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Synthesis and crystal structure of $Zn[(C_6H_5N_3)_4(H_2O)_2](ClO_4)_2$ and $Cu[(C_6H_5N_3)_4(H_2O)_2](ClO_4)_2$

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Abstract

Two novel octahedral complexes with formula of $Zn[(C_6H_5N_3)_4(H_2O)_2](ClO_4)_2$ **1** and $Cu[(C_6H_5N_3)_4(H_2O)_2](ClO_4)_2$ **2** have been obtained by the reaction of benzotriazole (BTA) ligand with zinc(II) salt and copper(II) salt in ethanol–water solution, respectively. Elemental analysis, IR spectra and X-ray crystal structure analysis were carried out to determine the compositions and crystal structures of the two compounds. The complex **1** crystallizes in monoclinic $C2/c$ space group, with lattice parameters $a = 13.838(2)$, $b = 13.374(4)$, and $c = 16.944(3)$ Å. $\beta = 103.206(9)°$, $V = 3053.1(11)$ Å^3, $Z = 4$, $R_1 = 0.0411$. The complex **2** crystallizes also in monoclinic $C2/c$ space group, with lattice parameters $a = 13.919(7)$, $b = 13.380(7)$, and $c = 16.733(9)$ Å. $\beta = 103.206(9)°$, $V = 3026$ Å^3, $Z = 4$, $R_1 = 0.0423$. The two complexes are isostructural. Both are mononuclear compounds, with similar coordination modes and packing arrangement in crystals. Every center metal ion is coordinated by four nitrogen atoms from four BTA ligands and two oxygen atoms from two water molecules, forming an octahedral coordination polyhedron. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Crystal structure; Benzotriazole; Zinc complex; Copper complex

1. Introduction

Metal protection with reactive materials capable of forming surface-phase coordination compounds is an area of chemistry which is of considerable scientific and technological importance [1–3]. Besides its uses as antiwear and antifouling reagents [4,5], the ability of BTA and its derivations to inhibit corrosion has focused attention on their transition metal complexes in general, especially on copper, zinc, cobalt complexes. Numerous complexes have been synthesized and a few compounds show some special structure in which BTA ligands adopt a variety of coordination modes [6–8]. Despite of the extensive uses of BTA and its derivations as corrosion inhibitors for zinc, copper and their alloys, only a few compounds have been structurally characterized by X-ray diffraction [9–11]. Here, we report the synthesis and crystal structures of two novel complexes with high symmetry formed by coordination of BTA to Zn^{2+}, Cu^{2+}, respectively.

2. Experimental

2.1. Reagents and materials

Zinc acetate and benzotriazole were purchased from commercial sources and used as received. Copper(II) perchlorate hexahydrate was obtained by the literature methods [12]. Other chemical reagents were of reagent grade, obtained from commercial sources and used without further purification.

Caution! Perchlorate salts of metal complexes are potentially explosive. Only a small amount of material should be prepared, and should be handled with care.

2.2. Synthesis and crystal growth

The complex **1** was prepared by dissolving BTA (0.2385 g, 0.002 mol) in ethanol solution, and an aqueous solution of $Zn(CH_3COO)_2{\cdot}2H_2O$ (0.2195 g, 0.001

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mol) was added to it. In the environment of pH = 7, white deposition was produced immediately. Using $HClO_4$ to adapt the pH to 4, the white deposition was dissolved and a clear solution was obtained. The mixture was stirred for 30 min at room temperature and then filtered to remove any solid particles. By slow evaporation of the filtrate at room temperature about 2 weeks, colorless prism crystals of **1** suitable for X-ray analysis were obtained.

The complex **2** was prepared in the similar process as mentioned above. An aqueous solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.3705 g, 0.001 mol) was added to an ethanol solution of BTA (0.2386 g, 0.002 mol). After stirred for 30 min at room temperature, the blue solution was filtered and evaporated slowly. Three weeks later, some blue prism crystals of **2** suitable for X-ray analysis were obtained.

2.3. Physical measurements

IR spectra of the complexes in the range of 400–4000 cm^{-1} were recorded in their tablets with KBr by using AVATAR 360 FT–IR E. SP from Nicolet Corporation.

Elemental analyses were performed by the instrument of Erba Strumentazion. The analysis results are: complex **1** found (%): C, 37.87, N, 21.55, H, 2.91. Calculated for complex **1** (%): C, 37.11, N, 21.64, H, 3.11. Complex **2** found (%): C, 37.22, N, 21.81, H, 3.00. Calculated for complex **2** (%): C, 37.20, N, 21.69, H, 3.12.

2.4. X-ray structure determination

The room temperature (294 ± 1 K) single-crystal X-ray experiments were performed on a Brüker P4 diffractometer equipped with graphite monochromatized Mo K_α radiation. Unit cell of complex **1** was obtained and refined by 35 well centered reflections with $4.6° < \theta < 18.5°$. Data collection was monitored by three standards every 100 reflection collected. No decay was observed except the statistic fluctuation in the range of ±2.2%. Raw intensities were corrected for Lorentz and polarization effects, and for absorption by empirical method based on ψ-scan data (Kopfmann and Huber, 1968). Direct phase determination yielded the positions of Zn, Cl, N and the most C and O atoms, and the other C and O atoms were located in successive difference Fourier syntheses. Hydrogen atoms, except those of aqua, were generated theoretically and rided on their parent atoms in the final refinement. All non-hydrogen atoms were subjected to anisotropic refinement. The final full-matric least-square refinement on F^2 converged with $R_1 = 0.0411$ and $wR_2 = 0.0855$ for 2794 observed reflections $[I \geqslant 2\sigma(I)]$. The final difference electron density map shows no features.

Unit cell of complex **2** was obtained and refined by 25 well centered reflections with $5.3° < \theta < 12.2°$. No decay was observed except the statistic fluctuation in the range of ±4.3%. The final full-matric least-square refinement on F^2 converged with $R_1 = 0.0423$ and $wR_2 = 0.0948$ for 2082 observed reflections $[I \geqslant 2\sigma(I)]$.

Details of the crystal parameters, data collection and structure refinement are given in Table 1. Data collection was controlled by XSCANS program. Computations were performed using the SHELXTL NT ver. 5.10 program package (Sheldrick, 1985) on an IBM PC 586 computer. Analytic expressions of atomic scattering factors were employed, and anomalous dispersion corrections were incorporated. Crystal drawings were produced with XP.

Table 1
Details of data collection, processing and structure refinement

	1	2
Chem. formula	$C_{24}H_{24}Cl_2N_{12}O_{10}Zn$	$C_{24}H_{24}Cl_2N_{12}O_{10}Cu$
Molecular weight	776.8	774.9
Crystal system	monoclinic	monoclinic
Space group	$C2/c$	$C2/c$
Unit cell parameters	$a = 13.838(2)$ (Å)	$a = 13.919(7)$ (Å)
	$b = 13.374(4)$ (Å)	$b = 13.380(7)$ (Å)
	$c = 16.944(3)$ (Å)	$c = 16.733(9)$ (Å)
	$\beta = 103.206(9)°$	$\beta = 103.84(2)°$
V (Å^3)	3053.1(11)	3026(3)
Z	4	4
D_{calc} (g/cm^3)	1.690	1.692
R_1	0.0411 (for observed data)	0.0423 (for observed data)
wR_2	0.0855 (for observed data)	0.0948 (for observed data)
λ (Å)	0.71073	0.71073
GOF	1.002	1.054

$$R_1 = \frac{\sum \| F_o | - | F_c \|}{\sum | F_o |}, \quad wR_2 = \sqrt{\frac{\sum \left[w(F_o^2 - F_c^2)^2 \right]}{\sum w(F_o^2)^2}}, \quad GOF = \sqrt{\frac{\sum \left[w(F_o^2 - F_c^2)^2 \right]}{n - p}}.$$

Table 2
IR spectral data for the complexes

Compound	υ(M–N)	υ(N–H)	υ(N=N)	υ(C–N)
$Zn[(C_6H_5N_3)_4(H_2O)_2](ClO_4)_2$	429.82	3198.21	1622.33	1210.35
$Cu[(C_6H_5N_3)_4(H_2O)_2](ClO_4)_2$	430.23	3252.96	1622.60	1220.08

3. Results and discussion

3.1. Spectroscopic analysis

The complex **1** is the product of a coordination reaction of zinc acetate with BTA. The IR spectra of the complex **1** confirms the existence of Zn–N bonds. The complex do not show any typical C=O stretching absorption band in the region around 1740 cm^{-1}, suggesting that acetic anions has been substituted by BTA ligands. At the same time, the three strong absorption peaks in the range of 1150–1090 cm^{-1} indicate the existence of ClO_4^- as balance anions. The complex **2** has similar IR spectra as complex **1**. The detail IR data of the two complexes are given in Table 2.

3.2. Crystal structure

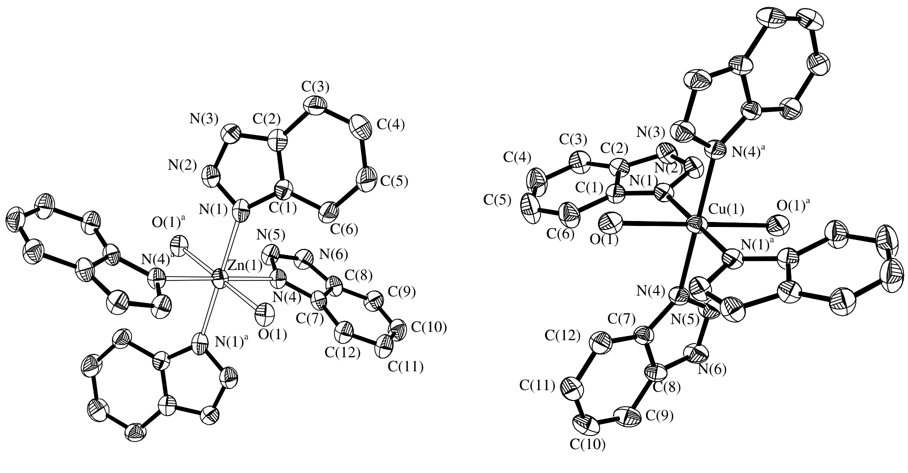
ORTEP drawings for the two title complexes are show in Fig. 1. They both are monomeric complexes, with similar coordination mode and molecular assembly order in crystal, forming two coordination isostructural molecules. In each of mononuclear molecule, the center metal ion (Zn^{2+} or Cu^{2+}) is coordinated by four nitrogen atoms from four BTA ligands and two oxygen atoms from two water molecules, forming an octahedral coordination polyhedron, respectively.

In the two complexes, the nine atoms of every BTA ligand are kept in a ring-plane very well, with the mean deviations from plane of 0.0045 Å, 0.0057 Å (for complex **1**) and 0.0027 Å, 0.0086 Å (for complex **2**), respectively. Every BTA ligand's ring-plane is strictly parallel to that of its opposite BTA ring-plane, and nearly perpendicular to the other ligand ring-planes, with the space dihedral angles of 99.7° (for complex **1**) and 96.5° (for complex **2**), forming two highly symmetric $C2/c$ space structures.

Although the two complex structures are very similar, there are significant difference in bond lengths caused by Jahn–Teller effect. In complex **2**, since the d^9 electron structure of center ion, Cu^{2+}, strong Jahn–Teller effect exists that makes the Cu–O bonds (2.393 Å) much longer than Cu–N bonds (2.009 Å, 2.090 Å). And there is no Jahn–Teller effect in the Zn^{2+} (d^{10}) complex. Selected bond lengths and bond angles are summarized in Table 3. From the bond length data we can confirm that.

We also notice the small differences of coordination bond lengths between Zn–N(1) (2.119 Å) and Zn–N(4) (2.223 Å) in complex **1**, and between Cu–N(1) (2.009 Å) and Cu–N(4) (2.090 Å) in complex **2**. We contribute them to the hydrogen bonds of the nitrogen atoms of BTA ligands with oxygen atoms of ClO_4^- anions. Strong and effective hydrogen bonds pull the ligands molecules powerfully, which make the corresponding coordination bond become longer. Hydrogen bonding data are shown in Table 4.

Of the three N atoms in BTA ligand, N(1) is the only one electron donor atom to center metal ion, with η^1-monodentate coordinating mode. We calculated the electron distribution in a conjugated BTA molecule by using HMO method [13]. The calculation result is shown in Table 5. Where BTA

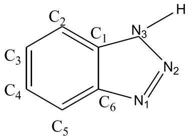


Complex **1** Complex **2**

Fig. 1. ORTEP drawings for diaquatetra(benzotriazole)zinc perchlorid and diaquatetra(benzotriazole)copper perchlorid with 35% probability ellipsoids, showing the atomic numbering scheme (H atoms and ClO_4^- are omitted for clarity).

Table 3
Selected bond lengths and bond angles

Complex **1**		Complex **2**	
Bond lengths (Å)		Bond lengths (Å)	
Zn(1)–N(1)	2.119(3)	Cu(1)–N(1)	2.009(3)
Zn(1)–O(1)	2.157(2)	Cu(1)–O(1)	2.393(3)
Zn(1)–N(4)	2.223(3)	Cu(1)–N(4)	2.090(3)
N(1)–N(2)	1.296(4)	N(1)–N(2)	1.302(4)
N(2)–N(3)	1.341(4)	N(2)–N(3)	1.336(4)
N(4)–N(5)	1.310(4)	N(4)–N(5)	1.315(4)
N(5)–N(6)	1.329(4)	N(5)–N(6)	1.337(4)
Bond angles (°)		Bond angles (°)	
N(1)^a–Zn(1)–N(1)	180	N(1)^a–Cu(1)–N(1)	180.0
N(1)–Zn(1)–O(1)^a	90.62(11)	N(1)^a–Cu(1)–O(1)	88.85(11)
N(1)–Zn(1)–O(1)^a	89.38(11)	N(1)–Cu(1)–O(1)	91.15(11)
O(1)^a–Zn(1)–O(1)	180.0	O(1)^a–Cu(1)–O(1)	180.00(13)
N(1)^a–Zn(1)–N(4)	89.92(11)	N(1)^a–Cu(1)–N(4)	89.71(12)
N(1)–Zn(1)–N(4)	90.08(11)	N(1)–Cu(1)–N(4)	90.29(12)
O(1)^a–Zn(1)–N(4)	90.04(10)	N(4)–Cu(1)–O(1)	90.31(10)
O(1)–Zn(1)–N(4)	89.96(10)	N(4)^a–Cu(1)–O(1)	89.69(10)
N(4)–Zn(1)–N(4)^a	180.00(16)	N(4)–Cu(1)–N(4)^a	180.00(16)



From the calculated electron distribution, we can see that N(1) has the highest electron density in the BTA molecule. It means that N(1) is the best electron donor in the ligand. This result is consistent with that of crystal structure. The deprotonated coordination mode of N(3) is not found in this two complexes. There are maybe two reasons. Firstly, the N(3) atom is not the best electron donor in BTA ligand, and it is difficult for BTA molecule to work as a bidentate ligand because of space block. On the other hand, N(3) and its linked hydrogen atom are devoted to forming hydrogen bonds to stabilize the whole solid molecular assembly. That is also make it almost impossible for N(3) to be deprotonated and coordinate with center ions.

Table 4
Hydrogen bonding

Complex	Hydrogen bonding	Distance (Å)	Angle (°)
1	N(3)–H···O(5)	2.320	124.8
	N(6)–H···O(3)	2.081	160.6
2	N(3)–H···O(5)	2.268	127.1
	N(6)–H···O(3)	2.080	160.3

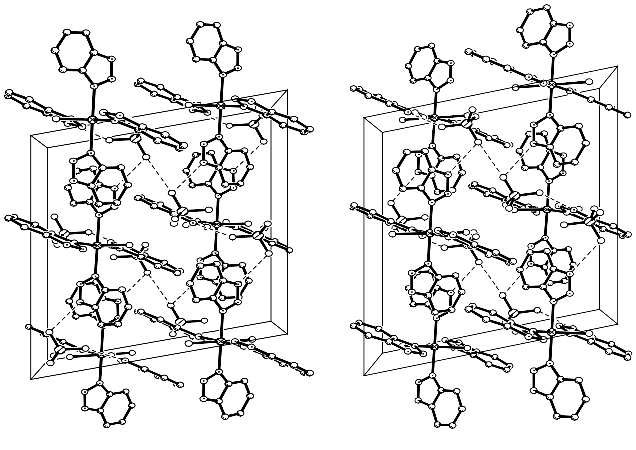

Complex **1** Complex **2**

Fig. 2. Crystal packing view along the *b* direction.

In the cell packing structures as shown in Fig. 2, we can see the hydrogen bonds between the uncoordinated N atoms of BTA ligands and O atoms of ClO_4^-, which link the mononuclear units to form three-dimensional solid structures. Because the distances between ligand ring-planes probably overlapping each other are more than 6 Å, we think there is no π–π interaction between the planes of adjacent ligands in these two complexes.

Table 5
Electron density (E.D) distribution of BTA

Atom	N_1	N_2	N_3	C_1	C_2	C_3	C_4	C_5	C_6
E.D	1.523,6	1.125,4	1.266,5	1.019,1	1.012,1	1.023,2	1.010,9	1.028,1	0.991,3

Supplementary material

X-ray crystallographic files in CIF format for the title compound and IR are available from authors.

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