Crystal structure of [(3-carboxyl-1-(4-carboxylphenylmethylene)-2-oxidopyrinium-κ^2O^1,O^2)chloride(pyrazino[2,3-*f*]-[1,10]phenanthroline-κ^2N^1,N^2)copper], $[Cu(C_{14}H_{10}NO_5)Cl(C_{14}H_8N_4)]$, $C_{28}H_{18}ClCuN_5O_5$

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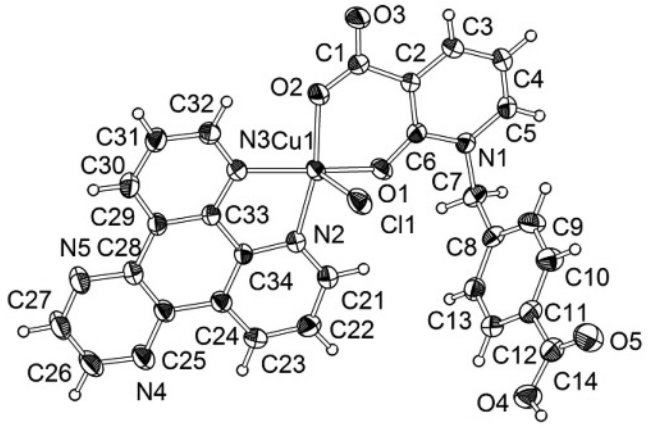

Abstract

$C_{28}H_{18}ClCuN_5O_5$, monoclinic, $P2_1/c$ (no. 14), a = 11.9225(1) Å, b = 8.2861(1) Å, c = 24.5789(3) Å, β = 91.619(1)°, V = 2427.2 Å^3, Z = 4, $R_{gt}(F)$ = 0.0477, $wR_{ref}(F^2)$ = 0.1358, T = 293 K.

Table 1. Data collection and handling.

Crystal:	blue blocks, size 0.08×0.08×0.15 mm
Wavelength:	Cu K_α radiation (1.54178 Å)
μ:	27.40 cm^{-1}
Diffractometer, scan mode:	Xcalibur, Ruby, Gemini ultra, ω
$2\theta_{max}$:	133.26°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11169, 4241
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3847
$N(param)_{refined}$:	361
Programs:	DIAMOND [8], SHELX [9]

Source of material

In a typical synthesis, 3-carboxyl-1-(4-carboxylphenylmethylene)-2-oxidopyrinium (0.029 g, 0.13 mmol), $CuCl_2{\cdot}2H_2O$ (0.021 g, 0.13 mmol), and pyrazino[2,3-*f*]-[1,10]phenanthroline (0.034, 0.13 mmol) were dissolved in the mixure of DMF (6 ml) and water (2 ml) under stirring. This mixture was sealed into a 15 ml autoclave and heated in the oven up to 358 K for 4 days. After cooling to room temperature, the blue block-shaped crystals were collected as a single phase.

Experimental details

The carbon H-atoms and carboxyl H-atom were placed in calculated positions (C–H (rings of L_1 and L_2) = 0.93 Å, C–H (methylene) = 0.97 Å, O–H (carboxyl) = 0.82 Å) and were included in the refinement in the riding-model approximation, with U_{iso}(H) = 1.2U_{eq}(C) and U_{iso}(H) = 1.2U_{eq}(O).

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Discussion

During the past decades, MOF materials have attracted huge attention due to the applications including gas absorption and catalysis [1,2]. At present, MOFs which are covalently built up from metal ion/metal oxide cluster and organic/organometallic linker can be rationally designed in some extent by manipulating the organic linker or the metal node. Nevertheless, it is still a great challenge to predict the exact structures and composition of polymeric compounds assembled by coordination bonds and/or π-π interactions [3]. The 1,10-phenanthroline and its derivatives as a candidate for non-covalent interactions have already been employed to construct coordination polymers [4-7]. A novel complex $[Cu(L_1)Cl(L_2)]$ (L_1 = 3-carboxyl-1-(4-carboxylphenylmethylene)-2-oxidopyrinium, L_2 = pyrazino[2,3-*f*][1,10]phenanthroline) has been synthesized and structurally determined. The asymmetric unit of title structure consists of one Cu(II) cation, one L_1 anion, one L_2 ligand and one chlorido ligand (Fig.). The Cu cation is pyramidly coordinated by one hydroxyl oxygen and one carboxyl oxygen of L_1, two nitrogens of L_2, and one chlorido ligand positioned on the apex of the pyramid. The Cu–O distances range from 1.925(2) Å to 1.965(2) Å, and the Cu–N distances from 2.010(2) Å to 2.028(2) Å, and a Cu–Cl distance of 2.504(1) Å. There are two interactions of H-bonds and π-π interactions in the title structure, responsible to build up the supermolecular net. The H-bonds between carboxyls of the adjacent L_1 result in the formation of chain paralleling with (001) direction. The π-π interacions of phenyl ring of L_1 and phen ring of L_2 give rise to the supermolecular net.

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

Atom	Site	x	y	z	U_{iso}
H(4A)	4*e*	0.2131	0.2746	0.0822	0.054
H(3)	4*e*	0.4084	0.5091	0.4935	0.044
H(4)	4*e*	0.5049	0.6911	0.4401	0.049
H(5)	4*e*	0.4112	0.8111	0.3684	0.042
H(7A)	4*e*	0.2445	0.8742	0.3206	0.039
H(7B)	4*e*	0.1322	0.7841	0.3330	0.039
H(9)	4*e*	0.3901	0.6080	0.2940	0.048
H(10)	4*e*	0.4166	0.4482	0.2195	0.049
H(12)	4*e*	0.0974	0.5223	0.1698	0.041
H(13)	4*e*	0.0716	0.6856	0.2447	0.040
H(21)	4*e*	–0.0377	0.5718	0.3104	0.043
H(22)	4*e*	–0.1937	0.6191	0.2554	0.044
H(23)	4*e*	–0.3647	0.5101	0.2779	0.040
H(26)	4*e*	–0.6636	0.2815	0.3313	0.055
H(27)	4*e*	–0.6624	0.1283	0.4084	0.054
H(30)	4*e*	–0.3556	0.0235	0.4971	0.041
H(31)	4*e*	–0.1840	0.0002	0.5424	0.043
H(32)	4*e*	–0.0332	0.1494	0.5142	0.039

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*	0.01619(3)	0.37918(4)	0.41644(1)	0.0220(2)	0.0407(3)	0.0311(3)	–0.0063(1)	–0.0033(2)	0.0082(1)
Cl(1)	4*e*	0.11277(5)	0.17198(9)	0.36023(3)	0.0263(3)	0.0489(4)	0.0500(4)	0.0049(3)	0.0004(3)	–0.0082(3)
O(1)	4*e*	0.1051(1)	0.5622(2)	0.39068(7)	0.0263(8)	0.041(1)	0.036(1)	–0.0059(7)	–0.0073(7)	0.0094(8)
O(2)	4*e*	0.1066(2)	0.3574(3)	0.48218(8)	0.033(1)	0.060(1)	0.035(1)	–0.0167(9)	–0.0065(8)	0.0166(9)
O(3)	4*e*	0.2629(2)	0.3584(3)	0.53114(9)	0.041(1)	0.072(1)	0.040(1)	–0.016(1)	–0.0153(9)	0.027(1)
O(4)	4*e*	0.1952(2)	0.3317(3)	0.10779(8)	0.045(1)	0.054(1)	0.035(1)	0.0048(9)	–0.0007(9)	–0.0113(9)
O(5)	4*e*	0.3775(2)	0.3159(3)	0.1301(1)	0.041(1)	0.082(2)	0.053(1)	0.010(1)	0.004(1)	–0.026(1)
C(1)	4*e*	0.2064(2)	0.4018(3)	0.4906(1)	0.030(1)	0.035(1)	0.026(1)	–0.002(1)	–0.001(1)	0.0042(9)
C(2)	4*e*	0.2621(2)	0.5165(3)	0.45228(9)	0.024(1)	0.035(1)	0.023(1)	–0.0039(9)	–0.0001(9)	0.0014(9)
C(3)	4*e*	0.3717(2)	0.5566(4)	0.4637(1)	0.027(1)	0.053(2)	0.031(1)	–0.004(1)	–0.004(1)	0.006(1)
C(4)	4*e*	0.4301(2)	0.6664(4)	0.4322(1)	0.029(1)	0.059(2)	0.035(1)	–0.014(1)	–0.000(1)	0.005(1)
C(5)	4*e*	0.3743(2)	0.7358(3)	0.3895(1)	0.031(1)	0.045(2)	0.031(1)	–0.012(1)	0.004(1)	–0.000(1)
C(6)	4*e*	0.2051(2)	0.5876(3)	0.40663(9)	0.027(1)	0.029(1)	0.023(1)	–0.0022(9)	0.0022(9)	–0.0016(9)
C(7)	4*e*	0.2117(2)	0.7691(3)	0.3273(1)	0.040(1)	0.030(1)	0.027(1)	0.002(1)	0.001(1)	0.0052(9)
C(8)	4*e*	0.2275(2)	0.6614(3)	0.2782(1)	0.037(1)	0.031(1)	0.023(1)	0.002(1)	0.003(1)	0.0051(9)
C(9)	4*e*	0.3308(2)	0.5906(4)	0.2693(1)	0.036(1)	0.049(2)	0.033(1)	0.008(1)	–0.008(1)	–0.005(1)
C(10)	4*e*	0.3468(2)	0.4952(4)	0.2245(1)	0.037(1)	0.049(2)	0.036(1)	0.014(1)	–0.002(1)	–0.004(1)
C(11)	4*e*	0.2608(2)	0.4677(3)	0.1866(1)	0.036(1)	0.036(1)	0.028(1)	0.003(1)	0.003(1)	0.001(1)
C(12)	4*e*	0.1563(2)	0.5395(3)	0.1947(1)	0.031(1)	0.042(1)	0.029(1)	–0.001(1)	–0.000(1)	0.001(1)
C(13)	4*e*	0.1408(2)	0.6366(3)	0.2399(1)	0.029(1)	0.039(1)	0.031(1)	0.003(1)	0.004(1)	0.005(1)
C(14)	4*e*	0.2845(2)	0.3637(3)	0.1386(1)	0.039(2)	0.039(1)	0.033(1)	0.003(1)	0.003(1)	0.001(1)
N(1)	4*e*	0.2651(2)	0.6979(2)	0.37678(8)	0.030(1)	0.030(1)	0.024(1)	–0.0058(8)	0.0016(8)	0.0008(8)
N(2)	4*e*	–0.1101(2)	0.4359(3)	0.36404(8)	0.025(1)	0.035(1)	0.030(1)	–0.0035(8)	0.0017(8)	0.0017(8)
N(3)	4*e*	–0.1077(2)	0.2511(3)	0.45125(8)	0.0242(9)	0.034(1)	0.029(1)	–0.0001(8)	0.0004(8)	0.0009(8)
N(4)	4*e*	–0.5046(2)	0.3395(3)	0.3331(1)	0.024(1)	0.050(1)	0.047(1)	–0.0006(9)	–0.003(1)	0.006(1)
N(5)	4*e*	–0.5034(2)	0.1438(3)	0.4270(1)	0.026(1)	0.044(1)	0.050(1)	–0.0046(9)	0.004(1)	0.005(1)
C(21)	4*e*	–0.1059(2)	0.5264(3)	0.3196(1)	0.030(1)	0.045(2)	0.034(1)	–0.007(1)	0.000(1)	0.006(1)
C(22)	4*e*	–0.1995(2)	0.5555(3)	0.2864(1)	0.041(1)	0.039(1)	0.030(1)	–0.002(1)	–0.001(1)	0.005(1)
C(23)	4*e*	–0.3010(2)	0.4899(3)	0.2995(1)	0.030(1)	0.038(1)	0.031(1)	0.001(1)	–0.005(1)	0.002(1)
C(24)	4*e*	–0.3074(2)	0.3921(3)	0.3459(1)	0.025(1)	0.031(1)	0.030(1)	0.0011(9)	–0.000(1)	–0.0014(9)
C(25)	4*e*	–0.4094(2)	0.3133(3)	0.3632(1)	0.022(1)	0.035(1)	0.034(1)	0.001(1)	0.0003(9)	–0.002(1)
C(26)	4*e*	–0.5963(2)	0.2678(4)	0.3508(1)	0.024(1)	0.057(2)	0.058(2)	–0.004(1)	–0.008(1)	0.006(1)
C(27)	4*e*	–0.5952(2)	0.1732(4)	0.3975(1)	0.023(1)	0.054(2)	0.059(2)	–0.007(1)	0.002(1)	0.005(1)
C(28)	4*e*	–0.4082(2)	0.2146(3)	0.4095(1)	0.025(1)	0.032(1)	0.036(1)	–0.0020(9)	0.004(1)	–0.001(1)
C(29)	4*e*	–0.3040(2)	0.1858(3)	0.4402(1)	0.024(1)	0.031(1)	0.031(1)	–0.0017(9)	0.0043(9)	–0.0004(9)
C(30)	4*e*	–0.2940(2)	0.0819(3)	0.4856(1)	0.031(1)	0.035(1)	0.037(1)	–0.003(1)	0.007(1)	0.005(1)
C(31)	4*e*	–0.1921(2)	0.0683(3)	0.5125(1)	0.033(1)	0.039(1)	0.035(1)	–0.001(1)	0.004(1)	0.009(1)
C(32)	4*e*	–0.1011(2)	0.1567(3)	0.4948(1)	0.029(1)	0.036(1)	0.032(1)	0.002(1)	–0.001(1)	0.005(1)
C(33)	4*e*	–0.2078(2)	0.2652(3)	0.42435(9)	0.022(1)	0.029(1)	0.026(1)	0.0005(9)	0.0024(9)	–0.0002(9)
C(34)	4*e*	–0.2092(2)	0.3681(3)	0.3767(1)	0.022(1)	0.030(1)	0.025(1)	–0.0018(9)	0.0033(9)	–0.0014(9)

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