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The crystal structure of bis(*N,N*-dimethylformamide- κO)-tetrakis(9*H*-xanthene-9-carboxylic-carboxylate- $\kappa^2 O:O'$)dicopper(II) - acetonitrile (1/2), $C_{66}H_{56}Cu_2N_4O_{14}$

Table 1: Data collection and handling.

Crystal:	Metallic light green block
Size:	0.22 × 0.19 × 0.18 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.80 mm ⁻¹
Diffractometer, scan mode:	Xcalibur, ω
$\theta_{\max}$, completeness:	27.0°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	11692, 6227, 0.022
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 5277
$N(\text{param})_{\text{refined}}$:	391
Programs:	CrysAlis ^{PRO} [1], Olex2 [2], SHELX [3, 4]

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

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.40458(2)	0.45576(2)	0.51231(2)	0.02469(8)
O1	0.54020(18)	0.71482(16)	0.00253(15)	0.0673(5)
O2	0.41485(14)	0.46165(13)	0.35307(11)	0.0359(3)
O3	0.57462(14)	0.54092(14)	0.33147(11)	0.0374(3)
O4	0.7095(2)	−0.01371(18)	0.42413(17)	0.0696(5)
O5	0.53535(14)	0.28645(12)	0.53747(12)	0.0356(3)
O6	0.69722(14)	0.36228(12)	0.51851(12)	0.0379(3)
O7	0.23464(14)	0.40557(14)	0.55135(12)	0.0398(4)
N1	0.04749(18)	0.44364(19)	0.64540(16)	0.0462(5)
N2	0.8470(3)	0.7900(3)	0.1032(3)	0.1095(11)
C1	0.4798(2)	0.5248(2)	0.17049(15)	0.0352(5)
H1	0.444378	0.463147	0.155375	0.042*
C2	0.3848(2)	0.6552(2)	0.12706(16)	0.0366(5)
C3	0.2595(2)	0.6934(2)	0.1640(2)	0.0510(6)
H3	0.233909	0.638166	0.218434	0.061*
C4	0.1709(3)	0.8105(3)	0.1231(2)	0.0629(7)
H4	0.087011	0.833245	0.149274	0.075*
C5	0.2076(3)	0.8935(3)	0.0432(2)	0.0649(8)
H5	0.148630	0.972758	0.014897	0.078*
C6	0.3314(3)	0.8590(2)	0.0054(2)	0.0630(8)
H6	0.356774	0.915030	−0.048441	0.076*
C7	0.4188(2)	0.7410(2)	0.04717(19)	0.0459(6)
C8	0.6312(2)	0.5973(2)	0.03547(18)	0.0456(6)
C9	0.7491(3)	0.5779(3)	−0.0165(2)	0.0600(7)
H9	0.762791	0.642543	−0.068892	0.072*
C10	0.8446(3)	0.4642(3)	0.0093(2)	0.0643(8)
H10	0.923823	0.450975	−0.025552	0.077*
C11	0.8249(3)	0.3689(3)	0.0861(2)	0.0691(8)
H11	0.890262	0.290956	0.103341	0.083*
C12	0.7072(3)	0.3893(2)	0.1381(2)	0.0573(7)

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Abstract

$C_{66}H_{56}Cu_2N_4O_{14}$, triclinic, $P\bar{1}$ (no. 2), $a = 11.0791(5)$ Å, $b = 11.5747(5)$ Å, $c = 12.4037(6)$ Å, $\alpha = 77.782(4)^\circ$, $\beta = 86.304(4)^\circ$, $\gamma = 69.491(4)^\circ$, $V = 1455.97(12)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0361$, $wR_{\text{ref}}(F^2) = 0.0830$, $T = 293(2)$ K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

The complex was prepared as follows: a mixture of copper(II) chloride dihydrate (0.2 mmol), xanthene-9-carboxylic

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Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
H12	0.694537	0.324311	0.190646	0.069*
C13	0.6080(2)	0.5037(2)	0.11379(16)	0.0383(5)
C14	0.4919(2)	0.50644(18)	0.29605(15)	0.0310(4)
C15	0.6521(2)	0.27406(18)	0.53719(15)	0.0299(4)
C16	0.7531(2)	0.14110(18)	0.55913(17)	0.0345(5)
H16	0.814280	0.138371	0.614115	0.041*
C17	0.8275(2)	0.11612(19)	0.45487(19)	0.0392(5)
C18	0.9247(2)	0.1643(2)	0.4189(2)	0.0516(6)
H18	0.946734	0.211774	0.460960	0.062*
C19	0.9893(3)	0.1434(3)	0.3224(3)	0.0689(8)
H19	1.054163	0.176541	0.299619	0.083*
C20	0.9577(4)	0.0740(3)	0.2607(3)	0.0825(11)
H20	1.000790	0.060475	0.195164	0.099*
C21	0.8633(3)	0.0239(3)	0.2938(2)	0.0748(9)
H21	0.841957	−0.023279	0.251056	0.090*
C22	0.7997(3)	0.0440(2)	0.3919(2)	0.0526(6)
C23	0.6812(2)	−0.0342(2)	0.5349(2)	0.0542(7)
C24	0.6349(3)	−0.1322(3)	0.5742(3)	0.0773(10)
H24	0.621701	−0.178703	0.526348	0.093*
C25	0.6089(3)	−0.1597(3)	0.6840(4)	0.0871(11)
H25	0.577593	−0.225028	0.710770	0.104*
C26	0.6284(3)	−0.0919(3)	0.7550(3)	0.0811(10)
H26	0.611565	−0.111714	0.829760	0.097*
C27	0.6735(3)	0.0067(2)	0.7145(2)	0.0599(7)
H27	0.686671	0.052874	0.762740	0.072*
C28	0.6992(2)	0.03730(19)	0.6039(2)	0.0410(5)
C29	0.1540(2)	0.4654(2)	0.61136(19)	0.0431(5)
H29	0.169781	0.530380	0.634093	0.052*
C30	−0.0443(3)	0.5183(3)	0.7146(3)	0.0878(11)
H30A	−0.015295	0.583220	0.727652	0.132*
H30B	−0.051530	0.465166	0.783664	0.132*
H30C	−0.126940	0.556013	0.678216	0.132*
C31	0.0188(3)	0.3405(2)	0.6168(2)	0.0609(7)
H31A	0.079305	0.305607	0.563194	0.091*
H31B	−0.066963	0.371206	0.586631	0.091*
H31C	0.024980	0.276443	0.681773	0.091*
C32	0.7555(4)	0.7991(3)	0.1515(3)	0.0758(9)
C33	0.6401(3)	0.8137(3)	0.2131(3)	0.0909(11)
H33A	0.567504	0.867371	0.166794	0.136*
H33B	0.643379	0.850811	0.274677	0.136*
H33C	0.631601	0.732786	0.239534	0.136*

acid (0.2 mmol), was suspended in a mixed solvent of ethanol (20 mL) and water (20 mL). An amount of 0.1 M potassium hydroxide was used to adjust the pH to 5.50 and then heated at 80 °C to reflux for 3 hours. The precipitations were recrystallized by a mixture of DMF/acetonitrile/methyl alcohol (40%: 40%: 20% v/v) for three days. Bright green crystals were obtained. The yield is ca. 41% based on Cu.

Experimental details

H atoms attached to C atoms were placed in geometrically idealized positions.

Comment

Owing to their wide antibacterial, catalysis, fluorescence switch and so on, great attention has been drawn to binuclear copper(II) complexes [5–7]. However, a limited number of binuclear copper complexes with bulky ring skeleton ligands are reported. We have successfully synthesized a binuclear copper complex containing macrocyclic skeleton ligands.

The single crystal X-ray diffraction showed that the distance of Cu–Cu of the dinuclear copper(II) complex is 2.6295 Å. Each copper(II) ion is pentacoordinated by four oxygen atoms originated from four xanthene-9-carboxylic-carboxylate ligands (see the figure), as well as one oxygen atoms from a DMF ligand. Furthermore, weak $\pi \cdots \pi$ interactions were found in the crystal. The centroid-to-centroid distance between a pair of aromatic groups on the xanthene-9-carboxylic-carboxylate ligands possessing $\pi \cdots \pi$ stacking interactions is 3.9020(2) Å.

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