

A Two-Dimensional Terrace-Like *N*-heterocyclic-Pb(II) Coordination Compound: Structure and Photoluminescence Property

Kui-Rong Ma,* Yu-Lan Zhu, Yu Zhang, Rong-Qing Li, and Li Cao

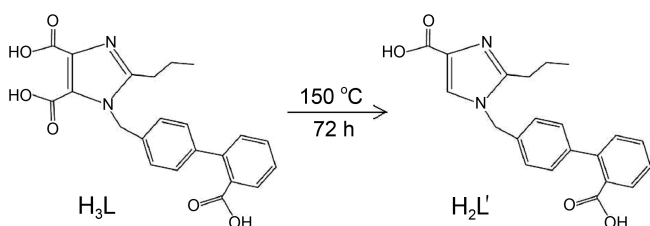
Jiangsu Key Laboratory for Chemistry of Low-dimensional Materials, School of Chemistry and Chemical Engineering, Huaiyin Normal University, Huaian 223300, P.R. China. *E-mail: kuirongma@163.com
Received December 6, 2010, Accepted January 7, 2011

The first example of lead compound from $\text{Pb}(\text{NO}_3)_2$ and H_3L *N*-heterocyclic ligand ($\text{H}_3\text{L} = (\text{HO}_2\text{C})_2(\text{C}_3\text{N}_2)(\text{C}_3\text{H}_7)\text{CH}_2(\text{C}_6\text{H}_4)(\text{C}_6\text{H}_3\text{CO}_2\text{H})$), $[\text{Pb}_4(\text{L}')_4] \cdot 5\text{H}_2\text{O}$ **1** ($\text{L}' = \text{OOC}(\text{C}_3\text{H}_7)(\text{C}_3\text{N}_2)\text{CH}_2(\text{C}_6\text{H}_4)(\text{C}_6\text{H}_3\text{COO})$), has been obtained under hydrothermal condition by decarboxylation, and characterized by elemental analysis, IR, TG-DTA, and single-crystal X-ray diffraction. Compound **1** possesses a rare two-dimensional upper-lower offset terrace-like layer structure. In **1**, crystallographic distinct Pb(II) ion adopts five-coordination geometry, and two lattice water molecules occupy the voids between 2-D layers. Results of solid state fluorescence measurement indicate that the emission band 458 nm may be assigned to $\pi^* \rightarrow n$ and $\pi^* \rightarrow \pi$ electronic transitions within the aromatic systems of the ligand L' , however, the emission bands centred at 555 nm, 600 nm and 719 nm may be derived from phosphorescent emission ($\lambda_{\text{excitation}} = 390$ nm).

Key Words : *N*-heterocyclic, Lead compound, Crystal structure, Photoluminescence

Introduction

Because of toxicity of lead, the study of lead compounds and removal of lead by chelating agents through coordination in biological system always attracts investigator's attention.¹ Lead(II) ion possesses a large radius, a variable stereochemical activity and a flexible coordination environment, which can provide unique opportunities for the construction of novel metal-organic frameworks (MOFs).^{2,3} The construction of Pb(II)-MOFs with fascinating architectures is a rapidly developing area of research in recent years.⁴⁻¹⁰ 1-[(2-Carboxybiphenyl-4-yl)methyl]-2-propylimidazole-4,5-dicarboxylic acid (H_3L), as a type of *N*-heterocyclic ligand (O- or N-donor), can be protonated or deprotonated to produce an infinite variety of MOF structures. When the ligand H_3L is conducted at 150 °C in the presence of organic amine and H_2O , regioselectivity of decarboxylation can happen.¹¹ Then a new ligand, 1-[(2-carboxybiphenyl-4-yl)methyl]-2-propylimidazole-4-carboxylic acid ($\text{H}_2\text{L}'$), is obtained (Scheme 1). The architecture of Pb(II)-MOF constructed from the ligand H_3L has never reported to date. Accordingly, we firstly reported the synthesis and crystal structure of a new 2-D lead-MOF $[\text{Pb}_4(\text{L}')_4] \cdot 5\text{H}_2\text{O}$ **1**. Moreover, the heat-treated products at various temperatures were analyzed by the solid-state photoluminescence.



Scheme 1. Decarboxylation of ligand H_3L .

Experimental Section

Materials and General Methods. All chemical reagents were obtained from commercial sources and used without further purification. The elemental analysis was conducted on a Perkin-Elmer 2400 LC II elemental analyzer. IR spectrum was carried out on an AVATAR-360 FT-IR spectrometer with KBr pellets in the 400 cm^{-1} - 4000 cm^{-1} region. Thermo-gravimetric (TG) and differential thermal analysis (DTA) were performed on a TG/SDTA851e analyzer by METTLER-TOLEDO Co. of Switzerland in an atmospheric environment at a heating rate of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$. Emission and excitation spectra were recorded on a PerkinElmer LS 55 fluorescence spectrometer. The powder x-ray diffraction (XRD) patterns was collected on a Thermo ARL X'TRA diffractometer using graphite-monochromated $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418\text{ \AA}$) in the angular range $2\theta = 4^\circ$ - 40° with stepping size of 0.02° and counting time of 4 s per step.

Synthesis of $[\text{Pb}_4(\text{L}')_4] \cdot 5\text{H}_2\text{O}$ **1.** A mixture of 0.265 g (0.8 mmol) $\text{Pb}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.183 g (0.4 mmol) H_3L and 10.0 mL (555 mmol) deionized water was sealed in a 15 mL Teflon-lined stainless steel autoclave. The initial pH value of solution was adjusted to 10.2, and then it was heated in molar ratio 0.8:0.4:555 at 150 °C for 72 h. The final pH value was 9.5. The crystalline of **1** (colorless block-shaped) was collected by vacuum filtration, washed thoroughly with deionized water and dried in air (yield 59% based on Lead). Elemental analysis (%), $\text{C}_{84}\text{H}_{82}\text{N}_8\text{O}_{21}\text{Pb}_4$: C, 42.62; H, 3.55; N, 4.79. Calcd.: C, 42.56; H, 3.46; N, 4.73. IR data (cm^{-1}) 3606 (w), 3392 (s), 3226 (w), 2962 (m), 2929 (w), 2869 (w), 1625 (w), 1584 (s), 1510 (w), 1444 (w), 1376 (s), 1332 (m), 1253 (s), 1143 (m), 1081 (m), 1004 (m), 862 (w), 833 (m), 752 (m), 665 (w), 572 (w), 528 (w), 482 (w) (see supplement figure S1).

X-ray Crystallography. Intensity data were collected on a Bruker SMART APEX II diffractometer equipped with a graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 293 K using the ω -2 θ scan technique. The structure was solved by direct methods and refined by full-matrix least-squares fitting on F^2 by SHELXL-97. A total of 14922 reflections were collected, of which 4020 ($R_{\text{int}} = 0.0468$) were unique. All non-hydrogen atoms were located from the initial solution and refined with anisotropic thermal parameters. The position of hydrogen atoms were either located by difference Fourier maps or calculated geometrically and their contributions in structural factor calculations were included. CCDC 765594 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Description of Structure. Compound **1** possesses a 2-D architecture by single-crystal X-ray diffraction, in which the asymmetric unit (Figure 1) contains one crystallographic unique Pb(II) ion, one L' ligand and two lattice water molecules. Crystallographic data and structural refinements are summarized in Table 1.

Pb(1) ion in the asymmetry unit is five-coordinated with four O atoms and one N atom from three organic ligands L', O(1), O(2), O(3A), O(3B) and N(2A). The coordination geometry around the Pb(1) ion can be described as a {PbO₄N} trigonal bipyramid geometry. The Pb-O/N distances are from 2.354(3) to 2.665(4) Å in a normal bond length range of 2.2–2.8 Å. The O-Pb-O/N angles range from 51.36(1)° to 130.45(1)°. Owing to stereochemical activity of the 6s electrons, five-coordinate Pb(II) ion is inclined to form hemi-directed coordination geometry which will produce distinct voids or gaps in the coordination sphere.¹²

When the bond length around Pb(II) ion extends from 2.8 Å to 3.1 Å, weak Pb-O interactions can be discovered in the direction of the void or gap derived from the repulsion of the 6s electrons. Pb(1)-O(1w) distance is 2.887(4) Å, and O/N-

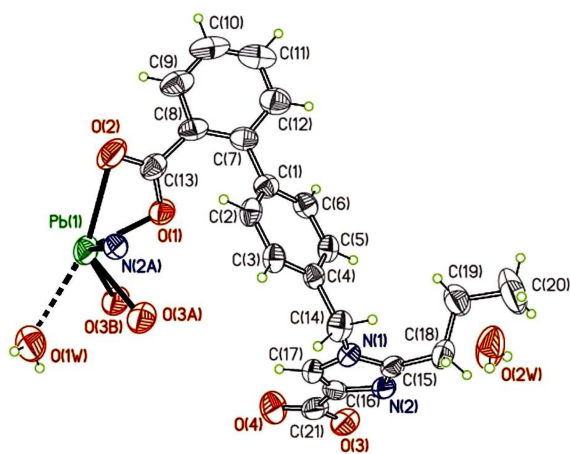


Figure 1. ORTEP view of **1** showing the atom-labeling scheme (50% thermal ellipsoids).

Pb(1)-O(1w) bond angles are from 68.17(1)° to 158.65(1)°. As a result, the coordination numbers of Pb(II) ion increase from five to six. At the same time the coordination geometry of Pb(II) ion is also changed from a distorted trigonal bipyramid to distorted octahedron. Selected bond lengths

Table 1. Crystallographic data for **1**

1	
Empirical formula	C ₈₄ H ₈₂ N ₈ O ₂₁ Pb ₄
Formula weight	592.08
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 21/ <i>c</i>
Unit cell dimensions	
<i>a</i> (Å)	13.0529(2)
<i>b</i> (Å)	13.822(2)
<i>c</i> (Å)	11.5345(2)
β (°)	100.298(2)
Volume (Å ³)	2047.5(5)
<i>Z</i>	1
Calculated density (g/cm ³)	1.921
Absorption coefficient (mm ⁻¹)	8.276
<i>F</i> (000)	1138
Theta range for data collection (°)	2.16–26.00
Limiting indices	–16 ≤ <i>h</i> ≤ 16 –14 ≤ <i>k</i> ≤ 17 –13 ≤ <i>l</i> ≤ 14
Unique (<i>R</i> (int))	4020 (0.0468)
Max. and min. transmission	0.191 and 0.087
Data / restraints / parameters	4020/0/272
Goodness-of-fit on F^2	0.966
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0327, <i>wR</i> ₂ = 0.0641
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0663, <i>wR</i> ₂ = 0.0703
Largest diff. peak and hole (eÅ ⁻³)	0.516 and –0.860

Table 2. Selected bond lengths [Å] and angles [°] for **1**

bond lengths			
O(1)-Pb(1)	2.354(3)	Pb(1)-O(3) ^d	2.532(4)
O(2)-Pb(1)	2.665(4)	Pb(1)-N(2) ^c	2.535(4)
Pb(1)-O(3) ^c	2.393(4)	O(1w)-Pb(1)	2.887(4)
angles			
C(15)-N(2)-Pb(1) ^a	140.5(4)	O(3) ^c -Pb(1)-N(2) ^c	67.08(1)
C(16)-N(2)-Pb(1) ^a	112.8(3)	O(3) ^d -Pb(1)-N(2) ^c	130.45(1)
C(13)-O(1)-Pb(1)	101.0(3)	O(1)-Pb(1)-O(2)	51.36(1)
C(13)-O(2)-Pb(1)	87.5(3)	O(3) ^c -Pb(1)-O(2)	122.68(1)
C(21)-O(3)-Pb(1) ^a	124.9(4)	O(3) ^d -Pb(1)-O(2)	122.73(1)
C(21)-O(3)-Pb(1) ^b	118.9(4)	N(2) ^c -Pb(1)-O(2)	77.91(1)
Pb(1) ^a -O(3)-Pb(1) ^b	115.85(2)	O(1)-Pb(1)-O(1w)	147.58(1)
O(1)-Pb(1)-O(3) ^c	81.33(1)	O(3) ^c -Pb(1)-O(1w)	68.17(1)
O(1)-Pb(1)-O(3) ^d	78.88(1)	O(3) ^d -Pb(1)-O(1w)	78.12(1)
O(3) ^c -Pb(1)-O(3) ^d	64.15(2)	N(2) ^c -Pb(1)-O(1w)	91.91(1)
O(1)-Pb(1)-N(2) ^c	85.90(1)	O(2)-Pb(1)-O(1w)	158.65(1)

Symmetry transformations used to generate equivalent atoms: ^a*x*, –*y*+3/2, *z*+1/2. ^b–*x*+2, *y*–1/2, –*z*+5/2. ^c*x*, –*y*+3/2, *z*–1/2. ^d–*x*+2, *y*+1/2, –*z*+5/2

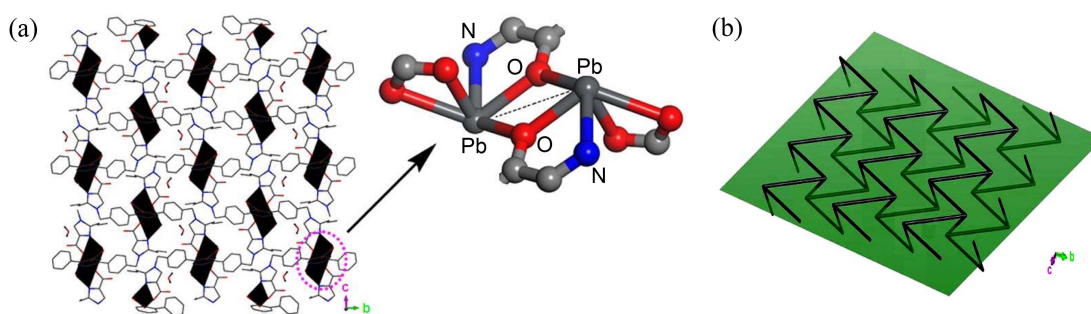


Figure 2. (a) 2-D layer built from double chains in the *bc* plane. (b) 2-D terrace-like topological structure *via* lead ion as a node in the *bc* plane.

and angles are listed in Table 2.

The ligand L' acts as a tetradentate role in $\mu_3:\eta^2:\eta^2:\eta^1$ mode in which carboxyl oxygen atoms (O(1), O(2)) from biphenyl moiety chelating with one Pb(II) ion, the carboxyl oxygen atom (O(3)) from *N*-heterocyclic moiety in μ_2 -O(3) monodentate mode connecting to two Pb(II) ions, and nitrogen atom (N(2)) from *N*-heterocyclic moiety bonding to one Pb(II) ion.

The compound **1** contains a $\{\text{Pb}_2\text{O}_6\text{N}_2\}$ (Figure 2a) core that can be described as an edge-shared dinuclear polyhedron with two μ_2 -O(3) atoms. In particular, the Pb(1)-Pb(1) contact is 4.174 Å that the weaker metal-metal interactions further reinforce the dinuclear structure. Three types of four/five-membered rings, [-Pb(1)-O(3)-Pb(1)-O(3)-], [-Pb(1)-O(1)-C(13)-O(2)] and [-Pb(1)-O(3)-C(21)-C(16)-N(2)], are assembled in the $\{\text{Pb}_2\text{O}_6\text{N}_2\}$ core. The dinuclear core $\{\text{Pb}_2\text{O}_6\text{N}_2\}$, as a basic structural unit, is joined together by the organic ligand L' to form a 2-D metal-organic framework in the *bc* plane (Figure 2a). Regarding Pb(II) ion as node, the 2-D layer actually comprises the upper-lower terrace-like double chains which further link together through μ_2 -O(3) (Figure 2b). It should be noted that the 2-D structure is the first example of this complicated ligand L', based on a Cambridge Structure Database (CSD) (Aug, 2010) search until now.¹³ The lattice water molecule (O2w) occupies the voids between the layers and is involved in hydrogen bonds. Due to the existence of the lattice water molecule, few of the voids are observed in the overall 2-D crystalline lattice. After the removal of solvent, the volume of tunnel formed by 2-D layers is 36.2 Å³ per unit cell using PLATON based on the crystal structures, comprising 1.8% of the crystal volume.¹⁴

Except for that long Pb-O(1w) contact, there also have two types of hydrogen bonds (O-H...O and C-H...O) in **1**. These hydrogen bonds are formed between the ligand L' (O(1), O(2), O(4), C(11), C(18)) and the two water molecules (O(1w), O(2w)). The hydrogen bonds (C(11)...O(2w), O(2w)...O(2) C(18)...O(2w) and O(2w)...O(4)) distances and angles are 3.209(1) Å, 2.748(1) Å, 3.352(2) Å, 2.620(1) Å, 128.9°, 129.6°, 149.3° and 160.2°, respectively. Accordingly, the above 2-D layers are further joined together by hydrogen bond interactions to lead to a 3-D supramolecular framework (Figure 3). The lattice water molecules play a

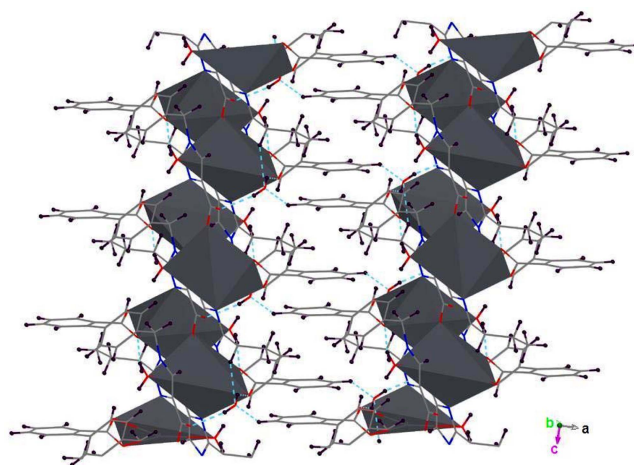


Figure 3. 3-D supramolecular network created from 2-D layers *via* hydrogen bond. Hydrogen bonds are drawn as blue dotted lines.

very important role in the formation of 3-D supramolecule. Hydrogen bonds and angles are given in Table 3.

XRD and TG-DTA Study. The powder XRD pattern of **1** indicates that as-synthesized product is a new material, and the pattern is entirely consistent with the simulated one from the single-crystal X-ray diffraction. Thermodiffractograms of **1** heated up to 520 °C in air are shown in Figure 4. Results reveal no phase transformation was observed in thermodiffraction powder at a temperature below 320 °C except thermal dilatation. It means the 2-D lattice of **1** began to collapse above a temperature of 320 °C.

The combined TG-DTA analysis (see supplement figure S2) shows two major weight losses. The first mass loss of 3.74% from 60 °C to 130 °C, with an endothermic peak

Table 3. Hydrogen bond lengths [Å] and angles [°] for **1**

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1w)-H(1wA)...O(1) ^a	0.85	2.01	2.771(5)	148.5
O(2w)-H(2w1)...O(4) ^b	0.72	1.93	2.620(1)	160.2
O(2w)-H(2w2)...O(2) ^c	0.71	2.24	2.748(1)	129.6
C(11)-H(11)...O(2w) ^d	0.93	2.54	3.209(1)	128.9
C(18)-H(18B)...O(2w)	0.93	2.48	3.352(2)	149.3

Symmetry transformations used to generate equivalent atoms: ^a-x+2, -y+2, -z+2. ^b-x+2, -y+1, -z+2. ^cx, y-1, z. ^d-x+1, y-1/2, -z+1/2

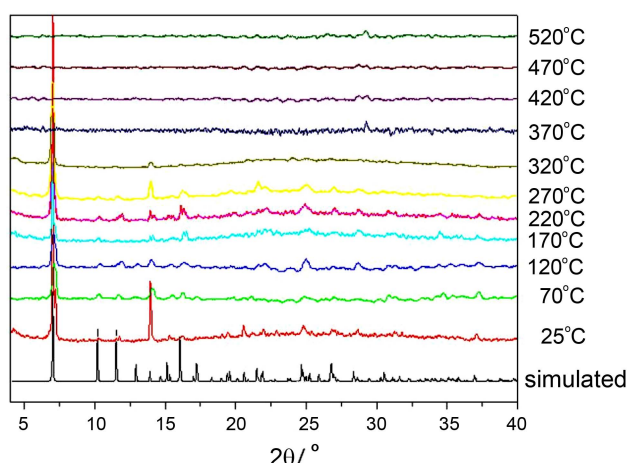


Figure 4. The powder XRD patterns of **1**.

centered at 80 °C, corresponds to the loss of two lattice water molecules (calc. 3.80%). The broad range to lose the lattice water molecules is much more likely to attribute to those complicated hydrogen bonds.¹⁵ The second mass loss of about 58.16% (calc. 58.50%), in the range of 320–500 °C, can be assigned to the pyrolysis of the organic ligand. Three exothermic peaks, centered at 328 °C, 409 °C and 455 °C, indicate structural changes. These changes are reflected in diffraction patterns at 370, 420, 470 and 520 °C. The final thermal decomposition residue at 800 °C is PbO, which possesses a mass of 38.1% (calc. 37.7%).

Photoluminescent Property. According to work reported previously, coordination polymers containing Pb(II) ions can exhibit photoluminescent properties.^{4–6} Here, we investigated the solid-state photoluminescent property of **1** heated at different temperatures (Figure 5). The free raw material H₃L shows a fluorescent emission in the visible region at 482 nm ($\lambda_{\text{excitation}} = 390$ nm), whereas the compound **1** shows four emission bands at 458 nm, 555 nm, 600 nm and 719 nm ($\lambda_{\text{excitation}} = 390$ nm), respectively. Three small emission bands at 545 nm, 585 nm and 703 nm ($\lambda_{\text{excitation}} = 390$ nm) are still observed even though the samples were heat-treated at above 320°C. This suggests that an emission maximum at

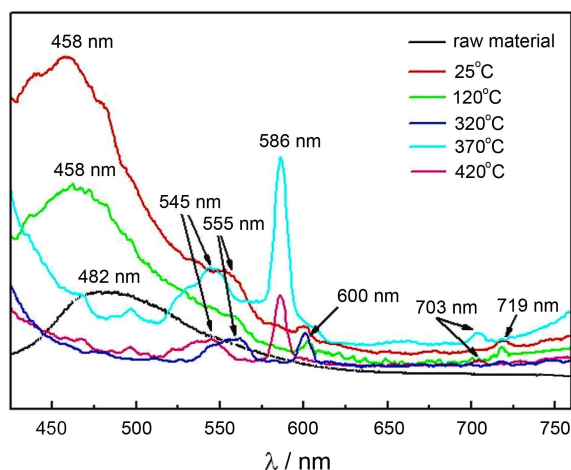


Figure 5. Solid-state emission spectra of **1**.

458 nm may be assigned to $\pi^* \rightarrow n$ and $\pi^* \rightarrow \pi$ electronic transitions within the aromatic systems of the ligand L'. The blue shift about 24 nm, compared to that of the free H₃L, may be due to the coordination or an excited state of a metal-perturbing intraligand. After the title compound was heat treated at the temperature of above 320 °C, X-ray powder diffraction show that the originally crystalline material changes take place. So the bands 555 nm, 600 nm and 719 nm may be assigned to phosphorescent emission. Owing to the presence of a heavy metal lead(II) ion, the radiationless deactivations of the triplet state can facilitate the intersystem crossing successfully. These results indicate the Pb(II) ion might give rise to effect on the photoluminescent properties through structural modifications by change organic ligand.

Conclusions

In summary, we have successfully synthesized a novel 2-D Pb(II)-L' compound under hydrothermal condition by decarboxylation. The compound **1** displays 2-D layer architecture with three types of four/five-membered rings around Pb(II) ion. The Pb(II) ion is five-coordinated with three adjacent organic ligand L' and an upper-lower double layer topological structure has been further built from {Pb₂O₆N₂} core. In addition, hydrogen bonds have also led to the production of 3-D supramolecular structure. The solid-state fluorescence measurement of **1** reveals a fluorescent emission band at 458 nm under excitation of 390 nm, likely caused by the ligand L' and lone electron pair of lead (II) ion.

Acknowledgments. The authors are grateful to the financial support from The National Natural Science Foundation of China, Open Fund of Jiangsu Key Laboratory for Chemistry of Low-dimensional Materials, Huai'an Scientific and technological support industrial projects and the Natural Science Foundation of the Higher Education Institutions of Jiangsu Province, China, (Projects Nos. 20671038, JSKC09068, HAG09054-12 and 10KJD150001).

Supporting Information Available. Supporting Information are available on request from the correspondence author (fax: +86 517 83525100 email: kuirongma@163.com)

References

- Fan, S. R.; Zhu, L. G. *Inorg. Chem.* **2007**, *46*, 6785.
- Ma, K. R.; Zhang, D. J.; Zhu, Y. L. *Aust. J. Chem.* **2010**, *63*, 452.
- Yang, J.; Ma, J. F.; Liu, Y. Y.; Ma, J. C.; Batten, S. R. *Inorg. Chem.* **2007**, *46*, 6542.
- Chen, S. C.; Zhang, Z. H.; Chen, Q.; Gao, H. B.; Liu, Q.; He, M.; Du, Y. M. *Inorg. Chem. Commu.* **2009**, *12*, 835.
- Ma, K. R.; Xu, J. N.; Wang, L.; Shi, J.; Wang, Y.; Ha, J.; Ning, D. K.; Fan, Y.; Song, T. Y. *Chem. J. Chinese U.* **2007**, *28*, 1434.
- Zhang, K. L.; Pan, Z. C.; Chang, Y.; Liu, W. L.; Ng, S. W. *Mater. Lett.* **2009**, *63*, 2136.
- Zhao, Y. H.; Xu, H. B.; Shao, K. Z.; Xing, Y.; Su, Z. M.; Ma, J. F. *Cryst. Growth Des.* **2007**, *7*, 513.
- Zhu, X. D.; Li, X. J.; Liu, Q. Y.; Lv, J.; Guo, Z. G.; He, J. R.; Li, Y. F.; Cao, R. *J. Solid State Chem.* **2007**, *180*, 2386.

9. Zhang, K. L.; Zhou, F.; Wub, R.; Yang, B.; Ng, S. W. *Inorg. Chim. Acta.* **2009**, 362, 4255.
 10. Zhang, K. L.; Liang, W.; Chang, Y.; Yuan, L. M.; Ng, S. W. *Polyhedron* **2009**, 28, 647.
 11. Collman, J. P.; Boulatov, R.; Sunderland, C. J.; Zhong, M. J. *Fluorine Chem.* **2000**, 106, 189.
 12. Shimoni-Livny, L.; Glusker, J. P.; Bock, C. W. *Inorg. Chem.* **1998**, 37, 1853.
 13. Allen, F. H. *Acta Crystallogr. Sect. B: Struct. Sci.* **2002**, 58, 380.
 14. Spek, A. L. *J. Appl. Cryst.* **2003**, 36, 7.
 15. Kong, D. Y.; Clearfield, A. *Cryst. Growth Des.* **2005**, 5, 1263.
-