

Note

Synthesis and Crystal Structure of Two-dimensional Network Supramolecular Complex $[\text{Cu}(\text{dafo})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$

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In an attempt to synthesize supra-molecular complex of copper (II) with mixed ligands in a solution reaction of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ with 4,5-diazafluorene-9-one (dafo) and *o*-phthalic acid, the bright blue column-like crystal $[\text{Cu}(\text{dafo})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ was obtained. Its structure was determined by single-crystal X-ray diffraction study. The crystal belongs to monoclinic system, space group $P2(1)/n$ with cell dimensions: $a = 0.7947(3)$ nm, $b = 1.2021(5)$ nm, $c = 1.3190(5)$ nm, $\alpha = 90.000(5)^\circ$, $\beta = 90.000(5)^\circ$, $\gamma = 90.000(5)^\circ$, $V = 1.2600(9)$ nm³, $Z = 2$, $F(000) = 670$, $M_r = 662.83$, $D_c = 1.747$ g/cm³, $\mu(\text{Mo K}\alpha) = 1.154$ mm⁻¹, $R_1 = 0.0455$, $wR_2 = 0.1041$. The analysis of the crystal structure indicates that the complex has a two-dimensional network structure which is formed by hydrogen bonds.

Keywords copper(II) complex, synthesis, crystal structure, supramolecular, two-dimensional network structure

Introduction

The supramolecular complexes formed by the weak interactions (electrostatic interaction, hydrogen bonds, van der Waals force, short-range exclusion force, etc.) of more than two sorts of species is an organizing entity that usually possesses special structure and function.¹ Supramolecular complexes have wide application in various fields such as material, catalysis, conductor, semiconductor, medicine, biotechnology, etc.²⁻⁶ We attempted to synthesize supramolecular complex of copper(II)

with mixed ligands by the reaction of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ with dafo and *o*-phthalic acid. But the anticipatory complex was not obtained, accidentally, a supramolecular complex $[\text{Cu}(\text{dafo})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ (dafo = 4,5, diazafluorene-9-one) that had a two-dimensional network structure was formed. In the present paper, the synthesis and crystal structure of the title complex are reported.

Experimental

Apparatus and reagents

Elemental analysis was performed on a Germany Vario EL III CHNOS analyzer. Crystal structure was obtained on a Bruker Smart-1000CCD diffractometer. All reagents were of A. R. grade. Dafo was prepared following the literature method.⁷ *O*-phthalic acid was obtained by hydrolysis of *o*-phthalic anhydride. Copper(II) perchlorate was prepared by ourselves.⁸

Preparation of ligand

Dafo was prepared following the reported method.⁷ The equation of the reaction is Eq. (1)

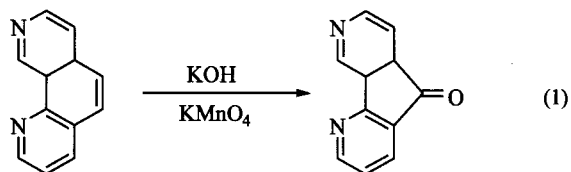
Preparation of complex

A solution of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.1850 g, 0.0005

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mol) in 3 mL of 95% ethanol and an aqueous solution of perchlorate acid were added dropwise into a solution of dafo (0.1818 g, 0.001 mol) in 10 mL of 95% ethanol under stirring at 60 °C. After mixing and refluxing for 1 h, a solution of *o*-phthalic acid (0.0840 g, 0.0005 mol) in 3 mL of 95% ethanol was added. Refluxing for an additional 1 h, the reaction solution turned blue and was standing for 10 d at room temperature. Bright blue column-like crystals suitable for X-ray diffraction analysis were formed. Yield, 60.3%, m. p. 253–254 °C. Anal. calcd for $C_{22}H_{16}CuN_4O_{12}$: C 39.80, N 8.45, H 2.41; found C 39.91, N 8.48, H 2.49.

X-Ray diffraction study

A single crystal with dimensions 0.25 mm × 0.36 mm × 0.28 mm was selected for data collection, using a Bruker Smart-1000CCD diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.071073$ nm). Data were collected by ω -2 θ scan technique. A total reflections of 6110 were collected, of which independent reflections of 2091 could be observed and used in the structure analysis. The structure was solved by direct methods. The positions of all remaining non-H atoms were obtained from successive Fourier syntheses. The positions of

all non-H atoms were refined anisotropically with full-matrix least-squares on F^2 . In the final difference map, the residuals are 616 e/nm³ and -424 e/nm³, respectively. The crystallographic data and analysis parameters are showed in Table 1: monoclinic system, space group $P2(1)/n$ with cell dimensions: $a = 0.7947(3)$ nm, $b = 1.2021(5)$ nm, $c = 1.3190(5)$ nm, $\alpha = 90.000(5)^\circ$, $\beta = 90.000(5)^\circ$, $\gamma = 90.000(5)^\circ$, $V = 1.2600(9)$ nm³, $Z = 2$, $F(000) = 670$, $M_r = 662.83$, $D_c = 1.747$ g/cm³, μ (Mo K α) = 1.154 mm⁻¹, $R_1 = 0.0455$, $wR_2 = 0.1041$.

Results and discussion

The non-H atomic coordinates and thermal parameters of the title complex are listed in Table 2, and the selected bonds length and bond angles are listed in Table 3. All of the data in brackets are standard deviation. The structure unit cell of the complex consists of $[Cu(dafo)_2(H_2O)_2]^{2+}$ and ClO_4^- . The copper atom is in a square planar coordination environment, two nitrogen atoms are from two dafo which are monodentate ligands here, and two oxygen atoms are from two water molecules, respectively. The bond length data: Cu(1)—N(1A) 0.1987(3) nm, Cu(1)—N(1) 0.1987(3) nm, Cu(1)—O(2) 0.1996(4) nm, Cu(1)—O(2) 0.1996(4) nm and bond angles data N(1A)-Cu(1)-N(1) 180.00(15)°, N(1A)-Cu(1)-O(2A) 90.15(16)°, N(1)-Cu(1)-O(2) 89.85(16)°, N(1A)-Cu(1)-O(2A) 89.85(16)°, N(1)-Cu(1)-O(2A) 90.15(16)°, O(2)-Cu(1)-O(2A)

Table 1 Crystal data and structure analysis parameters

Formula	$[Cu(dafo)_2(H_2O)_2](ClO_4)_2$	V (nm ³)	1.2600(9)
Crystal size (mm)	0.20 × 0.20 × 0.15	Z	2
Empirical formula	$C_{22}H_{16}Cl_2CuN_4O_{12}$	D_c (g·cm ⁻³)	1.747
Temperature (K)	299(2)	$F(000)$	670
Wavelength (nm)	0.071073	Scan mode	ω -2 θ
Formula weight	662.83	θ range for data collection (°)	2.29–24.72
Crystal system	monoclinic	Scan speed (min)	16°
Space group	$P2(1)/n$	Reflections collected	6110
a (nm)	0.7947(3)	Independent reflections	2091
b (nm)	1.2021(5)	Goodness-of-fit (F^2)	0.951
c (nm)	1.3190(5)	Refinement method	Full-matrix least-squares on F^2
α (°)	90.000(5)	$R [I > 2\sigma(I)]$	0.0455
β (°)	90.000(6)	R (all data)	0.0690
γ (°)	90.000(5)	Largest diff. peak and hole (e·nm ⁻³)	616 and -424

Table 2 Atomic coordinates ($\times 10^4$) and thermal parameters ($\times 10 \text{ nm}^2$)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}	Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Cu(1)	0	5000	0	36(1)	C(2)	4751(6)	5628(4)	1446(3)	48(1)
Cl(1)	3687(1)	8077(1)	8614(1)	47(1)	C(3)	4578(6)	6742(5)	1737(4)	53(1)
N(1)	1992(4)	5614(3)	718(2)	35(1)	C(4)	3095(5)	7272(4)	1511(3)	42(1)
N(2)	-951(4)	7040(3)	336(2)	41(1)	C(5)	1865(5)	6665(4)	1005(3)	35(1)
O(1)	3175(4)	9174(3)	2092(3)	65(1)	C(6)	415(5)	7372(3)	811(3)	35(1)
O(2)	956(5)	5513(4)	-1319(3)	54(1)	C(7)	729(5)	8428(4)	1193(3)	43(1)
O(3)	4047(4)	8656(3)	9521(2)	71(1)	C(8)	-493(7)	9228(4)	1078(4)	56(1)
O(4)	3744(6)	8758(4)	7767(3)	108(2)	C(9)	-1944(7)	8916(5)	584(4)	62(1)
O(5)	4648(8)	7137(4)	8534(4)	144(2)	C(10)	-2121(6)	7835(4)	231(4)	55(1)
O(6)	1936(5)	7736(4)	8702(3)	102(1)	C(11)	2451(5)	8419(4)	1664(3)	46(1)
C(1)	3457(5)	5100(4)	954(3)	42(1)					

Table 3 Selected bonds Lengths (nm) and bond angles ($^\circ$)

Cu(1)-N(1A)	0.1987(3)	N(1)-C(1)	0.355(5)
Cu(1)-N(1)	0.1987(3)	N(2)-C(6)	0.1315(5)
Cu(1)-O(2)	0.1996(4)	N(2)-C(10)	0.1341(6)
Cu(1)-O(2A)	0.1996(4)	O(1)-C(11)	0.1213(5)
N(1)-C(5)	0.1322(5)	C(5)-C(6)	0.1455(5)
N(1)-Cu(1)-O(2)	89.85(16)	C(5)-N(1)-C(1)	115.8(3)
N(1A)-Cu(1)-O(2A)	89.85(16)	C(6)-N(2)-C(10)	113.9(4)
O(2)-Cu(1)-O(2A)	180.0(3)	N(1)-C(5)-C(4)	125.8(4)
C(1)-N(1)-Cu(1)	128.7(3)	N(1)-C(5)-C(6)	124.7(3)
C(5)-N(1)-Cu(1)	115.5(3)	N(2)-C(6)-C(7)	126.8(4)
N(1A)-Cu(1)-N(1)	180.00(15)	N(2)-C(6)-C(5)	124.0(4)
N(1A)-Cu(1)-O(2)	90.15(16)	N(2)-C(10)-C(9)	124.3(5)
N(1)-Cu(1)-O(2A)	90.15(16)		

180.0(3) $^\circ$. These data suggest that copper constitutes a square planar complex with four coordination atoms, and the copper ion lies in the center of the square plane. Most of dafo reported in literature were involved in coordination as bidentate ligands.^{7,9} The copper ion of the complex [Cu(dafo)₂(H₂O)₂](NO₃)₂ reported in literature⁹ is coordinated by six atoms, four nitrogen atoms from two dafos which are coplanar with copper atom, two oxygen atoms from two water molecules which are vertical to the plane. And the copper ion lies in the center of distorted octahedron because of the Jahn-Teller effect. As far as the constitution concerned, the title complex differs this complex reported in literature⁹ only from the outside acid radical, so the structures of them should be probably similar. However, there is great difference in the structure. Because of the larger steric effect of ClO₄⁻ and rigidity of the

framework of dafo, the other nitrogen atom of dafo does not coordinate to copper(1) and copper(1) can not form normal octahedral structure. The result leads to the longer distance existing between N(2), N(2A) of the two dafo and Cu(1). The energy of e_g and t_{2g} sets, splitted into by 5 initial degenerated orbitals of metal cation, would give a corresponding change. The energy of e_g orbitals split because of the energy of d_{z²} orbital decreasing. On the other hand, the energy of t_{2g} orbitals split because of the energy of d_{xy} orbital increasing. So the degeneracy goes down. The interaction of N(2), N(2A) and the central metal cation vanished, therefore, the square planar complex is formed. It can be observed that the acid radical perhaps influences the coordination fashion of dafo: when the steric effect of acid radical is weaker, dafo maybe coordinates as bidentate ligand, and when the steric effect of acid

radical is stronger, dafo maybe coordinates as monodentate ligand. So we will give a further research on it. From Fig. 1, it can be seen that the two hydrogen atoms of the water molecule in $[\text{Cu}(\text{dafo})_2(\text{H}_2\text{O})_2]^{2+}$ form hydrogen bonds with oxygen atoms of two ClO_4^- . In Fig. 2, the two oxygen atoms of each ClO_4^- form two hydrogen bonds with the hydrogen atoms of the water molecules which come from two different complex ions $[\text{Cu}(\text{dafo})_2(\text{H}_2\text{O})_2]^{2+}$. So there are not only intramolecular hydrogen bonds but also intermolecular hydrogen bonds in the complex $[\text{Cu}(\text{dafo})_2(\text{H}_2\text{O})_2]^{2+}$.

$(\text{dafo})_2(\text{H}_2\text{O})_2]^{2+}(\text{ClO}_4)_2$. The distances of the two kind-of hydrogen bonds are 0.2780 nm and 0.2848 nm, respectively. Because of the existence of hydrogenbond, the supra-molecular complex is shown in Fig. 3, which possesses the two-dimensional network structure is formed.

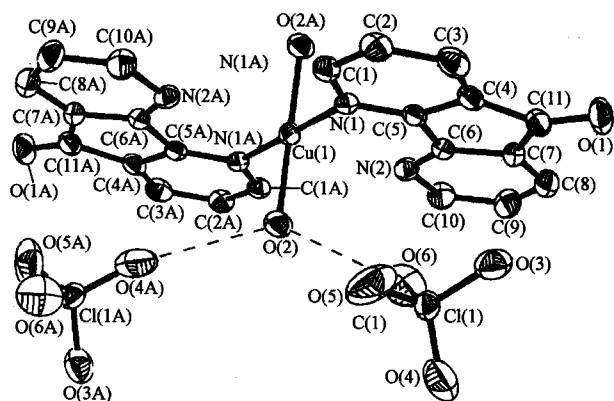


Fig. 1 Crystal structure of $[\text{Cu}(\text{dafo})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$.

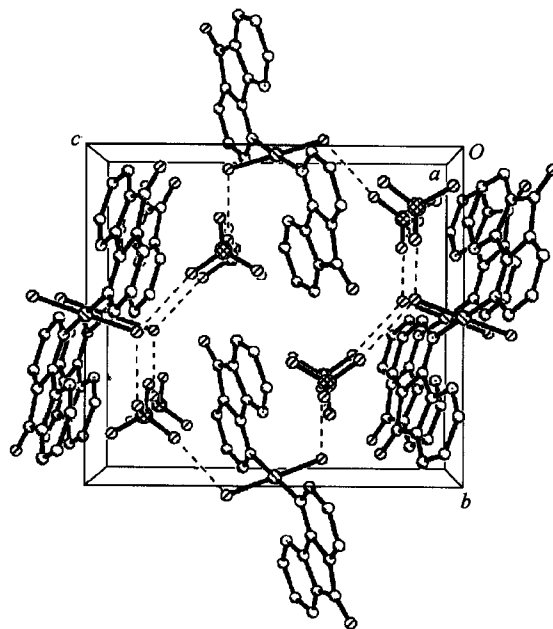


Fig. 2 Crystal cell of $[\text{Cu}(\text{dafo})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$.

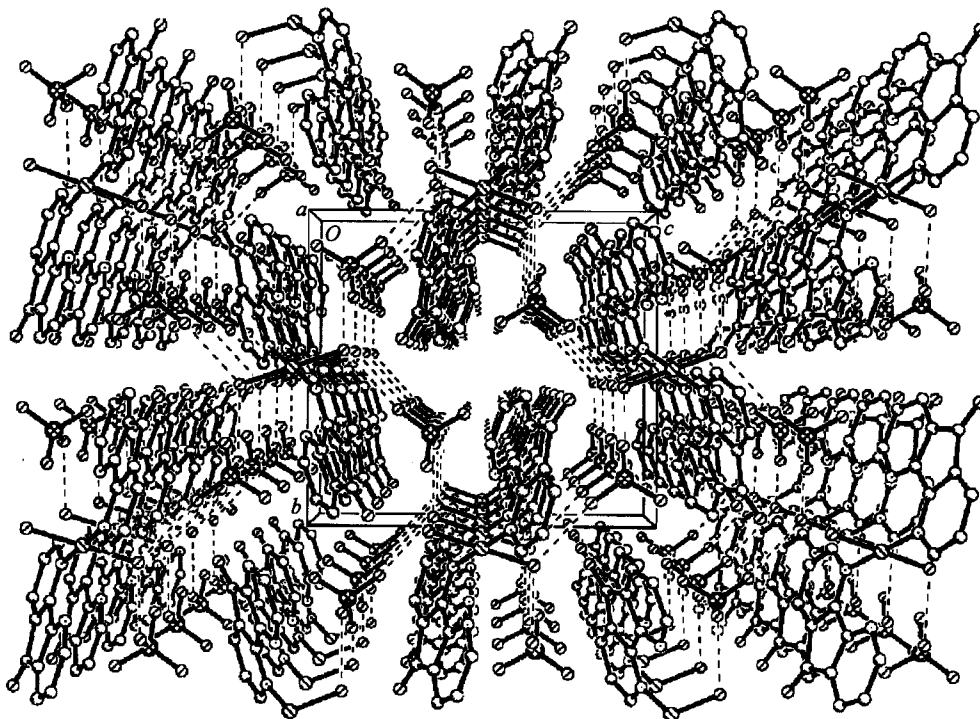


Fig. 3 Two-dimensional network structure of $[\text{Cu}(\text{dafo})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$.

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