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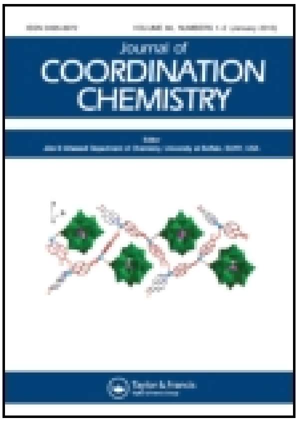

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A lead(II) coordination polymer containing 2-carboxycinnamic acid and 1,10-phenanthroline and its 3-D supramolecular network

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A lead(II) coordination polymer containing 2-carboxycinnamic acid and 1,10-phenanthroline and its 3-D supramolecular network

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The coordination polymer $\{[Pb(cca)(phen)]H_2O\}_n$ (H_2cca = 2-carboxycinnamic acid and phen = 1,10-phenanthroline) was synthesized by hydrothermal reaction and structurally characterized by single-crystal X-ray diffraction. The complex possesses a 1-D chain structure composed of infinite Pb-cca-Pb linkages, in which the $[PbO_4N_2]$ subunits are linked by bridging cca in bis(chelating-bridging) coordination mode. The coordination around the lead(II) is hemi-directed and weak $Pb\cdots O$ interactions are observed that result in a double-chain structure. The chains are combined to generate a 3-D supramolecular structure through interchain $C–H\cdots\pi$, $C–H\cdots O$, and $\pi\cdots\pi$ stacking interactions. Fluorescence of the complex originates from $\pi^*–\pi$ transitions of the ligand.

Keywords: Lead coordination polymer; 2-Carboxycinnamic acid; Crystal structure

1. Introduction

Design and synthesis of metal-organic polymeric complexes have attracted interest owing to intriguing structures and potential applications in magnetism, catalysis, gas-storage, nonlinear optics, etc. [1–8]. 2-Carboxycinnamic acid (H_2cca) with both aromatic rigidity and aliphatic flexibility is a good candidate as a bridging ligand for the construction of metal coordination polymers. The flexibility and conformational changes may cause diverse coordination modes and show significant structure diversity.

Bivalent transition metal complexes with H_2cca and/or different auxiliary ligands have been reported [9–13]. However, the coordination chemistry of main group elements of H_2cca has not been reported. Lead(II) complexes have stereochemical activity of lone pair valence shell electrons, extensively studied by Shimoni-Livny and co-workers [14]. Holo-directed and hemi-directed lead coordination geometries have been defined. The hemi-directed coordination geometry can form weak interactions between lead(II) with a significant gap and oxygen atoms of ligands [14–30]. Understanding the factors that control the stereoactivity of the lone pair in lead(II) complexes should be important for the design of complexing agents that can remove the toxic metal selectively from biological systems [14]. Thus, we have synthesized the

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coordination polymer $\{[Pb(cca)(phen)]H_2O\}_n$ and herein, we report the synthesis and structure of the compound and investigate the stereo-chemical activity of valence shell electron lone pairs. Weak supramolecular interactions control the final array and dimensionality of the complex.

2. Experimental

2.1. *Materials and physical measurements*

2-Carboxycinnamic acid with purity 97% was purchased from Alfa Aesar company. 1,10-Phenanthroline was purchased from Beijing Duxin Chemical company. All other reagents were commercially available and used as received.

Elemental analyses (C, H, and N) were determined on an Elementar Vario EL elemental analyzer. Infrared (IR) spectra were recorded on a Nicolet Avatar 360 FT-IR spectrometer using KBr pellets from 400 to 4000 cm^{-1}. Excitation and emission spectra of the solid samples were recorded on an F-4500 Fluorescence Spectrophotometer at room temperature. Thermogravimetric (TG) analyses were carried out on a WCT-1A Thermal Analyzer at a heating rate of 10°C min^{-1} from room temperature to 1000°C in air.

2.2. *Synthesis of Pb(II) complex*

0.1 mmol of $Pb(NO_3)_2$, 0.1 mmol of 2-carboxycinnamic acid, and 0.1 mmol 1,10-phenanthroline were mixed in 5 mL deionized water. The pH of the solution was adjusted to 5.5 with 0.2 mL NaOH (1 mol L^{-1}) aqueous solution. The mixture was transferred to a 25 mL Teflon-lined stainless steel bomb and kept at 140°C under autogenous pressure for 3 days. The mixture was cooled to room temperature at 5°C h^{-1} and filtered, colorless block crystals were obtained. Yield: 76% (based on Pb). Anal. Calcd for $C_{22}H_{16}N_2O_5Pb$(595.57) (%): C, 44.37; H, 2.71; N, 4.70. Found (%): C, 44.06; H, 2.50; N, 4.89. Selected IR (KBr pellet, cm^{-1}): 3441(s, br), 1640(m), 1571(m), 1528(s), 1386(vs), 1287(w), 1202(w), 861(m), 853(m), 776(m), 729(m), 598(m), 415(w).

2.3. *Single-crystal X-ray diffraction*

X-ray single-crystal data collections for the complex were performed on a Bruker SMART CCD diffractometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 296(2) K. Semi-empirical absorption corrections were applied. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXS-97 and SHELXL-97 programs [31, 32]. All non-hydrogen atoms in the complex were refined anisotropically. Hydrogen atoms were generated geometrically and treated by a mixture of independent and constrained refinement. A summary of the crystallographic data and details of the structure refinements are listed in table 1. Selected bond distances and angles for the complex are listed in table 2.

Table 1. Crystallographic data and structure refinement of the complex.

Empirical formula	$C_{22}H_{16}N_2O_5Pb$
Formula weight	595.57
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions (Å, °)	
a	23.1614(4)
b	10.7241(2)
c	17.4725(3)
β	115.306(1)
Volume (Å^3), Z	3923.44(12), 8
Calculated density (Mg m^{-3})	2.016
Absorption coefficient (mm^{-1})	8.638
$F(000)$	2272
Crystal size (mm^3)	0.30 × 0.20 × 0.10
θ range for data collection (°)	2.1–27.5
Limiting indices	$-30 \le h \le 28$; $-13 \le k \le 13$; $-22 \le l \le 22$
Reflections collected/unique	26,394/4502
Reflections observed [$I > 2\sigma(I)$]	3901
Data/restraints/parameters	4502/279
Goodness-of-fit on F^2	1.072
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0191$, $wR_2 = 0.0423$
R indices (all data)	$R_1 = 0.0256$, $wR_2 = 0.0443$
Largest difference peak and hole (e Å^{-3})	−1.136 and 0.490

Table 2. Selected bond lengths (Å) and angles (°) for the complex.

N(1)–Pb(1)	2.759(3)	N(2)–Pb(1)	2.553(3)
O(1)–Pb(1)#1	2.671(3)	O(2)–Pb(1)#1	2.511(2)
O(3)–Pb(1)	2.718(2)	O(4)–Pb(1)	2.454(2)
O(4)–Pb(1)–N(2)	72.01(8)	O(2)#2–Pb(1)–N(2)	77.63(8)
O(4)–Pb(1)–O(1)#2	70.48(8)	O(2)#2–Pb(1)–O(1)#2	50.45(7)
N(2)–Pb(1)–O(1)#2	118.40(8)	O(4)–Pb(1)–O(3)	50.05(7)
O(2)#2–Pb(1)–O(3)	131.90(7)	N(2)–Pb(1)–O(3)	82.16(8)
O(1)#2–Pb(1)–O(3)	107.20(8)	O(4)–Pb(1)–N(1)	107.39(8)
O(2)#2–Pb(1)–N(1)	131.62(8)	N(2)–Pb(1)–N(1)	62.01(8)
O(1)#2–Pb(1)–N(1)	177.16(8)	O(3)–Pb(1)–N(1)	69.98(8)

Symmetry transformations used to generate equivalent atoms: #1: $1/2 - x$, $5/2 + y$, $3/2 - z$; #2: $1/2 - x$, $5/2 + y$, $1/2 - z$.

3. Results and discussion

3.1. *Structural description*

The crystal structure of the complex is shown in figure 1. The complex features a 1-D chain structure constructed from single cca as a long bridge that links Pb^{2+} ions, a rare example of lead(II)-carboxylate complexes [22–30]. The asymmetric unit of the complex contains [Pb(cca)(phen)] and a lattice water. The Pb^{2+} is six coordinate by four oxygen atoms from two cca ligands and two nitrogen atoms from chelating phen (figure 1a). The bond distances of Pb–O vary from 2.454(2) to 2.718(2) Å with the an average value of 2.589 Å. The bond distances of Pb–N are 2.553(3) and 2.759(3) Å, respectively, with an average value of 2.656 Å. Pb–O and Pb–N distances are close to the reported ones [22, 23, 33–35]. The cca ligand adopts bis(bidentate-chelating) mode to coordinate two Pb^{2+} ions, forming a Pb-cca-Pb linkage. A 1-D chain is formed through the infinite

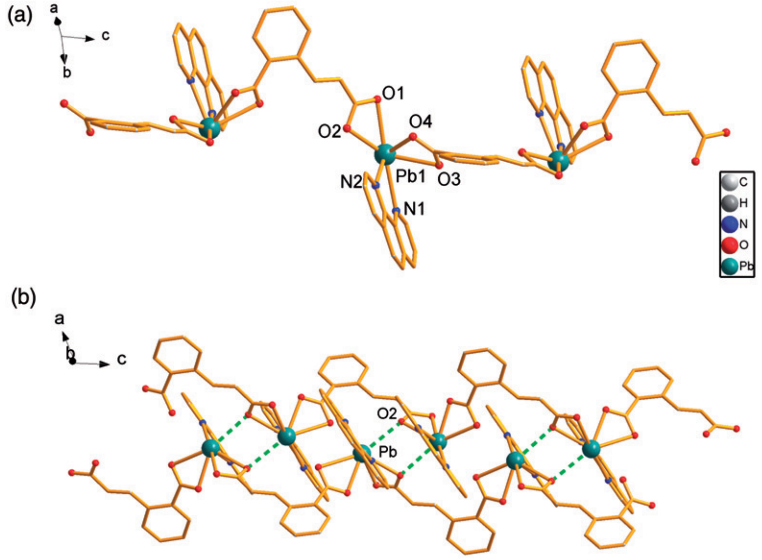

Figure 1. View of the structure of the complex: (a) The coordination environment of Pb^{2+} and the 1-D chain. All hydrogen atoms and free water molecules are omitted for clarity. (b) 1-D double chain *via* weak Pb···O bonds. (c) 3-D network and C–H···O, C–H···π, O1W–H1W···O4, and $\pi\cdots\pi$ stacking interactions.

extension Pb-cca-Pb. The distance between two neighboring Pb^{2+} ions is 8.755 Å. The chelating phen ligands around Pb^{2+} are almost parallel with the dihedral angle of 4.42°.

The distance between Pb^{2+} and O2 is 2.929 Å, significantly shorter than the sum of the van der Waals radii (Pb···O, 3.40 Å) [36, 37], indicating a weak interaction between Pb^{2+} and oxygen of cca dianion. The complex is hemi-directed with a significant gap on $Pb^{2+,}$ indicating that the lone pair of electrons on Pb^{2+} is stereochemically active. Such an environment leaves space for the bonding of oxygen atoms of cca dianions from adjacent 1-D chains, resulting in an infinite double-chain structure (figure 1b).

C–H···π interactions exist between phen and cca from the neighboring chain [C12–H12(phen)···Cg^{j}(cca), 3.576(5) Å, 148° (Cg is the centroid of aromatic ring (C4/C9) of cca; symmetry codes: $j = -x,\ 1-y,\ 1-z$)]. C–H···O hydrogen bonds are formed between phen and cca [C15–H15···$O1^{a}$, 3.329(5) Å, 165°; symmetry codes: $a = x,\ 1-y,\ -1/2+z$]. Face-to-face $\pi\cdots\pi$ stacking interactions occur between adjacent phen molecules from neighboring chains at 3.678 Å. The uncoordinated water and chain are connected by hydrogen bonds [O1W–H1WA···O4, 2.990(7) Å, 137(10)°]. The stability of the complex is further enhanced by the weak interchain contacts and the 1-D chain is developed into a 3-D supramolecular network (figure 1c).

3.2. *Fluorescence spectra*

The fluorescence spectra of the complex and the free ligand in the solid state were recorded at room temperature upon excitation at 380 nm (figure 2). The compound exhibits two intense emission bands with one maximum peak at 409 nm, the other at 435 nm with a shoulder at 459 nm. Free H_2cca and phen exhibit two emission bands at

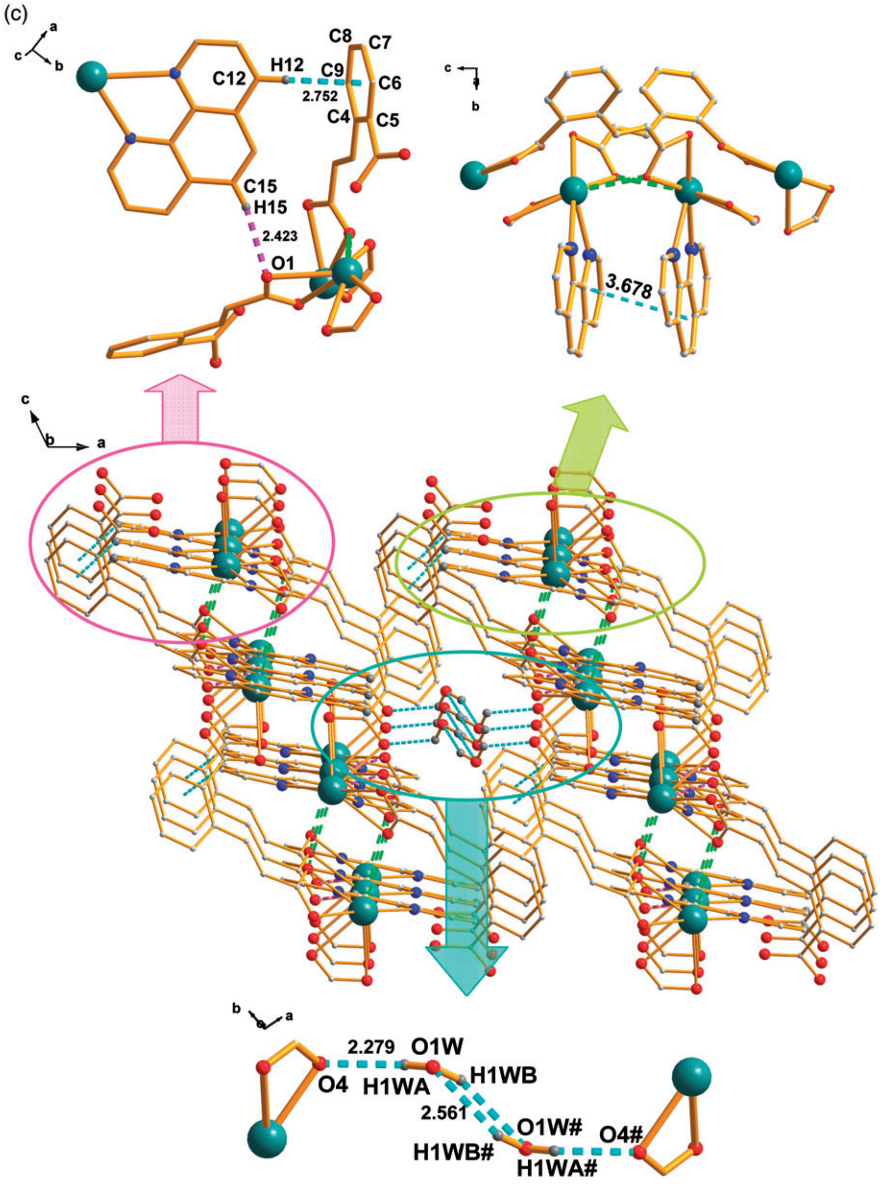

Figure 1. Continued.

409 and 439 nm. The fluorescence spectrum of the complex can be attributed to the π^*–π transition of the ligands [22, 38–42].

3.3. *TG analysis*

TGA-DTA analyses of the complex were studied from room temperature to 1000°C (figure 3). A thermal gravimetric analysis indicates that the first weight loss of 3.13%

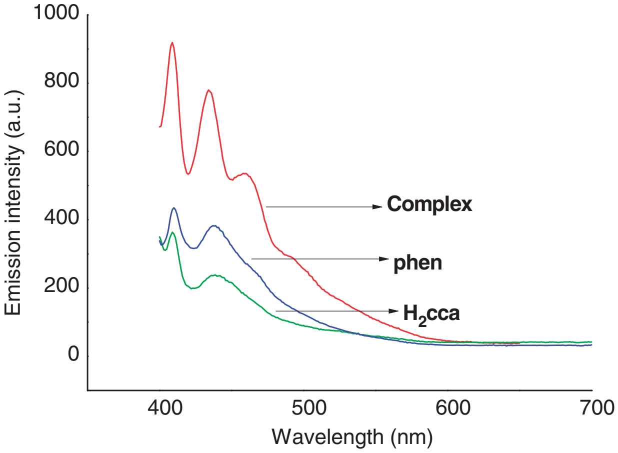

Figure 2. The emission spectra of the complex, phen, and H_2cca ligands ($\lambda_{ex} = 385$ nm).

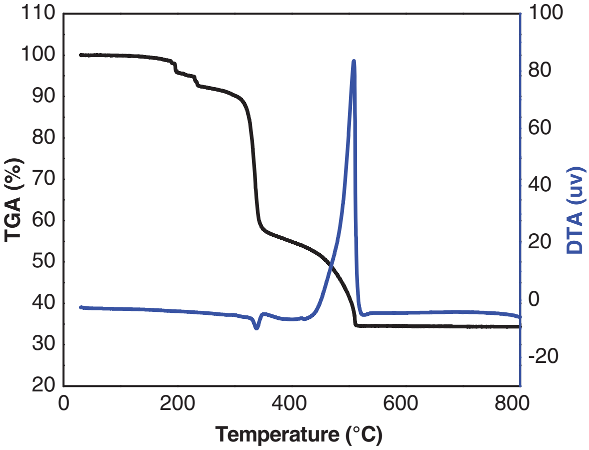

Figure 3. The DTA-TGA graph of the complex.

occurred at 113°C, equivalent to the removal of lattice water (Calcd 3.03%). A complicated decomposition reaction then takes place with continued heating. By 514°C the complex was completely degraded and the final residue weight is 36.42%, which corresponds to the PbO as a final product (Calcd 37.45%). These weight losses are accompanied by endothermic effect with maximum at 340°C and intense exothermic effect with maximum at 508°C on the DTA curve.

4. Conclusion

The coordination polymer $\{[Pb(cca)(phen)]H_2O\}_n$ possesses a 1-D chain of infinite Pb-cca-Pb linkages. Pb^{2+} is in a hemi-directed six-coordinate polyhedron. Pb$\cdots$O weak interaction leads to 1-D double-chain which further interacts with each other *via* C–H$\cdots\pi$, C–H$\cdots$O, and $\pi\cdots\pi$ interactions to create a 3-D supramolecular network.

Supplementary material

Crystallographic data for the compound has have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference number 770588 for the complex. Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Tel: (44) 01223 762910; Fax: (44) 01223 336033; Email: deposit@ccdc.cam.ac.uk or visit website: http://www.ccdc.cam.ac.uk/deposit).

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