Two New Hemidirected Lead(II) Complexes: [Pb(pcih)(bha)] and [Pb(pcih)(NO_3)]

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Two new lead(II) complexes [Pb(pcih)(bha)] (**1**) and [Pb(pcih)(NO_3)] (**2**, Hpcih = 1,4-bis(3-pyridyl)-2,3-diazo-1,3-butadiene, Hbha = 2-hydroxybenzoic acid) have been synthesized by solvothermal methods and structurally characterized. The single-crystal X-ray data show that the coordination spheres of the Pb^{2+} ions in **1** and **2** are hemidirected with stereochemically active electron lone pairs. There are some significant secondary Pb···N and Pb···O interactions which produce two different extended structures, namely a 1D chain in **1** and a 2D layer in **2**. Both **1** and **2** exhibit fluorescence properties at room temperature.

Key words: Lead(II) Complex, Crystal Structure, Solvothermal Synthesis, Hemidirected

Introduction

The rational design and synthesis of metal-organic coordination polymers have attracted intense interest owing to their fascinating structural diversities and their potential for use as functional materials in catalysis, molecular recognition, separation, and nonlinear optics [1]. The control over the network dimensionality and topology of these polymers can be achieved from judicious considerations of a variety of influencing factors, basically including structural characteristics of the organic ligand spacers and the coordination environment of the metal nodes. Among various ligands, rigid bipyridyl-based ligands containing free organic functional groups (such as -CONH-, -CR=N-, and -CH=N-) are often employed to construct extended frameworks with high structural stability and special topologies, as exemplified by 1D chain polymers $M(L_1)_2(NO_3)_2$ (M = Co and Cd; L_1 = 2,5-bis(3-pyridyl)-3,4-diaza-2,4-hexadiene) [2], 2D brick wall sheets of the types $[Cd(NO_3)_2(L_2)_{1.5}\cdot 0.5(L_2)]_n$ and $[Co(L_2)_{1.5}(NO_3)_2(H_2O)(CH_2Cl_2)_2]_n$ (L_2 = 1,4-bis(3-pyridyl)-2,3-diaza-1,3-butadiene) [2, 3], a 3D interpenetrating rhombus-grid polymer $[Ni(L_2)_2(NO_3)_2$-$(OC_4H_8)_{1.66}(H_2O)_{0.33}]_n$ [3], and 3D open framework polymers $\{[CuL_3(H_2O)(SO_4)](H_2O)_2\}_n$ and $\{[CdL_3$-$(NCS)_2](CH_3OH)_{1.5}\}_n$ (L_3 = 2,5-bis(4-pyridyl)1,3,4-thiadiazole) [4]. The above-mentioned frameworks are all built from metal ions and bridging ligands linked by normal coordinative covalent bonds, but extended polymers of bipyridyl ligands based on the combination of normal coordinative covalent bonds and secondary coordinative interactions are relatively rare.

Furthermore, the design and control over metal-organic coordination polymers has mainly focused on the incorporation of *d*- or *f*-block metals as coordination centers, whereas less attention has been paid to the *p*-block metals [5]. Pb^{2+}, as a heavy *p*-block metal ion, possesses a large radius, a stereochemically active lone pair, and a flexible coordination environment, which leads to new classes of coordination polymers with novel structures coupled with unusual properties. However, very little research has been carried out on a systematic elucidation of the structure formation of lead(II) complexes with rigid organic bipyridyl-based ligands. To understand the Pb^{2+} chemistry with bipyridyl-based ligands, the 1,4-bis(3-pyridyl)-2,3-diazo-1,3-butadiene ligand (Hpcih) has been selected for synthesizing novel coordination polymers in our laboratory, and a 3D extended lead(II) coordination polymer $[Pb(pcih)]_2(NO_3)_2(H_2O)$ has been synthesized [6]. As part of the continuing work in this system, here we report the solvothermal synthesis, structure, and characterization of the two new lead(II) complexes [Pb(pcih)(bha)] (**1**; Hbha = 2-hydroxybenzoic acid) and [Pb(pcih)(NO_3)] (**2**). The hemidirecting Pb^{2+} ions in **1** and **2** are further linked *via* secondary Pb···N and Pb···O interactions, forming a 1D extended chain in **1** and a 2D extended layer in **2**.

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Results and Discussion

Complex **1** crystallizes in the triclinic crystal system with space group $P\bar{1}$. The asymmetric unit of **1** contains one unique Pb^{2+} ion, one deprotonated Hpcih ligand and one deprotonated Hbha ligand (Fig. 1a). The Pb^{2+} ion is coordinated by two N atoms and one O atom of one $pcih^-$ ligand, and two O atoms of one bha^- anion (2.390(3) – 2.744(3) Å for Pb–O and 2.436(3) – 2.563(4) Å for Pb–N) to form a hemidirected pentahedral geometry [7], which suggests a gap or hole in the coordination sphere around the Pb^{2+} ion occupied by a stereochemically active lone pair of electrons on the Pb^{2+} ion. The shorter Pb1–O2 bond (2.390(3) Å) is observed opposite to the position of the putative lone pair, while the longer Pb1–O3 bond (2.744(3) Å) is adjacent to the position of the lone pair. Such a coordination environment of the Pb^{2+} ion leaves space for the bonding of N atoms of an adjacent $pcih^-$ ligand and of an O atom of a bha^- ligand. In this way, the Pb atoms also have significant secondary Pb···N and Pb···O interactions, whose distances are longer than the sum of the ionic radii but significantly shorter than the sum of the van der Waals radii (3.54 Å for Pb···N and 3.40 Å for Pb···O) [6, 8]. The Pb1 atom in **1** exhibits two long additional contacts with N and O atoms (3.107 Å for Pb1···N3A and 3.115 Å for Pb1···O4B) to form another hemidirected heptahedral geometry (Fig. 1b). Pairs of adjacent neutral [Pb(pcih)(bha)] molecules are bridged into centrosymmetric dimeric units $[Pb(pcih)(bha)]_2$ by two secondary Pb···N interactions, which are further interconnected *via* secondary Pb···O interactions resulting in a 1D chain structure (Fig. 1c). In addition, there are obviously face-to-face π-π stacking interactions between aromatic rings belonging to adjacent non-coordinating and coordinating pyridyl rings in **1**. The nearest distance between the neighboring pyridyl rings is 3.224 Å, suggesting an important role in stabilizing **1** in the solid state.

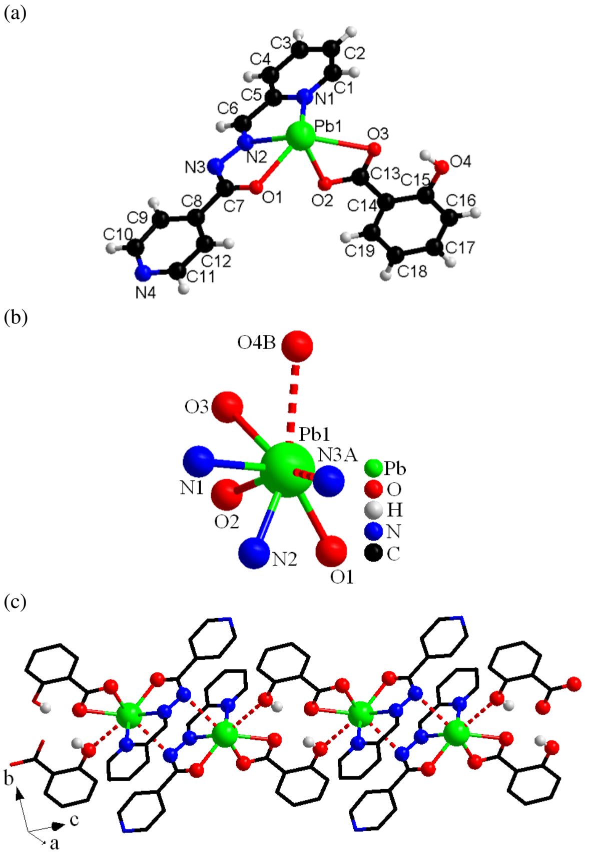

Fig. 1 (color online). (a) Molecular structure of **1**, showing the atom labeling scheme; (b) the coordination environment of the Pb atom in **1**, showing secondary Pb···N and Pb···O interactions [symmetry operations: (A) $1-x$, $1-y$, $-z$; (B) $2-x$, $1-y$, $1-z$]; (c) part of the crystal structure of **1**, showing the formation of a 1D chain constructed by secondary Pb···N and Pb···O interactions.

Complex **2** crystallizes in the monoclinic crystal system with space group $P2_1/c$. The asymmetric unit of **2** is composed of one unique Pb^{2+} ion, one deprotonated Hpcih ligand and one nitrate anion (Fig. 2a). The Pb^{2+} ion is surrounded by two N atoms and one O atom of a $bipd^-$ anion, and one O atom of one NO_3^- anion to form a hemidirected tetrahedral geometry [7] with Pb–O bonds lengths between 2.382(4) and 2.394(4) Å and Pb–N bonds varying from 2.474(5) to 2.677(5) Å. Apparently, the coordinative bonds around the Pb^{2+} ion lie in an irregular hemisphere with N1 near the equator, and with N2, O1 and O2 approximately opposite to the lone pair. The hemidirected coordination environment of the Pb^{2+} ion in **2** resembles that of **1** in that the Pb atom also has secondary Pb···O and Pb···N interactions and displays three long additional contacts with N and O atoms (2.810 Å for Pb1–O4, 3.205 Å for Pb1···N3A and 2.823 Å for Pb1···N4B) to form another hemidirected heptahedral geometry (Fig. 2b). The adjacent neutral $[Pb(pcih)(NO_3)]$ molecules are linked by secondary Pb1···N4 interactions to form an infinite zigzag chain along the [010] direction. These chains are aligned in an antiparallel fashion and are further connected *via* secondary Pb1···N3 interactions forming a layered arrangement parallel to the (001) plane (Fig. 2c). The

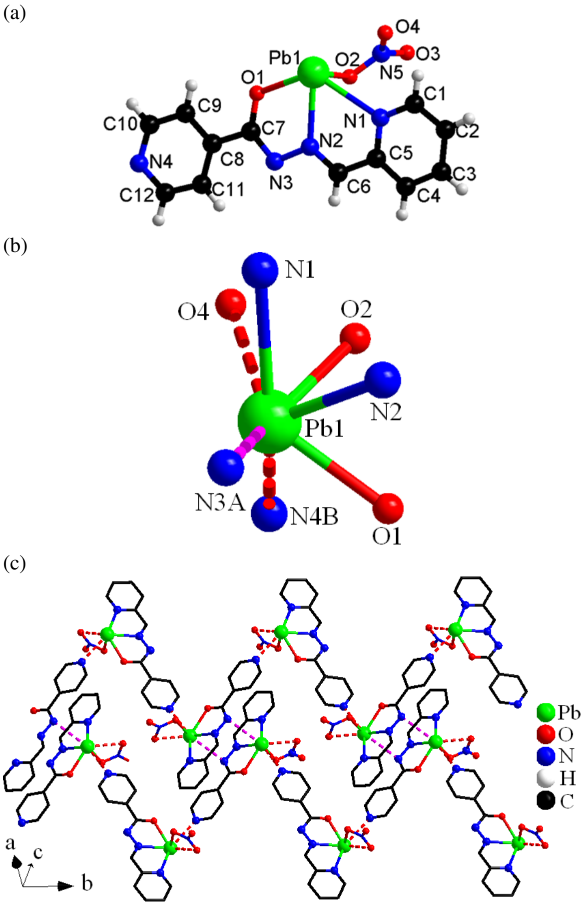

Fig. 2 (color online). (a) Molecular structure of **2**, showing the atom labeling scheme; (b) the coordination environment of the Pb atom in **2**, showing secondary Pb···N and Pb···O interactions [symmetry operations: (A) $-4-x$, $-y$, $-2-z$; (B) $-3-x$, $-0.5+y$, $-1.5-z$]; (c) part of the crystal structure of **2**, showing the formation of a 2D chain constructed by secondary Pb···N and Pb···O interactions.

face-to-face π-π stacking interactions (the nearest distance between neighboring pyridyl rings is 3.375 Å), which are similar to those of **1**, play an important role in stabilizing **2** in the solid state.

So far, the reported complexes of the neutral and deprotonated Hpcih ligand are usually discrete, as exemplified by $[Co(pcih)_2CoCl_3] \cdot 2H_2O$ [9], $[\{MnCl_2(DMSO)(Hpcih)\}_2Mn(DMSO)_2Cl_2]$ [9], $[Cu(pcih)_2]$ [9], $[Co(Hpcih)(pcih)](NO_3)_2 \cdot H_2O \cdot 0.5CH_3OH$ [9], $[Ni(pcih)_2] \cdot 2H_2O$ [9] and $[Cu(Hpcih)(PPh_3)_2]ClO_4 \cdot C_2H_5OH$ [10], mainly because the pyridyl N atom of isonicotinic acid hydrazide is not coordinated. Coordination polymers are relatively rare, the limited examples including the 3D polymer $[Zn(Hpcih)SO_4]$ [9], whose 3D framework is constructed by the linkage of 2D $[Zn(Hpcih)^{2+}]_n$ layers and sulfate anions, and $\{[Pb(pcih)]_2(NO_3)_2\}$-(H_2O), in which the 3D framework is built from 1D $\{[Pb(pcih)]_2(NO_3)_2\}_n$ zigzag chains connected *via* secondary Pb···N and Pb···O bonds [6]. However, 1D or 2D coordination polymers of the Hpcih ligand to the best of our knowledge have not been observed until now. Therefore, both **1** and **2** provide the only examples of 1D or 2D coordination polymers of the Hpcih ligand.

Another unusual feature of **1** and **2** is that the Pb atoms do not complete their coordination spheres by socalled secondary bonds to N or O atoms. The reported hemidirected lead environments, which bear a stereochemically active lone pair, leave space for bonding of other donor atoms (such as O and N atoms) of adjacent molecules, and the hemidirected system is usually extended to a holodirected system *via* weaker secondary coordinative bonds to have the coordination sphere completed [6, 8, 11]. For instance, in $[Pb(ampy)(sac)_2]$ (ampy = 2-aminomethylpyridine, sac = saccharinate) [11a], the mono-nuclear hemidirected lead(II) centers are linked into 1D chains with holodirected lead(II) by weak Pb···O interactions, and the hemidirected dimeric mixed-ligands lead(II) centers in $[Pb_2(2,2'\text{-bipy})_2(\mu\text{-}4,4'\text{-bipy})(NO_3)_4]$ (2,2′-bipy =2,2′-bipyridine and 4,4′-bipy = 4,4′-bipyridine) [11b] are extended to holodirected 2D layers by similar weak interactions. Therefore, the extended polymers of **1** and **2** with incomplete coordination spheres are significantly different from the reported lead(II) complexes and represent a new type.

The solid-state fluorescent spectra of Hpcih, **1** and **2** were investigated at room temperature upon excita-

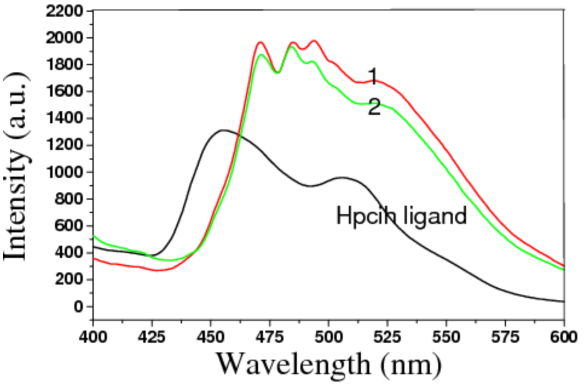

Fig. 3 (color online). The solid-state emission spectra of Hpcih, **1** and **2** at room temperature.

tion at 344 nm wavelength (Fig. 3). The emission spectra show that **1** and **2** possess nearly identical emission intensity, which probably means that the fluorescence emission of **1** and **2** is not related to the NO_3^- ion or to the bha ligand. The emission maxima are at 455 and 507 nm for Hpcih, at 471, 484, 494, and 521 nm for **1** and **2**. The emissions at 471 and 521 nm for **1** and **2** are significantly red-shifted compared to those of the free Hpcih ligand, which may likely be caused by the coordination of the pcih ligand or an interaction between ligands perturbed by the lead(II) ion [8a, 12]. Both **1** and **2** exhibit intense emissions at 484 and 494 nm not observed in the free Hpcih, which can be caused by the enolic form of the Hpcih ligand with the conjugated C=N–N=C–O- moiety. The enhanced luminescence may be attributed to the coordination of the ligand to the lead(II) ion, which effectively increases the rigidity of the ligand and reduces the non-radiative decay through the vibration manifold in the excited state.

Conclusion

Two new hemidirected lead(II) complexes, [Pb(pcih)(bha)] and [Pb(pcih)(NO_3)], have been synthesized under solvothermal conditions. Both **1** and **2** are rare examples of extended hemidirected lead polymers, because the hemidirected system of previously reported Pb(II) complexes is usually extended to a holodirected system *via* weaker secondary coordinative bonds, whereas the hemidirected system in **1** and **2** is not converted into a holodirected system by similar bonds. The successful synthesis of **1** and **2** not only enriches the structure types of lead complexes but also opens possibilities for synthesizing novel hemidirected lead polymers using different organic bipyridyl ligands and lead(II) salts.

Experimental Section

General: All analytically pure starting materials were purchased and used without additional purification. FT-IR spectra were recorded with a Nicolet Magna-IR 550 spectrometer from dry KBr pellets. Elemental analysis was carried out on an EA-1110 elemental analyzer. Fluorescence spectral analyses were performed using a Cary Eclips fluorescence spectrometer.

Synthesis of [Pb(pcih)(bha)] (1)

[Pb(pcih)(bha)] (**1**) was synthesized solvothermally in a 23-mL Teflon-lined autoclave by heating a mixture of Hpcih (0.0452 g, 0.2 mmol), Pb(Ac_2)·$3H_2O$ (0.0759 g, 0.2 mmol), bha (0.0276 g, 0.2 mmol), and CH_3OH (6 mL) at 80 °C for 5 d. After the mixture was slowly cooled to r. t., yellow crystals were obtained (yield: 53 % based on Pb). – Anal. for **1**: calcd. C 40.07, H 2.48, N 9.84; found C 39.86, H 2.58, N 9.75. – IR (KBr disk, cm^{-1}): ν = 3500(s), 1580(s), 1476(w), 1390(s), 1252(s), 1220(s), 1154(w), 1046(w), 942(vw), 864(m), 814(m), 768(m), 696(m), 524(m), 482(m).

Table 1. Crystal structure data for complexes **1** and **2**.

	1	**2**
Formula	$C_{19}H_{14}N_4O_4Pb$	$C_{12}H_9N_5O_4Pb$
F_w	569.54	494.44
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a, Å	7.4125(3)	7.2094(18)
b, Å	10.9230(4)	12.928(3)
c, Å	12.0868(4)	16.536(4)
α, deg	98.0730(10)	90
β, deg	106.4500(10)	115.624(9)
γ, deg	99.9800(10)	90
V, Å^3	905.57(6)	1389.6(6)
Z	2	4
T, K	296(2)	273(2)
Calcd. density, g cm^{-3}	2.09	2.37
Abs. coeff., mm^{-1}	9.4	12.2
$F(000)$, e	540	920
$2\theta_{max}$, deg	50.20	50.18
Total reflns. collected	10538	9913
Unique reflns.	3177	2478
No. of ref. param.	253	199
$R1$ [$I \geq 2\,\sigma(I)$]	0.0208	0.0270
$wR2$ (all data)	0.0470	0.0633
GOF on F^2	1.071	1.063
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	0.61 / −0.45	1.68 / −0.78

Synthesis of [Pb(pcih)(NO$_3$)] (2)

[Pb(pcih)(NO_3)] (**2**) was synthesized solvothermally in a 23-mL Teflon-lined autoclave by heating a mixture of bipd (0.0452 g, 0.2 mmol), Pb$(NO_3)_2$ (0.0662 g, 0.2 mmol), and CH_3OH (6 mL) at 80 °C for 5 d. After the mixture was slowly cooled to r. t., yellow crystals were obtained (yield: 53 % based on Pb). – Anal. for **2**: calcd. C 29.15, H 1.83, N 14.16; found C 28.86, H 2.03, N 13.98. – IR (KBr disk, cm^{-1}): ν = 3426(s), 3056(s), 1666(s), 1587(s), 1544(s), 1500(w), 1452(w), 1360(s), 1213(s), 1001(w), 927(vw), 811(m), 781(m), 728(m), 530(m), 482(m).

X-Ray structure determination

Data collections were performed on a Rigaku Mercury CCD diffractometer with graphite-monochromatized MoK_α radiation (λ = 0.71073 Å) at 296(2) (**1**) or 273(2) K (**2**) with a maximum 2θ value of 50.2°. The intensities were corrected for Lorentz and polarization effects. The structures were solved with Direct Methods using the SHELXS-97 program [13], and the refinement was performed against F^2 using SHELXL-97 [14]. All non-hydrogen atoms were refined anisotropically. The H atoms were positioned with idealized geometries and refined with fixed isotropic displacement parameters. Relevant crystal data and parameters pertinent to data collection and structure refinement can be found in Table 1. Selected bond lengths and angles for compounds **1** and **2** are listed in Table 2.

CCDC 769401 (**1**) and 769402 (**2**) contain 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.

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