

Two New Copper Complexes by H₄AQTC (Anthraquinone-1,4,5,8-tetracarboxylic Acid): Syntheses, Structures and Properties^①

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ABSTRACT Two new complexes [Cu(AQTC)_{0.5}(H₂O)₃]·3H₂O)_n (**1**, H₄AQTC = anthraquinone-1,4,5,8-tetracarboxylic acid) and Cu[(Py)₂C(OH)₂]₂(H₂AQTC)·2H₂O (**2**, (Py)₂CO = di-2-pyridyl ketone) have been prepared and characterized by elemental analyses and IR spectroscopy. X-ray crystallographic studies show that complex **1** crystallizes in monoclinic space group *C2/m* and complex **2** in monoclinic space group *P2₁/c*. Complex **1** features a 1D chain structure by carboxyl oxygen atoms. Complex **2** displays a mononuclear structure and anions and cations are separated. What's interesting is that the ligand of H₄AQTC with eight carboxyl oxygen atoms and two quinone oxygen atoms does not directly coordinate with metals, and only exist as a counter-anion in complex **2**. Three-dimensional structures of two complexes are formed by intermolecular interactions. The thermogravimetric analyses of two complexes are investigated. The luminescent properties of complex **1** are investigated as well.

Keywords: anthraquinone-1,4,5,8-tetracarboxylic acid, di-2-pyridyl ketone, syntheses, crystal structure;
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1 INTRODUCTION

There has been much interest in molecular materials, especially in coordination supramolecular materials. They have always been the focus of research because of their fascinating structures and potential application in many fields^[1-12]. Hitherto, many research groups have done a lot of significant work and a great number of complexes with abundant structural features and interesting properties have been deliberately prepared and reported. One of the effective strategies for construction of coordination complexes is to select suitable multidentate organic ligands. In particular, the ligands with N or O atom are preferred objects. So the research of carboxylic acid complexes is still in the ascendant^[13-15]. In our previous studies, we have successfully obtained a series of complexes by using H₄AQTC as the main ligand with rare earth metals, transition metals (Co(II), Ni(II) and barium salt. H₄AQTC has two quinone oxygen atoms which can be involved in coordination in addition to the other eight carboxylate ones^[16-18]. The study

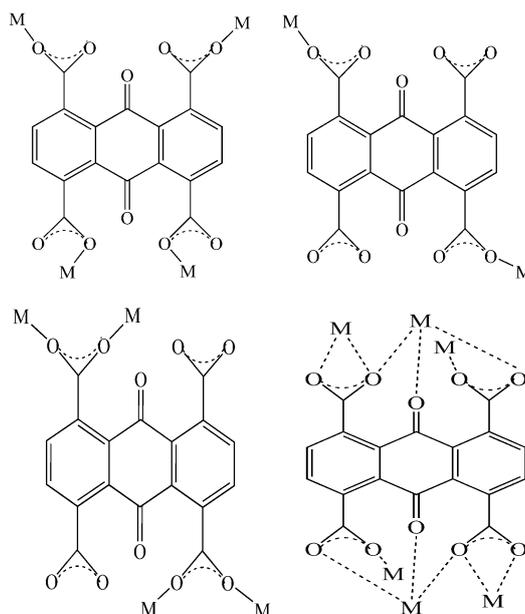
result confirms that the ligand has rich coordination modes (shown in Scheme 1). However, in this series of complexes, copper complexes have never been reported.

As an extension of these studies, we choose auxiliary ligand di-2-pyridyl ketone ((Py)₂CO) to react with copper salts. Similar attention has been paid to (Py)₂CO ligand. It has three potential coordination atoms, namely two pyridine nitrogen atoms and one carbonyl oxygen atom. (Py)₂CO can be *in situ* transformed into a new specimen in an aqueous medium through nucleophilic attack on the keto group in the presence of metal ions. The derivative (py)₂C(OH)₂ can coordinate to the metal ion as a neutral molecule or a monovalent anion^[19]. Di(2-pyridyl)ketone plays an important role in transition metal complexes because of its changeable coordination modes^[20-24]. In this paper, we describe the syntheses, crystal structures, thermal stability and luminescent property of two new copper complexes [Cu(AQTC)_{0.5}(H₂O)₃]·3H₂O)_n (**1**) and Cu[(Py)₂C(OH)₂]₂(H₂AQTC)·2H₂O (**2**).

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Scheme 1. Coordination modes of H₄AQTC

2 EXPERIMENTAL

2.1 Reagents and instruments

All reagents and solvents were purchased from commercial sources and used without further purification. H₄AQTC was prepared according to the literature^[25, 26]. Elemental analyses were performed on a PE-240C elemental analyzer. Thermal analyses were performed in nitrogen in the temperature range 30 to 700 °C with a heating rate of 10 °C min⁻¹ on a Mettler-Toledo TGA/DSC STARE system. The infrared spectra were recorded on a VECTOR 22 spectrometer with pressed KBr pellets in the range of 4000 to 400 cm⁻¹. The luminescent spectra were measured on a Perkin Elmer LS55 fluorescence spectrometer.

2.2 Synthesis of complex

[Cu(AQTC)_{0.5}(H₂O)₃] 3H₂O]_n (1)

A mixture of H₄AQTC (0.0079 g, 0.02 mmol), Cu(NO₃)₂ · 3H₂O (0.0098 g, 0.04 mmol), water (5 mL), 1 drop of 3 M HCl and 1 drop of DMF was sealed in a 25 mL Teflon-lined stainless-steel container and heated at 110 °C for 3 days. Blue needle crystals of **1** were obtained by filtration and washed by water several times. Yield: 32% based on Cu. Anal. Calcd. for C₉H₁₄CuO₁₁ (361.74) (%): C, 29.88; H, 3.90. Found: C, 29.86; H, 3.91. IR (KBr, cm⁻¹): 3483(m), 1673(m), 1616(s), 1477(w), 1390(s), 1325(w), 1251(m), 1079(w), 1174(w), 1086(w), 777(w).

2.3 Synthesis of complex

Cu[(Py)₂C(OH)₂]₂(H₂AQTC) 2H₂O (2)

Complex **2** was synthesized hydrothermally in a Teflon-lined stainless-steel container by heating a mixture of H₄AQTC (0.0082 g, 0.02 mmol), (Py)₂CO (0.0076 g, 0.04 mmol), Cu(CH₃COO)₂ · H₂O (0.0041 g, 0.02 mmol), 1 drop of 3 M HCl in distilled water (6 mL) at 120 °C for 3 days, and then cooled to room temperature. Purple crystals were obtained with 11% yield based on Cu. Anal. Calcd. for C₄₀H₃₀CuN₄O₁₆ (886.22) (%): C, 54.21; H, 3.41; N, 6.32. Found (%): C, 54.19; H, 3.43; N, 6.34. IR (KBr, cm⁻¹): 3510(w), 1722(s), 1679(m), 1567(m), 1393(s), 1331(m), 1242(m), 1164(m), 1003(w), 802(m), 641(w).

2.4 Structure determination and refinement

Suitable single crystals of two complexes were mounted on a Bruker Smart Apex CCD diffractometer with graphite-monochromated MoK α radiation with $\lambda = 0.71073$ Å. A hemisphere of the data was collected at room temperature for complexes **1** and **2**. The numbers of observed and unique reflections are 3771 and 1458 ($R_{\text{int}} = 0.0923$) for **1**, 13472 and 3485 ($R_{\text{int}} = 0.0817$) for **2**. The data were integrated using the Siemens *SAINTE* program^[27]. The structures were solved by direct methods and refined by full-matrix least-squares against F^2 using the SHELXTL crystallographic software package^[28, 29]. All non-hydrogen atoms were refined anisotropically. Complex **1** is of monoclinic system, space group $C2/m$ with $a = 20.220(7)$, $b = 10.827(4)$, $c = 6.597(2)$ Å, $\beta = 103.439(6)^\circ$; $V = 1404.7(8)$ Å³, $Z = 4$, $S = 1.101$, $R^a = 0.0482$ and $wR^b = 0.1260$ ($I > 2\sigma(I)$). Complex **2** adopts monoclinic space group $P2_1/c$ with $a = 14.0126(16)$,

$b = 10.3985(12)$, $c = 13.6734(16)$ Å, $\beta = 116.319(2)^\circ$; $V = 1785.8(4)$ Å³, $Z = 2$, $S = 1.012$, $R^a = 0.0560$ and $wR^b = 0.1580$ ($I > 2\sigma(I)$). The selected bond lengths and bond

angles are given in Table 1, and the selected hydrogen bond distances and bond angles in Table 2.

Table 1. Selected Bond Lengths (Å) and Bond Angles (°) for Complexes 1 and 2

1					
Bond	Dist.	Bond	Dist.	Bond	Dist.
Cu(1)–O(1)	1.948(3)	Cu(1)–O(1)A	1.948(3)	Cu(1)–O(4)	1.952(5)
Cu(1)–O(5)	2.301(5)	Cu(1)–O(1)	1.899(4)		
Angle	(°)	Angle	(°)	Angle	(°)
O(6)–Cu(1)–O(4)	175.6(2)	O(6)–Cu(1)–O(1)A	91.73(8)	O(4)–Cu(1)–O(1)A	88.21(8)
O(6)–Cu(1)–O(1)	91.73(8)	O(4)–Cu(1)–O(1)	88.21(8)	O(1)–Cu(1)–O(1)A	176.15(17)
O(6)–Cu(1)–O(5)	97.2(2)	O(4)–Cu(1)–O(5)	87.2(2)	O(1)A–Cu(1)–O(5)	90.63(8)
O(1)–Cu(1)–O(5)	90.63(8)				
2					
Bond	Dist.	Bond	Dist.	Bond	Dist.
Cu(1)–N(1)	1.993(3)	Cu(1)–N(1)A	1.993(3)	Cu(1)–N(2)	2.003(3)
Cu(1)–N(2)A	2.003(3)				
Angle	(°)	Angle	(°)	Angle	(°)
N(1)–Cu(1)–N(1)A	180.000(1)	N(1)–Cu(1)–N(2)	89.66(11)	N(1)A–Cu(1)–N(2)	90.34(11)
N(1)–Cu(1)–N(2)A	90.34(11)	N(1)A–Cu(1)–N(2)A	89.66(11)	N(2)–Cu(1)–N(2)A	180.0

Symmetry codes: 1. A: $x, 1-y, z$; 2. A: $2-x, 1-y, 1-z$

Table 2. Selected Hydrogen Bond Lengths (Å) and Bond Angles (°) for Complexes 1 and 2

1				
D–H···A	d(D–H)	D(H···A)	d(D···A)	∠DHA
O(9)–H···O(1)	0.85	2.49	3.188(7)	140
O(6)–H···O(7)	0.85	2.14	2.530(7)	108
O(7)–H···O(2)B	0.85	2.38	2.832(6)	119
O(5)C–H···O(2)	0.85	2.22	2.822(4)	128
2				
O(6C)–H···O(4)B	0.82	1.81	2.630(4)	174
O(7C)–H···O(3)B	0.82	1.88	2.697(4)	173
O(1W)C–H···O(2)E	0.85	2.19	3.040(5)	176
C(1)D–H···O(1W)C	0.93	2.54	3.200(6)	128
C(2)D–H···O(1W)C	0.93	2.82	3.332(5)	116
C(4)E–H···O(1)E	0.93	2.98	3.183(6)	94

Symmetry codes: 1. B: $0.5-x, 0.5+y, 1-z$; C: $x, y, -1+z$; 2. B: $1-x, -0.5+y, 0.5-z$;

C: $x, 0.5-y, -0.5+z$; D: $2-x, -0.5+y, 0.5-z$; E: $x, 1.5-y, -0.5+z$

3 RESULTS AND DISCUSSION

3.1 IR spectral analysis

IR spectra were recorded on a VECTOR 22 spectrometer with pressed KBr pellets in the range of 4000 to 400 cm⁻¹. Complexes **1** and **2** show peaks at 3483 cm⁻¹ for **1** and 3510 cm⁻¹ for **2**, respectively, which is the characteristic peak of OH group in H₂O. Peaks at 1616, 1390 cm⁻¹ for **1** and 1722, 1393 cm⁻¹ for **2** could be attributed to ν_{as} and ν_s stretching vibrations of coordinated carboxyl^[30]. The bands at 1679, 1567 cm⁻¹ for **2** are attributable to the C=N of pyridine rings^[31]. The IR spectra agree with the X-ray crystal

structures of the title complexes.

3.2 Crystal structural description

Complex **1** crystallizes in monoclinic space group *C2/m*. The asymmetric unit of **1** consists of one Cu, 0.5 AQTC⁻, and three coordinated and three lattice water molecules. As shown in Fig. 1, the Cu(II) ion is coordinated by five oxygen atoms. Two of them (O(1) and O(1A)) are from H₄AQTC and the remaining three oxygen atoms (O(4), O(5) and O(6)) from coordinating water molecules. The Cu(1)–O distances and O–Cu(1)–O angles are 1.899(4) ~ 2.301(5) Å and 88.21(8) ~ 176.15(2)°, respectively.

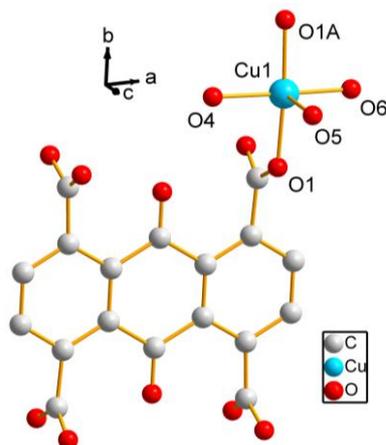


Fig. 1. Coordination environment of complex **1**. The hydrogen atoms and lattice water molecules are omitted for clarity. Symmetry codes: A: $x, 1-y, z$

As shown in Fig. 2, the H₄AQTC functions as a bridge. The Cu(II) is connected by the AQTC⁴⁻ ligand through carboxylate oxygen atoms O(1) and O(1)A, leading to a 1-D chain running along the *b*-axis.

Extensive hydrogen-bonding interactions are observed in complex **1** between carboxylate oxygen atoms of AQTC⁴⁻

and water molecules^[32]. The intermolecular hydrogen bonds mainly include O(9)–H··O(1) (O(9)··O(1) 3.188(7) Å), O(6)–H··O(7) (O(6)··O(7) 2.530(7) Å), O(7)–H··O(2)B (O(7)··O(2)B 2.832(6) Å) and O(5)C–H··O(2) (O(5)C··O(2) 2.822(4) Å) (Fig. 2). A supramolecular network structure is thus constructed as demonstrated in Fig. 2.

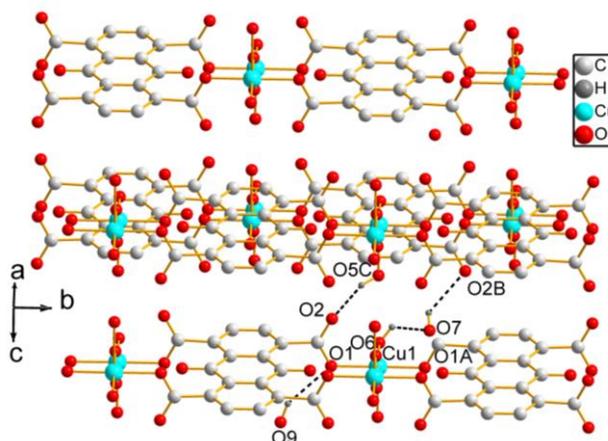


Fig. 2. Three-dimensional stacking diagram of structure **1** formed by hydrogen bonding interactions. The redundant hydrogen atoms and lattice water molecules are omitted for clarity. Symmetry codes: B: $0.5 - x, 0.5 + y, 1 - z$; C: $x, y, -1 + z$

The crystal of **2** belongs to a monoclinic system with space group $P2_1/c$. As shown in Fig. 5, anions and cations are separated. In a cation structure, the Cu(II) is four-coordinated with four nitrogen atoms (N(1), N(2), N(1)A, N(2)A) from two neutral molecules (Py)₂C(OH)₂. Each (Py)₂CO serves as a bidentate chelate ligand. The Cu–N bond lengths are in the range of 1.993(3)~2.003(3) Å while the N–Cu(1)–N bond angles are 89.66(11)~180.0°. Rich hydrogen-bonding interactions are found among cations, anions and water molecules (Fig. 4, Table 2). There are also

C–H·· π interactions between the pyridine carbon atom (C(2F)) and pyridine ring. The distance of C(2F) and the pyridine ring center is 3.580(5) Å^[33]. As shown in Fig. 4, a three-dimensional supramolecular network structure is built through these common weak interactions.

Compared with structure **1**, a very interesting result has emerged except for the coordination number of copper in complex **2**, that is to say, the H₄AQTC ligand is not directly coordinated with copper in complex **2**. This condition of the H₄AQTC ligand has never been reported. Anthraquinone

tetracarboxylic acid itself has eight carboxyl oxygen atoms and two quinone oxygen atoms. Therefore, the ligand has a strong coordination ability and rich coordination mode. This fact has been confirmed in the literature, such as bridging,

chelation, quinone-oxygen coordination, and so on (shown in Scheme 1). When it reacts with $(\text{Py})_2\text{CO}$, $(\text{Py})_2\text{CO}$ shows a stronger coordination ability.

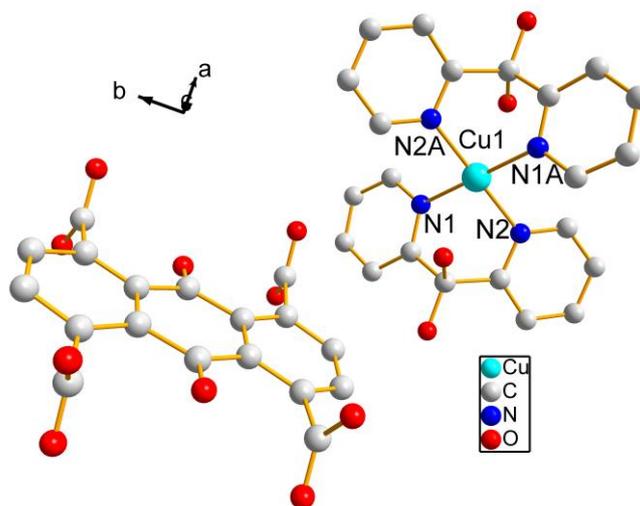


Fig. 3. Coordination environment of complex 2. The hydrogen atoms and lattice water molecules are omitted for clarity. Symmetry code: A: $2 - x, 1 - y, 1 - z$

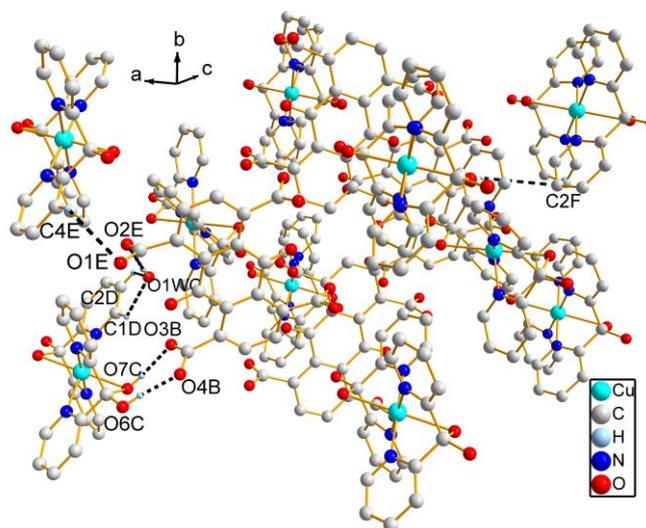


Fig. 4. Three-dimensional stacking diagram of structure 2 formed by intermolecular interactions. The redundant hydrogen atoms and lattice water molecules are omitted for clarity. Symmetry codes: B: $1 - x, -0.5 + y, 0.5 - z$; C: $x, 0.5 - y, -0.5 + z$; D: $2 - x, -0.5 + y, 0.5 - z$; E: $x, 1.5 - y, -0.5 + z$; F: $-1 + x, 1.5 - y, 0.5 + z$

3.3 Thermal stability

To further fully characterize the title complexes, their thermal stabilities were examined by using TG (Fig. 5). The TG curve of complex 1 displayed a weight loss (29.85%) below 244 °C, corresponding to the release of six water molecules (calcd. 29.87%). Complex 2 shows a weight loss

(4.03%) below 237 °C, corresponding to the release of two water molecules (calcd. 4.06%). Further weight losses above 244 °C for 1 and 237 °C for 2 correspond to the decomposition of the organic ligand and then the framework starts to decompose, respectively.

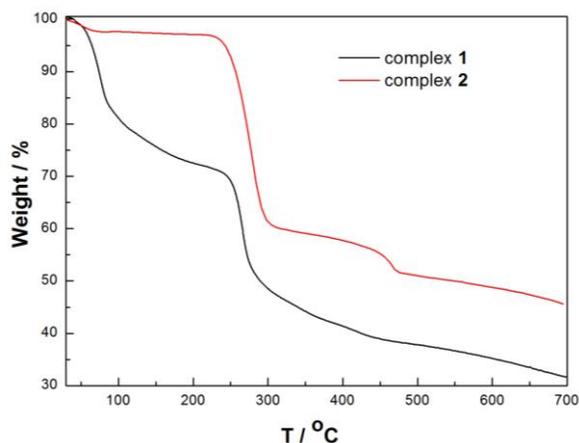


Fig. 5. TGA curves for complexes 1 and 2

3.4 Luminescent properties

Luminescence of solid-state complex **1** as well as free ligands H₄AQTC was investigated at room temperature under the excitation at 378 nm for **1** and 378 nm for H₄AQTC (Fig. 6), respectively. The intense emissions are observed with peak wavelengths at 490, 533 and 576 nm for

1. Free H₄AQTC emits luminescence with peak wavelengths at 485, 530 and 569 nm. The luminescence spectra of complex **1** resemble those of free H₄AQTC ligand. Therefore, the luminescence of the complex mainly originates from the ligand and the emissions can be tentatively assigned to intraligand transitions at the excited state.

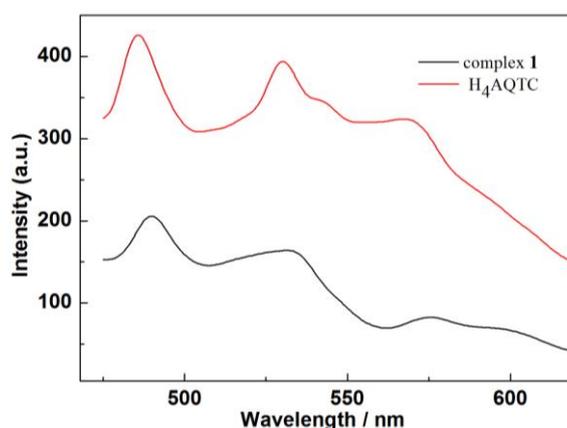


Fig. 6. Fluorescent emission spectra of complex **1** and free ligand in the solid state at room temperature

4 CONCLUSION

In summary, we describe the syntheses, structures and properties of two new complexes [Cu(AQTC)_{0.5}(H₂O)₃] · 3H₂O (**1**) and Cu[(Py)₂C(OH)₂]₂(H₂AQTC) · 2H₂O (**2**). H₄AQTC serves as a bridge ligand in complex **1**, but it does not directly coordinate with metals and only exists as a

counter-anion in complex **2**, in which the second ligand (Py)₂CO shows stronger coordination ability. Our work also provides experimental data for further study of these ligands. Further work is in progress to explore new materials based on the H₄AQTC and (Py)₂CO ligands which may show interesting physical or chemical properties. The results will be reported in due course.

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