由肉桂酸和甲基联吡啶喹喔啉配体构筑的双核铅(Ⅱ)的配合物的水热合成、表征及自然键轨道(NBO)分析

方 燕[1]   王 蕾[1]   倪 良[*,1]   姚 加[2]

([1] 江苏大学化学化工学院,镇江   212013)

([2] 浙江大学化学系,杭州   310027)

摘要: 采用水热法合成了一种新型双核铅(Ⅱ)配合物[Pb₂(CA)₄(Medpq)₂](HCA=cinnamic acid,Medpq=2-methyldipyrido[3,2-f:2,3′-h] quinoxaline),并对其进行了元素分析、红外光谱、紫外可见光光谱、热重表征、荧光光谱、X 射线单晶衍射测定和理论计算。标题配合物属于三斜晶系,空间群为 $P\bar{1}$。在晶体中,铅与来自 Medpq 配体的 2 个氮原子和 3 个肉桂酸配体的 5 个氧原子形成七配位。应用 Gaussian 03 程序,对标题配合物进行了自然键轨道(NBO)分析,结果表明 Pb(Ⅱ)与配位原子间的价键类型都属于共价键范畴。

关键词: 双核;Pb(Ⅱ)配合物;晶体结构;肉桂酸;自然键轨道

Hydrothermal Synthesis, Characterization and Natural Bond Orbital(NBO) Analysis of a Binuclear Lead(Ⅱ) Complex with Cinnamic Acid and Medpq Ligands

FANG Yan[1]   WANG Lei[1]   NI Liang[*,1]   YAO Jia[2]

([1]School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang, Jiangsu 212013, China)

([2]Department of Chemistry, Zhejiang University, Hangzhou 310027, China)

Abstract: A binuclear Pb(Ⅱ) complex [Pb₂(CA)₄(Medpq)₂] (HCA=cinnamic acid, Medpq=2-methyldipyrido[3,2-f: 2,3′-h]quinoxaline) has been hydrothermally synthesized and structurally characterized by elemental analysis, IR spectrum, UV-Vis spectrum, TG, fluorescent emission, single-crystal X-ray diffraction and theoretical calculations. Title compound crystallizes in triclinic, space group $P\bar{1}$ with a=0.854 35(17) nm, b=1.250 9(3) nm, c=1.436 6 (3) nm, α=107.45 (3)°, β=105.63 (3)°, γ=97.04 (3)°. In the crystal structure, the lead atom is seven-coordinated with two nitrogen atoms from Medpq ligand and five oxygen atoms from three cinnamic acid ligands. Natural bond orbital (NBO) analysis was performed by using the NBO method built in Gaussian 03 Program. The calculation results shown an covalent interaction between the coordinated atoms and Pb(Ⅱ) ion. CCDC: 859036.

Key words: binuclear; Pb(Ⅱ) complex; crystal structure; cinnamic acid; natural bond orbital

　　The design and synthesis of coordination complexes are attracting increasing attention, not only for their interesting molecular topologies, but also for their potential applications as functional materials in catalysis, molecular adsorption, magnetism, nonlinear optics and molecular sensing[1-9]. As one kind of important elements of *N*-containing heterocyclic ring systems in coordination chemistry, phenanthroline

(phen) and its derivatives are reported to have been widely used in the construction of metal-organic coordination complexes[10-15]. 2-methyldipyrido[3,2-f:2′, 3′-h]quinoxaline (Medpq) as one of the phen derivatives and possessing an extended aromatic system, is a planar rigid bidentate chelating reagent which can not only act as a terminal ligand but also potentially provide supramolecular interactions such as aromatic stacking to construct intriguing structures[16]. Aromatic carboxylic acids have been extensively studied in metal-organic coordination complexes not only due to their multiple coordination sites but also because of the π-band of the aromatic ring and excellent hydrogen-banding abilities[17-18].

However, cinnamic acid, one kind of aromatic carboxylic acids, has not been studied extensively to construct coordination compounds containing transition and main group metals. Up to now, only a few transition-metal-based MOFs constructed from cinnamic acid were reported, e.g. [Cd(cinnamato)₂(Phen)]₂, [Cd(bpy)(H₂O)(PhCH=CHCO₂)₂] (bpy=2,2′-bipyridine)[19-20].

Based on above reasons, we adopted cinnamic acid (HCA) as an organic linker, Medpq as a secondary ligand, divalent lead ion as the metal center, synthesized a new metal-organic coordination complex: [Pb₂(CA)₄(Medpq)₂].

1 Experimental

1.1 Materials

The Medpq ligand was synthesized according to the literature method[21-22]. Pb(CH₃COO)₂·3H₂O, cinnamic acid and NaOH were purchased commercially and used without further purification.

1.2 Instrument and measurements

Elemental analysis was carried out with a Perkin-Elmer 240C analyzer. Transmission mode FT-IR spectra were obtained between 4 000 and 400 cm^{-1} using a Nicolet Nexus 470 infrared spectrometer. UV-Vis absorption spectrum was recorded on a Hitachi UV-2450 spectrophotometer at room temperature. Thermogravimetric analysis (TG) analysis of the precursor powders was performed on a Germany Netzsch STA449C with heating rate of 10 ℃·min^{-1}

under flowing nitrogen.

1.3 Synthesis of the title compound

Pb(CH₃COO)₂·3H₂O (0.191 g, 0.5 mmol), cinnamic acid (0.074 g, 0.5 mmol), Medpq (0.124 g, 0.5 mmol) and H₂O (18 mL) were mixed by stirring at room temperature. When the pH value of the mixture was adjusted to about 8 with NaOH, the solution was put into a 25 mL Teflon-lined autoclave under autogenous pressure at 180℃ for seven days. After cooling to room temperature, pale red crystals of the title compound were collected by filtration and washed with distilled water in 62% yield (based on Pb). Anal. Calcd.(%) for C₃₃H₂₄N₄O₄Pb: Pb,27.7; C,53.0; H,3.2; O, 8.6; N,7.5. Found (%): Pb,27.7; C,52.9; H,3.1; O,8.7; N,7.6. IR (KBr, cm^{-1}): 1 637s, 1 529s, 1 494m, 1 369s, 1 238, 1 077m, 973m, 772m, 738s, 730m.

1.4 Structure determination

A single crystal with dimensions of 0.26 mm × 0.24 mm×0.21 mm was mounted on a Bruker Smart Apex Ⅱ CCD diffractmeter equipped with a grahite-monochromatic Mo $K\alpha$ radiation (λ=0.071 073 nm) by using an φ-ω scan mode (3.39°<2θ<25.35°) at 293(2) K. The structure was solved by direct methods with SHELXS-97 program[23] and refined by SHELXL-97[24] using full-matrix least-squares techniques on F^2. All non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically. All H atoms were positioned geometrically (C-H 0.093 nm for CH or 0.096 nm for CH₃) and refined as riding mode. The final R=0.028 2 and wR=0.054 6. The detailed crystallographic data and structure refinement parameters for the title complex are summarized in Table 1.

CCDC: 859036.

2 Result and discussion

2.1 Description of crystal structure

Single-crystal X-ray diffraction analysis reveals that the compound [Pb₂(CA)₄(Medpq)₂] crystallizes in $P\overline{1}$ space group. In the molecular structure of the title complex, there are two lead atoms, two Medpq ligands, and four CA ligands. The carboxylate groups of CA ligands present two different kinds of coordination modes (A and B, see Scheme 1).

Table 1　Crystallographic data for the title complex

Empirical formula	$C_{33}H_{24}N_4O_4Pb$	α / (°)	107.45(3)
Formula mass	747.75	β / (°)	105.63(3)
D_c / (g·cm^{-3})	1.805	γ / (°)	97.04(3)
μ(Mo $K\alpha$) / mm^{-1}	6.18	V / nm^3	1.375 5(5)
Crystal system	Triclinic	Z	2
Space group	$P\bar{1}$	R_1, wR_2 ($I>2\sigma(I)$)	0.028 2, 0.054 6
Crystal size / mm	0.26×0.24×0.21	$F(000)$	728
a / nm	0.854 35(17)	Collected reflections / unique	9 582 / 4934
b / nm	1.250 9(3)	Rint	0.025 1
c / nm	1.436 6(3)	Goodness-of-fit (GOF) on F^2	1.009

Pb(1) adopts a seven-coordinate manner by coordinating to two nitrogen atoms (N(1), N(2)) from one chelating Medpq ligand and five oxygen atoms (O(1), O(2), O(3), O(4), O(1^i)) of two chelating carboxylate groups (mode A),and one bridging carboxylate group (mode B), from three cinnamic acid ligands, respectively. The coordination environment of Pb(1^i) is the same as that of Pb(1), as shown in Fig.1. The Pb-O bond distances are in the range of 0.237 5 (3)~0.291 5(1) nm, the Pb-N(1) bond distance is 0.267 5(3) nm and Pb-N(2) bond distance is 0.268 1(3) nm, the N(O) - Pb-O(N) angles range from 70.08(19)° to 164.35(10)°. The selected important bond parameters are given in Table 2. For the title complex, the CA ligand has two coordination fashions as shown in Scheme 1. In one fashion, the ligand contains one chelating bidentate carboxylate group (Scheme 1a). In the second fashion, the carboxylate group acts as chelating ligand, also bridges two mental centers (Scheme 1b).
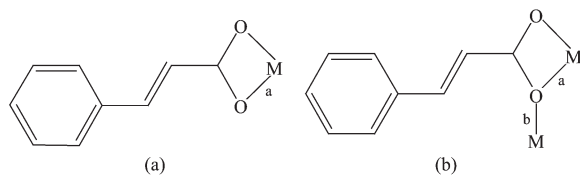
Scheme 1　Coordination fashions of cinnamic acid in the title compound

There are obviously π-π stacking interactions in the compound. The first is face-to-face π-π stacking interaction with the distance of 0.353 0 nm between the pyrazine rings and the benzene units of Medpq ligands in the adjacent unit. The second π-π stacking interactions occur between aromatic rings of cinnamic acid ligands in an edge-to-face fashion with a distance of 0.349 6 nm. The π-π stacking interactions are shown in Fig.2. At one time, intramolecular and intermolecular C –H ⋯ O hydrogen bonding interactions are observed between O(1), O(2), O(3) and O(4) (Fig.3,
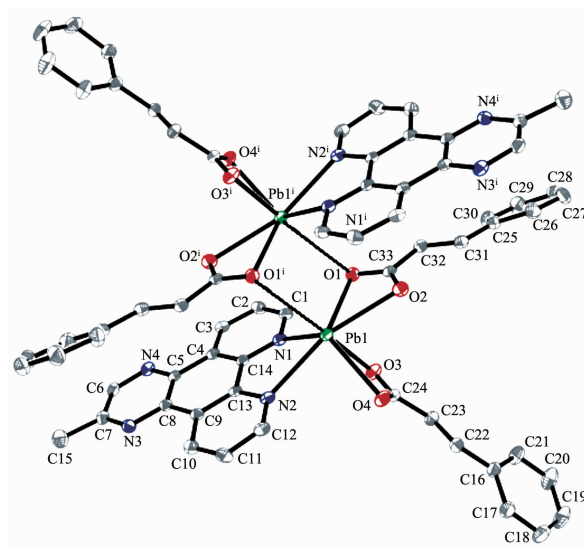
Thermal ellipsoids at 30% probability level, Hydrogen atoms are omitted for clarity; Symmetry code: ^{i} 1−x, −y, 2−z

Fig.1　ORTEP drawing of the molecule showing the local coordination environment of Pb(Ⅱ)
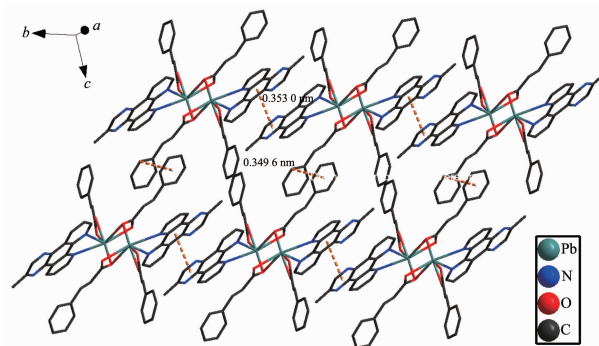
Fig.2　π-π stacking interactions in the title complex

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

Pb(1)-N(1)	0.267 5(3)	Pb(1)-N(2)	0.268 1(3)	Pb(1)-O(1)	0.255 3(3)
Pb(1)-O(2)	0.267 2(3)	Pb(1)-O(3)	0.237 5(3)	Pb(1)-O(4)	0.266 5(3)
Pb(1)-O(1^i)	0.291 5(1)				
N(1)-Pb(1)-O(1)	75.93(9)	N(1)-Pb(1)-O(2)	123.85(9)	N(1)-Pb(1)-O(3)	80.39(10)
N(1)-Pb(1)-O(4)	121.20(10)	N(1)-Pb(1)-O(1^i)	70.08(19)	N(2)-Pb(1)-O(1^i)	85.76(22)
N(2)-Pb(1)-O(1)	136.77(9)	N(2)-Pb(1)-O(2)	164.35(10)	N(2)-Pb(1)-O(3)	91.03(11)
N(2)-Pb(1)-O(4)	85.32(10)	O(1)-Pb(1)-O(2)	50.30(8)	O(1)-Pb(1)-O(3)	79.92(10)
O(1)-Pb(1)-O(4)	118.51(9)	O(2)-Pb(1)-O(3)	75.99(10)	O(2)-Pb(1)-O(4)	79.78(9)
O(3)-Pb(1)-O(4)	51.71(9)	O(1i)-Pb(1)-O(1)	80.70(18)	O(1^i)-Pb(1)-O(2)	109.89(18)
O(1i)-Pb(1)-O(3)	147.80(20)	O(1i)-Pb(1)-O(4)	158.70(25)		

Symmetry code: ^{i} 1−x, −y, 2−z.

Table 3 Hydrogen bond lengths and bond angles for the title complex

D–H⋯A	d(D-H) / nm	d(H⋯A) / nm	d(D⋯A) / nm	∠DHA / (°)
C(1)–H(1A)⋯O(1)	0.093	0.239	0.305 1(6)	128
C(12)–H(12A)⋯O(2)^i	0.093	0.236	0.313 6(5)	141
C(15)–H(15B)⋯O(3)^{ii}	0.096	0.238	0.327 0(6)	154
C(22)–H(22A)⋯O(4)	0.093	0.254	0.285 5(5)	100
C(31)–H(31A)⋯O(2)	0.093	0.253	0.284 9(5)	100

Symmetry codes: ^{i} −x, −y, 2−z; ^{ii} 1−x, 1−y, 2−z.

Table 3),which play an important role in stabilizing the structure. Additionally, the π-π interactions and hydrogen bonding interactions can make the title compound be further assembled into a 3D network, comparable to [Cd(cinnamato)$_2$(Phen)]$_2$[19].
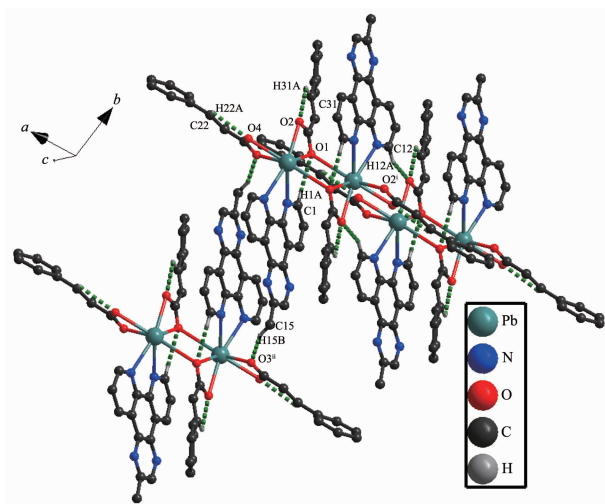

Some hydrogen atoms are omitted for clarity; Symmetry codes:
^{i} −x, −y, 2−z; ^{ii} 1−x, 1−y, 2−z

Fig.3 Hydrogen bonds of the title complex

2.2 Thermal analysis

The TG curve of the title compound is shown in Fig.4. It shows that the first weight loss of 41.99% from 19.2 to 479.8 ℃ corresponds to the removal of cinnamic acid ligand （Calcd. 39.61%）. Upon further heating, an obvious weight loss (29.74%) occurs in the temperature range of 479.8~1 125.7 ℃, corresponding to the release of Medpq ligand （Calcd. 32.93%）. The residual weight 28.27% （Calcd. 27.46%）corresponds to PbO.
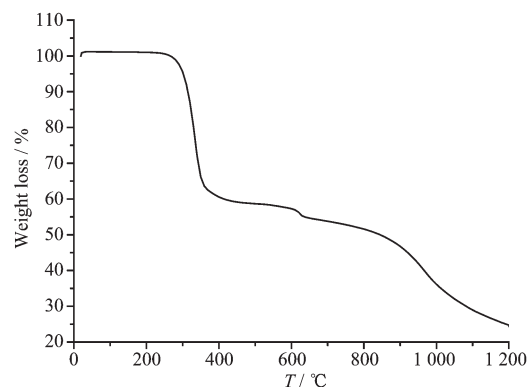

Fig.4 TG of the title complex

2.3 UV-Vis spectrum analysis

The optical property of the title compound is characterized by UV-Vis spectrum at room temperature in solid state, as shown in Fig.5. The

experimental bands in the 200~346 nm region result from ligand-mental charge transfer and ligand-ligand charge transfer transitions. The absorption band at 406 nm is assigned to the electronic transitions (metal-ligand charge transfer)[25]. The results indicate the good optical quality of the title compound.
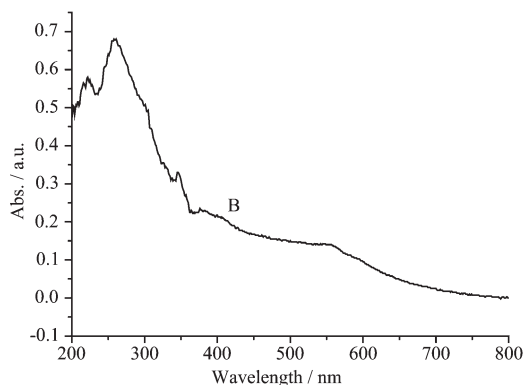

Fig.5　UV-Vis spectrum of the title complex

3.4　Fluorescent property

In this paper, the luminescent property of the title compound was investigated in solid state at room temperature. The compound exhibited an intense emission peak at 468 nm　(λ_{ex}=255 nm) as shown in
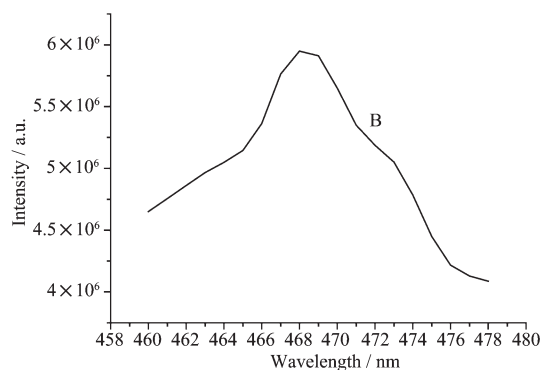

Fig.6　Luminescence spectrum of the compound at room temperature

Fig.6. According to the literature[26], the emission peak of free Medpq ligand was at wavelengths of 535 nm. Compared to luminescence spectrum of free Medpq ligands, the compound shows a blue-shift, which is probably due to the intraligand transition of the coordinated ligands[27].

3.5　Theoretical calculations

The Gaussian 03 program[28] was used in the calculation. The parameters of the molecular structure for the calculation were all from the experimental data of the crystal structure of the title compound. Natural bond orbital (NBO) analysis was performed by B3LYP method in Lanl2dz basis set.

The selected natural atomic charges, natural electron configuration, Wiberg bond indexes and NBO bond order　(a.u.) for title compound are shown in Table 4. It is indicated from Table 3 that the electronic configurations of Pb (Ⅱ) ion, O and N atoms are $6s^{1.92}6p^{0.63}7p^{0.01}$, $2s^{1.72~1.74}2p^{5.02~5.07}3p^{0.01}$ and $2s^{1.38~1.39}2p^{4.13~4.14}3p^{0.02}$, respectively. Based on the above results, one can conclude that the Pb(Ⅱ) ion coordinated with O and N atoms is mainly on 6s and 6p orbits (the electron number of 7p orbit is so small that can be omitted)[29], four O atoms and two N atoms bonding with Pb (Ⅱ) atom are all on 2s and 2p orbits (the electron number of 3p is so small that can be omitted). Therefore, the Pb (Ⅱ) ion obtained some electrons from two nitrogen atoms of Medpq ligand and four oxygen atoms of cinnamic acid ligand. Thus, according to valence-bond theory, the atomic net charge distribution and the NBO bond orders of the title compound　(See Table 4) show the covalent interaction between the coordinated atoms and Pb(Ⅱ)

Table 4　Natural atomic charges, natural valence electron configurations, Wiberg bond indexes and NBO bond orders (a.u.) for the title complex

Atom	Net charge / e	Valence electron configuration	Bond	Wiberg bond index	NBO bond order
Pb	1.438 94	[core]$6s(1.92)6p(0.63)7p(0.01)$			
O(1)	−0.819 38	[core]$2s(1.74)2p(5.07)3p(0.01)$	Pb-O(1)	0.177 7	0.142 6
O(2)	−0.759 72	[core]$2s(1.73)2p(5.02)3p(0.01)$	Pb-O(2)	0.138 9	0.119 5
O(3)	−0.804 91	[core]$2s(1.74)2p(5.06)3p(0.01)$	Pb-O(3)	0.247 6	0.183 4
O(4)	−0.751 03	[core]$2s(1.72)2p(5.02)3p(0.01)$	Pb-O(4)	0.145 8	0.120 8
N(1)	−0.538 82	[core]$2s(1.39)2p(4.13)3p(0.02)$	Pb-N(1)	0.126 4	0.154 7
N(2)	−0.542 47	[core]$2s(1.38)2p(4.14)3p(0.02)$	Pb-N(2)	0.097 8	0.133 6

ion. The differences of the NBO bond orders for Pb-O and Pb-N bonds make their bond lengths be different[30], which is good agreement with the X-ray crystal structural data of the title compound.

As can be seen from the Fig.7, lowest unoccupied molecular orbital (LUMO) was composed of π orbits of pyridine rings in Medpq, whereas highest occupied molecular orbital (HOMO) consists of π orbits of benzene rings and carboxyl mainly in cinnamic acid. So, ligand to ligand charge transition may be inferred from some contours of molecular orbitals of the title compound.
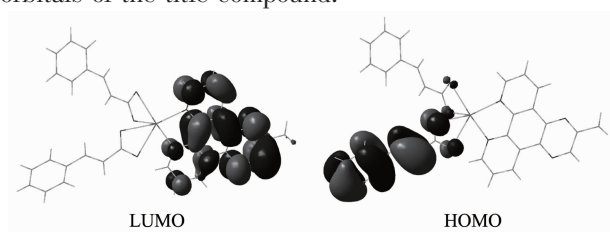

Fig.7　Molecular orbitals of the title complex

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