

溶剂对三(苯并咪唑-2-甲基)胺和间苯二胺四乙酸的铜配合物晶体结构的影响

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摘要: 本文利用三(苯并咪唑-2-甲基)胺和间苯二胺四乙酸为配体与硝酸铜在 $\text{CH}_3\text{COCH}_3/\text{CH}_3\text{OH}/\text{H}_2\text{O}$ 混合溶液中反应得到配合物 $[\text{Cu}(\text{ntb})(\text{H}_2\text{mpda})] \cdot 0.5\text{CH}_3\text{COCH}_3 \cdot 2\text{H}_2\text{O}$ (**1**), 在 $\text{DMF}/\text{CH}_3\text{OH}/\text{H}_2\text{O}$ 混合溶液中反应得到配合物 $[\text{Cu}(\text{ntb})(\text{H}_2\text{mpda})] \cdot \text{DMF} \cdot \text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$ (**2**) (ntb =三(苯并咪唑-2-甲基)胺, H_2mpda =间苯二胺四乙酸)。2 个配合物的中心的铜离子分别与 1 个 ntb 配体的 4 个氮原子和 1 个 H_2mpda 的氧原子配位形成三角双锥的配位构型。受溶剂的影响, 配合物中配体的相对位置和构象有较大的区别, 配合物 **2** 的配位构型更加扭曲。两个配合物均通过氢键连接形成不同的复杂三维网络。

关键词: 铜配合物; 对三(苯并咪唑-2-甲基)胺; 间苯二胺四乙酸; 溶剂调控

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Two Solvent-Controlled Copper(II) Complexes Constructed from Tris[(benzimidazol-2-yl)methyl]amine and *m*-Phenylenediaminetetraacetic Acid

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Abstract: The reactions of tris[(benzimidazol-2-yl)methyl]amine (ntb) and 1,3-phenylenedinitrilotetraacetic acid (H_2mpda) with copper nitrate can produce complex **1** from $\text{CH}_3\text{COCH}_3/\text{CH}_3\text{OH}/\text{H}_2\text{O}$ and complex **2** from $\text{DMF}/\text{CH}_3\text{OH}/\text{H}_2\text{O}$. Complexes with the formula of $[\text{Cu}(\text{ntb})(\text{H}_2\text{mpda})] \cdot 0.5\text{CH}_3\text{COCH}_3 \cdot 2\text{H}_2\text{O}$ (**1**) and $[\text{Cu}(\text{ntb})(\text{H}_2\text{mpda})] \cdot \text{DMF} \cdot \text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$ (**2**) both have $[\text{Cu}(\text{ntb})(\text{H}_2\text{mpda})]$ structural units, in which $\text{Cu}(\text{II})$ centers always have a five-coordination number bound to one ntb ligand and one H_2mpda anion. All these complexes possess trigonal bipyramidal coordination geometry. However, metal ions show remarkable differences in structures due to the effects of solvents. Comparing to complex **1**, complex **2** possesses more distorted coordination geometry. The positions of ntb and H_2mpda ligands in **1** and **2** are very different. The mononuclear coordination units are extended by hydrogen-bonding into different three dimensional networks. CCDC: 893363, **1**; 893364, **2**.

Key words: copper complex; tris[(benzimidazol-2-yl)methyl]amine; 1,3-phenylenedinitrilotetraacetic acid; solvent-dependence

0 Introduction

The design and preparation of novel metal-organic complexes and their potential applications have been

one of the major challenges during the past decades^[1]. In the self-assembly process of metal based structures, efforts were mainly focused on the choosing organic ligands, central metals, solvents, templates, as well as

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anions^[2]. Recently, researchers are interested in tris[(benzimidazol-2-yl)methyl]amine (ntb) due to its excellent ability of forming structural dissimilarity and its unique properties. The ligand is characterized by the versatile coordination mode and its ability of forming multiple inter-molecular interactions^[3]. Thermally stable 3D lanthanide complexes participating hydrogen bonded coordination networks based on ntb ligand have been constructed to display dual properties of robustness and dynamics^[4]. Ntb ligand containing chiral mononuclear complexes in clockwise (Δ) and anticlockwise (Λ) propeller coordination fashion can form *meso*-one-dimensional coordination polymer^[5], *meso*-helical cylindrical arrays^[6], and 2D Borromean network^[7]. Ntb-zinc complexes can be used as structural carbonic anhydrase models and in CO₂ hydration^[8]. The ntb-Ru^{III} complexes are used as the catalyst in allylic oxidation, epoxidation, and alkane functionalization^[9]. The DNA-condensing property of dicarboxylate-bridged ntb-Cu(II) polycationic complexes has been demonstrated^[10]. However, there are much less reports on those solvent controlled structures comparing to the large amounts of second ligand controlled examples^[11]. In this paper, we reported the synthesis of two solvent controlled complexes [Cu(ntb)(H₂mpda)] · 0.5CH₃COCH₃ · 2H₂O (**1**) and [Cu(ntb)(H₂mpda)] · DMF · CH₃OH · 2H₂O (**2**).

1 Experimental

The tris[(benzimidazol-2-yl)methyl]amine (ntb) ligand was prepared following the literature^[12]. Yield: *ca.* 72%. 1,3-phenylenedinitrilotetraacetic acid (H₄mpda) was synthesized by a previously reported method^[13]. Yield: *ca.* 94%. All other reagents and solvents were commercially available analytical grade materials without any further purification. IR spectra were recorded on a Perkin Elmer Spectre One spectrometer (range 4 00~500 cm⁻¹) as KBr pellets. ¹H NMR spectra were recorded on a Varian/Mercury-Plus 300 instrument. Elemental analyses were determined on an Elementar Vario EL elemental analyzer.

1.1 Synthesis of complex 1

A solution of Cu(NO₃) · 3H₂O (0.1 mmol) in H₂O

(2 mL) was added dropwise to a solution of ntb (0.1 mmol) in 10 mL of methanol. Then H₄mpda (0.1 mmol) was slowly mixed to it. The mixture was heated for 2 h to produce a nearly clear solution, followed by the addition of 1 mL of acetone. After cooling to room temperature, the reaction mixture was filtered. By slow evaporation of the solvent, blue block-shape single crystals were obtained in several days. Yield: 36.8%. IR (KBr, cm⁻¹): 3 342, 1 729, 1 648, 1 615, 1 496, 1 446, 1 406, 1 050, 876. The sample lost solvent molecules quickly while being exposed to air. After solvent molecules were removed under vacuum, the elemental analysis based on Cu(ntb)(H₂mpda) was performed. Anal. Calcd. C₃₈H₃₅CuN₉O₈ (%): C, 56.40; H, 4.36; N, 15.58. Found(%): C, 56.17; H, 4.61; N, 15.94.

1.2 Synthesis of complex 2

A solution of Cu(NO₃) · 3H₂O (0.1 mmol) in H₂O (2 mL) was added dropwise to a solution of ntb (0.1 mmol) in 20 mL of methanol. Then H₄mpda (0.1 mmol) in DMF (5 mL) was also slowly added. The mixture was heated for 5 min. After the composite solution was cooled to room temperature, the block crystals of **2** appeared in several days due to the slow solvent evaporation. Yield: 48.2 %. IR (KBr, cm⁻¹): 3 424, 1 725, 1 659, 1 607, 1 502, 1 440, 1 403, 1 048, 876. Similar to complex **1**, complex **2** also lost solvent molecules quickly when it was exposed to air. After solvent molecules were removed under vacuum, the elemental analysis based on Cu (ntb) (H₂mpda) was performed. Anal. Calcd. C₃₈H₃₅CuN₉O₈(%): C, 56.40; H, 4.36; N, 15.58. Found(%): C, 56.03; H, 4.69; N, 15.72.

1.3 X-ray crystallography

Intensity data were obtained on a Bruker SMART CCD diffractometer equipped with a graphite-monochromatic Mo K α radiation (λ =0.071 073 nm) at 185(2) K. Data for **1** and **2** were corrected for absorption using the SADABS program^[14]. The structure was obtained by direct methods using SHELXS97 and subsequent Fourier analyses and refined by the full-matrix least-squares method using SHELXL97 based on F^2 with all reflections^[15]. All the calculations were performed using the WINGX System, Ver 1.70.01^[16].

Table 1 Crystal data and structure refinements for complexes **1** and **2**

Complex	1	2
Empirical formula	C ₇₉ H ₈₄ Cu ₂ N ₁₈ O ₂₁	C ₄₂ H ₅₀ CuN ₁₀ O ₁₂
Measurement temperature / K	185(2)	185(2)
Formula weight	1748.72	950.47
Crystal system	Triclinic	Monoclinic
Crystal dimensions / mm	0.25×0.20×0.18	0.36×0.21×0.20
Space group	$P\bar{1}$	$P2_1/c$
<i>a</i> / nm	1.243 1(2)	1.249 8(1)
<i>b</i> / nm	1.2920(2)	1.4043(1)
<i>c</i> / nm	1.4562(3)	2.6044(2)
α / (°)	76.751(3)	
β / (°)	66.515(3)	97.249(1)
γ / (°)	77.469(3)	
<i>V</i> / nm ³	2.067 2(7)	4.534 5(5)
<i>Z</i>	1	4
<i>D_c</i> / (g·cm ⁻³)	1.405	1.392
μ / mm ⁻¹	0.598	0.554
<i>F</i> (000)	910	1 988
θ range / (°)	1.54~25.00	1.58~25.00
Reflections collected	10 817	7 988
Independent reflections	7 170	5 651
<i>R_{int}</i>	0.036 4	0.050 2
Parameters	572	601
Goodness-of-fit on <i>F</i> ²	1.036	1.049
Final <i>R</i> indices (<i>I</i> >2σ(<i>I</i>))	<i>R</i> ₁ =0.077 5, <i>wR</i> ₂ =0.189 2	<i>R</i> ₁ =0.067 0, <i>wR</i> ₂ =0.180 0
$\Delta\rho_{\max}$ and $\Delta\rho_{\min}$ / (e·nm ⁻³)	626 and -421	1 757* and -801

* Significant residual electron density maxima of the complex **2** are near the disordered oxygen atom (0.120 0 nm) of DMF.

Details of crystal data, data collection and refinement parameters for **1** and **2** are summarized in Table 1. In complex **1**, the disordered O10 of a water molecule has been split into two parts (O10A and O10B) with the occupancies of 0.7:0.3. In complex **2**, the disordered O12 of a water molecule has been split into two parts (O12A and O12B) with the occupancies of 0.7:0.3. When the oxygen atom of water is disordered over the possible positions in complex **1** and **2**, the addition of hydrogen atoms has not been performed.

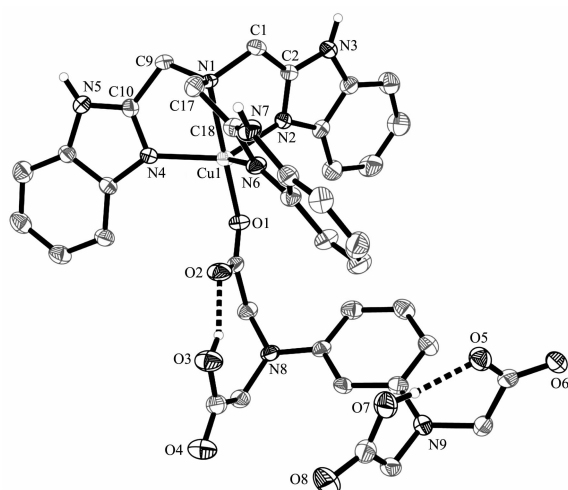
CCDC: 893363, **1**; 893364, **2**.

2 Results and discussion

The ntb ligands in these compounds demonstrated different coordination motifs with different conformations, where complex **1** and **2** showed different coordination environments. H₂mpda²⁻ anions in both comp-

lexes were all in monodentate coordination fashion.

The crystal structural analysis of complex **1** revealed the mononuclear structure (Fig.1). The coordination environment around the Cu(II) ion is five-coordinated trigonal-bipyramidal geometry, in which the Cu(II) is coordinated by four nitrogen atoms of a tetradentate ligand ntb and one oxygen atom of H₂mpda²⁻ anions. The tertiary amino nitrogen atom of ntb and one oxygen atom of the carboxylate ligand occupy axial positions; the other three nitrogen atoms of ntb are located in the equatorial plane. All bond lengths and bond angles are in the range of earlier reports. The tripodal ligand ntb wraps around the central metal ion through four nitrogen atoms in a propeller fashion. The ntb ligand exhibits a clockwise (Δ)-like conformational chirality around the metal center. For the symmetry, there are equal numbers of



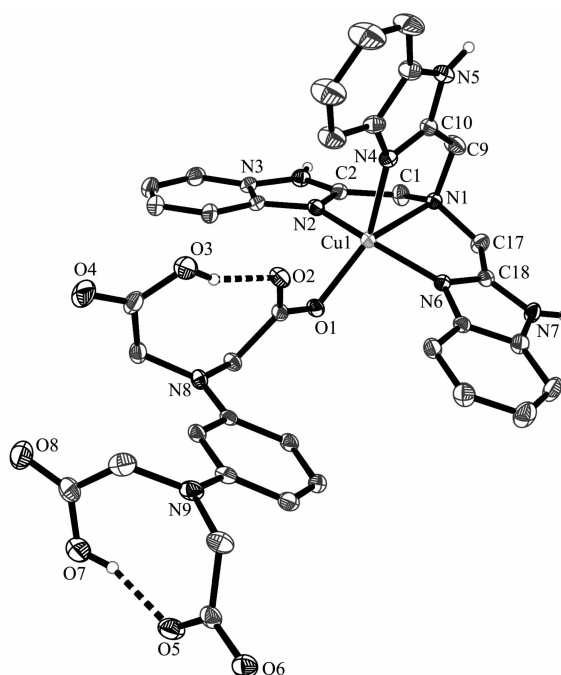
Displacement ellipsoids drawn at the 30% probability level; Hydrogen atoms have been omitted for clarity except these attaching nitrogen and oxygen atoms

Fig.1 Molecular structure of the complex **1**

anticlockwise (A) monomers in the crystal. In $\text{H}_2\text{mpda}^{2-}$ ligand, two nitrilodiacetic groups are in the same side of the phenyl ring, showing a cis-conformation. Every nitrilo nitrogen atom links an acetic acid group and an acetate group, which forms an eight-ring by intra-molecular hydrogen bonds ($\text{O3}-\text{H3A}\cdots\text{O2}$, $\text{O7}-\text{H7B}\cdots\text{O5}$).

The crystal structure of complex **2** is illustrated in Fig.2. The Cu(II) ion is also mononuclear in five-coordinated environment. The mcenter is coordinated by four N atoms from one ntb ligand and one oxygen atom of $\text{H}_2\text{mpda}^{2-}$. The coordination polyhedron around the Cu(II) ion lies between square-pyramidal and trigonal bipyramidal geometry. In **2**, ntb-Cu part displays a symmetric structure. Two nitrilodiacetic acid groups are in the different sides of the phenyl ring, showing a trans-conformation. In $\text{H}_2\text{mpda}^{2-}$ ligand, the formation of intra-molecular hydrogen bonds ($\text{O3}-\text{H3A}\cdots\text{O2}$, $\text{O7}-\text{H7B}\cdots\text{O5}$) is similar to that in complex **1**.

Because of the different coordination situation of the ligands, the coordination bond lengths and angles are significantly altered in complex **1** and **2**. The lengths of the equatorial Cu-N bonds are in the range of 0.199 6~0.216 6 nm (**1**) and 0.195 2~0.207 2 nm (**2**), while the lengths of the apical Cu-N bonds are 0.213 5 (**1**) and 0.233 40 nm (**2**). The longer distance



Displacement ellipsoids drawn at the 30% probability level; Hydrogen atoms have been omitted for clarity except these attaching nitrogen and oxygen atoms

Fig.2 Molecular structure of the complex **2**

between the tertiary amine nitrogen atom and the metal ion in complex **2** indicates the weaker interaction than that in complex **1**. The ntb-Cu coordination cation of complex **1** has approximate C_3 symmetry, with the nearly linear axis of $\text{N1}-\text{Cu1}-\text{O1}$ $173.37(19)^\circ$. The angle of $\text{N1}-\text{Cu1}-\text{O1}$ in complex **2** is $145.08(12)^\circ$, indicating that the metal center is in a distorted environment (Fig.3). A comparison of structural parameters of complex **1**, complex **2**, and earlier reported carboxylate bridged ntb-Cu(II) crystal structures show that in complex **1** and other similar structures^[10], the ntb ligands show a fan-like conformation^[17]. One oxygen atom of the monodentate carboxylate group is bonded to Cu(II) ion, while the other one fills in the space between the two benzimidazolyl rings. For these complexes, the average distance of axial Cu-N bond is 0.214 nm and Cu-O bond is 0.193 nm with the average O-Cu-N angle of 175.11° . In the reported ntb-Cu unit containing structures, the coordination oxygen atom of carboxylate deviates from the axial position with a high degree usually because of the crowding effect caused by the $\mu-\eta^1:\eta^1$ bridging bidentate mode

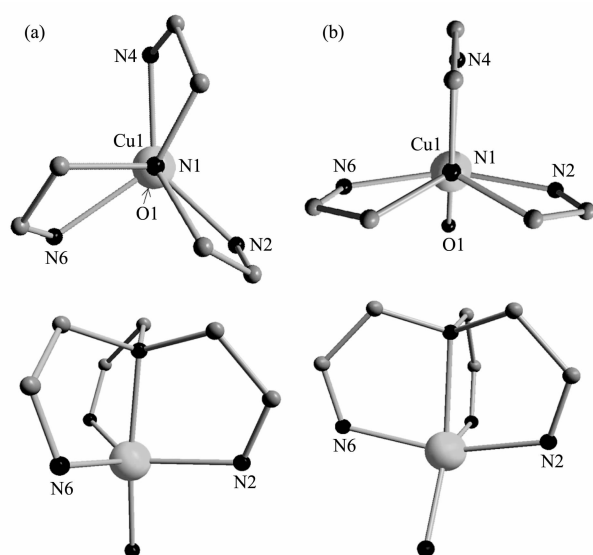


Fig.3 View of the coordination environment of Cu(II) ion from different directions in complex 1(a) and 2 (b)

of carboxylate^[18]. In complex **2**, the carboxylate group (O1/C25/O2) and a benzimidazolyl group (C11-C16/ N4/C10/N5) are in a plane with the mean deviation of 0.004 5 nm and the dihedral angle of 6.4°. In complex

2 and its related structure, the average distance between axial nitrogen atom and Cu(II) metal is 0.227 nm, which is larger than that in complex **1**.

The binuclear complex $\text{Na}_4[\text{Cu}_2(\text{mpda})_2] \cdot 18\text{H}_2\text{O}$ ^[19] is one of the few examples which are formed by the mpda ligand. It is interesting to compare the role played by the mpda ligand in this complex with that in **1** and **2**. In above mentioned complex, copper(II) is in highly distorted octahedral coordination geometry which is complete by N atom of iminodiacetate group. The axial Cu-O is 0.223 9(7) nm, while Cu-O_{axis} is 0.196 2(4) (**1**) and 0.197 2(3) nm (**2**), respectively.

In complex **1**, the hydrogen bonds (Table 2) formed by NH_{Bin} , carboxylic acid, carboxylate groups and water molecules link coordination units together to an intricate supramolecular network, in which solvated water molecules are in the bridging fashion and the acetone molecules lay in the cavity of crystal lattice by $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds with water molecules. In complex **2**, one water molecule and

Table 2 Hydrogen bond geometry of the complexes

D-H...A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle \text{DHA} / (^\circ)$
Complex 1				
N3-H3...O6 ⁱ	0.086	0.184	0.268 5(7)	167
N5-H5A...O9 ⁱⁱ	0.086	0.184	0.268 1(7)	167
N7-H7A...O3 ⁱⁱⁱ	0.086	0.202	0.285 9(7)	164
O3-H3A...O2	0.082	0.168	0.245 1(8)	156
O7-H7B...O5	0.082	0.175	0.253 8(7)	161
O7-H7B...N9	0.082	0.241	0.285 9(7)	116
O9-H9D...O6 ⁱ	0.085	0.205	0.276 7(7)	141
O9-H9C...O10A(B)*	0.085	0.189(0.201)	0.273 1(12)(0.277(2))	170(148)
Complex 2				
N3-H3...O10 ^{iv}	0.086	0.189	0.272 3(6)	163
O3-H3A...O2	0.082	0.178	0.257 1(5)	161
O3-H3A...N8	0.082	0.239	0.284 2(6)	116
N5-H5A...O9 ^v	0.086	0.188	0.273 8(6)	173
N7-H7A...O6 ^{vi}	0.086	0.203	0.283 2(5)	154
O7-H7B...O5	0.082	0.175	0.254 8(5)	162
O7-H7B...N9	0.082	0.241	0.285 8(6)	115
O9-H9C...O6 ^{vii}	0.085	0.19	0.272 1(5)	162
O9-H9D...O11 ^{viii}	0.085	0.226	0.309 5(16)	168
O10-H10...O6 ^{vii}	0.082	0.193	0.272 8(6)	163

Symmetry code: **1**: ⁱ 1-x, 1-y, -z; ⁱⁱ 1-x, -y, 1-z; ⁱⁱⁱ 1-x, -y, -z; **2**: ^{iv} 1-x, 1-y, -z; ^v -x, 1-y, -z; ^{vi} x, 5/2-y, -1/2+z; ^{vii} x, -1+y, z; ^{viii} -x, 1/2+y, 1/2-z.

methanol are in linking fashion, while another disordered water molecule and DMF are trapped in the hydrogen bonded complicated network.

The disordered O10 of a water molecule has been split into O10A and O10B with the occupancies of 0.7:0.3. The water molecule as hydrogen bond donor has not been included in because of it is difficult to attach hydrogen atoms to water oxygen atom in best position matching their hydrogen bond environment. So is it in complex **2**.

3 Conclusions

Based on the reaction of ntb, H₄mpda, and copper nitrate in different component solvents, two Cu (II) isomers have been synthesized and characterized. The structural dissimilarity between the two coordination units and supramolecular assemblies depended on the coordination environments of the metal center and conformations of the ntb/H₄mpda ligands influenced by solvent systems. The result suggests that structural transformations can be controlled by the appropriate solvent composition, which may be used in the adjustment of ntb-containing complexes properties in the solution and the solid state.

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