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三核镍簇合物的合成、晶体结构及红外光谱分析

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摘要:合成了一种新型的螯合双肟配体,4,4′-二氯-2,2′-[(1,3-亚丙基)二氧双(氮次甲基)]二酚(H_2L),及其三核镍簇合物,并通过元素分析,红外光谱以及 X-射线单晶衍射对其进行了结构表征。镍配合物晶体属单斜晶系,空间群为 $P2_1/n$。镍簇合物含有 3 个镍离子、2 个配体单元(提供 N_2O_2 给予体)、2 个乙酸根离子和 2 个配位的乙醇分子,围绕每个镍原子形成一个稍微扭曲的八面体配位结构。

关键词:4,4′-二氯-2,2′-[(1,3-亚丙基)二氧双(氮次甲基)]二酚;镍(Ⅱ)簇合物;合成;晶体结构
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Synthesis, Crystal Structure and Infrared Spectral Analysis for a Trinuclear Nickel(Ⅱ) Cluster

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Abstract: A novel chelating bisoxime ligand, 4,4′-dichloro-2,2′-[(1,3-propylene)dioxybis (nitrilomethylidyne)] diphenol (H_2L), and its corresponding trinuclear Ni(Ⅱ) cluster $\{[NiL(C_2H_5OH)]_2(OAc)_2Ni\}\cdot C_2H_5OH$ (**1**) have been synthesized and characterized by elemental analyses, IR, ^{1}H NMR and X-ray singel crystal diffraction method. The crystal of the Ni(Ⅱ) cluster belongs to monoclinic, space group $P2_1/n$ with cell dimensions a=1.336 53(18) nm, b=1.341 64(18) nm, c=1.549 8(2) nm, β=106.841(2)°, and V=2.659 8(6) nm^3, Z=2, R_1=0.051 6, wR_2=0.157 4. In the Ni(Ⅱ) cluster, there are three nickel(Ⅱ) atoms, two ligand moieties (which provide N_2O_2 donors), two acetate ions and two coordinated ethanol molecules, which result in the formation of a slightly distorted octahedral coordination geometry around each Ni(Ⅱ) ion respectively. CCDC: 644788.

Key words: 4,4′-dichloro-2,2′-[(1,3-propylene)dioxybis(nitrilomethylidyne)]diphenol; nickel(Ⅱ) cluster; synthesis; crystal structure

The Schiff base compounds have been intensively investigated in coordination chemistry mainly due to their facile synthesis and easily tunable steric, electronic, and catalytic properties. The complexes of nickel with a wide variety of Schiff bases having donor atoms such as N_2O_2, N_4 and N_2S_2 around the metal ion is of considerable interest since they derived from Schiff bases are reported to be used as catalysts for carbonylation, hydrogenation, hydroformylation and epoxidation reactions[1~6]. Therefore, synthesis of new Schiff bases and their nickel (Ⅱ) complexes still the aim of many recent investigations[7,8]. Here, in continuation of our previous studies on characterization of transition metal complexes[9~11], we reported the synthesis and structural characterization of a novel Schiff base ligand, 4,4′-dichloro-2,2′-[(1,3-propylene)dioxybis (nitrilomethylid-

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yne)]diphenol (H_2L) and its corresponding tri-nickel cluster {[NiL(C_2H_5OH)]$_2$(OAc)$_2$Ni}·C_2H_5OH (**1**), which has three octahedral geometries in single molecule.

1 Experimental

1.1 Reagents and physical measurements

5-Chloro-2-hydroxybenzaldehyde from Aldrich was used without further purification. 1,3-dibromopropane was dried and redistilled before use. 1,3-bis(aminooxy)propane was synthesized according to an analogous method reported earlier[12]. The other reagents and solvents were analytical grade reagents from Tianjin Chemical Reagent Factory. Elemental analysis for Ni was detected by an IRIS ER/S·WP-1 ICP atomic emission spectrometer. C, H and N analyses were carried out with a GmbH VariuoEL V3.00 automatic elemental analyzer. IR spectra were recorded on a VERTEX70 FTIR spectrophotometer, with samples prepared as KBr (500~4 000 cm^{-1}) and CsI (100~500 cm^{-1}) pellets. ^1H NMR spectra were recorded on a Mercury-400BB spectrometer. Single crystal structure was determined on a Bruker Smart APEX CCD X-ray single crystal diffractometer. Melting points were measured by the use of a microscopic melting point apparatus made in Beijing Taike Instrument Limited Company, and the thermometer was uncorrected.

1.2 Synthesis of H_2L

4,4′-Dichloro-2,2′-[(1,3-propylene)dioxybis(nitrilomethylidyne)]diphenol(H_2L) was synthesized according to a slightly modified method reported earlier[13,14]. To an ethanol solution (10 mL) of 5-chloro-2-hydroxybenzaldehyde (322.4 mg, 2.00 mmol) was added an ethanol solution (5 mL) of 1,3-bis(aminooxy)propane (109.8 mg, 1.0 mmol). After the solution had been stirred at 55 ℃ for 3 h, the mixture was filtered, washed successively with ethanol and hexane, respectively. The product was dried under reduced pressure and purified with recrystallization from ethanol to yield 295.0 mg of colorless crystalline solid. Yield, 74.4%, m.p. 164~166 ℃. Anal. calcd for $C_{17}H_{16}Cl_2N_2O_4$(H_2L) (%): C, 53.28; H, 4.21; N, 7.31; Found (%): C, 53.32; H,4.22; N, 6.78.

1.3 Synthesis of cluster 1

A solution of Ni(Ⅱ) acetate tetrahydrate (23.70 mg, 0.095 mmol) in ethanol (10 mL) was added dropwise to a solution of H_2L (36.3 mg, 0.095 mmol) in acetonitrile/acetone (5∶3) (24 mL). The color of the mixing solution turned pale green immediately, and then stirring was continued for 2 h at room temperature. The mixture was then filtered and the filtrate was allowed to stand at room temperature for about three weeks. The solvent was then partially evaporated and green block-shaped single crystals suitable for X-ray diffraction were obtained. Yield 0.013 5 g, 35.6%. Anal. Calcd. For $C_{44}H_{52}Cl_4N_4Ni_3O_{15}$ ({[NiL(C_2H_5OH)]$_2$(OAc)$_2$Ni}·C_2H_5OH) (%): C, 44.23; H, 4.39; N, 4.69; Ni, 14.74; Found (%): C, 44.57; H, 4.30; N, 4.87, Ni,14.88.

1.4 Crystal structure determination

A single crystal of 1 with approximate dimension of 0.43 mm × 0.38 mm × 0.04 mm was selected for the structure analysis. The diffraction data was collected on a Bruker Smart Apex CCD diffractometer using a graphite monochromatized Mo $K\alpha$ radition (λ=0.071 073 nm) at 298(2) K. The structure was solved by direct methods and difference Fourier techniques (SHELXS-97)[15], refined by full matrix least squares on F^2 using the program (SHELXL-97)[16]. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were added theoretically. The crystal data and experimental parameters relevant to the structure determination are listed in Table 1.

Table 1　Crystallographic data collection and structure refinement for 1

Empirical formula	$C_{44}H_{52}Cl_4N_4Ni_3O_{15}$	Crystal size / mm	0.43 × 0.38 × 0.04
Formula weight	1194.83	θ range / (°)	1.78~25.01
T / K	298(2)	Limiting indices	$-15 \leqslant h \leqslant 15, -15 \leqslant k \leqslant 14, -18 \leqslant l \leqslant 7$
Wavelength / nm	0.071 073	Reflections collected	107 65
Crystal system	Monoclinic	Reflections indeendent	4 663 (R_{int}=0.033 6)
Space group	$P2_1/n$	Reflections observed [$I>2\sigma(I)$]	3 577
a / nm	1.336 53(18)	Completeness to θ=25.01°	99.60%

Continued Table 1

b / nm	1.341 64(18)	Absorption correction	Semi-empiricalfrom equivalents
c / nm	1.549 8(2)	Max. and min. transmission	0.949 2 and 0.601 1
β / (°)	106.841(2)	Refinement method	Full-matrix least-squares on F^2
V / nm^3	2.659 8(6)	Data / restraints / parameters	4663 / 58 / 331
Z	2	Goodness-of-fit on F^2	1.026
D_c / (Mg·m^{-3})	1.492	Final R indices [$I>2\sigma(I)$]	0.051 6, 0.157 4
μ / mm^{-1}	1.318	R indices (all data)	0.071 3, 0.185 9
Absorption corrections	Multi-scan	$(\Delta\rho)_{max}$ /(e·nm^{-3})	1 316
F(000)	1 232	$(\Delta\rho)_{min}$ / (e·nm^{-3})	−358

CCDC: 644788.

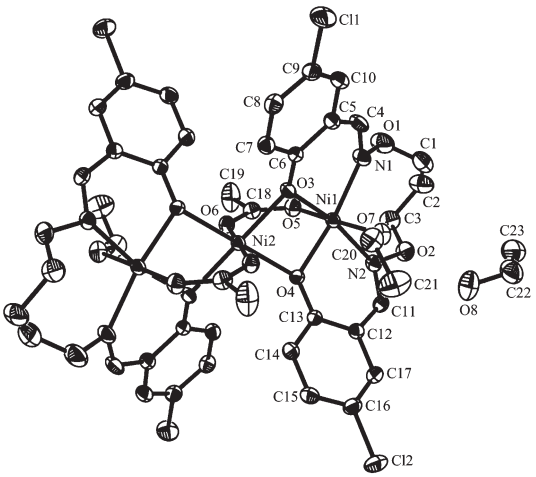
2 Results and discussion

2.1 Crystal structure of 1

Crystal structure shows that Ni(2) is located on a centre of inversion. The cluster ion consists of three nickel(Ⅱ) atoms, two L^{2-} units, two acetate ions, two coordinated ethanol molecules and one crystallizing ethanol molecule (Fig.1). The selected bond lengthes and angles are listed in Table 2.

The nickel atom (Ni(1)) is six-coordinated by two nitrogen (N(1), N(2)) atoms and two oxygen atoms (O(3), O(4)) in the N_2O_2 moieties of the ligand, one oxygen atom (O(5)) from the bridging acetate ion and one oxygen atom (O(7)) from the coordinated ethanol molecule. Consequently, around Ni(1) atoms is a slightly distorted octahedral geometry.

In addition the central nickel′s (Ni (2)) coordination sphere is completed by quadruple μ-phenoxo oxygen atoms (O(3), O(4), O(3)#, O(4)#) from two [NiL]



Displacementellipsoids for non-H atoms are drawn at the 30% probability level. Each of the nickel atoms sit in an octahedral geometry

Fig.1 Structure of **1** with the atom numbering

Table 2 Selected bond distances (nm) and bond angles (°) for 1

Ni(1)-O(3)	0.202 2(3)	N(1)-O(1)	0.143 4(6)	C(5)-C(6)	0.143 2(6)
Ni(1)-O(5)	0.202 6(3)	N(2)-C(11)	0.129 1(6)	C(6)-C(7)	0.139 9(6)
Ni(1)-O(4)	0.203 2(3)	N(2)-O(2)	0.142 2(5)	C(7)-C(8)	0.138 6(7)
Ni(1)-N(1)	0.207 0(4)	O(1)-C(1)	0.136 6(9)	C(8)-C(9)	0.137 0(7)
Ni(1)-N(2)	0.211 2(4)	O(2)-C(3)	0.143 0(7)	C(9)-C(10)	0.136 0(8)
Ni(1)-O(7)	0.216 7(4)	O(3)-C(6)	0.131 1(5)	C(11)-C(12)	0.144 0(7)
Ni(2)-O(6)#1	0.203 2(3)	O(4)-C(13)	0.131 6(5)	C(12)-C(17)	0.140 4(7)
Ni(2)-O(6)	0.203 2(3)	O(5)-C(18)	0.126 5(6)	C(12)-C(13)	0.141 3(6)
Ni(2)-O(3)	0.208 7(3)	O(6)-C(18)	0.124 3(6)	C(13)-C(14)	0.141 2(6)
Ni(2)-O(3)#1	0.208 7(3)	O(7)-C(20)	0.145 1(6)	C(14)-C(15)	0.138 3(7)
Ni(2)-O(4)#1	0.210 0(3)	O(8)-C(22)	0.134 0(13)	C(15)-C(16)	0.137 1(7)
Ni(2)-O(4)	0.210 0(3)	C(1)-C(2)	0.155 4(10)	C(16)-C(17)	0.136 5(7)
Cl(1)-C(9)	0.174 8(5)	C(2)-C(3)	0.151 9(9)	C(18)-C(19)	0.150 9(7)
Cl(2)-C(16)	0.175 4(5)	C(4)-C(5)	0.144 1(7)	C(20)-C(21)	0.146 1(9)
N(1)-C(4)	0.128 5(7)	C(5)-C(10)	0.140 5(7)	C(22)-C(23)	0.140 0(15)

Continued Table 2

O(3)-Ni(1)-O(5)	91.70(13)	O(6)-Ni(2)-O(6)#1	180.000(1)	O(4)-Ni(2)-O(4)#1	180.00(17)
O(3)-Ni(1)-O(4)	81.78(12)	O(6)#1-Ni(2)-O(3)	91.25(13)	C(4)-N(1)-Ni(1)	125.3(3)
O(5)-Ni(1)-O(4)	92.50(13)	O(6)-Ni(2)-O(3)	88.75(13)	O(1)-N(1)-Ni(1)	125.3(3)
O(3)-Ni(1)-N(1)	86.75(14)	O(6)#1-Ni(2)-O(3)#1	88.75(13)	C(11)-N(2)-Ni(1)	121.6(3)
O(5)-Ni(1)-N(1)	89.70(16)	O(6)-Ni(2)-O(3)#1	91.25(13)	O(2)-N(2)-Ni(1)	127.9(3)
O(4)-Ni(1)-N(1)	168.38(15)	O(3)-Ni(2)-O(3)#1	180.000(1)	C(6)-O(3)-Ni(1)	127.7(3)
O(3)-Ni(1)-N(2)	166.70(14)	O(6)#1-Ni(2)-O(4)	91.96(12)	C(6)-O(3)-Ni(2)	132.9(3)
O(5)-Ni(1)-N(2)	93.67(15)	O(6)-Ni(2)-O(4)	88.04(12)	Ni(1)-O(3)-Ni(2)	97.05(13)
O(4)-Ni(1)-N(2)	85.83(14)	O(3)#1-Ni(2)-O(4)	101.32(12)	C(13)-O(4)-Ni(1)	125.5(3)
N(1)-Ni(1)-N(2)	105.42(16)	O(3)-Ni(2)-O(4)	78.68(12)	C(13)-O(4)-Ni(2)	131.5(3)
O(3)-Ni(1)-O(7)	90.02(13)	O(6)#1-Ni(2)-O(4)#1	88.04(12)	Ni(1)-O(4)-Ni(2	96.33(12)
O(5)-Ni(1)-O(7)	177.56(14)	O(6)-Ni(2)-O(4)#1	91.96(12)	C(18)-O(5)-Ni(1)	125.7(3)
O(4)-Ni(1)-O(7)	89.46(14)	O(3)#1-Ni(2)-O(4)#1	78.68(12)	C(18)-O(6)-Ni(2)	131.6(3)
N(1)-Ni(1)-O(7)	88.67(16)	O(3)-Ni(2)-O(4)#1	101.32(12)	C(20)-O(7)-Ni(1)	127.5(3)
N(2)-Ni(1)-O(7)	85.02(15)				

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

chelates, and both of oxygen atoms (O(6), O(6)#) from the ligating acetate ions which adopt a familiar μ-O-C-O fashion, and constitute another octahedral geometry. Therefore, all of the nickel atoms are six-coordinated. Furthermore, the trinuclear structure is probably stabilized by the two μ-acetato ligand, which neutralize the whole charge of the cluster.

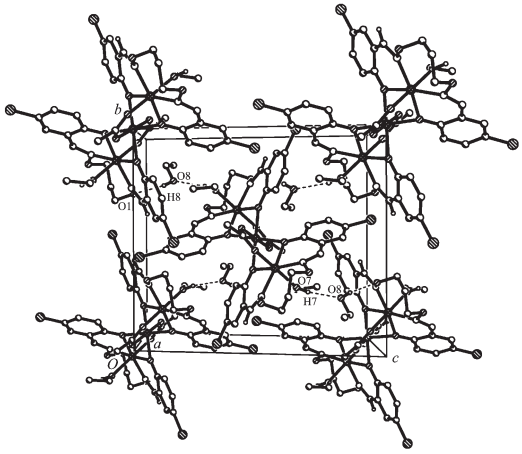
The interatomic distance of Ni(2)-Ni(1) (0.307 9(5) nm) is significantly longer than all that of the Ni-O and Ni-N bonds in the cluster (Table 2), which is also essentially similar to our previously reported bisoxime octanuclear analogue of $[Zn_8L_4(H_2O)_2X]\cdot 2H_2O\cdot 1.5CHCl_3\cdot 0.5$hexane (X=$H_2O$ or EtOH)[9].

The unit cell packing of Ni(Ⅱ) cluster was formed by one cluster molecule and one crystallizing ethanol molecule (Fig.2). The extended hydrogen bonding network is formed by strong O–H⋯O hydrogen bonds (O(7)–H(7)⋯O(8) and O(8)–H(8)⋯O(1)) between coordinated ethanol molecule and the oxygen atom [O(8)] of crystallizing ethanol molecule, crystallizing ethanol molecule and the oxygen atom [O(1)] of N-O-CH_2-CH_2-CH_2-O-N- unit, respectively (Fig.2 and Table 3). It also could be pointed out that the hydrogen bonds interactions play a critical role in formation, stability and crystallization of the cluster.

Table 3　Hydrogen bonds for 1

D–H⋯A	d(D-H) / nm	d(H⋯A) / nm	∠DHA / (°)	d(D⋯A) / nm
O7–H7⋯O8	0.082 0	0.212 8	165.74	0.292 9
O8–H8⋯O1^{i}	0.082 0	0.244 4	171.10	0.325 7

Symmetry codes: ^{i} $x+1/2$, $-y+1/2$, $z+1/2$.



H atoms are omitted for clarity

Fig.2　Packing diagram of **1**

2.2　IR spectra

IR spectral details of H_2L and {$[NiL(C_2H_5OH)]_2(OAc)_2Ni\}\cdot C_2H_5OH$ show the bands due to $\nu_{C=N}$ and $\nu_{Ar\text{-}O}$ of the cluster were lowered by 4 and 83 cm^{-1} respectively, as compared to H_2L values ($\nu_{C=N}$ and $\nu_{Ar\text{-}O}$ appear at 1 610 and 1 265 cm^{-1} respectively). These provide evidence for the coordination of H_2L with Ni(Ⅱ) ions. In addition, a strong band at 3 431 cm^{-1} was observed in the infrared spectrum of the Ni(Ⅱ) cluster and assigned to the O-H stretching mode of ethanol[17].

The far-infrared spectrum of the Ni(Ⅱ) cluster was also obtained in the region 500~100 cm^{-1} in order to identify frequencies due to the Ni-O and Ni-N bonds. The IR spectrum of the cluster shows vibrational absorption frequencies at 445 cm^{-1} and 412 cm^{-1}, which were assigned to ν(Ni-O) and ν(Ni-N), respectively. These assignments are consistent with the literature frequency values[18].

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