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不对称大环双核铜(Ⅱ)配合物$[Cu_2(C_{23}H_{26}Cl_2N_4O_2)](ClO_4)_2$的合成、晶体结构及磁性

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摘要:大环双核铜(Ⅱ)配合物由 *N*,*N*′-二甲基-*N*,*N*′-二(3-甲酰基-5-氯水杨醛)乙二胺和 1,3-丙二胺,与铜(Ⅱ)反应形成的,经过 X-射线单晶衍射结果表明:*a*=0.871 05(16) nm,*b*=0.957 78(18) nm,*c*=1.810 4(3) nm,*β*=100.761(18)°,*V*=1.483 8(5) nm^3,*Z*=2,D_c=1.762 Mg·m^{-3},*μ*=1.85 mm^{-1},*F*(000)=796,and final R_1=0.061,wR_2=0.126。晶体结构表明:两个铜离子位于双核大环中间,与大环的胺、亚胺以及酚羟基的氧进行配位。磁性结果表明配合物为反铁磁性。

关键词:晶体结构;双核铜配合物;磁性
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Synthesis, Crystal Structure and Magnetic Properties of the Asymmetric Dinuclear Copper(Ⅱ) Macrocyclic Complex $[Cu_2(C_{23}H_{26}Cl_2N_4O_2)](ClO_4)_2$

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Abstract: The dinuclear copper(Ⅱ) macrocyclic complex has been synthesized by condensation between *N*,*N*′-dimethyl-*N*,*N*′-bis(3-formyl-5-chlorosalicylidene)ethylene diamine and 1,3-propanediamine in the presence of copper(Ⅱ). The complex was determined by X-ray diffractions single crystal structure analysis. The results indicates that the complex crystallizes in monoclinic, space group $P2_1$, Flack parameters(*x*) =0.06(2), with *a*=0.871 05(16) nm, *b*=0.957 78 (18) nm, *c*=1.810 4 (3) nm, *β*=100.761 (18)°, *V*=1.483 8 (5) nm^3, *Z*=2, D_c=1.762 Mg·m^{-3}, *μ*=1.85 mm^{-1}, *F*(000)=796, and final R_1=0.061, wR_2=0.126, The crystal structure shows that the two copper(Ⅱ) ions in the phenol-based macrocyclic dinuclear complex, are coordinated with $(N_{amine})_2O_2$ and $(N_{imine})_2O_2$ sites. Magnetic measurements reveal an antiferromagentic interaction in the complex. CCDC: 624712.

Key words: crystal structure; dinuclear copper complex; magnetic properties

0 Introduction

The dinuclear metals macrocyclic complex with aminic and iminic sites are of current interest due to unique physicochemical properties[1-4]. Phenol-based macrocyclic ligands, having dissimilar $(N_{amine})_2O_2$ and $(N_{imine})_2O_2$ metal-binding sites sharing the phenolic oxygen atoms, have been used for bounding two metals

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to form asymmetric compartmental dinuclear copper(Ⅱ) complex[5-8]. The proligand *N*,*N*′-dimethyl-*N*,*N*′-bis(3-formyl-5-chlorosalicylidene)ethylenediamine have been developed for providing heterodinuclear, tetranuclear or pentanuclear metal complexes[9-11]. In this paper, we report on synthesis, crystal structure and magnetic property of this complex $[Cu_2(C_{23}H_{26}Cl_2N_4O_2)](ClO_4)_2$.

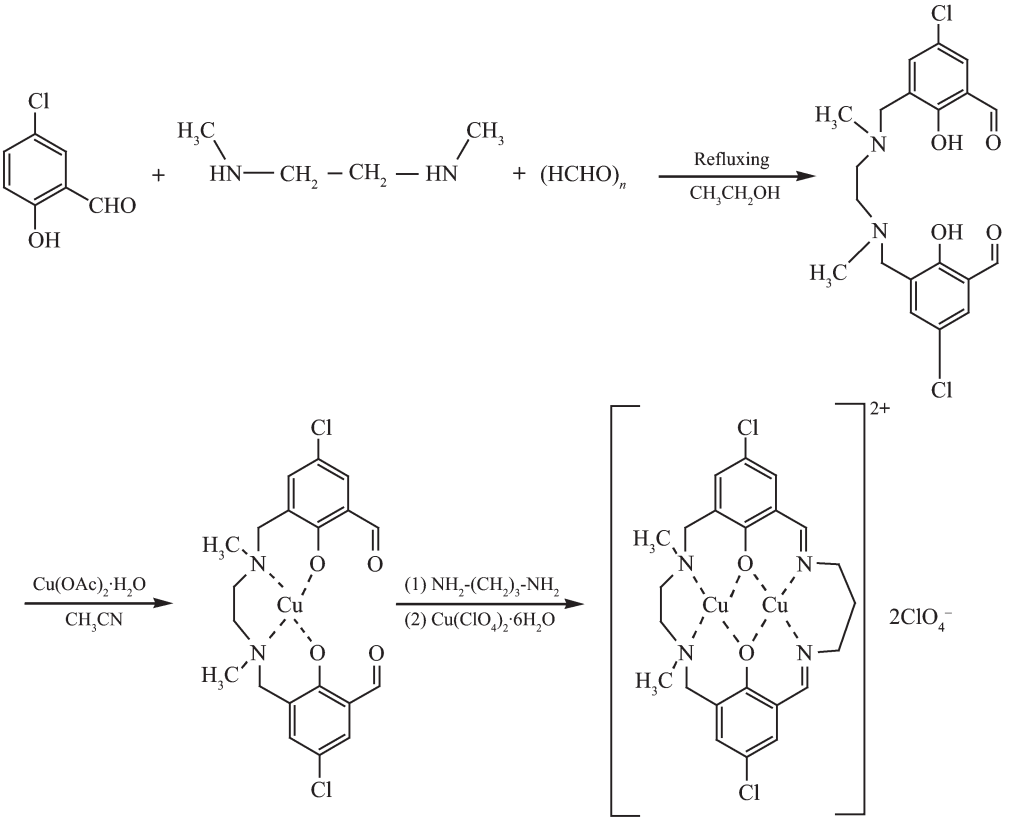
1 Experimental

1.1 General procedures

All commercially available chemicals and solvents are reagent grade and used as received without further purification. Elemental analysis for C, H and N were performed on a Perkin-Elmer 240 analyzer. Variable-temperature magnetic susceptibilities (1.8~300 K) of a power sample were measured on a SQUID MPMS XL-7, and were corrected for diamagnetism by Pascal constants. IR spectrum was recorded using KBr disc on a vector 22 FTIR spectrophotometer.

1.2 Synthesis of the complex

N, *N*′-Dimethylethylenediamine (0.176 g, 2.0 mmol), 5-chlorosalicylaldehyde (0.800 g, 4.0 mmol), and paraformaldehyde (0.160 g, 5.3 mmol) were dissolved in methanol (50 mL), and the mixture was refluxed for 1 week to form a white powder. The white powder and copper(II) acetate tetrahydrate (0.448 g, 2.0 mmol) were dissolved in solution of acetonitrile (50 mL) at ambient temperature with stirring for 4 h. To this solution, $Cu(ClO_4)_2\cdot 6H_2O$ (0.755 g, 2.0 mmol) and 1,3-propanediamine (0.148 g, 2.0 mmol) was dropped with stirring, respectively (Scheme 1). The mixture was stirred for 10 h was concentrated to afford a dark green precipitate (0.620 g, yield 53%). Elemental analysis calculated for $Cu_2C_{24}H_{27}N_4Cl_3O_{12}$ (%): C, 36.17; H, 3.41; N, 7.03. Found(%): C, 36.15; H, 3.44; N, 7.01. IR (KBr): 3 419.14, 1 631, 1 555.32, 1 296.46 cm^{-1}.



Scheme 1　Reaction equation for the title complex

1.3 Crystal structure determination

A single crystal with dimensions of 0.32 mm×0.26 mm×0.24 mm was selected for X-ray structure analysis. The data were collected on a Bruker Smart Apex CCD diffractometer equipped with a Mo *Kα* radiation (λ = 0.071 073 nm) at 298 K. A total of 15 477 reflections

were collected in the range of 1.14° ≤θ ≤26.00° by using an ω-2θ scan mode, of which 5 798 were unique with R_{int}=0.055 and 4 438 observed reflections with $I>2\sigma(I)$. Data reduction and cell refinement were performed by the SMART and SAINT Program[12]. The structures were determined by the direct method (Bruker Shelxtl) and refined on F^2 by full-matrix least squares (Bruker Shelxtl) using all unique data[13]. The non-H atoms in the structure were anisotropic. All the hydrogen atoms were placed in calculated positions assigned fixed isotropic thermal parameter at 1.2 times the equivalent isotropic U of the atoms to which they are attached (1.5 times for methyl group) and allowed to ride on their respective parent atoms. Details of the crystal parameters, data collection, and refinements of the title complex are summarized in Table 1.

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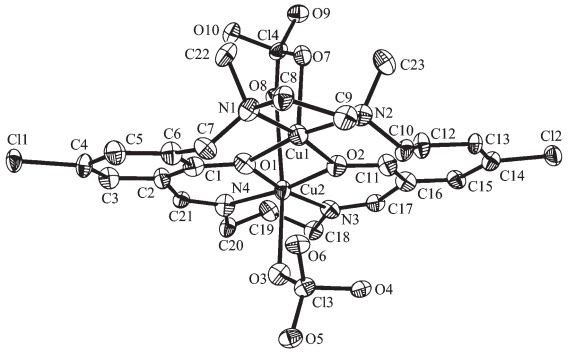
Table 1 Crysta data and structure refinement parameters for the title complex

Empirical formula	$C_{23}H_{26}Cl_4Cu_2N_4O_{10}$	Limiting indices	$-10<h<10, -11<k<11, -22<l<22$
Formula weight	787.36	Absorption coefficient / mm^{-1}	1.854
Temperature / K	298(2)	F(000)	796
Crystal system	Monoclinic	θ range for data collection / (°)	1.14~26.00
Space group	$P2_1$	Reflections collected	15 477
a / nm	0.871 05(16)	Independent reflections (R_{int})	5 798 (0.054 5)
b / nm	0.957 78(18)	Reflections observed ($I>2\sigma(I)$)	4 438
c / nm	1.810 4(3)	Data / restraints / parameters	5 798 / 1 / 390
β / (°)	100.761(18)	Goodness-of-fit on F^2	1.005
V / nm^3	1.483 8(5)	Final R indices ($I>2\sigma(I)$)	R_1=0.061 2, wR_2=0.121 7
Z	2	R indices (all data)	R_1=0.077 9, wR_2=0.126 0
D_c / (g·cm^{-3})	1.762	$\Delta\rho_{max}$, $\Delta\rho_{min}$ / (e·nm^{-3})	365 and −670
Size / mm	0.32×0.26×0.24	Flack parameters (x)	0.06(2)

2 Results and discussion

2.1 Crystal structure

The crystal structure $[Cu_2(C_{23}H_{26}Cl_2N_4O_2)](ClO_4)_2$ were shown in Fig.1. The selected bond lengths and bond angles of non-hydrogen atoms are listed in Table 2. The crystal structure of complex reveals that the title complex is dinuclear Cu(Ⅱ) macrocyclic complex with $(N_{amine})_2O_2$ and $(N_{imine})_2O_2$ metal-binding sites and each Cu(Ⅱ) ion is six-coordinate. Atom Cu1 is coordinated by two amine and two phenoxide donors, while Cu2 is coordinated by two imine and two phenoxide donors. The basal Cu1-to-ligand bond distances rang from 0.189 2 to 0.196 8 nm and the basal Cu2-to-ligand bond distances rang from 0.191 5 to 0.198 8 nm. The perchlorate anions coordinate weakly to Cu1 and Cu2 with Cu-O distances of 0.282 4(5) nm (Cu1-O6), 0.251 1(6) nm (Cu1-O7), 0.256 5(5) nm (Cu2-O3) and 0.264 8(6) nm (Cu2-O8). Two Cu(Ⅱ) centers are equivalently bridged by the phenolic oxygens with the intermetallic separation of 0.301 4 nm.



Symmetry code: A: $-x$, y+1/2, $-z$+1/2

Fig.1 A view of the title compound, displacement ellipsoids are drawn at the 30% probability level

The dihedral angle between the $(N_{amine})_2O_2$ and $(N_{imine})_2O_2$ planes is 1.2(3)°. The deviations of Cu1 and Cu2 from these planes are 0.011 80(9) and 0.003 38(9) nm, respectively. The N1 and N2 have S and R configurations, respectively. The two methyl groups attached to atoms N1 and N2 are cis to each other, the

Table 2　Selected bond lengths (nm) and bond angles (°) for the title complex

Cu1-O1	0.190 0(5)	Cu1-N1	0.196 8(6)	Cu2-O2	0.198 8(5)
Cu1-N2	0.196 0(6)	Cu2-O1	0.194 1(5)	Cu2-N4	0.191 5(6)
Cu1-O2	0.189 2(5)	Cu2-N3	0.195 9(6)		
O1-Cu1-O2	78.9(2)	O1-Cu1-N1	95.9(3)	O1-Cu2-N3	167.5(2)
O2-Cu1-N2	96.0(2)	N2-Cu1-N1	88.4(3)	N4-Cu2-O2	168.7(2)
O1-Cu1-N2	170.9(3)	N4-Cu2-O1	93.3(2)	O1-Cu2-O2	75.6(2)
O2-Cu1-N1	172.1(3)	N4-Cu2-N3	99.0(3)	N3-Cu2-O2	91.9(2)

Cu1-N2-C23 and Cu1-N1-C22 angles are 110.28° and 111.44°.

Moreover, the perchlorate anions play a key role in maintaining the three-dimensional structure of the complex. To illustrate the role, the interactions of one perchlorate anion with the adjacent macrocyclic rings are shown in Fig.2, two macrocyclic rings in adjacent chains through C–H⋯O hydrogen-bond interactions, where the O atoms are from perchlorate anions. It is obvious that there are two hydrogen bond interactions in each macrocyclic unit of the complex, the hydrogen bond lengths are 0.2398 nm for O(9A)⋯H(18C) and 0.2396 nm for O(8A)⋯H(5A).

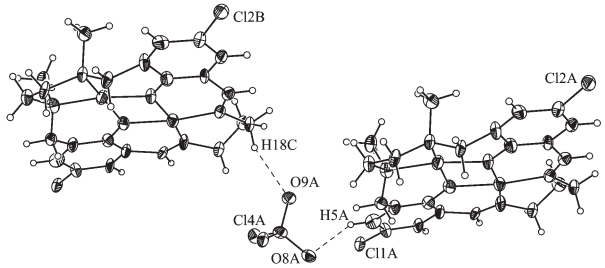


Fig.2　A perspective view of complex showing the interactions of perchlorate anions with adjacent macrocyclic rings, drawn with ellipsoids at 30% probability level

2.2　Magnetic properties

The magnetic susceptibility of [$Cu_2(C_{23}H_{26}Cl_2N_4O_2)$]$(ClO_4)_2$ was measured in the temperature range of 1.79~300 K, and the data are shown in Fig.3 as plot of $\chi_m T$ versus temperature (T). The temperature dependence of magnetic susceptibility (χ_m) of the title complex is typical of antiferromagnnetically interacting $Cu^{Ⅱ}Cu^{Ⅱ}$. The $\chi_m T$ data is fitted to Bleaney-Bowers equation (**1**). In this expression N is Avogadro′s number, β is Bohr magneton, g is the Landé g value, J is the exchange integral, T is the absolute temperature, k is the Boltzmann constant, ρ is the fraction of a paramagnetic impurity, and N_α is the temperature-independent paramagnetism[14-16]. The best-fit parameters obtained using the parameters are J=−369.3 cm^{-1}, g=2.01, ρ=0.002 6, N_α=0.000 44 $cm^3 \cdot mol^{-1}$.

$$\chi_M = \frac{2Ng^2\beta^2}{kT} \times \frac{1}{3+e^{\frac{-2J}{kT}}} \times (1-\rho) + \rho \times \frac{Ng^2\beta^2}{2kT} + N_\alpha \qquad (1)$$

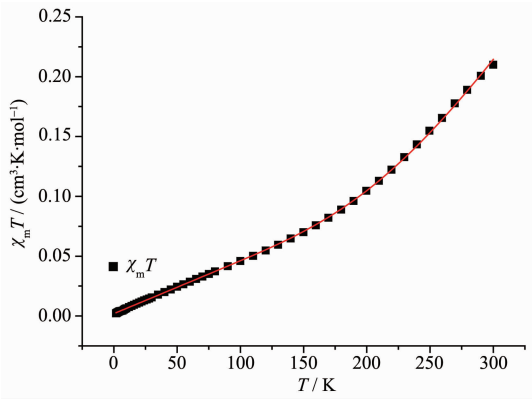


Fig.3　Polt of $\chi_m T$ vs T for the title complex

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