Hydrothermal Synthesis, Crystal Structure and Properties of a Novel Phosphorus-containing 3D Metal-Organic Cd(II) Coordination Polymer

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A metal-organic framework $[Cd(dppip)]_n$ (**1**) based on 5-(diphenylphosphino)isophthalic acid (H_2dppip) has been synthesized hydrothermally and characterized by IR spectroscopy, elemental analysis, and X-ray crystallography. $[Cd(dppip)]_n$ shows a sheet structure owing to carboxylate bridging with windows with dimensions 10.692×9.325 Å^2. The layers are further connected through P–Cd interactions to give a three-dimensional supramolecular network. The thermal analysis (DTA) of complex **1** exhibited an exceptionally high thermal stability (m. p. 452.8 °C). The compound shows fluorescence at *ca.* 418 nm upon excitation at 314 nm.

Key words: 5-(Diphenylphosphino)isophthalic Acid, P–Cd Interactions, 3D Metal-Organic Framework

Introduction

In recent years, metal-organic frameworks (MOFs) have been rapidly developed because of their fascinating variety of architecture topologies and potential applications as functional materials, such as for gas adsorption, separation, catalytic activities, optoelectronic materials, luminescence, and magnetism [1 – 3]. The self-assembly of multidentate organic ligands and metal ions is currently the most efficient approach towards coordination polymer frameworks, whose structures are influenced by the subtle interplay of many factors, such as the geometric preference of metal ions, and the sizes and shapes of the organic building blocks [4 – 6]. In many studies, multicarboxylate ligands separated by various rigid or flexible spacers are good candidates for the construction of coordination frameworks [7 – 11]. On the other hand, phosphine ligands have been intensively used in coordination chemistry because of their specific electron-donating power [12 – 19]. The rich diversity of functional groups which can be bonded to the central phosphorus atom is reflected in the large activity in this field.

According to the situation above, and based on our work done before [9 – 11], we focused on the design and synthesis of hybrid ligands which contain tertiary phosphine and multicarboxylate groups that will selectively coordinate to transition metals [20 – 24]. With the aim of better understanding the influence of phosphines on the resultant structure, we have selected the asymmetrical ligand 5-(diphenylphosphino)isophthalic acid (H_2dppip) to carry out a self-assembly of a novel 3D Cd(II) coordination polymer $[Cd(dppip)]_n$ (**1**). Furthermore, the photoluminescence and thermal properties of **1** have been investigated.

Experimental Section

Materials and physical measurements

5-(Diphenylphosphino)isophthalic acid (H_2dppip) was prepared according to the literature [25, 26], and the crystals were purified by washing with hydrochloric acid and recrystallization. All the reagents and solvents for the synthesis were commercially available at analytical grade and used without further purification or with purification by standard methods prior to use. Elemental analyses for C, H and N were carried out on a Perkin-Elmer 240 elemental analyzer. The Fourier transform infrared (FT-IR) spectra were obtained in the range of 4000 – 400 cm^{-1} on KBr pellets with a Bruker Vector 22 spectrometer. Thermogravimetric measurements were carried out from room temperature to 700 °C on crystalline samples in a nitrogen stream using a SDT 2960 thermal analyzer at a heating rate of 20 °C min^{-1}. Luminescence spectra for the solid samples were recorded on a Hitachi 850 fluorescence spectrophotometer.

*Preparation of the complex $[Cd(dppip)]_n$ (**1**)*

Compound **1** was synthesized hydrothermally in a Teflon-lined stainless-steel container by heating a mixture of 5-(diphenylphosphino)isophthalic acid (0.0175 g, 0.05 mmol), $Cd(NO_3)_2 \cdot 6H_2O$ (0.0154 g, 0.05 mmol) and LiOH (0.0043 g, 0.1 mmol) in 7 mL of distilled water at 120 °C for 3 days. After cooling to room temperature, colorless needle-shaped crystals of **1** were obtained in 82 % yield

based on Cd. – Anal. for $C_{20}H_{13}PO_4Cd$ (460.67): calcd. C 52.14, H 2.84; found C 52.12, H 2.79. – IR (KBr, cm^{-1}): $\nu = 3059$ (w), 1598 (s), 1546 (s), 1436 (vs), 1367 (vs), 1188 (m), 1118 (m), 997 (w), 873 (w), 773 (m), 744 (m), 691 (m).

Crystal structure determination

Single crystals suitable for X-ray analysis were used for intensity data collection on a Bruker Smart Apex CCD diffractometer [27] using graphite-monochromatized MoK_α radiation ($\lambda = 0.71073$ Å) at room temperature using the ω-scan technique. Lorentz, polarization and absorption corrections were applied. The structures were solved by Direct Methods with SHELXS-97 [28] and refined with full-matrix least-squares using the SHELXL-97 program [29]. Anisotropic displacement parameters were assigned to all non-hydrogen atoms. Analytical expressions of neutral atom scattering factors were employed, and anomalous dispersion corrections were incorporated. Crystal data and numbers pertinent to data collection and structure refinement are summarized in Table 1. Selected bond lengths and bond angles are listed in Table 2.

CCDC 852817 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystal and structure refinement data for **1**.

Formula	$C_{20}H_{13}PO_4Cd$
M_r	460.67
Crystal size, mm^3	$0.21 \times 0.20 \times 0.19$
Crystal system	monoclinic
Space group	$P2_1/c$
a, Å	10.808(3)
b, Å	14.067(2)
c, Å	15.788(4)
β, deg	132.447(15)
V, $Å^3$	1771.2(7)
Z	4
D_{calcd}, g cm^{-3}	1.73
μ(MoK_α), mm^{-1}	1.4
F(000), e	912
θ range data collection, deg	2.94 – 24.71
hkl range	$-12 \rightarrow 11$, ± 16, $-18 \rightarrow 17$
Refl. measd / unique / R_{int}	6953 / 3010 / 0.0872
Param. refined	235
$R1^a$ / $wR2^b$ [$I > 2\,\sigma(I)$]	0.0960 / 0.1796
$R1^a$ / $wR2^b$ (all data)	0.1809 / 0.2138
GoF^c (F^2)	1.062
$\Delta\rho_{fin}$ (max / min), e $Å^{-3}$	1.53 / −1.65

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$; [c] $GoF = [\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

Table 2. Selected bond lengths (Å) and angles (deg) for **1**[a].

Distances			
Cd(1)–O(1)$^{\#1}$	2.225(9)	Cd(1)–O(2)$^{\#2}$	2.227(11)
Cd(1)–O(3)	2.342(9)	Cd(1)–O(4)	2.333(10)
Cd(1)–P(1)$^{\#3}$	2.802(4)		
Angles			
O(1)$^{\#1}$–Cd(1)–O(3)	108.5(4)	O(2)$^{\#2}$–Cd(1)–O(3)	87.1(4)
O(4)–Cd(1)–O(3)	55.0(3)	P(1)$^{\#3}$–Cd(1)–O(3)	141.7(3)
O(1)$^{\#1}$–Cd(1)–O(4)	88.9(4)	O(2)$^{\#2}$–Cd(1)–O(4)	139.9(3)
P(1)$^{\#3}$–Cd(1)–O(4)	100.8(3)	O(1)$^{\#1}$–Cd(1)–O(2)$^{\#2}$	118.5(4)
P(1)$^{\#3}$–Cd(1)–O(2)$^{\#2}$	102.7(3)	P(1)$^{\#3}$–Cd(1)–O(1)$^{\#1}$	99.2(3)

[a] Symmetry codes: $^{\#1}$ $1-x$, $-0.5+y$, $1.5-z$; $^{\#2}$ $1+x$, $1.5-y$, $0.5+z$; $^{\#3}$ $1-x$, $1-y$, $1-z$.

Results and Discussions

*Structural description of [Cd(dppip)]$_n$ (**1**)*

X-Ray crystallographic analysis revealed that complex **1** crystallizes in the monoclinic space group $P2_1/c$. The metal-ligand connectivity pattern is depicted in Fig. 1. Table 2 contains important bond lengths and angles. Each asymmetric unit consists of one Cd(II) ion and one dppip^{2-} anion. Each Cd(II) ion is fourfold-coordinated by the two chelating oxygen atoms O3 and O4 from one carboxylate group of the ligand and the two bridging oxygen atoms O1#2 and O2#3 from carboxylate groups of two different dppip^{2-} ligands. A weaker P1–Cd interaction (2.802(4) Å) leads to a distorted trigonal-bipyramidal geometry with O1#2, O2#3 and O4 in the equatorial plane, and P1#1 and O3 in the axial positions. The cadmium ion is 0.085 Å out of

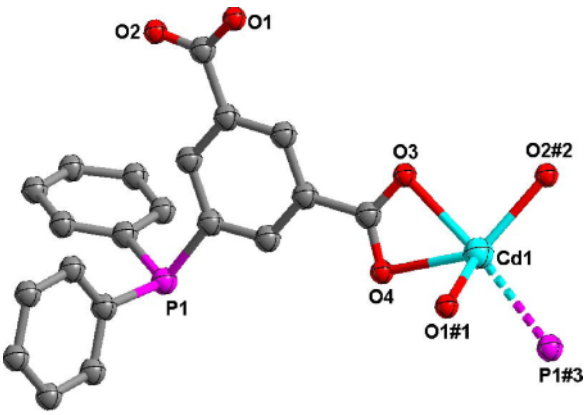

Fig. 1 (color online). Metal coordination and atom labeling in complex **1** (ellipsoids at 50% probability level). All hydrogen atoms are omitted for clarity.

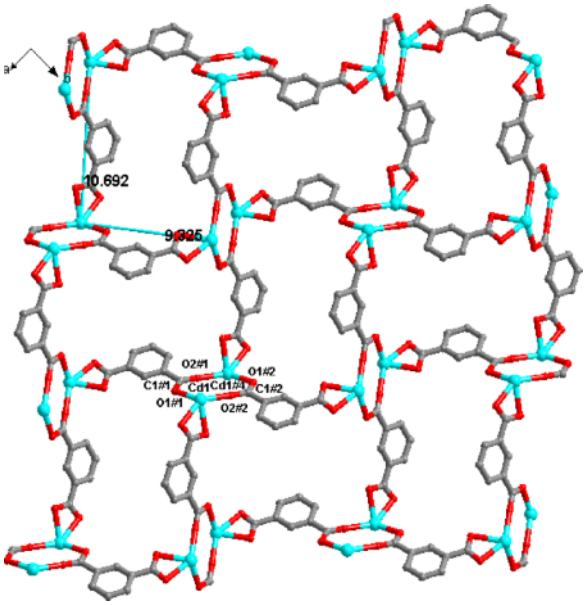

Fig. 2 (color online). View of extended sheets of **1** being located parallel to the crystallographic *ab* plane.

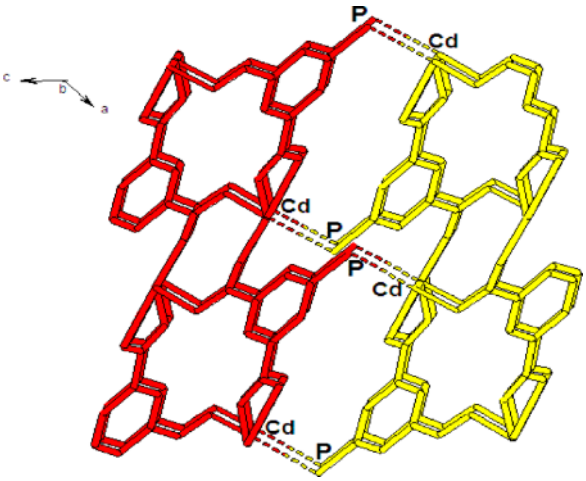

Fig. 3 (color online). The 3D network structure linked by P–Cd interactions.

the equatorial plane. Angular distortions are observed both in the equatorial plane, with bond angles in the range 88.98(8) – 139.77(6)°, and along the axial direction of the bipyramid with a P1#1–Cd–O3 angle of 141.7(3)°. The two carboxylate groups of $dppip^{2-}$ show bidentate chelating and bidentate bridging coordination modes. Two neighboring Cd(II) ions are joined together to produce a small eight-membered bimetallic $[Cd_2(CO_2)_2]$ ring, with a Cd···Cd distance of 4.215 Å. Each bimetallic unit connects four isophthalic acid anions $dppip^{2-}$, and in turn each isophthalate anion links two bimetallic units to give a sheet, showing a window with dimensions 10.692 × 9.325 $Å^2$ (Fig. 2). These sheets are linked together through P–Cd interactions into a 3D network structure (Fig. 3). From the topological view, if each dimeric $[Cd_2(CO_2)_2]$ unit is considered as a 6-connected node (being coordinated by six $dppip^{2-}$ ligands) and the $dppip^{2-}$ ligand as a 3-connected node, we reach a 3D supramolecular network with 6^3 topology (Fig. 4).

*Thermal analysis of complex **1***

The thermogravimetric analysis (TGA) experiment was conducted to determine the thermal stability of this complex, which is an important aspect for metal-organic frameworks. TGA was performed on crys-

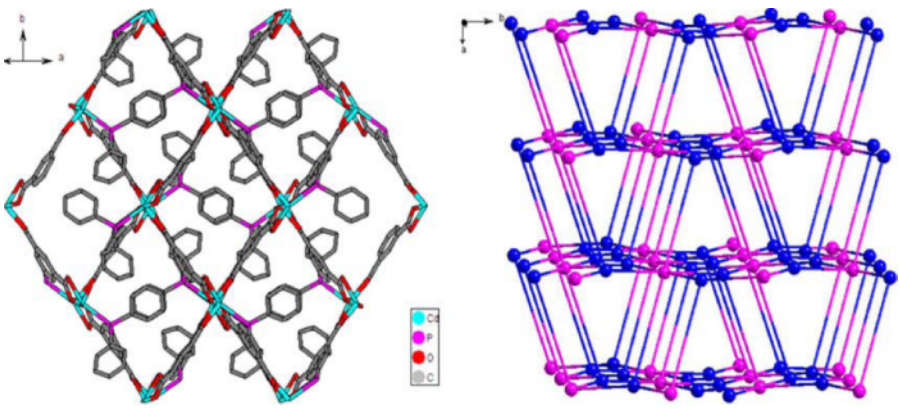

Fig. 4 (color online). 3D framework structure and schematic view of the 6^3 topology of **1**. Schematic presentations of a single 3D net of **1**: Six-connecting nodes as $[Cd_2(CO_2)_2]$ units are represented by red balls, and three-connecting nodes as $dppip^{2-}$ ligands represented by blue balls.

talline samples of **1** in the range of 25 – 700 °C. The host framework is stable up to 452.8 °C and the one-step weight loss rapidly happens from 452 to 500 °C probably to be attributed to the complete decomposition of the ligand.

*Luminescence properties of complex **1***

The luminescence properties of complex **1** were investigated in the solid state at room temperature. Compound **1** exhibits an intense green-blue emission at 418 nm upon excitation at 314 nm. The ligand exhibits an emission maximum at around 563 nm (λ_{ex} = 284 nm). In comparison, the emission frequency of compound **1** is obviously blue-shifted and may be assigned to the ligand-to-metal charge transfer (LMCT).

Conclusion

In summary, we present here a novel three-dimensional Cd(II) coordination polymer $[Cd(dppip)]_n$ assembled from the relatively rigid phosphorus-containing asymmetrical linker H_2dppip under hydrothermal conditions. We have observed that the long P–Cd bond is strong enough to stabilize a 3D framework. More importantly, compound **1** may have potential use as a heat resistant and fire retardant material because of its high thermal stability.

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