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Crystal structure of bis(4-phenylpiperazin-1-ium) bis(2-(4-phenylpiperazin-1-yl)succinato- $\kappa^2\text{O},\text{O}'$)copper(II) tetrahydrate, $\text{C}_{48}\text{H}_{70}\text{CuN}_8\text{O}_{12}$, $[\text{C}_{10}\text{H}_{14}\text{N}_2]_2[\text{Cu}(\text{C}_{14}\text{H}_{17}\text{N}_2\text{O}_4)_2] \cdot 4 \text{H}_2\text{O}$

Abstract

$\text{C}_{48}\text{H}_{70}\text{CuN}_8\text{O}_{12}$, triclinic, $P\bar{1}$ (no. 2), $a = 9.4869(1) \text{ \AA}$, $b = 11.2213(1) \text{ \AA}$, $c = 12.0819(1) \text{ \AA}$, $\alpha = 74.608(1)^\circ$, $\beta = 78.441(1)^\circ$, $\gamma = 86.820(1)^\circ$, $V = 1214.90(2) \text{ \AA}^3$, $Z = 1$, $R_{\text{gt}}(F) = 0.0460$, $wR_{\text{ref}}(F^2) = 0.1239$, $T = 296(2) \text{ K}$.

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The molecular structure is shown in the figure (Carbon-bound hydrogen atoms are removed for clarity.). Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Green polyhedron
Size:	$0.57 \times 0.38 \times 0.35 \text{ mm}$
Wavelength:	Mo $K\alpha$ radiation ($0.71073 \text{ \AA}$)
μ :	0.52 mm^{-1}
Diffractometer, scan mode:	Bruker P4, ω
θ_{max} , completeness:	33.1° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	19878, 7895, 0.027
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 5851
$N(\text{param})_{\text{refined}}$:	329
Programs:	Bruker [1], SHELX [2, 3], Diamond [4]

Source of material

The mixture of CuCl_2 (0.040 g, 0.3 mmol), 1-phenylpiperazine (0.136 mL, 0.9 mmol), maleic acid (0.035 g, 0.3 mmol) in water (1.0 mL) was sealed under vacuum in a Pyrex tube and heated to 70°C for 68 h, then cooled to room temperature at 20°C/h . The pH before and after the reaction were 7 and 6, respectively. The green polyhedral crystals were recovered by vacuum filtration and washed with distilled water. The product is stable in air.

Experimental details

All hydrogen atoms bound to carbon and nitrogen atoms were placed in calculated positions and refined as riding model except for the hydrogen atoms in water molecules, which were located in difference Fourier maps, and their positions and isotropic displacement parameters were refined.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
Cu1	0.500000	0.000000	1.000000	0.02852(9)
O1	0.60683(14)	0.07860(11)	1.08400(10)	0.0368(3)
O2	0.67703(15)	0.26125(12)	1.08993(12)	0.0415(3)
O3	0.29525(15)	0.12342(12)	1.05074(13)	0.0480(3)
O4	0.16977(15)	0.29763(13)	1.02906(14)	0.0508(4)
C1	0.62013(17)	0.19420(15)	1.04447(14)	0.0314(3)
C2	0.56250(18)	0.25435(14)	0.93191(14)	0.0315(3)
H2	0.631230	0.318164	0.882920	0.038*
C3	0.41848(19)	0.31806(15)	0.96113(16)	0.0365(4)
H3A	0.399048	0.373154	0.889030	0.044*
H3B	0.429895	0.369234	1.012043	0.044*
C4	0.28521(19)	0.23769(16)	1.01912(15)	0.0361(4)
N1	0.55865(14)	0.15839(12)	0.86617(11)	0.0281(3)
N2	0.66399(15)	0.26522(13)	0.61478(12)	0.0322(3)
C5	0.70816(18)	0.14099(16)	0.80379(14)	0.0331(3)
H5A	0.711600	0.064693	0.779969	0.040*
H5B	0.772977	0.131858	0.858248	0.040*
C6	0.76259(19)	0.24560(17)	0.69645(15)	0.0364(4)
H6A	0.770146	0.320834	0.719965	0.044*
H6B	0.857496	0.225155	0.658508	0.044*
C7	0.46615(18)	0.18571(17)	0.77738(15)	0.0356(4)
H7A	0.370036	0.205211	0.813775	0.043*
H7B	0.459601	0.112138	0.750961	0.043*
C8	0.51955(19)	0.29179(17)	0.67196(15)	0.0387(4)
H8A	0.454744	0.304121	0.617141	0.046*
H8B	0.520890	0.367177	0.696611	0.046*
C9	0.71200(19)	0.34301(15)	0.50067(14)	0.0323(3)
C10	0.6303(2)	0.34785(17)	0.41577(15)	0.0391(4)
H10	0.544062	0.304677	0.435892	0.047*
C11	0.6766(2)	0.41664(18)	0.30132(16)	0.0456(4)
H11	0.621858	0.417929	0.245202	0.055*
C12	0.8025(2)	0.48283(19)	0.27006(17)	0.0505(5)
H12	0.832363	0.529796	0.193585	0.061*
C13	0.8837(2)	0.4787(2)	0.35344(18)	0.0523(5)
H13	0.969014	0.523182	0.332920	0.063*
C14	0.8398(2)	0.40853(18)	0.46829(16)	0.0432(4)
H14	0.896475	0.405736	0.523424	0.052*
N3	0.06144(17)	−0.16510(15)	0.82835(14)	0.0421(4)
H3C	−0.005416	−0.206132	0.886691	0.050*
H3D	0.146541	−0.198979	0.838451	0.050*
N4	0.12882(17)	0.02941(14)	0.61656(13)	0.0381(3)
C15	0.0615(2)	−0.0340(2)	0.83097(18)	0.0470(4)
H15A	0.090381	−0.028486	0.902048	0.056*
H15B	−0.035049	−0.000468	0.831465	0.056*
C16	0.1627(2)	0.04076(18)	0.72656(17)	0.0425(4)
H16A	0.156593	0.126960	0.727888	0.051*
H16B	0.260546	0.012896	0.730839	0.051*
C17	0.0319(3)	−0.17569(19)	0.71499(19)	0.0528(5)
H17A	−0.065496	−0.148024	0.708322	0.063*
H17B	0.039661	−0.261543	0.712532	0.063*
C18	0.1361(3)	−0.09928(19)	0.61428(19)	0.0516(5)
H18A	0.232987	−0.130238	0.618314	0.062*
H18B	0.114102	−0.106358	0.541273	0.062*
C19	0.2047(2)	0.11313(18)	0.51468(16)	0.0402(4)
C20	0.2934(3)	0.0740(2)	0.42412(19)	0.0554(5)

Table 2 (continued)

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
H20	0.310649	−0.009858	0.431675	0.067*
C21	0.3559(3)	0.1598(3)	0.3228(2)	0.0663(7)
H21	0.415058	0.132456	0.263096	0.080*
C22	0.3321(3)	0.2835(3)	0.3090(2)	0.0660(7)
H22	0.372110	0.340106	0.239758	0.079*
C23	0.2484(3)	0.3229(2)	0.3988(3)	0.0677(7)
H23	0.233534	0.407077	0.391009	0.081*
C24	0.1856(2)	0.2393(2)	0.5009(2)	0.0561(5)
H24	0.129844	0.267964	0.561132	0.067*
WO1	0.9865(2)	0.2556(2)	0.87464(19)	0.0715(5)
H25	0.945(4)	0.336(4)	0.876(3)	0.111(13)*
H26	1.059(4)	0.255(3)	0.907(3)	0.087(11)*
WO2	0.8163(3)	0.4660(2)	0.9187(2)	0.0881(7)
H27	0.835(4)	0.531(3)	0.935(3)	0.096(11)*
H28	0.789(5)	0.428(4)	0.983(4)	0.140(19)*

Comment

Recently, we reported a series of “unnatural”, tailor-made α -amino acid metal complexes containing racemic mixtures of the chiral ligands, which are formed under mild hydrothermal conditions *in situ* by Michael addition of amine to fumaric acid or *trans*-muconic acid [5–8]. For example, the hydrothermal reaction of a nickel salt, benzylamine, and fumaric acid in water can produce a nickel *N*-benzyl aspartate complex [6]. This type of Michael reaction, *i.e.*, the direct amination of α,β -unsaturated dicarboxylic acid is rarely reported, although several synthetic methods for amination of α,β -unsaturated dicarboxylic acid derivatives, such as mono- or diester and monoamide, are well known [9]. In this study we report a new complex containing the racemic 2-(4-phenylpiperazin-1-yl)succinato ligand, which is formed *in situ* by Michael addition of 4-phenylpiperazine to maleic acid.

The crystal structure of the title complex contains discrete centrosymmetric mononuclear Cu(C₁₄H₁₇N₂O₄)₂^{2−} anions. One crystallographically unique copper atom is coordinated by two racemic 2-(4-phenylpiperazin-1-yl)succinato ligands to form a Cu(*rac*-phenylpiperazinyl succinato)₂ unit. One nitrogen and two oxygen atoms in each D- and L-piperazinyl succinate are bonded to the Cu to complete a distorted octahedral arrangement with distances in the range of 1.955(1) Å–2.396(1) Å. The other two oxygen atoms in each carboxylate group of the phenylpiperazinyl succinate keep uncoordinated. A bond valence sum (BVS) calculation gives a value of 1.81 for Cu(1) indicating an oxidation state of +2.00 [10]. The [Cu(C₁₄H₁₇N₂O₄)₂]^{2−} anion charge is balanced by two mono-protonated phenylpiperazinium cations (see the figure). Water molecules occupy

the remaining lattice volume. The formula can be represented by $[\text{phenylpiperazinium}^+]_2[\text{Cu}^{2+}(\text{rac-phenylpiperazinyl succinate}^{2-})_2] \cdot 4 \text{H}_2\text{O}$.

The structure of $\text{Cu}(\text{rac-phenylpiperazinyl succinate})_2^{2-}$ is very similar to $\text{Cu}(\text{rac-piperazinyl succinate})_2$ in ref. 7. The major difference arises from the charge of the ligands. Unlike the divalent phenylpiperazinyl succinate in the title complex, monovalent piperazinyl succinate anion is produced in $\text{Cu}(\text{rac-piperazinyl succinate})_2$ complex from addition of fumaric acid to diamine, piperazine forming a zwitterion, i.e., the positive charge is localized at the protonated terminal nitrogen atom of piperazine moiety and the negative charge in the vicinity of carboxylate, to form neutral $\text{Cu}^{2+}(\text{rac-piperazinyl succinate}^-)_2$ complex [7].

The $\text{Cu}(\text{phenylpiperazinyl succinate})_2^{2-}$ anion forms extended networks of $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds with the phenylpiperazinium cation with the distance of $d(\text{N} \cdots \text{O}) = 2.735(2) \text{ \AA}$ and $2.904(2) \text{ \AA}$ respectively. Furthermore, the lattice water molecules are hydrogen bonded to the not Cu-coordinated (O2, O4) oxygen atoms in phenylpiperazinyl succinate ligand [$d(\text{O} \cdots \text{O}) = 2.833(2) \text{ \AA}$, $2.900 \text{ \AA}$, and $2.930 \text{ \AA}$] or to each other in a complicated arrangement, which results in the formation of layers in the *ab*-plane. Thus the hydrogen bonded layers stack along the *c*-axis and interact through van der Waals forces.

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