Crystal structure of trikis(4,4′-bipyridine)bis(*N*-dimethylformamide)-copper(II) bis(perchlorate) — pyridine (1:2), $[Cu(C_{10}H_8N_2)_3(C_3H_7O)_2][ClO_4]_2 \cdot 2C_{10}H_8N_2$

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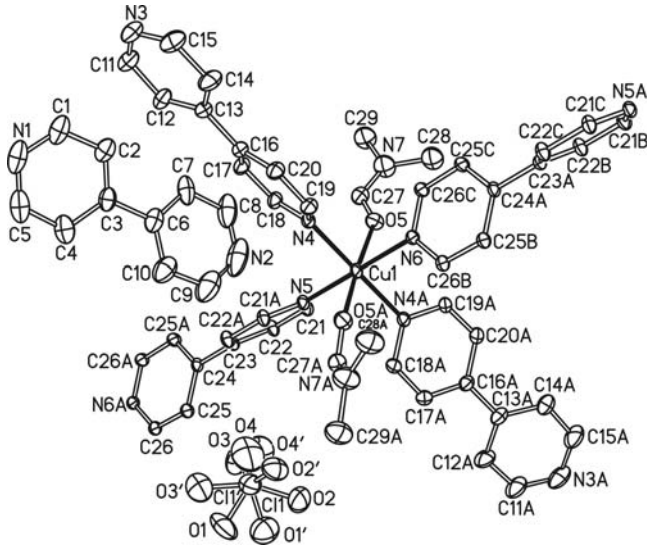

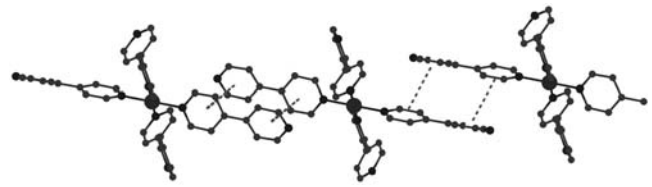

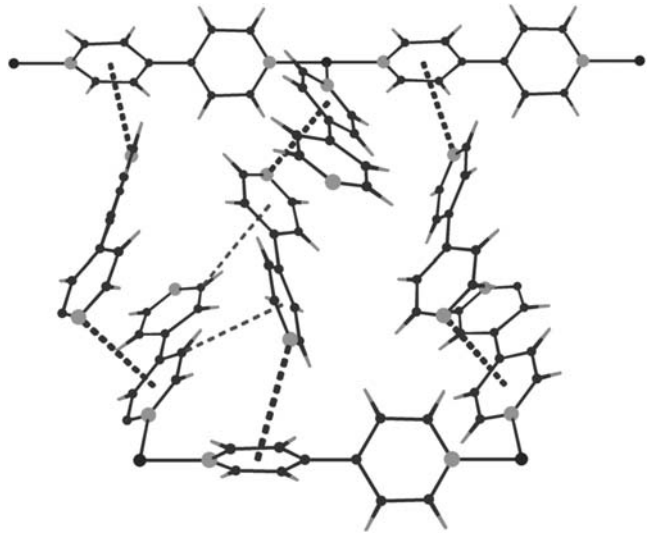

Abstract

$C_{56}H_{54}Cl_2CuN_{12}O_{10}$, monoclinic, *C*12/*c*1 (no. 15), a = 29.30(1) Å, b = 11.041(5) Å, c = 20.924(8) Å, β = 120.94(4)°, V = 5806.5 Å^3, Z = 4, $R_{gt}(F)$ = 0.064, $wR_{ref}(F^2)$ = 0.195, T = 293 K.

Source of material

All reagents were available commercially and were used without further purification. 4,4′-Bipyridine (156 mg) was added to $Cu(ClO_4)_2$ (1 mmol, 260 mg) in 10 ml of water. The suspension was stirred for 4 h and filtered. After leaving the filtrate in air for one week, blue block-shaped crystals of the title compound were formed. The crystals were isolated, washed with water three times and dried in a vacuum desiccator using silica gel (yield 75 %). Elemental analysis — found: C, 56.47 %; H, 4.51 %; N, 14.16 %; calculated for $C_{56}H_{54}Cl_2CuN_{12}O_{10}$: C, 56.54 %; H, 4.58 %; N, 14.13 %.

Experimental details

All the H atoms bonded to carbon atoms were located at the ideal positions with d(C—H) = 0.93 Å (aromatic), 0.97 Å (methylene) and 0.96 Å (methyl) and U_{iso}(H) = 1.2 U_{eq}($C_{aromatic,\ methylene}$) or 1.5 U_{eq}(C_{methyl}). The perchlorate anion is disordered in two orientation with occupancy 0.59 : 0.41.

Discussion

4,4′-Bipyridine spacers have been recognized to have strong hydrogen bonding capability with water molecules in supramolecular chemistry and crystal engineering. They are good hosts for inducing water aggregation. A number of one-, two-, and three-dimensional metal-4,4′-bipy frameworks have already been generated.

In the title crystal structure, the Cu(II) atom is in a distorted octahedral environment. The equatorial plane is constructed by four N atoms from 4,4′-bipyridine molecules, and two O atoms from two *N*-dimethylformamide molecules occupying the axial positions (figure, top). Isolated 4,4′-bipyridine molecules and perchlorate anions are encapsulated inside the channels which formed by the 4,4′-bipyridine and the metal.

Analysis of the crystal packing of the title compound reveals the existence of multiple intermolecular C–H···O, $\pi\cdots\pi$, lone pair···π and C–H···π interactions linking the molecule into three-dimensional networks (figure, middle, bottom). The relevant distances are d(Cg1···Cg1^{i}) = 3.96(1) Å, d(N3···Cg2) = 3.42 Å; Cg1

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is the centroid of the ring defined by the atoms C11-C15/N3, and Cg2 is the centroid of the ring defined by the atoms C16-C20/N4 (symmetry code i: 3/2–*x*,3/2–*y*,2–*z*).

Table 1. Data collection and handling.

Crystal:	blue block, size 0.35 × 0.35 × 0.35 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	5.36 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	50.02°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	13291, 5117
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4176
$N(param)_{refined}$:	407
Programs:	SHELXS-97, SHELXL-97 [3]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	8*f*	0.8854	0.1085	0.8630	0.126
H(2)	8*f*	0.7996	0.1392	0.8371	0.100
H(4)	8*f*	0.7504	–0.1272	0.6848	0.117
H(5)	8*f*	0.8389	–0.1429	0.7137	0.134
H(7)	8*f*	0.7295	0.0882	0.8458	0.115
H(8)	8*f*	0.6418	0.1149	0.8162	0.160
H(9)	8*f*	0.5872	0.0026	0.6128	0.183
H(10)	8*f*	0.6727	–0.0307	0.6356	0.130
H(11)	8*f*	0.8575	0.5221	1.0362	0.118
H(12)	8*f*	0.7659	0.5126	0.9742	0.098
H(14)	8*f*	0.7619	0.8363	0.8843	0.098
H(15)	8*f*	0.8539	0.8346	0.9511	0.119
H(17)	8*f*	0.6843	0.5412	0.9410	0.063
H(18)	8*f*	0.5934	0.5418	0.8777	0.057
H(19)	8*f*	0.5882	0.7944	0.7438	0.057
H(20)	8*f*	0.6793	0.8001	0.8042	0.063
H(21)	8*f*	0.4570	0.4674	0.7969	0.049
H(22)	8*f*	0.4562	0.2586	0.7987	0.050
H(25)	8*f*	0.4559	0.0778	0.6384	0.051
H(26)	8*f*	0.4544	–0.1308	0.6417	0.050
H(27)	8*f*	0.5369	0.5705	0.9398	0.072
H(28A)	8*f*	0.5166	0.8803	0.9660	0.147
H(28B)	8*f*	0.4835	0.8406	1.0022	0.147
H(28C)	8*f*	0.4602	0.8219	0.9166	0.147
H(29A)	8*f*	0.5545	0.5759	1.0576	0.146
H(29B)	8*f*	0.5158	0.6549	1.0712	0.146
H(29C)	8*f*	0.5705	0.7084	1.0881	0.146

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*		½	0.66787(5)	¾	0.0335(3)	0.0181(3)	0.0505(4)	0	0.0160(3)	0
N(1)	8*f*		0.8697(3)	–0.0182(7)	0.7913(4)	0.091(4)	0.130(5)	0.150(6)	0.045(4)	0.084(4)	0.053(4)
N(2)	8*f*		0.6073(3)	0.0600(7)	0.7120(8)	0.084(5)	0.099(5)	0.34(2)	0.006(4)	0.114(8)	0.042(7)
N(3)	8*f*		0.8646(2)	0.6775(6)	0.9999(3)	0.041(2)	0.129(5)	0.106(4)	0.004(3)	0.018(2)	–0.022(3)
N(4)	8*f*		0.5816(1)	0.6685(2)	0.8050(2)	0.037(2)	0.027(1)	0.049(2)	0.000(1)	0.019(1)	0.001(1)
N(5)	4*e*		½	0.4863(3)	¾	0.037(2)	0.023(2)	0.049(2)	0	0.022(2)	0
N(6)	4*e*		½	0.8503(3)	¾	0.038(2)	0.024(2)	0.043(2)	0	0.014(2)	0
N(7)	8*f*		0.5163(2)	0.7020(5)	0.9794(3)	0.120(4)	0.101(4)	0.071(3)	0.011(3)	0.057(3)	0.005(3)
O(1)	8*f*	0.59(2)	0.3609(7)	0.212(1)	0.4588(9)	0.20(2)	0.100(7)	0.18(1)	–0.018(9)	0.11(1)	–0.066(8)
O(2)	8*f*	0.59	0.3208(6)	0.366(2)	0.4836(6)	0.18(1)	0.21(2)	0.094(7)	0.10(1)	0.037(7)	0.001(8)
O(3)	8*f*	0.59	0.378(2)	0.242(3)	0.582(2)	0.21(2)	0.23(3)	0.12(1)	0.10(2)	0.08(1)	0.10(2)
O(4)	8*f*	0.59	0.4109(8)	0.376(2)	0.531(2)	0.15(2)	0.16(2)	0.36(3)	–0.08(1)	0.13(2)	–0.09(2)
Cl(1)	8*f*	0.59	0.36910(7)	0.2932(2)	0.5151(1)	0.104(1)	0.085(1)	0.090(1)	–0.0018(9)	0.0370(9)	–0.0073(8)
Cl(1')	8*f*	0.41	0.36910(7)	0.2932(2)	0.5151(1)	0.104(1)	0.085(1)	0.090(1)	–0.0018(9)	0.0370(9)	–0.0073(8)
O(3')	8*f*	0.41	0.406(1)	0.201(2)	0.520(1)	0.18(2)	0.16(2)	0.16(2)	0.02(1)	0.09(2)	–0.01(1)
O(1')	8*f*	0.41	0.3183(7)	0.254(2)	0.456(1)	0.14(1)	0.15(2)	0.15(1)	–0.01(1)	0.06(1)	0.00(1)
O(2')	8*f*	0.41	0.3809(8)	0.411(2)	0.5046(9)	0.14(2)	0.080(8)	0.107(9)	–0.020(9)	0.06(1)	–0.006(7)
O(4')	8*f*	0.41	0.369(2)	0.290(4)	0.584(3)	0.19(3)	0.17(3)	0.17(2)	0.01(2)	0.10(2)	0.02(2)
O(5)	8*f*		0.4990(1)	0.6777(3)	0.8634(2)	0.069(2)	0.053(2)	0.054(2)	–0.004(1)	0.032(2)	–0.002(1)
C(1)	8*f*		0.8581(3)	0.0615(7)	0.8264(4)	0.072(4)	0.129(6)	0.124(5)	0.027(4)	0.057(4)	0.031(4)
C(2)	8*f*		0.8064(2)	0.0797(6)	0.8116(3)	0.061(3)	0.102(4)	0.086(4)	0.010(3)	0.039(3)	0.015(3)
C(3)	8*f*		0.7658(2)	0.0095(5)	0.7593(3)	0.070(3)	0.065(3)	0.085(3)	0.019(2)	0.048(3)	0.024(3)
C(4)	8*f*		0.7769(3)	–0.0777(6)	0.7207(4)	0.118(5)	0.078(4)	0.126(5)	0.022(3)	0.085(5)	0.019(4)
C(5)	8*f*		0.8305(4)	–0.0866(7)	0.7391(5)	0.133(7)	0.095(5)	0.154(7)	0.044(5)	0.107(6)	0.037(5)
C(6)	8*f*		0.7101(2)	0.0260(5)	0.7426(3)	0.066(3)	0.055(3)	0.111(4)	0.005(2)	0.049(3)	0.022(3)
C(7)	8*f*		0.7013(3)	0.0701(5)	0.7984(5)	0.104(4)	0.062(3)	0.170(6)	0.014(3)	0.105(5)	0.015(4)
C(8)	8*f*		0.6485(4)	0.0858(7)	0.7801(7)	0.112(6)	0.075(4)	0.26(1)	0.011(4)	0.127(8)	0.024(6)
C(9)	8*f*		0.6162(4)	0.019(1)	0.6599(7)	0.082(6)	0.141(9)	0.21(1)	0.003(5)	0.058(6)	0.025(8)
C(10)	8*f*		0.6675(2)	–0.0006(7)	0.6730(4)	0.074(4)	0.096(5)	0.135(6)	–0.006(3)	0.038(4)	0.018(4)
C(11)	8*f*		0.8381(2)	0.5863(7)	1.0055(4)	0.047(3)	0.101(5)	0.109(5)	0.006(3)	0.013(3)	–0.010(4)
C(12)	8*f*		0.7825(2)	0.5796(5)	0.9679(3)	0.047(3)	0.082(4)	0.085(3)	0.017(2)	0.012(2)	0.003(3)
C(13)	8*f*		0.7525(2)	0.6730(4)	0.9217(2)	0.040(2)	0.063(3)	0.057(2)	–0.001(2)	0.017(2)	–0.012(2)
C(14)	8*f*		0.7802(2)	0.7710(6)	0.9150(3)	0.045(3)	0.095(4)	0.090(4)	–0.015(3)	0.025(2)	0.000(3)
C(15)	8*f*		0.8359(2)	0.7688(7)	0.9555(4)	0.050(3)	0.119(5)	0.113(5)	–0.018(3)	0.031(3)	–0.010(4)
C(16)	8*f*		0.6932(2)	0.6705(3)	0.8807(2)	0.038(2)	0.047(2)	0.049(2)	–0.000(2)	0.017(2)	–0.004(2)
C(17)	8*f*		0.6658(2)	0.5939(4)	0.9011(2)	0.043(2)	0.050(2)	0.055(2)	0.006(2)	0.017(2)	0.010(2)
C(18)	8*f*		0.6108(2)	0.5948(3)	0.8627(2)	0.044(2)	0.037(2)	0.054(2)	0.005(2)	0.020(2)	0.009(2)
C(19)	8*f*		0.6077(1)	0.7431(3)	0.7842(2)	0.040(2)	0.038(2)	0.056(2)	–0.006(2)	0.019(2)	0.005(2)
C(20)	8*f*		0.6627(2)	0.7467(4)	0.8203(2)	0.043(2)	0.047(2)	0.061(2)	–0.006(2)	0.022(2)	0.004(2)
C(21)	8*f*		0.4746(1)	0.4247(3)	0.7778(2)	0.043(2)	0.027(2)	0.057(2)	–0.003(1)	0.030(2)	–0.001(2)

Table 3. Continued.

Atom	Site	OCc.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(22)	8*f*		0.4739(2)	0.2993(3)	0.7789(2)	0.050(2)	0.025(2)	0.060(2)	–0.000(2)	0.035(2)	–0.001(2)
C(23)	4*e*		½	0.2355(4)	¾	0.037(2)	0.022(2)	0.039(2)	0	0.017(2)	0
C(24)	4*e*		½	0.1012(4)	¾	0.033(2)	0.023(2)	0.047(3)	0	0.021(2)	0
C(25)	8*f*		0.4735(1)	0.0372(3)	0.6838(2)	0.047(2)	0.026(2)	0.044(2)	0.003(1)	0.017(2)	0.001(1)
C(26)	8*f*		0.4735(1)	–0.0880(3)	0.6861(2)	0.043(2)	0.026(2)	0.044(2)	0.003(1)	0.015(2)	0.000(1)
C(27)	8*f*		0.5187(2)	0.6438(4)	0.9272(3)	0.055(2)	0.059(3)	0.063(3)	–0.001(2)	0.029(2)	0.006(2)
C(28)	8*f*		0.4921(3)	0.8213(6)	0.9648(3)	0.123(5)	0.101(5)	0.075(4)	0.013(4)	0.055(4)	0.003(3)
C(29)	8*f*		0.5414(3)	0.6564(6)	1.0556(3)	0.122(5)	0.103(5)	0.072(3)	0.009(4)	0.054(4)	0.008(3)

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