_2)(C_7H_3NO_4)_2 \cdot Cu_2(H_2O)(C_{10}H_8N_2)(C_7H_3NO_4)_2 \cdot 6H_2O$

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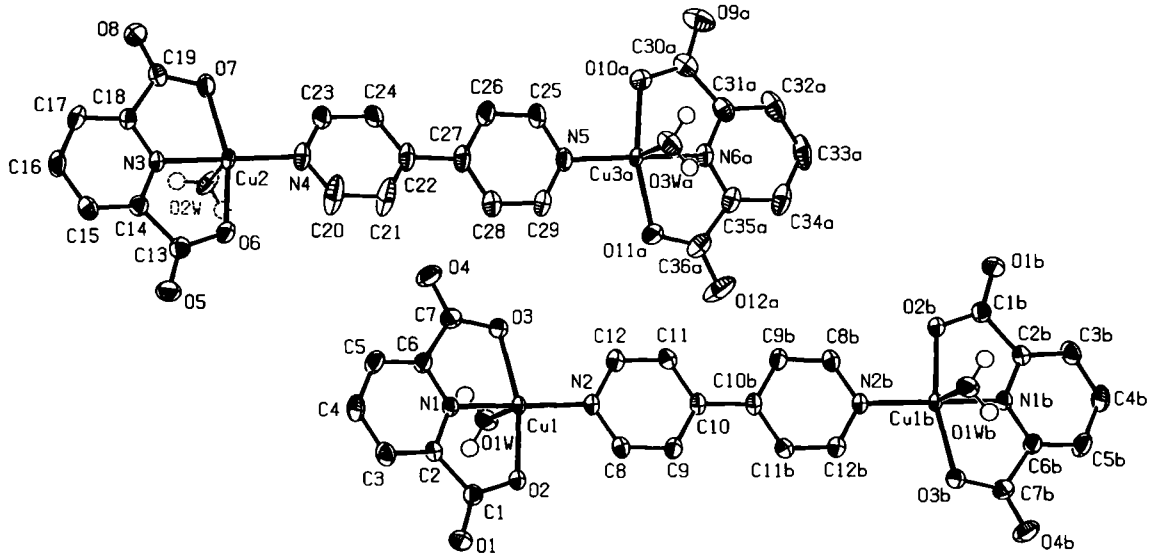

Abstract

$C_{72}H_{64}Cu_6N_{12}O_{35}$, triclinic, $P\bar{1}$ (no. 2), a = 10.5798(5) Å, b = 10.7076(5) Å, c = 18.6826(6) Å, α = 84.413(7)°, β = 86.541(8)°, γ = 62.797(4)°, V = 1873.1 Å^3, Z = 1, $R_{gt}(F)$ = 0.029, $wR_{ref}(F^2)$ = 0.087, T = 130 K.

Source of material

Copper nitrate trihydrate (121 mg, 0.5 mmol), pyridine-2,6-dicarboxylic acid (167 mg, 1 mmol), 4,4′-bipyridine (78 mg, 0.5 mmol) and water (18 ml) was sealed in a 25-ml Teflon-lined stainless-steel Parr bomb. The bomb was heated to 433K for 60 h and then cooled to room temperature over 60 h. Blue prismatic crystals were separated from reaction solution.

Experimental details

The H atoms of the coordinating water molecules (located from Fourier difference maps) and the aromatic H atoms (placed at calculated positions) were included in the refinement in riding model approximations with d(O—H) = 0.85 Å, d(C—H) = 0.93 Å and U_{iso}(H) set to 1.2U_{eq}(O,C), whereas the aqua H atoms were rotated to fit the electron density. One of the coordinating water molecules (O2w) was found to have a reduced occupancy factor of 0.5. The three lattice water molecules are each disordered over two sites. Their occupancies were refined, and their six hydrogen atoms were not localized.

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Discussion

The 4,4′-bipyridine heterocycle has been used as a linking molecule for many transition metal carboxylates, as noted the Cambridge Structure Database [1], e.g. this spacer affords with copper(II) pyridine-2,6-dicarboxylate, a dimeric 2:1 copper pyridine-2,6-dicarboxylate: 4,4′-bipyridine adduct in which the dianion also functions as a bridge to furnish a rectangle-shaped, tetranuclear species. The two independent copper atoms show square-pyramidal coordination; for one of them, the pentacoordinate status arises from such bridging whereas for the other, the pentacoordinate status arises from coordination by a water molecule [2]. A similar synthesis with a different copper reagent affords only a centrosymmetric, monomeric dinuclear molecule which crystallizes with two lattice water molecules.

The crystal structure of the title compound consists of three molecules of $[Cu_2(H_2O)_x(C_7H_3NO_4)_2(C_{10}H_8N_2)]$, for x = 2 one of these lies on a general position and a second on an inversion site. A complex with x = 1 is also situated on the general position. The copper atoms are O,N,O'-chelated by the dianions in all molecules, and the nitrogen atoms of the spacer heterocycles occupy the fourth position of the square. The environment is a square pyramid, when a water molecule occupies the apical site. The coordination architecture depends on the reaction conditions, including temperature, metal-to-ligand ratio, pH value, solvents and counteranions, which is the reason for different complexes of the present study and [2], cf. also [3]. Hydrogen bonds link the molecules of the title crystal structure into a 3D network structure.

Table 1. Data collection and handling.

Crystal:	blue prism, size 0.25 × 0.30 × 0.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	17.79 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC-7 & Mercury CCD, ω
$2\theta_{max}$:	55°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	14419, 8419
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 7646
$N(param)_{refined}$:	607
Programs:	SHELXS-97 [4], SHELXL-97 [5]

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

Atom	Site	Occ.	x	y	z	U_{iso}
H(1W1)	2*i*		0.8213	0.4760	0.7648	0.021
H(1W2)	2*i*		0.8300	0.3917	0.7110	0.021
H(2W1)	2*i*	0.50	1.1466	–0.0409	0.6281	0.021
H(2W2)	2*i*	0.50	1.1288	0.0011	0.5551	0.021
H(3W1)	2*i*		0.5201	1.1233	0.1869	0.025
H(3W2)	2*i*		0.5183	1.0382	0.1360	0.025
H(3)	2*i*		0.5305	0.1538	0.7914	0.020
H(4)	2*i*		0.5064	0.1925	0.9136	0.024
H(5)	2*i*		0.5173	0.3884	0.9518	0.022
H(8)	2*i*		0.5322	0.6306	0.5571	0.020
H(9)	2*i*		0.5006	0.8026	0.4663	0.021
H(11)	2*i*		0.5155	1.0446	0.6139	0.018
H(12)	2*i*		0.5419	0.8679	0.7011	0.018
H(15)	2*i*		0.8662	–0.3282	0.6946	0.021
H(16)	2*i*		0.8775	–0.3001	0.8163	0.024
H(17)	2*i*		0.8883	–0.1011	0.8507	0.022
H(20)	2*i*		0.7675	0.1963	0.4595	0.040
H(21)	2*i*		0.7537	0.3620	0.3681	0.036
H(23)	2*i*		0.8612	0.5549	0.5089	0.026
H(24)	2*i*		0.8785	0.3800	0.5959	0.025
H(25)	2*i*		0.7995	0.8898	0.3416	0.028
H(26)	2*i*		0.8034	0.7273	0.4331	0.028
H(28)	2*i*		0.8083	0.4798	0.2832	0.022
H(29)	2*i*		0.8064	0.6477	0.1960	0.021
H(32)	2*i*		0.7872	1.3779	0.1067	0.029
H(33)	2*i*		0.8136	1.3382	–0.0151	0.032
H(34)	2*i*		0.8332	1.1274	–0.0518	0.027

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)	2*i*		0.56466(2)	0.58007(2)	0.71225(1)	0.0192(1)	0.0090(1)	0.0082(1)	–0.00713(8)	0.00020(7)	0.00165(7)
Cu(2)	2*i*		0.84866(2)	0.11834(2)	0.60898(1)	0.0232(1)	0.0112(1)	0.0087(1)	–0.00765(9)	0.00058(8)	0.00303(7)
Cu(3)	2*i*		0.79340(2)	0.93342(2)	0.18772(1)	0.0215(1)	0.0108(1)	0.0078(1)	–0.00756(9)	0.00000(8)	0.00210(7)
O(1)	2*i*		0.5770(2)	0.2285(1)	0.64748(7)	0.0343(8)	0.0157(6)	0.0171(6)	–0.0143(6)	–0.0025(5)	–0.0024(5)
O(1W)	2*i*		0.8081(1)	0.4753(1)	0.72051(7)	0.0220(6)	0.0145(6)	0.0176(6)	–0.0098(5)	0.0016(5)	–0.0026(4)
O(2)	2*i*		0.5587(1)	0.4463(1)	0.64547(6)	0.0233(6)	0.0116(5)	0.0113(5)	–0.0085(5)	–0.0011(5)	0.0010(4)
O(2W)	2*i*	0.50	1.0923(3)	0.0208(3)	0.5969(1)	0.014(1)	0.026(1)	0.008(1)	–0.005(1)	0.0012(9)	–0.0008(9)
O(3)	2*i*		0.5508(1)	0.6757(1)	0.80448(6)	0.0208(6)	0.0128(6)	0.0122(5)	–0.0080(5)	0.0016(5)	–0.0008(4)
O(3W)	2*i*		0.5459(1)	1.0388(1)	0.17771(7)	0.0230(7)	0.0144(6)	0.0264(7)	–0.0092(5)	0.0019(5)	–0.0022(5)
O(4)	2*i*		0.5520(2)	0.6314(1)	0.92461(6)	0.0318(7)	0.0273(7)	0.0117(6)	–0.0181(6)	0.0033(5)	–0.0045(5)
O(5)	2*i*		0.8505(1)	–0.2321(1)	0.54962(6)	0.0250(7)	0.0183(6)	0.0186(6)	–0.0116(5)	0.0021(5)	–0.0053(5)
O(6)	2*i*		0.8330(1)	–0.0140(1)	0.54509(6)	0.0266(7)	0.0171(6)	0.0110(5)	–0.0122(5)	0.0000(5)	0.0008(4)
O(7)	2*i*		0.8735(1)	0.2011(1)	0.69790(6)	0.0220(6)	0.0133(6)	0.0161(6)	–0.0086(5)	–0.0053(5)	0.0035(4)
O(8)	2*i*		0.9136(1)	0.1482(1)	0.81613(7)	0.0273(7)	0.0187(6)	0.0171(6)	–0.0090(5)	–0.0068(5)	–0.0009(5)
O(9)	2*i*		0.7485(2)	1.3005(1)	0.25048(8)	0.0318(8)	0.0210(7)	0.0357(8)	–0.0152(6)	0.0041(6)	–0.0110(6)
O(10)	2*i*		0.7784(1)	1.0782(1)	0.25488(7)	0.0226(6)	0.0161(6)	0.0148(6)	–0.0093(5)	0.0005(5)	–0.0020(5)
O(11)	2*i*		0.8307(1)	0.8281(1)	0.09792(6)	0.0285(7)	0.0183(6)	0.0122(5)	–0.0125(5)	0.0019(5)	–0.0016(4)
O(12)	2*i*		0.8390(2)	0.8637(2)	–0.02192(7)	0.050(1)	0.0491(9)	0.0116(6)	–0.0361(8)	0.0051(6)	–0.0067(6)
N(1)	2*i*		0.5504(2)	0.4442(1)	0.78199(7)	0.0137(7)	0.0103(6)	0.0106(6)	–0.0056(5)	0.0007(5)	0.0011(5)
N(2)	2*i*		0.5404(2)	0.7318(1)	0.63766(7)	0.0173(7)	0.0106(6)	0.0112(6)	–0.0060(5)	–0.0014(5)	0.0025(5)
N(3)	2*i*		0.8691(2)	–0.0295(1)	0.68009(7)	0.0158(7)	0.0109(6)	0.0109(6)	–0.0064(5)	–0.0007(5)	0.0025(5)
N(4)	2*i*		0.8277(2)	0.2701(2)	0.53568(8)	0.0170(7)	0.0186(7)	0.0153(7)	–0.0082(6)	–0.0011(6)	0.0067(6)
N(5)	2*i*		0.8024(2)	0.7848(2)	0.26027(8)	0.0172(7)	0.0135(7)	0.0131(7)	–0.0043(6)	0.0011(5)	0.0034(5)
N(6)	2*i*		0.8029(2)	1.0716(1)	0.11822(7)	0.0138(7)	0.0128(6)	0.0142(7)	–0.0058(5)	–0.0004(5)	0.0026(5)
C(1)	2*i*		0.5611(2)	0.3331(2)	0.67713(9)	0.0137(8)	0.0127(7)	0.0136(7)	–0.0055(6)	–0.0017(6)	0.0004(6)
C(2)	2*i*		0.5463(2)	0.3326(2)	0.75861(9)	0.0138(8)	0.0111(7)	0.0124(7)	–0.0052(6)	–0.0009(6)	0.0006(6)
C(3)	2*i*		0.5317(2)	0.2331(2)	0.8070(1)	0.0204(9)	0.0141(8)	0.0185(8)	–0.0106(7)	–0.0006(7)	0.0023(6)
C(4)	2*i*		0.5189(2)	0.2562(2)	0.88004(9)	0.028(1)	0.0178(8)	0.0159(8)	–0.0129(8)	0.0019(7)	0.0058(6)
C(5)	2*i*		0.5245(2)	0.3734(2)	0.90318(9)	0.0218(9)	0.0206(9)	0.0106(7)	–0.0096(7)	0.0011(6)	0.0022(6)
C(6)	2*i*		0.5413(2)	0.4668(2)	0.85146(9)	0.0141(8)	0.0135(8)	0.0109(7)	–0.0060(6)	0.0004(6)	0.0002(6)
C(7)	2*i*		0.5493(2)	0.6015(2)	0.86289(9)	0.0159(8)	0.0153(8)	0.0136(7)	–0.0067(6)	0.0021(6)	–0.0022(6)
C(8)	2*i*		0.5284(2)	0.7150(2)	0.56850(9)	0.0244(9)	0.0117(8)	0.0145(8)	–0.0088(7)	–0.0022(7)	0.0020(6)
C(9)	2*i*		0.5105(2)	0.8178(2)	0.51340(9)	0.0262(9)	0.0145(8)	0.0122(8)	–0.0104(7)	–0.0043(7)	0.0024(6)
C(10)	2*i*		0.5073(2)	0.9446(2)	0.52879(9)	0.0150(8)	0.0117(7)	0.0130(8)	–0.0062(6)	–0.0019(6)	0.0031(6)
C(11)	2*i*		0.5187(2)	0.9615(2)	0.60095(9)	0.0197(8)	0.0111(7)	0.0141(8)	–0.0076(7)	0.0000(6)	–0.0001(6)
C(12)	2*i*		0.5347(2)	0.8545(2)	0.65332(9)	0.0195(8)	0.0134(8)	0.0118(7)	–0.0077(7)	–0.0008(6)	0.0009(6)
C(13)	2*i*		0.8484(2)	–0.1328(2)	0.57758(9)	0.0137(8)	0.0162(8)	0.0136(7)	–0.0065(6)	0.0021(6)	–0.0012(6)
C(14)	2*i*		0.8633(2)	–0.1418(2)	0.65871(9)	0.0141(8)	0.0134(7)	0.0127(7)	–0.0062(6)	0.0006(6)	–0.0001(6)
C(15)	2*i*		0.8682(2)	–0.2483(2)	0.7088(1)	0.0222(9)	0.0138(8)	0.0192(9)	–0.0105(7)	–0.0006(7)	0.0013(6)
C(16)	2*i*		0.8763(2)	–0.2313(2)	0.78144(9)	0.028(1)	0.0175(8)	0.0157(8)	–0.0132(7)	–0.0019(7)	0.0064(6)
C(17)	2*i*		0.8826(2)	–0.1126(2)	0.80244(9)	0.0229(9)	0.0199(8)	0.0103(7)	–0.0097(7)	–0.0021(6)	0.0033(6)

Table 3. Continued.

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(18)	2*i*		0.8802(2)	–0.0124(2)	0.74868(9)	0.0147(8)	0.0124(7)	0.0117(7)	–0.0047(6)	–0.0020(6)	0.0014(6)
C(19)	2*i*		0.8898(2)	0.1226(2)	0.75714(9)	0.0139(8)	0.0118(7)	0.0168(8)	–0.0043(6)	–0.0023(6)	0.0015(6)
C(20)	2*i*		0.7890(3)	0.2680(2)	0.4691(1)	0.047(1)	0.045(1)	0.026(1)	–0.038(1)	–0.0212(9)	0.0219(9)
C(21)	2*i*		0.7795(2)	0.3680(2)	0.4139(1)	0.037(1)	0.042(1)	0.0223(9)	–0.031(1)	–0.0166(8)	0.0188(8)
C(22)	2*i*		0.8087(2)	0.4771(2)	0.42724(9)	0.0140(8)	0.0170(8)	0.0159(8)	–0.0039(7)	0.0014(6)	0.0075(6)
C(23)	2*i*		0.8440(2)	0.4817(2)	0.49721(9)	0.034(1)	0.0122(8)	0.0149(8)	–0.0070(8)	0.0069(7)	0.0002(6)
C(24)	2*i*		0.8534(2)	0.3763(2)	0.54955(9)	0.030(1)	0.0143(8)	0.0131(8)	–0.0068(7)	0.0040(7)	0.0015(6)
C(25)	2*i*		0.8015(2)	0.8064(2)	0.3300(1)	0.034(1)	0.0146(8)	0.0150(8)	–0.0075(8)	0.0033(7)	0.0030(6)
C(26)	2*i*		0.8033(2)	0.7091(2)	0.3854(1)	0.032(1)	0.0180(9)	0.0120(8)	–0.0063(8)	0.0040(7)	0.0031(6)
C(27)	2*i*		0.8052(2)	0.5839(2)	0.36902(9)	0.0137(8)	0.0158(8)	0.0148(8)	–0.0034(6)	0.0025(6)	0.0058(6)
C(28)	2*i*		0.8066(2)	0.5621(2)	0.2964(1)	0.0191(9)	0.0162(8)	0.0182(8)	–0.0082(7)	–0.0013(7)	0.0041(6)
C(29)	2*i*		0.8053(2)	0.6638(2)	0.24416(9)	0.0199(9)	0.0193(8)	0.0138(8)	–0.0094(7)	–0.0021(6)	0.0052(6)
C(30)	2*i*		0.7709(2)	1.1934(2)	0.2221(1)	0.0142(8)	0.0161(8)	0.0227(9)	–0.0073(7)	0.0015(7)	–0.0029(6)
C(31)	2*i*		0.7905(2)	1.1905(2)	0.14093(9)	0.0122(8)	0.0128(8)	0.0216(8)	–0.0049(6)	0.0009(6)	0.0004(6)
C(32)	2*i*		0.7948(2)	1.2944(2)	0.0916(1)	0.0185(9)	0.0141(8)	0.036(1)	–0.0067(7)	0.0063(8)	0.0035(7)
C(33)	2*i*		0.8109(2)	1.2700(2)	0.0189(1)	0.023(1)	0.0195(9)	0.030(1)	–0.0069(8)	0.0061(8)	0.0127(7)
C(34)	2*i*		0.8229(2)	1.1441(2)	–0.0034(1)	0.0179(9)	0.028(1)	0.0162(8)	–0.0079(8)	0.0010(7)	0.0080(7)
C(35)	2*i*		0.8191(2)	1.0451(2)	0.04896(9)	0.0140(8)	0.0204(8)	0.0129(7)	–0.0072(7)	–0.0007(6)	0.0035(6)
C(36)	2*i*		0.8309(2)	0.9010(2)	0.03950(9)	0.0181(8)	0.0263(9)	0.0128(8)	–0.0119(7)	0.0007(6)	–0.0014(6)
O(5W)	2*i*	0.511(4)	0.9844(4)	0.5602(3)	0.9390(2)	0.064(3)	0.039(2)	0.043(2)	–0.029(2)	–0.028(2)	0.012(1)
O(5W')	2*i*	0.489	0.8058(3)	0.6295(3)	0.9671(2)	0.033(2)	0.023(2)	0.034(2)	–0.009(1)	–0.011(1)	–0.006(1)
O(4W)	2*i*	0.50(5)	0.869(2)	0.4281(7)	0.8612(3)	0.025(4)	0.022(2)	0.019(2)	–0.010(2)	–0.002(2)	–0.001(1)
O(4W')	2*i*	0.50	0.914(3)	0.446(1)	0.8612(3)	0.035(6)	0.024(3)	0.027(2)	0.001(3)	–0.005(2)	0.003(2)
O(6W)	2*i*	0.520(8)	0.4657(4)	1.0568(5)	0.0365(2)	0.042(2)	0.055(3)	0.035(2)	–0.020(2)	–0.011(2)	–0.001(2)
O(6W')	2*i*	0.480	0.4002(5)	1.1476(5)	0.0540(2)	0.051(3)	0.028(2)	0.034(2)	–0.020(2)	–0.015(2)	–0.001(2)

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