



草酰胺桥联异三核配合物 $\text{Cu}(\text{NiL})_2(\text{ClO}_4)_2$ 的合成、光谱表征和晶体结构

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关键词: 大环草酰胺配合物 晶体结构 光谱表征
分类号: O614.121 O614.81+3

Synthesis, Spectroscopic Characterization and Crystal Structure of A Novel Oxamido-Bridged Trinuclear Complex $\text{Cu}(\text{NiL})_2(\text{ClO}_4)_2$

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A novel oxamido-bridged trinuclear complex $\text{Cu}(\text{NiL})_2(\text{ClO}_4)_2$ (where $\text{H}_2\text{L}=2,3\text{-dioxo-}5,6,14,15\text{-dibenzo-}1,4,8,12\text{-tetraazacyclo-pentadeca-}7,3\text{-dien}$) has been synthesized and characterized by elemental analysis, IR spectrum, UV-Visible spectrum and single crystal X-ray diffraction. It crystallizes in the monoclinic system, space group $P2_1/n$. The lattice parameters are: $a=1.052\ 4(6)$ nm, $b=1.182\ 1(6)$ nm, $c=1.586\ 2(9)$ nm, $\beta=91.657(9)^\circ$, and $V=1.972\ 6(19)$ nm³, $Z=2$. The results show that the coordination geometry around copper(II) in the title complex is hexa-coordinated octahedron. CCDC: 232608.

Keywords: macrocyclic oxamide complex crystal structure spectroscopic characterization

0 Introduction

At the meeting point of molecular magnetism and macrocyclic compound, Polynuclear macrocyclic complexes are active fields of research encompassing chemistry, physics, biology, and materials science^[1-4] and have received considerable attention in the designing of new magnetic materials and investigating the structure as well as the role of the polymetallic active sites in biological systems^[2-11]. Recently, some

oxamido-bridged polynuclear complexes containing macrocyclic ligand have been prepared and characterized^[12]. In continuation of interest in polynuclear macrocyclic complex, We have designed and synthesized macrocyclic complex ligand NiL (where $\text{H}_2\text{L}=2,3\text{-dioxo-}5,6,14,15\text{-dibenzo-}1,4,8,12\text{-tetraazacyclo-pentadeca-}7,3\text{-dien}$) with oxamido bridge. Based on this complex ligand, we succeeded in obtaining a novel trinuclear complex $\text{Cu}(\text{NiL})_2(\text{ClO}_4)_2$.

收稿日期:2004-03-15。收修改稿日期:2004-07-29。

国家自然科学基金(No59973008)和天津市自然科学基金(No.013603711)资助项目。

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1 Experimental

1.1 Materials and Physical Measurements

All starting materials were of AR grade, obtained from commercial suppliers and used without further purification.

The elemental contents of C, H and N were determined on a Perkin-Elmer 240 Elemental analyzer. IR spectra were recorded as KBr discs on a Shimadzu IR-408 infrared spectrophotometer in the 4 000~600 cm^{-1} range. Electronic spectra in DMF were recorded on a Shimadzu UV-2101 PC scanning spectrophotometer.

1.2 Preparation of the Complex Ligand NiL

The complex ligand NiL was prepared by refluxing and stirring H_2L (H_2L =2,3-dioxo-5,6,14,15-dibenzo-1,4,8,12-tetraazacyclo-pentadeca-7,3-dien) ligand (0.01 mol), 1,3-propanediamine(0.03 mol), and $\text{NiAc} \cdot 4\text{H}_2\text{O}$ (0.01 mol) for 3 h in 50 mL of CH_3OH with the presence of 5 drops of 2 mol $\cdot \text{L}^{-1}$ NaOH. After the mixture was cooled and filtered, the precipitate thus obtained was washed with water, methanol, and diethyl ether successively and dried under vacuum.

1.3 Preparation of the Title Complex

A methanol solution of 0.2 mmol (0.073 0 g) of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ was added dropwise to a methanol solution (25 mL) of NiL (0.4 mmol, 0.156 4 g), the mixture was refluxed with stirring for 3 hours. The resulting green solution was cooled and filtered. Single crystals suitable for X-ray analysis were obtained by slow evaporation of the filtrate in the open air at room temperature. The C, H and N contents were determined by elemental analysis (Found (%): C, 43.43; H, 3.27; N, 10.60. Calcd.(%): C, 43.69; H, 3.09; N, 10.73).

1.4 X-ray Crystal Structure Analysis

A crystal suitable for X-ray diffraction analysis with dimensions of 0.30 mm \times 0.25 mm \times 0.20 mm was mounted on a glass fiber and diffraction experiments were performed on a Bruker Smart-1000-CCD area detector. Diffraction data were measured at 293 K using graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda =$

0.071 073 nm). Crystal data: $M_r=1\,044.58$, Monoclinic, space group $P2_1/n$, $a=1.052\,4(6)$ nm, $b=1.182\,1(6)$ nm, $c=1.586\,2(9)$ nm, $\beta=91.657(9)^\circ$, $V=1.972\,6(19)$ nm^3 , $D_c=1.759$ $\text{Mg} \cdot \text{m}^{-3}$, $F(000)=1\,062$, $Z=2$. A total of 9 045 reflections were measured in the setting angles $2.15^\circ < \theta < 26.48^\circ$ by ω -scan method, of which 4 022 were independent reflections. The crystal structure was solved by direct method and subsequent Fourier difference techniques and refined using full-matrix least squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXS-97 and SHELXL-97)^[13]. Hydrogen atoms were added geometrically and refined with riding model position parameters and fixed isotropic thermal parameters. Final R indices [$I > 2\sigma(I)$]:

Table 1 Crystal Data and Structure Refinement for the Title Complex

empirical formula	$\text{C}_{38}\text{H}_{32}\text{Cl}_2\text{CuN}_8\text{Ni}_2\text{O}_{12}$
formula weight	1 044.58
temperature / K	293(2)
wavelength / nm	0.071 073
crystal system	monoclinic
space group	$P2_1/n$
a / nm	1.052 4(6)
b / nm	1.182 1(6)
c / nm	1.586 2(9)
β / ($^\circ$)	91.657(9)
volume / nm^3	1.972 6(19)
Z	2
calculated density / ($\text{Mg} \cdot \text{m}^{-3}$)	1.759
absorption coefficient / mm^{-1}	1.691
$F(000)$	1 062
crystal size / mm^3	$0.3 \times 0.25 \times 0.20$
θ / ($^\circ$)	2.15 to 26.48
limiting indices	$-13 \leq h \leq 9,$ $-8 \leq k \leq 14,$ $-19 \leq l \leq 19$
reflections collected / unique	9 045/4 022 [$R(\text{int})=0.058\,3$]
completeness to $\theta=26.48$	98.7%
max. and min. transmission	0.728 5 and 0.630 9
refinement method	full-matrix least-squares on F^2
data / restraints / parameters	4 022 / 0 / 286
goodness-of-fit on F^2	1.052
final R indices [$I > 2\sigma(I)$]	$R_1=0.058\,0$, $wR_2=0.123\,3$
R indices (all data)	$R_1=0.128\,8$, $wR_2=0.147\,8$
largest diff. peak and hole / ($\text{e} \cdot \text{nm}^{-3}$)	785 and -555

Table 2 Bond Lengths (nm) and Angles ($^\circ$) for the Title Complex

Ni(1)-N(3)	1.874(4)	Ni(1)-N(2)	1.907(4)	Ni(1)-N(4)	1.879(4)
Ni(1)-N(1)	1.909(4)	Cu(1)-O(1)	1.933(4)	Cu(1)-O(2) ^{#1}	1.942(4)
Cu(1)-O(1) ^{#1}	1.933(4)	Cu(1)-O(2)	1.942(4)	Cu(1)-O(3)	2.547(5)
Cu(1)-O(3) ^{#1}	2.547(5)				
O(1)Cu(1)O(2)	84.25(16)	Cu(1)O(2)C(2)	112.3(3)	O(1)Cu(1)O(3)	90.53(17)
Cu(1)O(3)Cl(1)	135.8(3)	O(1)Cu(1)O(1) ^{#1}	180.00	Ni(1)N(1)C(1)	110.5(4)
O(1)Cu(1)O(2) ^{#1}	95.75(16)	Ni(1)N(1)C(19)	127.5(4)	O(1)Cu(1)O(3) ^{#1}	89.47(18)
C(1)N(1)C(19)	120.6(4)	O(2)Cu(1)O(3)	86.93(16)	Ni(1)N(2)C(2)	111.7(3)
O(1) ^{#1} Cu(1)O(2)	95.75(16)	Ni(1)N(2)C(3)	127.4(3)	O(2)Cu(1)O(2) ^{#1}	180.00
C(2)N(2)C(3)	120.9(4)	O(2)Cu(1)O(3) ^{#1}	93.07(16)	Ni(1)N(3)C(9)	126.6(4)
O(1) ^{#1} Cu(1)O(3)	89.47(18)	Ni(1)N(3)C(10)	116.3(4)	O(2) ^{#1} Cu(1)O(3)	93.07(16)
C(9)N(3)C(10)	116.5(4)	O(3)Cu(1)O(3) ^{#1}	180.00	Ni(1)N(4)C(12)	115.9(4)
O(1) ^{#1} Cu(1)O(2) ^{#1}	84.25(16)	Ni(1)N(4)C(13)	125.5(4)	O(1) ^{#1} Cu(1)O(3) ^{#1}	90.53(18)
C(12)N(4)C(13)	118.5(5)	O(2) ^{#1} Cu(1)O(3) ^{#1}	86.93(16)	O(1)C(1)N(1)	129.2(5)
N(1)Ni(1)N(2)	86.89(19)	O(1)C(1)C(2)	115.5(4)	N(1)Ni(1)N(3)	163.2(2)
N(1)C(1)C(2)	115.2(5)	N(1)Ni(1)N(4)	93.2(2)	O(2)C(2)N(2)	129.7(4)
N(2)Ni(1)N(3)	93.22(19)	O(2)C(2)C(1)	115.3(4)	N(2)Ni(1)N(4)	167.4(2)
N(2)C(2)C(1)	114.9(4)	N(3)Ni(1)N(4)	90.3(2)	N(2)C(3)C(4)	122.7(5)
O(3)Cl(1)O(4)	112.0(4)	N(2)C(3)C(8)	118.8(4)	O(3)Cl(1)O(5)	108.6(4)
O(4)Cl(1)O(6)	111.6(5)	O(3)Cl(1)O(6)	110.2(3)	O(5)Cl(1)O(6)	108.0(5)
O(4)Cl(1)O(5)	106.2(4)	Cu(1)O(1)C(1)	112.1(3)		

Symmetry transformations used to generate equivalent atoms: #1: $-x+1, -y+1, -z$.

$R_1=0.0580$, $wR_2=0.1233$. The largest peak and hole on the final difference-Fourier map were 785 and $-555 \text{ e} \cdot \text{nm}^{-3}$, respectively. A summary of the key crystallographic information is given in Table 1. Selected bond distances and angles are listed in Table 2.

CCDC: 232608.

2 Result and Discussion

2.1 Spectroscopic Characterization

The infrared spectrum shows the characteristics bands of the bridging oxamides moiety^[14] at around 1640 cm^{-1} ($\nu_{\text{C=O}}$, amido group), and $1595, 1575, 1550 \text{ cm}^{-1}$ ($\nu_{\text{C=N}}$, imido group). Peaks at around $1090, 1110, 1115 \text{ cm}^{-1}$ are attributed to the absorption of the perchlorate ions. Such a splitting pattern is consistent with coordinated tetrahedral ClO_4^- as shown in the crystal structural section.

The electronic absorption spectrum of the macrocyclic organic ligand [NiL] and the title complex $\text{Cu}(\text{NiL})_2(\text{ClO}_4)_2$ in DMF shows that intense bands

dominate regions below 500 nm. The presence of a series of bands at 1430, 1550, 1700 and 1770 nm due to intra-ligand and charge-transfer transitions in the [NiL] chromophore. A broad strong band centered at 580 nm and a broad weak band at 800 nm were also observed and can be attributed to the $d-d$ transitions of copper atoms in environments close to tetragonal-plane.

2.2 Crystal Structure of the Title Complex

Fig.1 shows the perspective view of monomeric unit with the atomic numbering scheme of the title complex. The complex has the centrosymmetric construction centered at the copper(II) ion which is six-coordinate in an octahedral geometry. The two primary ligands NiL (macrocyclic oxamide groups) participate in the coordination with oxygen donor atoms that forms the complete tetragonal-plane. The secondary ligands ClO_4^- take part in weak bonding with copper(II) through oxygen donor atoms on both sides of the tetragonal-plane ($d_{\text{O} \cdots \text{Cu}}=2.547 \text{ nm}$). The nickel(II) atom is

