研究简报

新颖的二维超分子化合物[Co^{Ⅲ}(aea)(2,2′-bipy)]Cl·H_2O的水热合成及结构表征

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Hydrothermal Synthesis and Structural Characterization of a Novel 2-D Supramolecular Compound [Co^{Ⅲ}(aea)(2,2′-bipy)]Cl·H_2O

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Abstract: A new compound [Co^{Ⅲ}(aea)(2,2′-bipy)]Cl·H_2O (aea=N-(2-aminoethyl)aspartate, 2,2′-bipy=2,2′-bipyridine) was hydrothermally synthesized and structurally characterized, which contains a new quadridentate ligand (aea) came from malic acid and ethylenediamine via *in-situ* reaction. The asymmetric molecules are interconnected through N–H···O hydrogen bond to form helical chains that are further hold together into a two-dimensional network via the N–H···Cl hydrogen bond. The formation of aea can be considered as the substitution of hydroxyl group in malate by ethylenediamino group, which presents a type of new *in-situ* ligand reaction. CCDC: 222018.

Key words: supramolecular network; *in-situ* reaction; cobalt(Ⅲ) complex; quadridentate

0 Introduction

In recent years great attention has been paid to supramolecular chemistry and a wide variety of networks have already been constructed based upon the principle of crystal engineering[1~3]. Usually, various multifunctional organic ligands, both rigid and flexible multicarboxylic acids, are employed to construct versatile networks, whereas the hydroxycarboxylic acids are less considered as building blocks in the construction of inorganic-organic hybrid or supramolecular networks. The hydroxyl polycarboxylic acids are useful biological reagents with excellent chelating ability, hydrophilic nature and biological properties. Citric acid and malic acid are often acted as the substitutes of homocitric acid in the synthetic model study of nitrogenase and their complexes of vanadium, molybdenum, or tungsten have been extensively studied[4~11], but the structurally characterized complexes of other transition metals with malate are relatively rare[12,13]. Several types of *in-situ* reactions have been reported[14~18] under hydro(solvo)thermal conditions up

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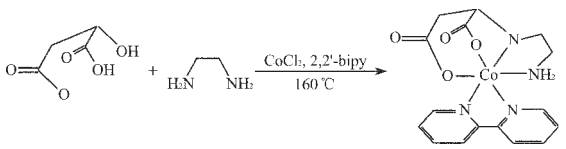
to now, which can generate some interesting organic species and various fascinating networks. Ethylenediamine (en) was acted as the adjuster of pH value in our reaction system of cobalt salt with malic acid, the unexpected complex of $[Co^{Ⅲ}(aea)(2,2'\text{-bipy})]Cl\cdot H_2O$ (**1**) (aea=N-(2-aminoethyl)aspartate, 2,2′-bipy=2,2′-bipyridine) was obtained under hydrothermal condition (Scheme 1).



Scheme 1

1 Experimental

1.1 Materials and methods

Regents were purchased commercially and used without further purification. The elemental analysis was conducted on a Perkin-Elmer 2400 elemental analyzer. Inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer Optima 3300DV spectrometer. Infrared spectrum was measured on KBr disk with a Perkin-Elmer Spectrometer in the 4 000~400 cm^{-1} region. A NETZSCH STA 449C unit was used to carry out the TGA and DTA analyses in air with a heating rate of 20 ℃·min^{-1}.

1.2 Synthesis

The mixture of $CoCl_2\cdot 6H_2O$ (0.5 g), malic acid (0.4 g), 2,2′-bipy (0.2 g) and 15 mL water was stirred for two hours at room temperature and the pH value was adjusted to about 6 with ethylenediamine. The mixture was heated at 160 ℃ for two days in a stainless steel autoclave, after cooling the red solution was allowed to stand at room temperature. Red brick crystals suitable for X-ray diffraction were isolated (yield 70% based on cobalt) five days later by slow evaporation of the solution. Element analysis for $C_{16}H_{20}ClCoN_4O_5$ (%), Calcd: Co, 13.31; C, 43.40; H, 4.55; N, 12.66; Found: Co, 13.18; C, 43.25; H, 4.38; N, 12.52. Main IR features (KBr, cm^{-1}): 3 411.0s, ν(O-H); 3 070.9w, 3 012.6s, 2 921.3w, 2 889.8w, ν(N-H, C-H); 1 665.7s, $\nu_{as}(COO^-)$; 1 612.5m, 1 591.5s, ν(C=N, C=C); 1 454.4m, 1 438.8w, 1 408.9m, δ(N-H, C-H); 1 384s $\nu_s(COO^-)$; 1 284w, 1 245w, 1 228w, 1 179w, 1 137w, 1 125w, 1 045w, 879w, 824w, 771s, 729m, 579w, 547w, 485w.

1.3 X-ray crystallography

A suitable single crystal having dimensions of 0.318 mm × 0.315 mm × 0.211 mm was mounted on a glass fiber. All measurement was made on a Rigaku RAXIS-RAPID diffractometer and data collection was performed at 293 K by using graphite-monochromated Mo $K\alpha$ (λ=0.071 073 nm). The structure was solved by direct methods using the program SHELXS-97 and refined by full-matrix least-squares methods on F^2. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located from the difference Fourier map and refined isotropically. Detailed information about the crystal data and structure determination is summarized in Table 1. The selected bond lengths and angles are listed in Table 2.

Table 1 Summary of crystallographic data for compound 1

Empirical formula	$C_{16}H_{20}ClCoN_4O_5$	F(000)	912
Formula weight	442.74	θ range for data collection / (°)	2.02~27.48
Temperature / K	293(2)	Index range	$0 \leqslant h \leqslant 10$,
Crystal system	Monoclinic		$0 \leqslant k \leqslant 15$,
Space group	$P2_1/n$		$-25 \leqslant l \leqslant 25$
a / nm	0.791 19(16)	Reflection collected	4 131
b / nm	1.175 6(2)	Independent reflection	3 379
c / nm	1.956 6(4)	Data/restrains/parameters	4 131 / 0 / 324
β / (°)	90.73(3)	Goodness-of-fit on F^2	1.015
V / nm^3	1.819 8(6)	Final R indices [$I > 2\sigma(I)$]	R_1=0.028 8, wR_2=0.070 7
Z	4	R indices (all data)	R_1=0.038 7, wR_2=0.078 9
D_{calc} / (g·cm^{-3})	1.616	Largest diff. peak and hole / (e·nm^{-3})	565 and −592
μ / mm^{-1}	1.127		

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

Co-O(2)	0.190 29(13)	O(1)-C(16)	0.123 3(2)
Co-O(4)	0.192 50(13)	O(2)-C(16)	0.129 4(2)
Co-N(1)	0.192 29(16)	O(3)-C(13)	0.123 6(2)
Co-N(2)	0.193 66(15)	O(4)-C(13)	0.128 1(2)
Co-N(3)	0.193 72(17)	N(3)-C(15)	0.148 8(2)
Co-N(4)	0.191 94(16)	C(13)-C(14)	0.152 1(3)
O(2)-Co-N(4)	91.20(7)	N(1)-Co-N(3)	175.24(7)
O(2)-Co-O(4)	91.03(6)	O(4)-Co-N(3)	93.99(6)
N(4)-Co-O(4)	177.61(6)	N(2)-Co-N(3)	100.57(7)
N(1)-Co-O(4)	89.12(6)	C(15)-N(3)-C(11)	112.15(15)
O(2)-Co-N(2)	175.58(6)	C(15)-N(3)-Co	104.03(12)
N(4)-Co-N(2)	91.50(7)	C(11)-N(3)-Co	109.08(12)
N(1)-Co-N(2)	83.21(6)	C(12)-N(4)-Co	108.70(12)
O(4)-Co-N(2)	86.23(6)	N(3)-C(15)-C(16)	106.18(15)
O(2)-Co-N(3)	83.06(6)	N(3)-C(15)-C(14)	110.43(16)
N(4)-Co-N(3)	87.13(7)	C(16)-C(15)-C(14)	110.97(16)

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2　Results and discussion

X-ray structure analysis reveals that the coordination sphere around cobalt is a distorted octahedron containing two nitrogen donor atoms of 2,2′-bipy, two nitrogen and two oxygen atoms came from the ligand aea, as shown in Fig.1. $\{CoN_4O_2\}$ has some deviations from the expected octahedral geometry due to the restrictions imposed by tetradentate aea. The cisoid and transoid N(/O)-Co-N(/O) bond angles fall in the region of 83.06(6)°~100.57(7)° and 175.24(7)°~177.61(6)° (Table 2). The bond lengths of Co(Ⅲ) with nitrogen atoms range from 0.191 94(16) to 0.193 72(17) nm, and the distances of Co-O(2), Co-O(4) are 0.190 29(13), 0.192 50(13) nm, respectively. The Co-O and Co-N distances in compound **1** are significantly shorter than those Co(Ⅱ) complexes due to the higher charge of cobalt centers, which are comparable with those previously reported six-coordination Co(Ⅲ) complexes [19-21]. The ligand aea serves as a quadridentate ligand giving rise to one seven-membered, one six-membered, and two five-membered chelate rings. Two five-membered rings are attached to Co(Ⅲ) ion in a facial mode and the corresponding bite angle of O(2)-Co-N(3) is 83.06(6)°, N(2)-Co-N(3) angle is 100.57(7)°. The bite angles of six- and seven-membered rings formed at Co(Ⅲ) ion are 93.99(6)° and 91.03(6)°, respectively. The angle of C(14)-C(15)-C(16) is reduced to 110.97(16)° due to the formation of new C(15)-N(3) bond, whose distance of 0.148 8(2) nm is smaller than that of N(3)-C(11) and N(4)-C(12).

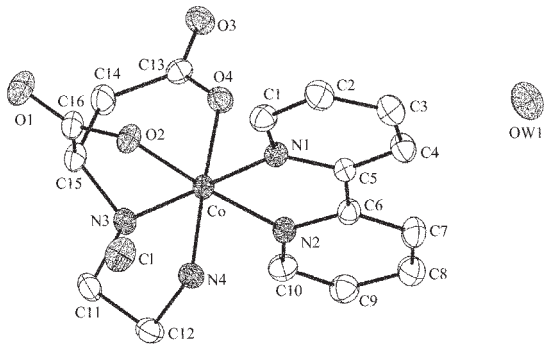

Fig.1　ORTEP drawing of the complex [Co(Ⅲ)(aea)(2,2′-bipy)]Cl·H_2O with thermal ellipsoids at 30% probability, the hydrogen atoms are omitted for clarity

In each complex molecule, the hydrogen atoms of N(4) are connected with O(3) of another adjacent molecule through N(4)–H(4B)⋯O(3) hydrogen bonds to generate one-dimensional helical chains along the twofold screw axis (Fig.2 and 3). Outside the coordination sphere, the counter anions Cl^- are also involved in the hydrogen bonds with N(3), N(4) and OW(1) atoms of different molecules. The N(3)–H(3B)⋯Cl and

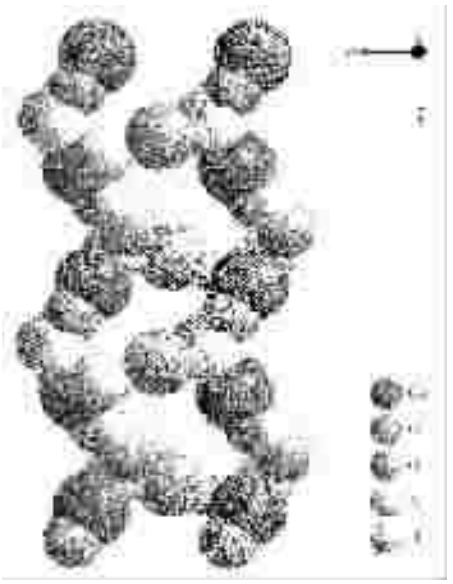

Fig.2　A view of the space-filling plot showing the hydrogen bonding helical chains, the water molecules are omitted for clarity

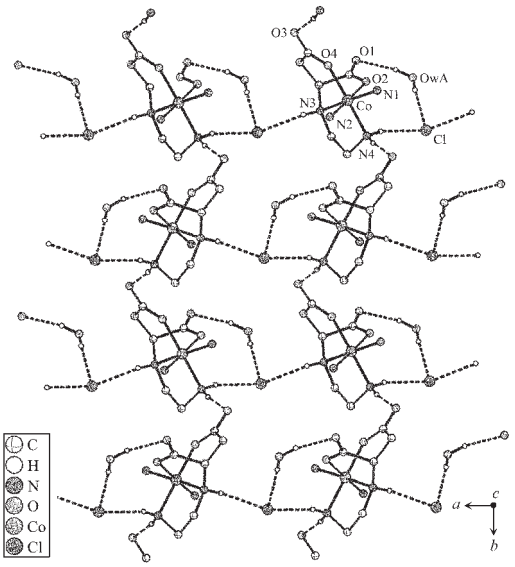

Fig.3 2-D hydrogen bonding network of compound **1** in *ab*-plane, the pyridine rings are omitted for clarity

N(4)–H(4C)···Cl bonds link the helical chains together to form a layer structure in the *ab* plane roughly. As a result, a novel two-dimensional supramolecular network was assembled through two types of hydrogen bonds (N–H···O and N–H···Cl) in the crystal of **1** (Fig.3). The OW(1) of water molecules also form hydrogen bonds with O(1) and Cl atoms, the geometry of the hydrogen bonding is showing in Table 3.

Although the exact mechanism is unclear completely, the formation of new quadridentate ligand (aea) can be considered as the substitution of -OH by $-HNCH_2CH_2NH_2$ accompanying the dehydration process under hydrothermal condition. It is noticeable that the acylation of carboxyl in malic acid should happen more easily than the substitution of hydroxyl by ethylenediamino group under general condition, so we can speculate that the carboxylic group must have coordinated to the metal before the substitution reaction occurs.

Table 3 Hydrogen bonding parameters (nm, °) for compound 1

D–H···A	*d*(D···H)	*d*(H···A)	∠(DHA)	*d*(D···A)	Position of A
OW(1)–H(1B)···O(1)	0.090 8	0.195 1	167.70	0.284 5	*x*+1/2, −*y*+3/2, *z*+1/2
OW(1)–H(1C)···Cl	0.073 6	0.247 3	175.24	0.320 7	*x*+1/2, −*y*+3/2, *z*+1/2
N(4)–H(4B)···O(3)	0.090 8	0.197 5	171.15	0.287 6	−*x*+3/2, *y*−1/2, −*z*+1/2
N(3)–H(3B)···Cl	0.084 0	0.231 5	157.29	0.310 7	*x*+1, *y*, *z*
N(4)–H(4C)···Cl	0.082 6	0.239 2	165.00	0.319 7	intramolecular

The thermal behavior of compound **1** is studied from 30 to 800 ℃. TG curve indicates that the crystalline sample lose its one lattice water molecule from 140 to 200℃ with 4.16% weight-loss, which is consistent with the calculated result of 4.07%. The dehydrated sample is stable without weight-loss until 270 ℃, the decomposition performed slowly upon further heating and completed at about 700 ℃. The final residue is identified as Co_2O_3 without further change from 700 to 800 ℃. According to the results of X-ray structural analysis, elemental analysis, IR spectra and thermal analysis, the new compound is formulated as $[Co(aea)(2,2'\text{-bipy})]Cl\cdot H_2O$. The +3 oxidation state of cobalt is consistent with the charge compensation and the bond lengths of six-coordinated Co(Ⅲ)-N and Co(Ⅲ)-O; ESR spectra of compound **1** shows no sign of Co(Ⅱ) even at 84 K and XPS spectra gives peak at 781.4 eV attributing to the $2p_{3/2}$ of Co(Ⅲ).

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