Crystal structure of 2,2'-bipyridino-tetrafluorophthalato-copper(II) $[Cu(C_8HF_4O_4)(C_{10}H_8N_2)_2](C_8H_2F_4O_4)(C_8HF_4O_4)$, $C_{44}H_{20}CuF_{12}N_4O_{12}$

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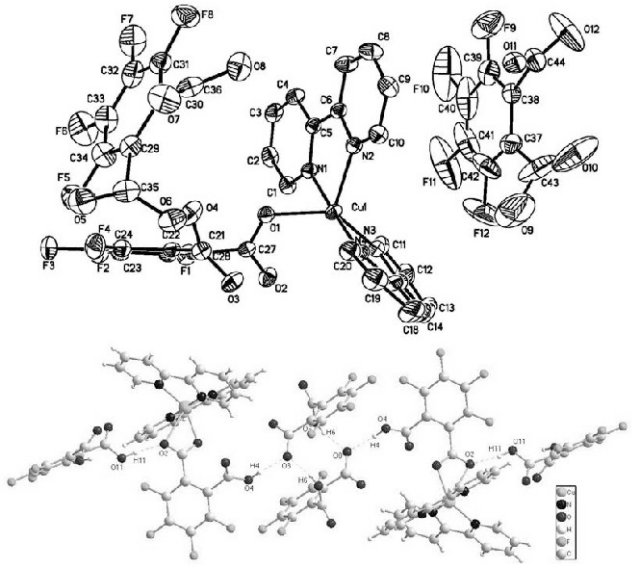

Abstract

$C_{44}H_{20}CuF_{12}N_4O_{12}$, triclinic, $P\bar{1}$ (no. 2), a = 12.274(1) Å, b = 14.621(3) Å, c = 14.623(2) Å, α = 104.891(2)°, β = 109.986(1)°, γ = 106.783(2)°, V = 2169.0 Å^3, Z = 2, $R_{gt}(F)$ = 0.0566, $wR_{ref}(F^2)$ = 0.1697, T = 296 K.

Table 1. Data collection and handling.

Crystal:	green blocks, size 0.15×0.22×0.25 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	6.26 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	16711, 8037
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5785
$N(param)_{refined}$:	661
Programs:	SHELXS-97 [7]

Source of material

A mixture of 2,2'-bipyridine (31.2 mg, 0.2 mmol), tetrafluorophthalic acid (23.6 mg, 0.1 mmol), $Cu(OAc)_2{\cdot}H_2O$ (20.0 mg, 0.1 mmol) and NaOH (8.2 mg, 0.2 mmol) were added to a H_2O solution (15 ml) in a Teflon-lined stainless steel reactor. The mixture was heated at 433 K for 3 days, and then slowly cooled down to room temperature over 24 hours. Green block-shaped crystals of the title compound were obtained.
Elemental analysis found:C: 48.58%; H: 1.88%; N: 5.17%;
calcd. for $C_{44}H_{20}CuF_{12}N_4O_{12}$: C: 48.55%; H: 1.84%; N: 5.15%.

Discussion

The design and synthesis of supramolecular coordination polymers, especially those constructed by hydrogen bonding and intermolecular weak interactions is a field of rapid growth due to their special physical properties and potential application in functional materials with electronic, magnetic, optical and catalytic applications. It is well know that organic ligands play a crucial role in the design and construction of desirable frameworks. The changes in symmetry flexibility and length of organic ligands can result in a remarkable class of materials bearing diverse architectures and functions. Phthalic acid and its derivatives present versatile coordination modes that can yield predetermined networks [1-6].
The asymmetric unit of the title compound contains one Cu(II) ion, one mono-dentate tetrafluorophthalate anion, and two 2,2'-bipyridine (bipy) ligands, one free tetrafluorophthalate anion, and one free tetrafluorophthalate acid molecule. Each copper(II) ion is distorted trigonal-biyramidally coordinated by four N atoms from two chelating bipy ligands and one O atom from the deprotonated 1-carboxyl group of the tetrafluorophthalate ligands. The bond lengths Cu–N are 1.962(3) Å, 1.997(3) Å, 2.038(3) Å and 2.131(3) Å. The bond lengths Cu–O are 2.083(2) Å. In the complex, there exist inter-molecular hydrogen bonds: O(4)–H(4)···O(8) = 2.612(4) Å, O(6)–H(6)···O(8) = 2.527(4) Å and O(11)–H(11)···O(2) = 2.594(4) Å (Fig. bottom).

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

Atom	Site	x	y	z	U_{iso}
H(4)	2*i*	0.7472	0.5590	0.9393	0.094
H(6)	2*i*	0.6755	0.5248	1.1063	0.089
H(9)	2*i*	0.5445	1.0613	0.9403	0.375
H(11)	2*i*	0.1129	0.8218	0.7409	0.083
H(1)	2*i*	0.8369	0.7239	0.5253	0.055
H(2)	2*i*	0.7580	0.6044	0.3546	0.063
H(3)	2*i*	0.5425	0.4995	0.2595	0.065
H(4A)	2*i*	0.4094	0.5139	0.3372	0.057
H(7)	2*i*	0.2953	0.5386	0.4180	0.064
H(8)	2*i*	0.1888	0.5656	0.5195	0.070
H(9A)	2*i*	0.2995	0.6924	0.6891	0.061
H(10)	2*i*	0.5162	0.7801	0.7590	0.053
H(11A)	2*i*	0.7980	0.8849	0.5311	0.066
H(12)	2*i*	0.9199	1.0470	0.5490	0.085
H(13)	2*i*	1.0172	1.1850	0.7106	0.095
H(14)	2*i*	0.9831	1.1586	0.8503	0.084
H(17)	2*i*	0.9193	1.1206	0.9709	0.083
H(18)	2*i*	0.8709	1.0624	1.0902	0.095
H(19)	2*i*	0.7735	0.8846	1.0449	0.082
H(20)	2*i*	0.7272	0.7711	0.8816	0.062

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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)	2*i*	0.73507(4)	0.78423(3)	0.68228(3)	0.0404(3)	0.0311(3)	0.0308(3)	0.0105(2)	0.0147(2)	0.0042(2)
N(1)	2*i*	0.6728(3)	0.6910(2)	0.5319(2)	0.041(2)	0.035(2)	0.029(2)	0.015(1)	0.016(1)	0.008(1)
N(2)	2*i*	0.5352(3)	0.7158(2)	0.6330(2)	0.040(2)	0.037(2)	0.032(2)	0.016(1)	0.016(1)	0.008(1)
N(3)	2*i*	0.8195(3)	0.9235(2)	0.6767(3)	0.042(2)	0.037(2)	0.045(2)	0.016(2)	0.015(2)	0.013(2)
N(4)	2*i*	0.7890(3)	0.8753(2)	0.8286(2)	0.041(2)	0.037(2)	0.033(2)	0.013(1)	0.013(1)	0.002(1)
O(1)	2*i*	0.7793(2)	0.6699(2)	0.7262(2)	0.037(1)	0.037(1)	0.040(1)	0.015(1)	0.019(1)	0.011(1)
O(2)	2*i*	0.9658(3)	0.7726(2)	0.7478(2)	0.052(2)	0.040(2)	0.068(2)	0.016(1)	0.038(2)	0.023(1)
O(3)	2*i*	0.9158(3)	0.6952(2)	0.9583(2)	0.062(2)	0.038(2)	0.045(2)	0.011(1)	0.026(2)	0.002(1)
O(4)	2*i*	0.7680(3)	0.5337(2)	0.8946(3)	0.076(2)	0.045(2)	0.074(2)	0.018(2)	0.053(2)	0.015(2)
O(5)	2*i*	0.7067(3)	0.3554(3)	1.1574(2)	0.074(2)	0.076(2)	0.048(2)	0.025(2)	0.021(2)	0.034(2)
O(6)	2*i*	0.7014(3)	0.5032(2)	1.1522(2)	0.065(2)	0.060(2)	0.037(2)	0.014(2)	0.021(2)	0.012(1)
O(7)	2*i*	0.4257(3)	0.3461(3)	1.0859(3)	0.071(2)	0.101(3)	0.056(2)	0.031(2)	0.041(2)	0.040(2)
O(8)	2*i*	0.3276(3)	0.4097(2)	0.9775(3)	0.075(2)	0.066(2)	0.069(2)	0.036(2)	0.051(2)	0.031(2)
O(9)	2*i*	0.5373(9)	1.0428(5)	0.8799(6)	0.262(9)	0.135(6)	0.137(6)	0.066(6)	–0.092(6)	0.003(4)
O(10)	2*i*	0.3521(9)	1.0548(5)	0.8313(5)	0.231(9)	0.096(5)	0.110(4)	–0.030(5)	0.110(6)	–0.021(3)
O(11)	2*i*	0.1743(3)	0.8311(2)	0.7281(2)	0.052(2)	0.058(2)	0.063(2)	0.017(2)	0.034(2)	0.029(2)
O(12)	2*i*	0.0704(5)	0.8835(5)	0.6120(5)	0.109(4)	0.263(7)	0.221(6)	0.132(4)	0.116(4)	0.202(6)
F(1)	2*i*	1.0055(2)	0.6083(2)	0.6260(2)	0.064(2)	0.057(1)	0.056(1)	0.022(1)	0.041(1)	0.020(1)
F(2)	2*i*	1.0632(2)	0.4479(2)	0.6320(2)	0.066(2)	0.068(2)	0.070(2)	0.037(1)	0.041(1)	0.011(1)
F(3)	2*i*	1.0266(3)	0.3581(2)	0.7675(2)	0.076(2)	0.053(2)	0.089(2)	0.042(1)	0.031(2)	0.024(1)
F(4)	2*i*	0.9312(3)	0.4302(2)	0.8937(2)	0.086(2)	0.061(2)	0.062(2)	0.036(2)	0.035(2)	0.036(1)
F(5)	2*i*	0.7745(3)	0.3395(3)	0.9762(2)	0.071(2)	0.120(3)	0.077(2)	0.048(2)	0.045(2)	0.044(2)
F(6)	2*i*	0.6471(4)	0.2521(3)	0.7636(2)	0.132(3)	0.136(3)	0.072(2)	0.083(2)	0.073(2)	0.038(2)
F(7)	2*i*	0.3979(3)	0.2109(2)	0.6658(2)	0.135(3)	0.093(2)	0.031(1)	0.059(2)	0.027(2)	0.010(1)
F(8)	2*i*	0.2778(3)	0.2665(2)	0.7775(2)	0.062(2)	0.081(2)	0.049(2)	0.022(2)	0.006(1)	0.010(1)
F(9)	2*i*	0.1253(5)	0.7640(3)	0.4624(3)	0.151(4)	0.091(3)	0.069(2)	0.022(3)	0.002(2)	0.012(2)
F(10)	2*i*	0.3027(8)	0.7840(5)	0.3968(5)	0.45(1)	0.273(7)	0.167(5)	0.267(8)	0.245(7)	0.148(5)
F(11)	2*i*	0.5439(7)	0.9182(6)	0.5280(7)	0.278(7)	0.394(9)	0.42(1)	0.278(7)	0.317(8)	0.352(9)
F(12)	2*i*	0.6092(3)	1.0325(5)	0.7258(6)	0.045(2)	0.222(6)	0.39(1)	0.018(3)	0.038(4)	0.226(7)
C(1)	2*i*	0.7501(4)	0.6815(3)	0.4869(3)	0.050(2)	0.051(2)	0.042(2)	0.025(2)	0.025(2)	0.017(2)
C(2)	2*i*	0.7032(4)	0.6099(3)	0.3846(3)	0.067(3)	0.065(3)	0.040(2)	0.040(2)	0.031(2)	0.020(2)
C(3)	2*i*	0.5755(4)	0.5476(3)	0.3284(3)	0.071(3)	0.049(2)	0.032(2)	0.026(2)	0.021(2)	0.004(2)
C(4)	2*i*	0.4962(4)	0.5565(3)	0.3743(3)	0.050(2)	0.042(2)	0.031(2)	0.012(2)	0.013(2)	0.003(2)
C(5)	2*i*	0.5468(3)	0.6295(3)	0.4763(3)	0.041(2)	0.033(2)	0.031(2)	0.014(2)	0.015(2)	0.011(2)
C(6)	2*i*	0.4697(3)	0.6440(3)	0.5329(3)	0.039(2)	0.033(2)	0.029(2)	0.013(2)	0.012(2)	0.010(2)
C(7)	2*i*	0.3394(4)	0.5873(3)	0.4876(3)	0.041(2)	0.057(3)	0.036(2)	0.006(2)	0.012(2)	0.005(2)
C(8)	2*i*	0.2760(4)	0.6044(4)	0.5478(4)	0.039(2)	0.069(3)	0.052(3)	0.010(2)	0.021(2)	0.017(2)
C(9)	2*i*	0.3415(4)	0.6782(3)	0.6487(3)	0.051(3)	0.067(3)	0.051(2)	0.029(2)	0.034(2)	0.027(2)
C(10)	2*i*	0.4710(4)	0.7313(3)	0.6894(3)	0.046(2)	0.052(2)	0.036(2)	0.023(2)	0.020(2)	0.013(2)
C(11)	2*i*	0.8366(4)	0.9404(3)	0.5963(4)	0.062(3)	0.048(2)	0.061(3)	0.025(2)	0.028(2)	0.027(2)
C(12)	2*i*	0.9095(5)	1.0375(4)	0.6065(5)	0.077(3)	0.062(3)	0.096(4)	0.033(3)	0.048(3)	0.047(3)
C(13)	2*i*	0.9662(5)	1.1193(4)	0.7018(5)	0.078(4)	0.043(3)	0.119(5)	0.021(3)	0.046(4)	0.037(3)
C(14)	2*i*	0.9468(5)	1.1034(3)	0.7852(5)	0.069(3)	0.035(2)	0.084(4)	0.017(2)	0.023(3)	0.011(2)
C(15)	2*i*	0.8729(4)	1.0044(3)	0.7708(3)	0.038(2)	0.038(2)	0.055(2)	0.016(2)	0.012(2)	0.010(2)
C(16)	2*i*	0.8471(4)	0.9783(3)	0.8540(3)	0.038(2)	0.037(2)	0.044(2)	0.013(2)	0.009(2)	–0.001(2)
C(17)	2*i*	0.8790(5)	1.0497(4)	0.9532(4)	0.065(3)	0.047(3)	0.055(3)	0.017(2)	0.014(2)	–0.011(2)
C(18)	2*i*	0.8510(5)	1.0152(4)	1.0243(4)	0.081(4)	0.075(4)	0.040(3)	0.025(3)	0.017(3)	–0.018(2)
C(19)	2*i*	0.7930(5)	0.9096(4)	0.9974(4)	0.070(3)	0.084(4)	0.039(2)	0.031(3)	0.023(2)	0.008(2)
C(20)	2*i*	0.7647(4)	0.8422(3)	0.8993(3)	0.052(2)	0.057(3)	0.038(2)	0.022(2)	0.019(2)	0.011(2)
C(21)	2*i*	0.9386(3)	0.6082(3)	0.7599(3)	0.028(2)	0.032(2)	0.031(2)	0.007(2)	0.010(2)	0.003(2)
C(22)	2*i*	0.9165(3)	0.5607(3)	0.8277(3)	0.032(2)	0.034(2)	0.030(2)	0.009(2)	0.009(2)	0.005(2)
C(23)	2*i*	0.9478(4)	0.4775(3)	0.8286(3)	0.042(2)	0.042(2)	0.042(2)	0.014(2)	0.014(2)	0.015(2)
C(24)	2*i*	0.9980(4)	0.4392(3)	0.7638(3)	0.042(2)	0.034(2)	0.052(2)	0.017(2)	0.013(2)	0.007(2)
C(25)	2*i*	1.0175(4)	0.4843(3)	0.6980(3)	0.038(2)	0.049(2)	0.048(2)	0.021(2)	0.022(2)	0.003(2)
C(26)	2*i*	0.9890(3)	0.5686(3)	0.6959(3)	0.034(2)	0.046(2)	0.038(2)	0.014(2)	0.018(2)	0.011(2)
C(27)	2*i*	0.8933(3)	0.6913(3)	0.7454(3)	0.040(2)	0.035(2)	0.024(2)	0.013(2)	0.016(2)	0.006(1)
C(28)	2*i*	0.8675(4)	0.6048(3)	0.9021(3)	0.045(2)	0.042(2)	0.035(2)	0.016(2)	0.020(2)	0.015(2)
C(29)	2*i*	0.5932(4)	0.3536(3)	0.9886(3)	0.053(2)	0.044(2)	0.034(2)	0.016(2)	0.024(2)	0.017(2)
C(30)	2*i*	0.4655(4)	0.3371(3)	0.9388(3)	0.054(2)	0.037(2)	0.034(2)	0.013(2)	0.023(2)	0.011(2)
C(31)	2*i*	0.4020(4)	0.2895(3)	0.8298(3)	0.059(3)	0.044(2)	0.037(2)	0.017(2)	0.016(2)	0.012(2)
C(32)	2*i*	0.4625(5)	0.2592(3)	0.7707(3)	0.098(4)	0.053(3)	0.031(2)	0.036(3)	0.029(2)	0.013(2)
C(33)	2*i*	0.5882(5)	0.2786(4)	0.8209(4)	0.088(4)	0.071(3)	0.049(3)	0.044(3)	0.047(3)	0.026(2)
C(34)	2*i*	0.6513(5)	0.3237(4)	0.9288(4)	0.064(3)	0.070(3)	0.053(3)	0.031(2)	0.035(2)	0.030(2)
C(35)	2*i*	0.6713(4)	0.4035(4)	1.1077(3)	0.052(3)	0.061(3)	0.042(2)	0.015(2)	0.027(2)	0.018(2)
C(36)	2*i*	0.4013(4)	0.3662(3)	1.0064(3)	0.049(2)	0.044(2)	0.037(2)	0.004(2)	0.026(2)	0.006(2)
C(37)	2*i*	0.3968(5)	0.9618(4)	0.7048(4)	0.059(3)	0.047(3)	0.074(3)	0.015(2)	0.016(3)	0.035(3)
C(38)	2*i*	0.2713(4)	0.8920(3)	0.6308(3)	0.053(2)	0.048(2)	0.055(2)	0.024(2)	0.033(2)	0.028(2)
C(39)	2*i*	0.2464(6)	0.8355(4)	0.5311(4)	0.094(4)	0.072(3)	0.063(3)	0.042(3)	0.039(3)	0.036(3)
C(40)	2*i*	0.341(1)	0.8469(8)	0.5003(7)	0.25(1)	0.169(8)	0.138(7)	0.162(9)	0.165(8)	0.119(7)

Table 3. continued.

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(41)	2*i*	0.457(1)	0.913(1)	0.564(1)	0.151(9)	0.22(1)	0.26(2)	0.146(9)	0.18(1)	0.21(1)
C(42)	2*i*	0.4873(6)	0.9681(6)	0.6646(8)	0.048(3)	0.127(6)	0.197(9)	0.040(4)	0.050(5)	0.130(7)
C(43)	2*i*	0.421(1)	1.0247(6)	0.8124(6)	0.17(1)	0.055(4)	0.064(5)	–0.020(5)	–0.006(5)	0.024(4)
C(44)	2*i*	0.1614(5)	0.8707(4)	0.6570(4)	0.061(3)	0.068(3)	0.084(3)	0.032(3)	0.043(3)	0.046(3)

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