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Synthesis, Crystal Structure and Thermal Stability of Copper Complex of 1,3-Propane Diamine

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Abstract: An unexpected complex with the maximum crystal size of about 7 mm×3 mm×5 mm was prepared by a reaction of CuCl₂ with 1,3-propane diamine(pn) in methanol. The characterization results with infrared spectroscopy, elemental analysis and X-ray diffraction show that the complex exhibits three dimensional network structure, which is contributed to the hydrogen bonding and electrostatic interactions between coordination ion [CuCl(pn)₂]⁺ and its counter anion Cl⁻, where CH₃OH also participates the hydrogen bonding interactions. In addition, thermogravimetric analysis and differential scanning calorimetry techniques show that the thermal stability of synergistic interactions increases in the order of electrostatic, coordination and hydrogen bond. The synergistic interactions are in favor of the formation of bigger size crystals of the complex.

Keywords: 1,3-propane diamine; crystal structure; copper(II) polymer; chlorine-containing-hydrogen bond

丙二胺铜配合物的合成、晶体结构和热稳定性

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摘要: CuCl₂与1,3-丙二胺(pn)在甲醇中反应获得了一个意想不到的络合物,其最大晶体尺寸约为7 mm×3 mm×5 mm。通过红外光谱,元素分析和X射线衍射表征该配合物,结果表明,该复合体具有三维网络结构。三维网状结构是由于配位离子[CuCl(pn)₂]⁺与Cl⁻之间的氢键和静电相互作用而形成的,其中CH₃OH也参与氢键相互作用。另外,使用热重分析和差示扫描量热技术研究了该络合物的热稳定性。结果表明,相互作用的热稳定序列(从强到弱)是静电作用,配位作用和氢键作用。协同相互作用有助于形成更大尺寸的配合物晶体。

关键词: 1,3-丙二胺;晶体结构;铜聚合物;含氯氢键

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The nitrogen-containing ligands have strong coordination ability with most of metal ions and are capable to form variety of complexes^[1-6]. The structures of these complexes vary with various kinds of factors such as ligands, metal ions as well as the

anions introduced by metal salts. Vezzosi and coworkers^[7] found that 1,3-propane diamine (pn) reacting with CuCl₂·2H₂O with mole ratio of Cu(II):pn=1:2 produced a dinuclear copper(II) complex with a pn as a bridged group. However, the same

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reaction with the mole ratio of 1: 2 led to a mononuclear copper(II) complex^[8]. Besides the coordination interactions in the complexes, there are also others such as hydrogen bond and p-p stacking, which are attributed to the formation of final space configuration. In the reported complexes, Cl⁻ is found to exhibit multifunction. Llobet and coworkers^[9] synthesized a chloro-bridged dimer ([Cu₂Cl₂(pn)₂]Cl₂) by the reaction of pn and CuCl₂ with mole ratio of 1:1 in methanol, where Cl⁻ exhibited strong coordination ability, hydrogen bonding and electrostatic interactions. The researches on the molecular structure will provide useful information not only to understand the constitution of the substances but also to reveal reasons for the existence of some unknown ones. Although many polyamine copper (II) complexes have been reported^[10-11], the complex with formula of [CuCl(pn)₂]Cl · CH₃OH has not been reported yet. In this work, this complex with unexpected maximum crystal size of about 7 mm × 3 mm × 5 mm was synthesized. The structure and the thermal stability of the complex have been thoroughly studied by infrared spectrum, X-ray diffraction, elementary and thermogravimetric analyses.

1 Experimental

1.1 Materials

Methanol was purified to anhydrous one by the general method, and other solvents and chemicals we used were of analytical grade and used as received. 1, 3-propane diamine was purchased from Aladdin (Shanghai, China) and used as received.

1.2 Synthesis of complex 1

The solution of CuCl₂ (1.709 9 g, 10 mmol) was added to methanol (20 mL). Then, 30 mL methanol solution containing pn (1.487 4 g, 20 mmol) was added dropwise under magnetic stirring. The resulting solution was stirred at room temperature for 24 h and filtered. The blue-black crystals suitable for the X-ray diffraction analysis were obtained by the diffusion of ethyl acetate into the filtration for a month. Yield: 56%. Anal Calcd for C₇H₂₄Cl₂CuN₄O (%): C, 26.71; H, 7.69; N, 17.80. Found (%): C, 26.34; H, 7.26; N, 17.58. FTIR (KBr: cm⁻¹): ν(C—H) 2 943 cm⁻¹, ν(N—H) 3 446 cm⁻¹, 3 371 cm⁻¹, ν(C—N)

1 168 cm⁻¹.

1.3 Physical measurements

A vector 22 FI-IR spectrophotometer using KBr disc was used to record on IR spectra. And a Vario EL III CHNOS elemental analyzer was used to perform on the Elemental. Thermogravimetric analysis (TGA) was performed on a SDT Q600Q50 TGA (USA). The obtained samples (20 mg) were placed in a platinum crucible, and heated from 25 °C to 800 °C in Ar atmosphere at a heating rate of 20 °C·min⁻¹.

1.4 Crystal structure determination

A single crystal with dimensions of 3.2 mm × 2.7 mm × 2.5 mm was mounted on a SMART-CCD area-detector diffractometer equipped with a graphite-monochromatic MoKα radiation (λ = 0.710 73 nm). The SMART and SAINT programs were used to reduce data and refine cell, respectively. The structure was solved by direct methods (Bruker SHELXTL) and refined on F² by full-matrix least-squares (Bruker SHELXTL) using all unique data. The non-H atoms were considered as anisotropic thermal parameters. Hydrogen atoms were located geometrically and refined in a riding mode.

2 Results and discussion

2.1 Crystal structure

The complex was obtained by one-pot reaction at room temperature. The result of the elemental analysis for the complex matched well with the complex' s composition. As shown in Fig. 1, the band at 2 942 cm⁻¹ can be assigned to the stretching vibration of CH₂. The absorption peaks at 3 446 cm⁻¹ and 3 371 cm⁻¹ are due to the existence of NH. And C—N stretching vibration is found in 1 168 cm⁻¹. These results are in agreement with the structure of the complex. The morphology of the complex is shown in Fig. 2(a). They were black block with the maximum crystal size of about 7 mm × 3 mm × 5 mm. The crystallographic data and details about the data collection are presented in Table 1. And selected bond lengths (nm) and angles (°) relevant to the metal coordination spheres of the complex are listed in Table 2. Some hydrogen bond data are shown in Table 3.

Tab. 1 Crystal data and structure refinement for the complex	
Empirical formula	C ₇ H ₂₄ Cl ₂ CuN ₄ O
Formula weight	314.74
Space group	P2 ₁ /c
Crystal system	Monoclinic
Temperature / K	291(2)
<i>a</i> / nm	8.538 9(4)
<i>b</i> / nm	16.159 2(7)
<i>c</i> / nm	10.274 7(4)
α / (°)	90
β / (°)	107.246(2)
γ / (°)	90
Volume / nm ³	1 353.98(10)
<i>Z</i>	4
<i>D</i> _{calcd} / (g/cm ³)	1.544
Mu(Mo K α) /mm	1.992
F(0 0 0)	660.0
Crystal size /mm ³	7 mm \times 3 mm \times 5 mm
Mo k α radiation/nm ³	0.710 73
Θ Range/(°)	2.17–26.00
Observed data [<i>I</i> > 2.0 sigma (<i>I</i>)]	2 366
Nref, Npar	2 380, 138
R, wR ₂ , S	0.020 6 , 0.051 3 , 1.026

The molecular structure of the complex is shown in Fig. 2(b). The complex crystallizes in monoclinic space group. It contains one coordination ion [Cu(pn)₂Cl]⁺, a counter anion Cl[−] and one CH₃OH molecule. Each Cu(II) in the [Cu(pn)₂Cl]⁺ unit coordinates with four nitrogen atoms from two pn molecules and one Cl[−]. The coordination configuration of Cu(II) can be approximately described as a square pyramid as ascertained by

Reedijk' st factor of 0.30^[12–15]. The four nitrogen atoms from two pn units are nearly coplanar constituting the base plane of the pyramid. The distances of Cu—N(1), Cu—N(2), Cu—N(3) and Cu—N(4) are 2.025, 2.038, 2.030 and 2.027 nm, respectively. As shown in the Fig. 2(b), Cl(1) occupies the apical position with the distance of Cu—Cl(1) of 2.717 nm, and Cu—Cl(1) is almost perpendicular to the base plane with the angle of 88.0°. In the crystal structure, one coordination unit [Cu(pn)₂Cl]⁺ connects with three Cl(2) anions, two Cl(1) anions and one CH₃OH through Cl—containing hydrogen bonding interactions, shown in Fig. 2(c). The uncoordinated Cl(2) resides in the voids of molecular architecture, acting as a counterion and a hydrogen acceptor to three pn with N—H $\times\times\times$ Cl interaction and one CH₃OH with C—H $\times\times\times$ Cl interaction. The distances of N $\times\times\times$ Cl are in the range of 3.207 nm–3.420 nm, and the angle of N—H $\times\times\times$ Cl is of 111.0°–176.6°. CH₃OH involving hydrogen bond parameters as well as the detailed information about the length and angle of N—H $\times\times\times$ Cl are listed in Table 2. And the three dimensional network is shown in Fig. 2(c). The 3D network frame of the complex is mainly contributed to the hydrogen bonding and electrostatic interactions between coordination ion [CuCl(pn)₂]⁺ and its counter anion Cl[−].

2.2 Thermal stability analysis

The thermal stability of the complex was quantitatively determined by TGA. The plots of weight loss and relative heat flow of the complex verse temperature are exhibited in Fig. 3. The weight loss between 25 °C and 164 °C could be assigned to the escape of methanol from the complex, the weight loss 10.2% matched very well with the content of one

Tab. 2 Selected bond distances (nm) and bond angles (°) for complex

Bond	Dist	Bond	Dist
Cu(1)—N(1)	2.025 2(13)	Cu(1)—N(4)	2.026 8(13)
Cu(1)—N(2)	2.038 2(12)	Cu(1)—Cl(1)	2.717 1(5)
Cu(1)—N(3)	2.030 2(13)		
Angle	(°)	Angle	(°)
N(1)—Cu(1)—N(2)	90.004(56)	N(2)—Cu(1)—N(4)	90.907(55)
N(1)—Cu(1)—N(3)	87.998(55)	N(2)—Cu(1)—Cl(1)	98.590(41)
N(1)—Cu(1)—N(4)	177.332(55)	N(3)—Cu(1)—N(4)	92.032(56)
N(1)—Cu(1)—Cl(1)	90.109(42)	N(3)—Cu(1)—Cl(1)	101.840(44)
N(2)—Cu(1)—N(3)	159.472(58)	N(4)—Cu(1)—Cl(1)	87.275(41)

Tab.3 Hydrogen bond date

D—H---A	d(D—H) /nm	d(H---A) /nm	d(D---A) /nm	∠DHA/(°)
N(1)—H(1D)---Cl(1)	0.910 3(15)	2.635 7(4)	3.407 7(14)	143.100(85)
O(1)—H(1)---Cl(1)	0.840 0(12)	2.296 0(4)	3.127 8(13)	170.654(94)
N(4)—H(4C1)---Cl(1)	0.910 5(15)	2.874 2(4)	3.311 6(16)	111.01(9)
N(4)—H(4C2)---Cl(1)	0.910 5(15)	2.650 2(4)	3.420 2(15)	142.825(86)
N(1)—H(1C)---Cl(2)	0.910 4(13)	2.494 8(2)	3.404 0(13)	176.589(85)
N(2)—H(2D)---Cl(2)	0.910 5(13)	2.619 8(4)	3.440 6(14)	150.335(82)
N(2)—H(2C)---Cl(2)	0.910 2(16)	2.518 6(5)	3.207 6(17)	132.823(92)
N(4)—H(4D)---Cl(2)	0.910 0(13)	2.470 3(4)	3.361 3(13)	166.289(85)
C(7)—H(7C)---Cl(2)	0.979 6(22)	2.763 0(5)	3.613 8(22)	145.577(111)

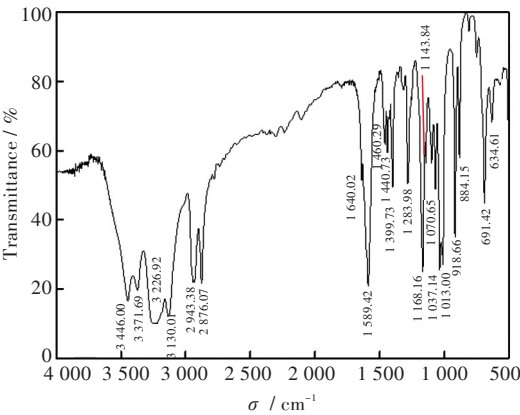


Fig. 1 FT-IR spectrum of the complex

molar CH₃OH in the complex formula. The weight lose between 164 °C and 230 °C was corresponding to the dissociation of one pn, and the loss of the second pn happened in the range of 230 –380 °C, the relative weight losses were in agreement with the relative molecule's dissociation. From 380 °C to 800 °C, the weight loss could be attributed to the decomposition of CuCl₂, where at 430 °C, CuCl₂ changed into CuCl, then it gradually decomposed into Cu and Cl₂. The content of residual sample was 22.87% at 789 °C, which was slightly larger than the content (20.19%)

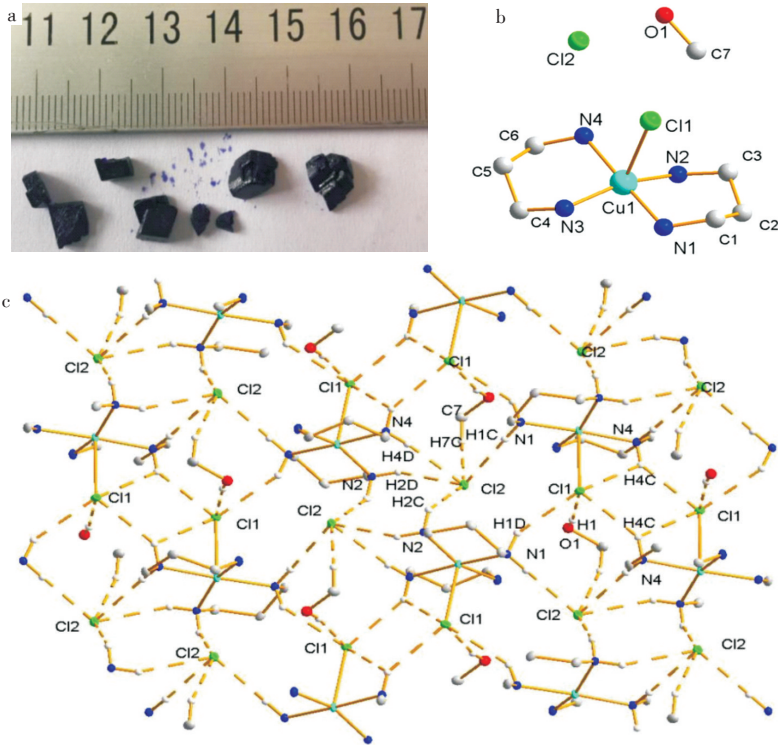


Fig. 2 (a) The morphology of the complex, (b) the molecular structure of the complex (Symmetry code a :2-x,0.5+y,1.5-z), (c) three-dimensional network of the complex showing the hydrogen bond interactions. The atoms that have not participated in the hydrogen bond interactions have not been marked for clarity

of Cu in the formula of the complex. According to the above analysis, the thermal decomposition scheme for the complex can be proposed, and the scheme for the suggested procedure can be described as Scheme 1. Differential scanning calorimetry has exhibited three endothermic reactions and two exothermic reactions. Methanol molecule produces a small sharp endothermic peak centered around 164 °C, two pn molecules produce two endothermic peaks at 230 °C and 330 °C, respectively. And the decomposition of CuCl₂ exhibits two exothermic peaks at 397 °C and 502 °C, respectively. The results show that methanol molecule in lattice can be easily escaped from the complex because of its weak hydrogen bonding interactions with the other components in the complex. The decomposition of two pn molecules at higher temperature range indicates that pn has stronger coordination interactions with copper(II) ions. Cl⁻ changed into Cl₂ and escaped from the sample at temperature range from about 400 °C to 800 °C, giving a strong support with the additional electrostatic interactions between Cu(II) and Cl⁻ besides their coordination interactions.

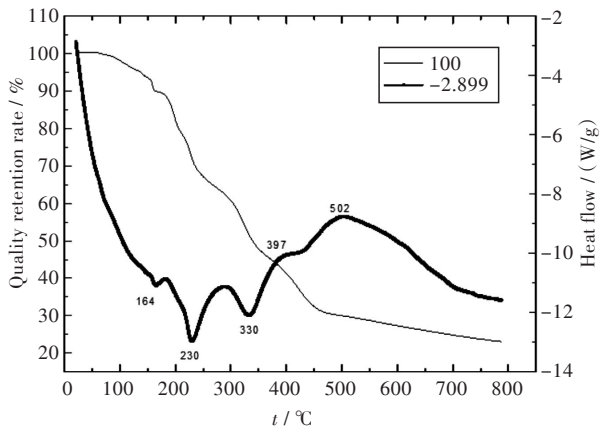
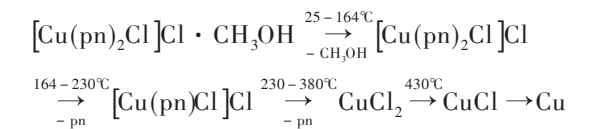


Fig. 3 TGA and DSC curves of the complex



Scheme 1 The thermal decomposition scheme for the complex

3 Conclusion

A three-dimensional network complex derived from the reaction of 1,3-propane diamine and Cu(II) was successfully obtained. The unit are joined together by the hydrogen bonding interaction in the

form of N—H---Cl and electrostatic interactions. The results show that the thermal stability is decreased in the order of electrostatic, coordination and hydrogen bond. The synergistic interactions contribute to the formation of bigger size crystals of the complexes. The study provides useful information to understand the constitution of the chloridion-containing substances.

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