第 25 卷第 12 期
2009 年 12 月

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CHINESE JOURNAL OF INORGANIC CHEMISTRY

Vol.25 No.12
2211~2214

研究简报

二维铅配合物$[Pb_2(C_8H_4O_4)_2(C_{19}H_{12}N_4O)_2]_n \cdot 3.5nH_2O$的水热合成、晶体结构与荧光性质研究

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关键词:铅;TCPP;1,4-苯二甲酸;晶体结构;荧光

中图分类号:O614.43+3 **文献标识码**:A **文章编号**:1001-4861(2009)12-2211-04

Hydrothermal Synthesis, Crystal Structure and Photoluminescence of a 2D Lead(Ⅱ) Complex: $[Pb_2(C_8H_4O_4)_2(C_{19}H_{12}N_4O)_2]_n \cdot 3.5nH_2O$

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Abstract: In the title compound, $[Pb_2(C_8H_4O_4)_2(C_{19}H_{12}N_4O)_2]_n \cdot 3.5nH_2O$ (**1**), has been synthesized by the hydrothermal assembly of 1,4-benzenedicarboxylate and 4-(1H-1,3,7,8-tetraazacyclopenta[*l*]-phenanthren-2-yl)phenol(TCPP) with lead acetate. Elemental analysis, X-ray crystal structure analysis, IR spectrum, thermogravimetric analysis and luminescence property were carried out for the structural determination and characterization of the title compound. Compound **1** crystallizes in triclinic, space group $P\bar{1}$ with a=1.013 54(10) nm, b=1.104 84(11) nm, c=1.210 05(12) nm, α=76.812 0(10)°, β=74.814 0(10)°, γ=86.030 0(10)°, V=1.273 1(2) nm^3, $Pb_2C_{54}H_{39}N_8O_{13.5}$, M_r=1 430.31, Z=1, D_c=1.866 g·cm^{-3}, μ=6.680 mm^{-1}, F(000)=691, R=0.027 3 and wR=0.068 7 for 4 042 observed reflections ($I>2\sigma(I)$). The compound **1** exhibits two-dimensional network structures, which are further stacked through π-π interactions and hydrogen bonds to form three-dimensional supramolecular polymer. Solid-state luminescent spectrum of the compound **1** indicates intense fluorescent emission. CCDC: 748883.

Key words: lead; TCPP; 1,4-benzenedicarboxylate; crystal structure; photoluminescence

The design and synthesis of metal-organic coordinated polymer have attracted considerable attention in recent years. Not only because of their intriguing structural diversity but also because of their tremendous potential applications in catalysis, molecular adsorption, magnetism, nonlinear optics and molecular sensing[1~3]. In general, two different types of interactions, viz. covalent bonds and non-covalent intermolecular forces, can be used to construct varied supramolecular architectures. 1,10-Phenanthroline (phen), as a common organic ligand, has been widely used in the construction of metal-organic coordination polymers[4~6]. The phen derivative 4-(1H-1,3,7,8-tetraazacyclopenta[*l*]-phenanthren-2-yl)phenol (TCPP) possesses an extended

收稿日期:2009-04-22。收修改稿日期:2009-09-19。

江苏省博士后基金项目(No.0801010B),吉林省自然科学基金项目(No.20082112)。

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delocalized aromatic system[7]. To date, only a handful of supramolecular architectures based on TCPP molecules have been described[8]. As a continuation of this work, we selected 1,4-benzenedicarboxylate (1,4-H_2BDC) to act as a metal-metal linker in its deprotonated form and TCPP as a terminal ligand, generating the title compound, $[Pb_2(C_8H_4O_4)_2(C_{19}H_{12}N_4O)_2]_n \cdot 3.5nH_2O$ (**1**), a novel coordination polymer, which is reported here. Whereas Pb^{2+} is employed in the present work for several reasons: (1) it has a $6s^2$ outer electron configuration and large radius, which can lead to interesting topological arrangements[9~11]; (2) the absence of crystal field stabilization energy effects allows the Pb^{2+} ion to adopt varied coordination geometries including octahedra, tetrahedra, or square planes amongst others, which give rise to novel coordination networks[12~14]; and (3) it has interesting photochemical and photophysical properties[15~18].

1 Experimental

1.1 Materials and general methods

The TCPP ligand was synthesized according to the literature method[19] and all A.R. grade chemicals were used as received without further purification. Elemental analyses were performed on a Perkin-Elmer 240C analyzer. The FTIR spectra were recorded on a Perkin-Elmer Spectrum One spectrometer using KBr pellets in the range of 4 000~450 cm^{-1}. Thermogravimetric analyses were performed on a SDT 2960 Simultaneous DSC-TGA analyzer, at a heating rate of 10 ℃·min^{-1} under an air atmosphere. Fluorescence spectra were recorded on a Perkin-Elmer LS 55 luminescence spectrometer.

1.2 Synthesis of $[Pb_2(C_8H_4O_4)_2(C_{19}H_{12}N_4O)_2]_n \cdot 3.5nH_2O$ (1)

The brown block crystals of **1** were synthesized hydrothermally which is an available way of growing complex crystals due to its effectiveness, simplicity, and environmental friendliness[20], from a mixture of $Pb(CH_3COO)_2$, 1,4-H_2BDC ligand, TCPP ligand and distilled water (molar ratio 1∶1∶2∶5 000) in a 20 mL Teflon-lined stainless steel autoclave (15 mL capacity) under autogenously pressure heated to 160 ℃ for 3 days and cooled to room temperature. Crystalline product was filtered, washed with distilled water, and dried to give 0.49 g of the compound (yield 47% based on lead). The pH of the solution plays an important role in the formation of this compound. The feature in this structure is that compound **1** crystallizes in the space group $P\bar{1}$ of the $[Pb_2(C_8H_4O_4)_2(C_{19}H_{12}N_4O)_2]_n \cdot 3.5nH_2O$ (1 430.31): calcd.(%): C 45.34, H 2.75, N 7.83; Found (%) C 45.31, H 2.76, N 7.80.

1.3 X-ray structure determination

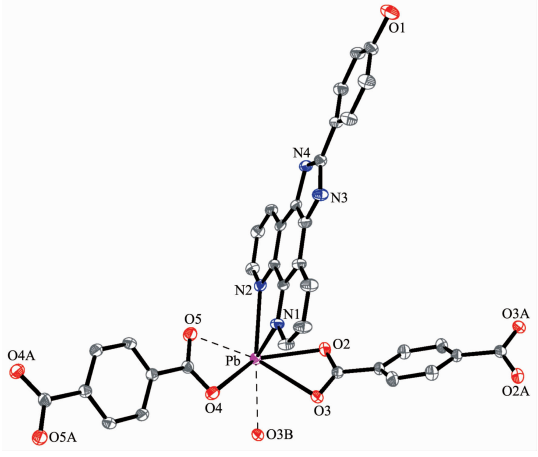
A suitable brown prismatic crystal of **1** was mounted on a Bruker SMART APEX CCD area-detector diffractometer, and the data were collected by using a graphite-monochromatized Mo $K\alpha$ radiation (λ = 0.071 073 nm) at 292(2) K in the range of $2.08° \leqslant \theta \leqslant 25.00°$. A total of 6 786 reflections were collected and 4 404 were unique (R_{int}=0.028 6), of which 4 042 were observed ($I>2\sigma(I)$). The structure was solved by direct methods with SHELXS-97 program and refined with SHELXL-97 by full-matrix least-squares techniques on F^2. All non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically. The H atoms of water molecules were located from difference Fourier map and refined freely. The final R =0.027 3 and wR =0.068 7 ($w=1/[\sigma^2(F_o^2)+(0.037\ 6P)^2]$, where $P=(F_o^2+2F_c^2)/3$).

CCDC: 748883.

2 Results and discussion

2.1 Structure description of $[Pb_2(C_8H_4O_4)_2(C_{19}H_{12}N_4O)_2]_n \cdot 3.5nH_2O$ (1)

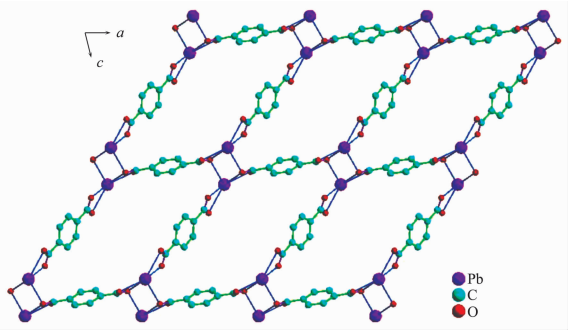
The asymmetric unit of compound **1** consists of one crystallographically independent lead(Ⅱ), one 1,4-BDC dianion, one TCPP ligand and one point seven five free lattice water molecules. As shown in Fig.1, the



Symmetry code: A: $-x-1, -y+2, -z+1$

Fig.1 Coordination and linkage modes of ligands and $Pb^{Ⅱ}$ in **1**, weak interaction in dashed

coordination environment of lead cation and the linkage modes of 1,4-BDC are well denoted. Pb^{II} is in a seven-coordinate environment, supplied by five O atoms from 1,4-BDC, two of which coordinated with center metal by weak interaction, two remainder positions are occupied by two N atoms from a bidentate TCPP ligand. The basic unit of **1** is dinuclear entity which is bonded by two O atom in $\mu_{1,1}$ mode, due to each Pb^{II} of the basic unit was chelated by one carboxylate group of 1,4-BDC extended to four direction, which results in two dimensional network (Fig.2). The bond lengths and angles are given in Table 1. There are π-π stacking interactions with π-π stacking distance the range from 0.338 8 to 0.378 1 nm between TCPP ligands. In this structure, there exist four types of hydrogen bonds (Table 2). Consequently, the three-dimensional supramolecular polymer is generated not only by coordination bonds and weak interactions but also by intermolecular hydrogen bonds and interchain π-π interactions (Fig.3).



All TCPP ligands omitted for clarity

Fig.2　2D network structure of **1** from *b* axis

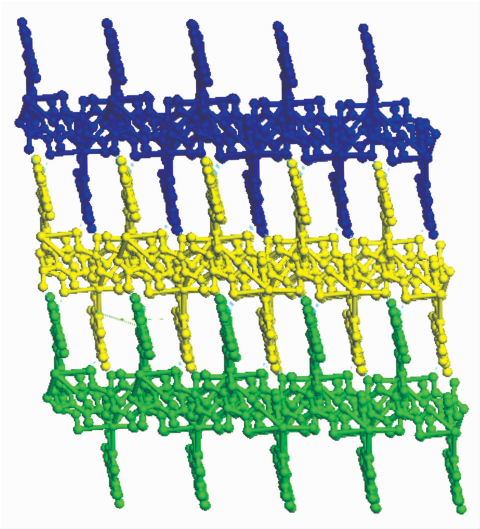


Fig.3　3D structure of **1** in the *ac* plane

Table 1　Selected bond lengths (nm) and bond angles (°)

Pb-O(2)	0.252 5(4)	Pb-O(3)	0.274 8(4)	Pb-N(1)	0.252 5(4)
Pb-O(5)	0.280 7(3)	Pb-O(4)	0.262 2(3)	Pb-O(3B)	0.283 4(3)
Pb-N(2)	0.263 6(4)				
O(2)-Pb-N(1)	75.28(13)	O(2)-Pb-O(3)	49.14(11)	O(2)-Pb-O(4)	133.84(12)
N(1)-Pb-O(3)	70.28(12)	N(1)-Pb-O(4)	78.28(12)	O(4)-Pb-O(3)	86.48(11)
O(2)-Pb-N(2)	78.48(12)	N(2)-Pb-O(3)	117.08(11)	N(1)-Pb-N(2)	63.92(12)
O(4)-Pb-O(5)	48.02(11)	O(4)-Pb-N(2)	121.45(11)	O(3)-Pb-O(3B)	67.20(11)

Table 2　Hydrogen bond lengths and bond angles

D–H···A	D-H / nm	H···A / nm	D···A / nm	∠DHA /(°)	Symmetry code
O(1)–H(1A)···O(2)	0.082 0	0.182 0	0.261 4(5)	163.1	$-x+1, -y+1, -z+1$
N(4)–H(4A)···O(5)	0.086 0	0.198 0	0.277 7(5)	153.5	$-x, -y+1, -z+1$
O(1W)–H(29)···N(3)	0.085 0	0.215 0	0.296 3(6)	160.4	$-x, -y+2, -z$
O(1W)–H(30)···O(4)	0.085 0	0.198 0	0.282 9(6)	173.9	$x, y, z-1$

2.2　IR spectra

The infrared spectrum of the compound **1** displays a broad strong absorption band at 3 380.74 cm^{-1} due to the vibrational modes of water and hydroxide of TCPP ligand. The vibration modes that involve the metal atoms are found in the low energy region. Bands at 1 382.40, 1 445.45, 1 483.10 and 1 546.93 cm^{-1} are the characteristic ones of phenyl and flex vibration of carbonyl group at 1 617.88 cm^{-1}. In the end of the spectra are a series of strong bands at 742.29, 847.26

and 955.37 cm^{-1}, due to the 1,4-BDC stretching.

2.3 Thermogravimetric analyses

The thermogravimetric analysis (TGA) curve recorded at 30~650 ℃ reveals that there are three stages weight losses for compound **1** (Fig.4). The first stage occurred between 90 and 202 ℃ and was attributed to the loss of the free water molecules per formula. The observed weight loss (4.43%) is in agreement with the calculated value (4.40%). The second weight loss from 370 to 430 ℃ (43.61%) corresponds to the removal of the TCPP ligands (Calc. 43.63%). After 430 ℃, the compound **1** begins to lose 1,4-BDC ligand (observed, 22.91%; calculated, 22.94%) and completely decompose until 530 ℃. The final product after 530 ℃ is mainly lead monoxide according to the residual weight.

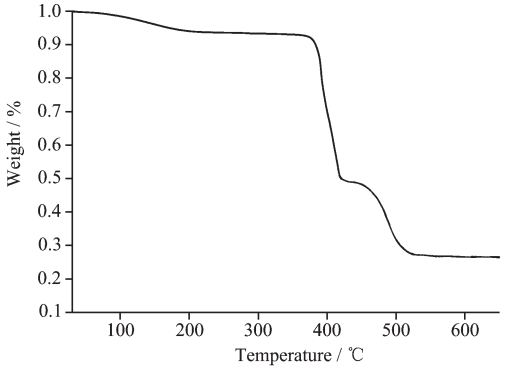


Fig.4 TG curve of complex **1**

2.4 Luminescence properties

Fig.5 shows the emission spectrum of **1** in the solid state measured at room temperature. The free 1,4-H_2BDC and TCPP ligands show emission bands at 407 nm (λ_{ex}=345 nm) and at 430 nm (λ_{ex}=267 nm). The emission band for the free ligand is attributable to the π^*-n transitions[8]. On complexation of the ligand with Pb^{2+} ion, the emission arising from the free ligands were not observable. Compound **1** exhibits photoluminescent emission maximum at 604 nm (λ_{ex}=365 nm) which is similar to those observed in other Pb organic complexes[8]. This emission can be assigned to a metal-centered transition involving the *s* and *p* metal orbitals, as proposed by Vogler et al.[21,22].

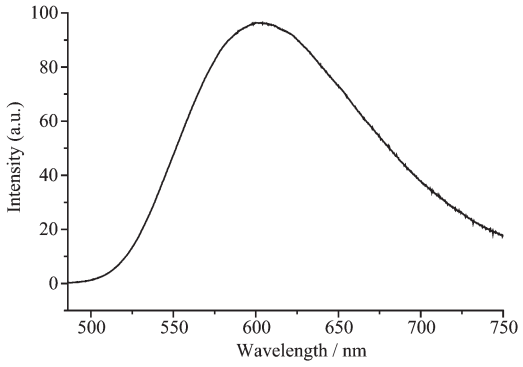


Fig.5 Luminescent spectrum of the compound **1** in the solid state at room temperature

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