研究简报

氨基酸配位聚合物[Co(*L*-trp)(*D*-trp)]$_n$

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An Amino Acid Coordination Polymer [Co(*L*-trp)(*D*-trp)]$_n$

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Abstract: The coordination polymer [Co(*L*-trp)(*D*-trp)]$_n$ (where *L*-trp is *L*-tryptophan or (*S*)-2-Amino-3-(3-indolyl) propionic acid and *D*-trp is *D*-tryptophan or (*R*)-2-Amino-3-(3-indolyl)propionic acid) was prepared by hydro-thermal method. The structure and physicochemical properties were characterized by single-crystal X-ray diffraction structure determination, infrared spectroscopy, elemental analysis and cyclic vohammogram. The crystal data for the title compound: Monoclinic, *P*2$_1$/*c*, β=98.024(2)°, *a*=1.959 5(3) nm, *b*=0.546 45(7) nm, *c*=0.905 54(17) nm, *Z*=2, μ= 0.934 mm⁻¹, R_1=0.063 2, wR_2=0.155 3. The crystal structure shows a two-dimensional double chain plane structure feature. The cyrstallized coordination polymer has a centrosymmetric space group. Each Co²⁺ is coordinated with a pair of racemes, and the complex is a mesomer. CCDC: 651088.

Key words: crystal structure; Co(Ⅱ) complex; tryptophan; polymer; synthesis

Trace amount of cobalt has important physiological function. In organisms, Co(Ⅱ) coordinats with amino acids to form stable complexes. Thus it is important to pharmacology, coordination chemistry and bioinorganic chemistry to study the structure, properties and stability of Co(Ⅱ)-amino acid complex[1-3].

The Co(Ⅱ) ion possesses a d⁷ outer layer electronic orbit. The most common three-dimensional structures are octahedron[4] or tetrahedron. Physiologically cobalt in our body is a biophilic element and plays an indispensable role as a trace element by coordination with amino acids[5-9]. Tryptophan is the only one complicated amino acid which has general-purpose physiological and biochemical functions[10]. In 1997, for example, Wang et al. using the linearity scanning adsorption volt-ampere method with a hanging mercury drop electrode, investigated the volt-ampere characteristics and mechanism of Co(Ⅱ) ion-tryptohan complex[11]. Zhen et

al. studied the interaction of copper-zinc superoxide dismutase with cobalt(Ⅱ)-tryptophane by VIS and ICP spectra analysis[12]. Li et al. determined the polarographic prewave of Co(Ⅱ) with tryptophan[13].

In metal-organic coordination polymers, there are bidentate and multidentate ligands to play a component part, and dominate space between metal atoms and dimension of crystal structure. Rigid organic ligands which have bifunctional were widely used, such as ligand contain N and O atoms [14]. Therefore, metal-organic coordination polymers have particular and special structural characteristics with some caves, holes and channels and can be applied in selected catalysis, molecular recognition, reversible exchange of host-guest molecules (ions), superpurity separation, biological conductor etc. In recent years, such polymers have been widely investigated[15~18]. However, a single-crystal structure of a coordination polymer formed with Co(Ⅱ) and trp has not been reported. In this report we will describe the preparation and characterization of a novel amino acid coordination polymer [Co(*L*-trp)(*D*-trp)]$_n$.

1 Experimental

1.1 Materials and methods

All the reagents were of AR grade and used without further purification. Elemental analyses were performed with a PE2400-Ⅱ instrument. IR spectro were recorded with a WGH-30A FTIR instrument (KBr discs) in the 4 000~400 cm^{-1} region. Cyclic vohammogram were determined with a CHI600b instrument in scanning scope −0.2 to −1.2 V.

1.2 Synthesis of [Co(*L*-trp)(*D*-trp)]$_n$

The title compound was prepared by the hydrothermal method. *L*-trp (1.0 mmol) and KOH (1.0 mmo1) were dissolved in 7.5 mL water and stirred for 0.5 h at room temperature. Then cobaltous perchlorate (0.5 mmol) aqueous solution was added dropwise. The resulted mixture was put into a Teflon-lined stainless steel autoclave (25 mL capacity) and undergone autogenous pressure heated to 150 ℃ for 72 h, and then cooled to room temperature. The light brown prismatic-folded plate crystals suitable for X-ray diffraction were obtained with a yield of 42%. The crystal is difficult to

dissolve in water, ethanol, acetonitrile. It can be slowly dissolved in DMF and DMSO, and be accelerated with ultrasonic. C, H and N analysis (%): Calcd. for C$_{22}$H$_{22}$Co N$_4$O$_4$: C 56.77; H 4.76; N 12.04. Found: C 56.55; H 4.71; N 12.09. IR (cm^{-1}, Fig.1): 3 397s, 3 296m, 2 910w, 1 595s, 1 454m, 1 417m, 1 319m, 1 223w, 1 093m, 1 036 m, 741s, 581m, 498m and 426m. The IR of *L*-trp is shown in Fig.2.
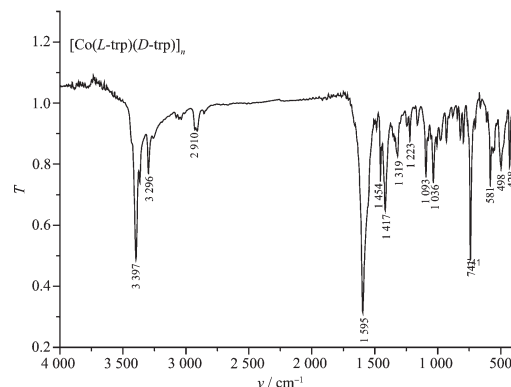

Fig.1　IR of [Co(*L*-trp)(*D*-trp)]$_n$

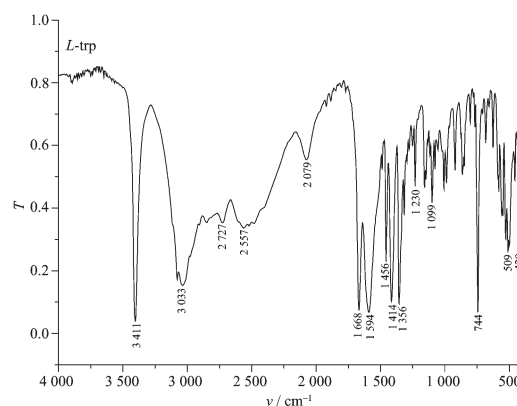Fig.2　IR of *L*-trp

1.3 Cyclic voltammetry (CV)

Cyclic vohammogram curve of [Co(*L*-trp)(*D*-trp)]$_n$ seeing Fig.3.
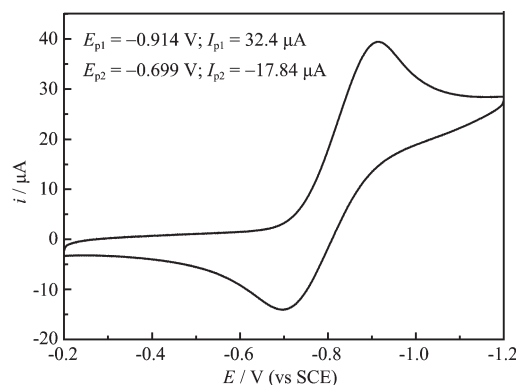

Fig.3　Cyclic vohammogram curve of [Co(*L*-trp)(*D*-trp)]$_n$

1.4 Crystal structure determination[19-21]

A single crystal of the complex with dimensions of 0.45 mm × 0.32 mm × 0.13 mm was selected for single-crystal X-ray structure analysis. Data colection was performed on a BRUKER SMART APEX 1000 CCD diffractometer equipped with a graphite-monochromatized Mo $K\alpha$ radiation (λ=0.071 073 nm) at 298(2) K in the range of $2.10°\leqslant\theta\leqslant25.00°$. A total of 4 366 reflections were collected with 1 680 unique ones(R_{int}=0.070 3), of which 1 237 with $I>2\sigma(I)$ were considered as observed and used in the succeeding structure solution and refinement. The intensity data were corrected for Lp factor. The structure of the compound was solved with direct methods to locate all the non-H atoms from the trial structure and then refined anisotropically using full-matrix least-squares procedure. All the H atoms were geometrically fixed at calculated positions. The final cycle of refinement converged to R=0.063 2, wR= 0.155 3 (w=1/[σ^2 (F_o^2)+(0.086 2)^2+2.011 4P], where P= (F_o^2+2F_c^2)/3, $(\Delta/\sigma)_{max}$=0.000, $\Delta\rho_{max}$=1 127 e·nm^{-3}, $\Delta\rho_{min}$= −1 015e·nm^{-3}.

CCDC: 651088.

2 Results and discussion

2.1 Synthesis

In our experiment, the title compound was prepared in aqueous solution. The pH value plays an important role in the ionization and coordinating action of the trp and the hydrolyzation of Co^{2+}. The suitable acidity for crystal growth is about pH=6.0. Furthermore reaction time and temperature can also influence the dimension and quality of the crystal.

2.2 IR spectroscopy

By comparison of Fig.2 and Fig.1, the IR between L-trp and [Co(L-trp)(D-trp)]$_n$, ν_{as}NH$_3^+$/NH$_2$ reduced from 3 411 to 3 397 cm^{-1}; ν_sNH$_3^+$/NH$_2$ reduced from 3 033 cm^{-1} to 2 910 cm^{-1}; δ_{as}NH$_3^+$/NH$_2$ disappeared from 1 668 cm^{-1}; The vibrations of indole nitrogen, νC$_7$H$_6$N has little changes from 744 cm^{-1} to 741 cm^{-1}, this shows indole nitrogen do not participate in forming coordination bond; ν_{as}COO$^-$ retain at 1 594; ν_s(COO$^-$) reduced from 1 356 cm^{-1} to 1 319 cm^{-1}, $\Delta\nu_{as-s}$COO$^-$ increased from 238 to 275 cm^{-1}. Compared with L-trp, the $\Delta\nu_{as-s}$ value of the complex slightly increased. However the added value is not very big. It indicates that carboxyl oxygen has high symmetry, the coordination modes of carboxyl can be oxo-bridging coordination.Otherwise the vibrations of 2 557 and 2 079 cm^{-1} disappeared from the coordination polymer.

2.3 Cyclic voltammetry

In DMF solution, 0.1 mol·L^{-1} of (n-Bu)$_4$NClO$_4$ was supporting electrolyte, the CV of 1×10^{-4} mol·L^{-1} of [Co (L-trp)(D-trp)]$_n$ was determined. In scanning scope −0.2 to −1.2V, CV shows two irreversible cathodic waves at −0.699 V and −0.914 V.

2.4 Description of the structure

The related crystallographic data of title complex specified in Table 1. The Selected bond lengths (nm) and angles (°) of the title complex were listed in Table 2.

Scheme 1 is the molecular structure of the cobalt complex. The ORTEP drawing of complex with the atom numbering scheme is shown in Fig.4. Fig.5 shows the

Table 1 Crystallographic data of the titled complex

Empirical	C$_{22}$H$_{22}$CoN$_4$O$_4$	μ(Mo $K\alpha$) / mm^{-1}	0.934
Formula weight	465.37	F(000)	482
Crystal system	Monoclinic	Range of θ / (°)	2.10~25.00
Space group	$P2_1/c$	Index range	−23 $\leqslant$ h $\leqslant$ 12, −6 $\leqslant$ k $\leqslant$ 6, −10 $\leqslant$ l $\leqslant$ 10
a / nm	1.959 5(3)	Reflections collected / unique (R_{int})	4 366 / 1 680 (0.070 3)
b / nm	0.546 45(7)	Observed data [$I>2\sigma(I)$]	1 237
c / nm	0.905 54(17)	R_1, wR_2 [$I>2\sigma(I)$]	0.063 2, 0.155 3
β / (°)	97.884(10)	R_1, wR_2 (all data)	0.091 7, 0.178 9
V / nm^3	0.960 1(3)	GOF	1.072
Z	2	Largest diff.peak and hole / (e·nm^{-3})	1 127 and −1 015
D_c / (g·cm^{-3})	1.610		

Table 2　Selected bond lengths (nm) and angles (°) of the titled complex

Co1-O1[i]	0.203 7(3)	Co1-O1	0.203 7(3)	Co1-O2[ii]	0.210 0(4)
Co1-O2[iii]	0.210 0(4)	Co1-N1[i]	0.212 8(4)	Co1-N1	0.212 8(4)
O1[i]-Co1-O1	180.0(2)	O1[i]-Co1-O2[ii]	90.11(15)	O1-Co1-O2[ii]	89.89(15)
O1[i]-Co1-O2[iii]	89.89(15)	O1-Co1-O2[iii]	90.11(15)	O2[ii]-Co1-O2[iii]	180.00(17)
O1[i]-Co1-N1[i]	80.15(15)	O1-Co1-N1[i]	99.85(15)	O2[ii]-Co1-N1[i]	86.13(16)
O2[iii]-Co1-N1[i]	93.87(16)	O1[i]-Co1-N1	99.85(15)	O1-Co1-N1	80.15(15)
O2[ii]-Co1-N1	93.87(16)	O2[iii]-Co1-N1	86.13(16)	N1[i]-Co1-N1	180.00(12)
C2-N1-Co1	109.5(3)				

Symmetry codes: [i] $-x+1$, $-y+1$, $-z+1$; [ii] $-x+1$, $y-1/2$, $-z+3/2$; [iii] x, $-y+3/2$, $z-1/2$; [iv] $-x+1$, $y+1/2$, $-z+3/2$.

packing diagram of the cobalt complex in a unit cell.
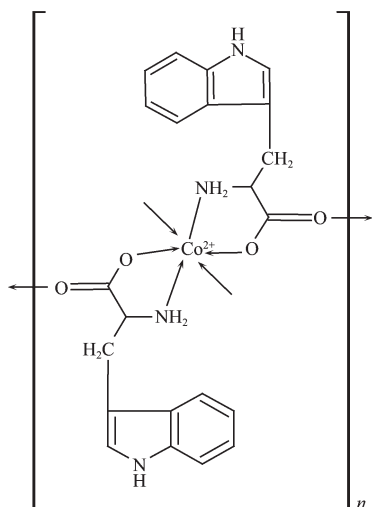
Scheme 1　Part of the crystal structure of the title complex, showing interactions of Co^{2+} with N and O atom
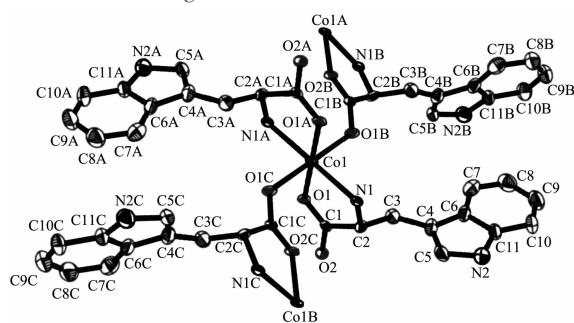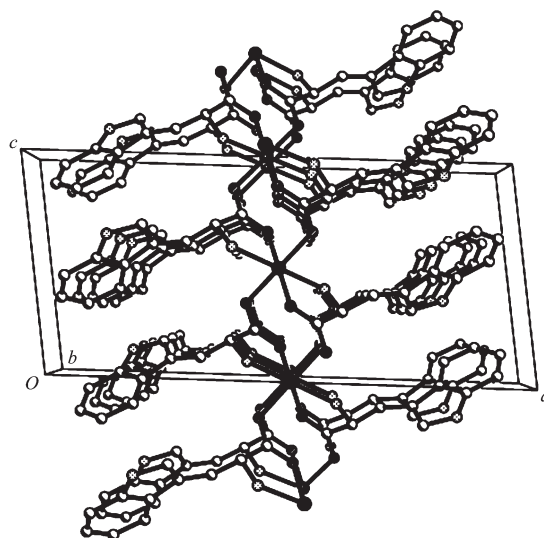

Symmetry codes: [i] x, y, z; [ii] $-x$, $1/2+y$, $1/2-z$; [iii] $-x$, $-y$, $-z$; [iv] x, $1/2-y$, $1/2+z$

Fig.4　Structure of the title complex, displacement ellipsoids are drawn at the 30% probability level

X-ray analysis reveals that the complex is a coordination polymer. Co(II) ion is six-coordinated to form a octahedron. Each Co(II) ion lies across centres of complex and contains two neutral tryptophan molecules: L-trp and D-trp. The complex shows a two-dimensional double chain structure along bc orientation assembled by bridging oxygen of carboxyl and cobalt into chains of ····O-C-O-Co-O-C-O-Co··· interactions. Each unit cell contains two title complex molecules. L-trp and D-trp are chiral molecules in the complex which crystallized in centrosymmetric space group. In the molecular structure of [Co(L-trp)(D-trp)]n, the cobalt atom is coordinated by two N atoms and two O atoms from a L-trp and a D-trp, and two O atoms from another two carboxy group of adjacent position L-trp and D-trp (shown at Scheme 1 and Fig.4). The equatorial Co-O bond lengths are Co1-O1 0.203 7(3) nm, Co1-O2 0.210 0(4) nm, and the axial Co-N distance is 0.212 8(4) nm. The angles in the octahedron are ∠O1[i]-Co1-O1 = ∠O2[ii]-Co1-O2[iii] =180.0(2)°, ∠O1[i]-Co1-O2[ii] = ∠O1-Co1-O2[iii]=90.11(15)°, ∠O1-Co1-O2[ii]= ∠O1[i]-Co1-O2[iii]=

Symmetry codes: [i] x, y, z; [ii] $-x$, $1/2+y$, $1/2-z$; [iii] $-x$, $-y$, $-z$; [iv] x, $1/2-y$, $1/2+z$

Fig.5　Crystal packing of the title complex

89.89(15)°, $\angle$ O1^i-Co1-N1^i=$\angle$ O1-Co1-N1=80.15(15)°, $\angle$ O1-Co1-N1^i=$\angle$ O1^i-Co1-N1=99.85(15)°, $\angle$ O2^{ii}-Co1-N1^i=$\angle$ O2^{iii}-Co1-N1=86.13(16)°, $\angle$ O2^{iii}-Co1-N1^i=$\angle$ O2^{ii}-Co1-N1=93.87(16)°, $\angle$ N1^i-Co1-N1=180.00(12)°, respectively. It shows each Co(Ⅱ) atom exhibits a slightly deformed octahedral environment with four oxygen atoms from four different *L*-trp and *D*-trp molecules in the equatorial plane, as well as two nitrogen atoms from a *L*-trp and a *D*-trp molecules at the axial positions.

Furthermore from Fig.5, the complex shows a two-dimensional structure assembled by linking into chains of head to tail ····O-C-O-Co-O-C-O-Co··· interactions. Bonds lengths and angles agree with accepted values. There is a chiral carbon atom in the *L*-trp or *D*-trp molecule, so the ligand is a chiral molecule. Since each Co^{2+} coordinate with a pair of racemes, thus the complexes is a mesomer. Consequently the cyrstallized coordination polymer has a centrosymmetric space group.

3　Conclusions

A novel two-dimensional double chain plane structure cobalt(Ⅱ) compound [Co(*L*-trp)(*D*-trp)]$_n$ was synthesized and structurally characterized. It crystallizes in monoclinic system, space group $P2_1/c$. Each Co (Ⅱ) atom locates in the center of a deformed octahedron configuration. The six vertexs of deformed octahedral forms 4O+2N coordination number environment with four oxygen atoms from four different *L*-trp and *D*-trp molecules, two nitrogen atoms from a *L*-trp and a *D*-trp molecules. The ligand is a chiral molecule. However each Co^{2+} coordinate with a pair of racemes, the complex is a mesomer. The cyrstallized coordination polymer has a centrosymmetric space group.

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