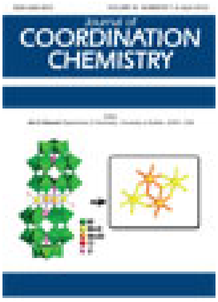
This article was downloaded by: [Renmin University of China]
On: 13 October 2013, At: 10:45
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

A holodirected Pb(II) architecture based on bifunctional tetrazole-carboxylate and photoluminescence

Jiyong Hu [a], Shenshen Li [b], Jin'an Zhao [a], Shufang Chen [b], Hongwei Hou [b] & Haipeng Zhao [a]

[a] Department of Chemistry and Chemical Engineering, Henan University of Urban Construction, Henan 467036, P.R. China

[b] Department of Chemistry, Zhengzhou University, Henan 450052, P.R. China

Published online: 20 Mar 2012.

To cite this article: Jiyong Hu, Shenshen Li, Jin'an Zhao, Shufang Chen, Hongwei Hou & Haipeng Zhao (2012) A holodirected Pb(II) architecture based on bifunctional tetrazole-carboxylate and photoluminescence, Journal of Coordination Chemistry, 65:7, 1258-1265, DOI: 10.1080/00958972.2012.670700

To link to this article: http://dx.doi.org/10.1080/00958972.2012.670700

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms &

Journal of Coordination Chemistry
Vol. 65, No. 7, 10 April 2012, 1258–1265

Taylor & Francis
Taylor & Francis Group

A holodirected Pb(II) architecture based on bifunctional tetrazole-carboxylate and photoluminescence

JIYONG HU*†, SHENSHEN LI‡, JIN'AN ZHAO*†, SHUFANG CHEN‡,
HONGWEI HOU‡ and HAIPENG ZHAO†

†Department of Chemistry and Chemical Engineering, Henan University of Urban Construction, Henan 467036, P.R. China
‡Department of Chemistry, Zhengzhou University, Henan 450052, P.R. China

(*Received 19 October 2011; in final form 23 January 2012*)

A new 1-D Pb(II) complex $\{[Pb_2(H_2O)_4(tppbc)_2] \cdot (CH_3)_2NCHO\}_n$ (**1**) based on tetrazole-carboxylate bifunctional ligand has been prepared and characterized (tppbc = 3-(4-(2-(1*H*-tetrazol-5-yl)phenyl-4-yl)phenyl)-2-ethoxy-3H-benzimidazole-4-carboxylic acid). Photoluminescence measurements indicate that although the fluorescence of tppbc is quenched after coordination, the Pb(II) complex shows strong intense phosphorescence emission. Lifetimes at 298 K and low temperatures agree with the large Stokes shift of **1**.

Keywords: Tetrazole-carboxylate; Pb(II) complex; Photoluminescence

1. Introduction

Construction of inorganic and organic hybrid materials has achieved great progress in forming intriguing topologies with applications in magnetism, electrical conductivity, luminescence, and separations [1]. Research on functional materials has concentrated on the incorporation of s-, d- and even f-metal ions as coordination centers. As a heavy p-block metal center, Pb(II) with a large radius, flexible coordination environment, and variable stereochemical activity is suitable to form unusual network topologies with interesting photophysics and photochemistry [2]. Pb(II) centers in complexes with six/seven coordination number and hard donors (e.g., N- or O-) are more likely to be hemidirected [3]. When the number of coordinated ligands around Pb(II) is high, the directional effect of the lone pair electrons is less evident.

Resulting architectures and properties of hybrid materials are mainly derived from the nature of metal centers and the organic synthons. Thus, organic ligands also play a great role in directing the coordination behavior of metal centers. Being small building units with different coordination properties, tetrazole derivatives can afford a wide range of extended network structures [4]. The bifunctional tetrazole-carboxylate synthon has been the subject of limited studies with metal centers, especially for

---

*Corresponding authors. Email: hujiyong@hncj.edu.cn; zjinan@zzu.edu.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2012 Taylor & Francis
http://dx.doi.org/10.1080/00958972.2012.670700

Pb(II) [5]. Accordingly, exploring the coordination chemistry of Pb(II) to ligands with oxygen and nitrogen donors is attractive [6]. Only one Pb(II) complex based on a tetrazole-carboxylate has been reported. As an excellent derivative of tetrazole, tppbc bears both carboxylate and tetrazole groups with good solubility and flexible structure, which is conducive to unique coordination configurations. After coordination with Pb(II), luminescence measurements reveal that although the strong fluorescence is quenched, broad phosphorescent emission is observed. This is attractive for mobile Pb(II) extraction and transport as well as for sensing applications.

2. Experimental

2.1. *Materials and general methods*

All chemicals were commercially available and used as purchased. Infrared data were recorded on a BRUKER TENSOR 27 spectrophotometer with KBr pellets from 400 to $4000\,\mathrm{cm}^{-1}$. Elemental analyses (C, H, and N) were carried out on a Flash EA 1112 elemental analyzer. Photoluminescence measurements were carried out on Edinburgh Analytical Instruments FLS920 (Spectrofluorimeter) at ambient temperature and low temperatures in the solid state. The excitation and emission slit widths are 0.5 nm and 1 nm, respectively. Thermogravimetric experiment was performed using a METTLER TGA instrument with N_2 as purge gas.

2.2. *Synthesis of* $\{[Pb_2(H_2O)_4(tppbc)_2]\cdot(CH_3)_2NCHO\}_n$ *(1)*

For preparation of **1**, a solution of tppbc (0.0852 g, 0.2 mmol) in methanol (7 mL) and an equivalent amount of $Pb(NO_3)_2$ in water (2 mL) were mixed, and colorless block crystals were obtained upon slow evaporation of the solution in the dark at ambient temperature (yield: 61%, based on Pb). Elemental Anal. Calcd for ($C_{51}H_{36}N_{13}O_{11}Pb_2$) (%): C, 43.10; H, 2.55; N, 12.81. Found: C, 42.81; H, 2.75; N, 12.53. IR (KBr): 3424m, 1682s, 1617s, 1552s, 1489m, 1388s, 1353s, 1287m, 1258m, 1139w, 1041s, 1009w, 760s, 741m.

2.3. *Crystal structure determination*

A crystal suitable for X-ray determination was mounted on a glass fiber. The data of **1** were collected at room temperature on a Rigaku Saturn 724 CCD with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods and expanded with Fourier techniques. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on observed reflections and variable parameters. All calculations were performed with the SHELXL-97 crystallographic software package [7]. Table 1 shows crystallographic crystal data and processing parameters for **1** and table 2 lists selected bond lengths and angles.

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

Complex	**1**
Empirical formula	$C_{51}H_{36}N_{13}O_{11}Pb_2$
Formula weight	1421.33
Temperature (K)	293(2)
Wavelength (Mo-Kα) (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	7.7185(15)
b	12.793(3)
c	14.139(3)
α	94.47(3)
β	99.78(3)
γ	97.71(3)
Volume (Å^3), Z	1356.1(5), 1
$2\theta_{max}$ (°)	55.84
$F(000)$	685
Goodness-of-fit on F^2	1.059
Final R_1[a], wR_2[b]	0.0373, 0.0817

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR_2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$. $w = 1/[\sigma^2(F_o)^2 + 0.0297P^2 + 27.5680P]$, where $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

N(2)–Pb(1)#2	2.722(4)	N(3)–Pb(1)	2.728(4)
O(1)–Pb(1)	2.642(4)	O(2)–Pb(1)	2.452(3)
O(2)–Pb(1)#1	2.496(3)	O(3)–Pb(1)	2.493(3)
O(4)–Pb(1)	2.780(4)	N(3)–Pb(1)–O(4)	78.75(15)
N(2)#2–Pb(1)–O(4)	100.62(15)	O(1)–Pb(1)–O(4)	144.76(13)
O(2)#1–Pb(1)–O(4)	85.82 (13)	O(3)–Pb(1)–O(4)	125.55(14)
O(2)–Pb(1)–O(4)	138.44(13)	N(2)#2–Pb(1)–N(3)	113.08(13)
O(1)–Pb(1)–N(3)	73.91(14)	O(2)#1–Pb(1)–N(3)	94.85(13)
O(3)–Pb(1)–N(3)	154.88(15)	O(2)–Pb(1)–N(3)	72.69(13)

Symmetry transformation used to generate equivalent atoms: #1 $-x$, $-y+1$, $-z+1$; #2 $-x-1$, $-y+1$, $-z+1$.

3. Results and discussion

3.1. *Crystal structure of 1*

As shown in figure 1, Pb(II) in **1** with the coordination number of seven possesses a stereochemically "inactive" electron lone pair, in which the equatorial positions are furnished by O1a, O2, O2a, O4w, and N2c with the deviation of 0.5839 Å. The axial sites are occupied by one water molecule and one nitrogen with angle of 154.9°. The coordination sphere is holodirected, completed by three carboxylate oxygen atoms, two tetrazole nitrogen atoms, and two water oxygen atoms. Therefore, holodirected geometry is also favored at intermediate coordination number (6–8) in the presence of hard donors. The bond lengths are 2.722 and 2.733 Å for Pb–N and 2.451–2.778 Å for Pb–O. The Pb–O/N distances fall in the normal range found in other Pb(II) complexes [8].

Pb(II) ions are bridged by carboxylate oxygen atoms and tetrazole alternatively, and the Pb···Pb distances separated by oxygen atoms and tetrazole are 4.1125 and

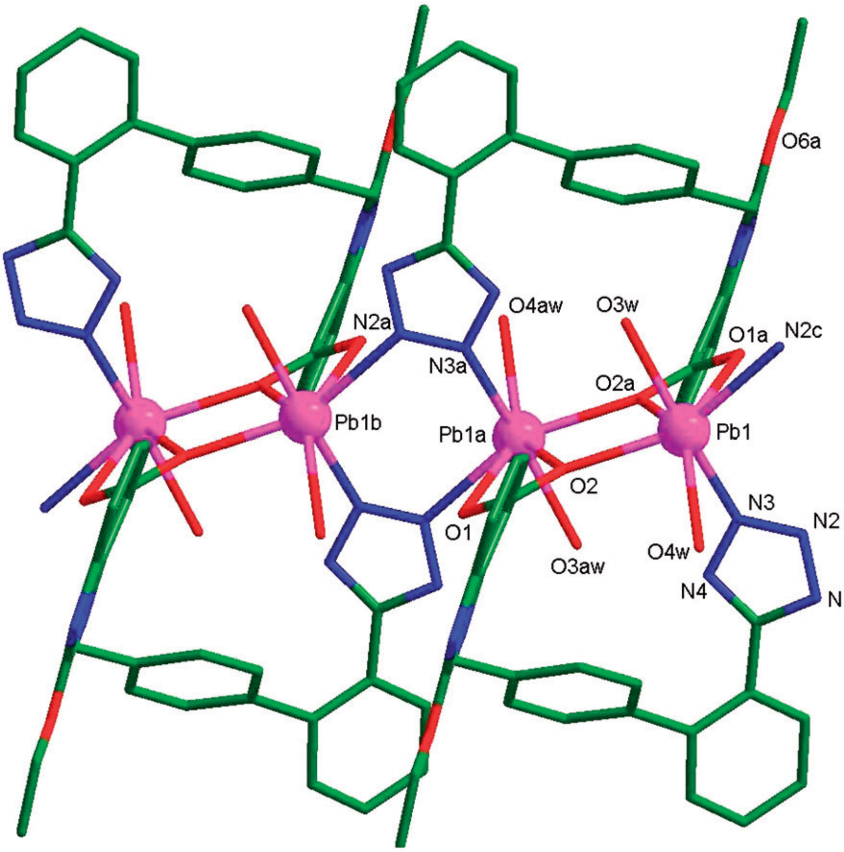


Figure 1. Coordination environment of Pb(II); hydrogen atoms and partial labels are omitted for clarity.

4.2294 Å, indicating that Pb···Pb contact exists [9]. In the complex, the ligand is a tetradentate connector *via* N and O and the bridging group (totally penta-dentate) in a chelating, bridging (μ_2-$\eta^2:\eta^1$) mode where the oxygen of carboxylate coordinates to a Pb(II) and also bridges an adjacent Pb(II), yielding the Pb_2O_2 entity. Further, the Pb(II) centers are bridged by tppbc to form a 1-D chain (figure 2). The solvent-accessible volume was estimated by PLATON to be 16.4% of the total crystal volume [10]. Up to now, only one example of Pb(II) complex, $[Pb(ttzCOO)(H_2O)_2]_n$, based on a bifunctional ligand with tetrazole and carboxylate was reported by the Yang group. For the reported Pb(II) complex, the ligand is bidentate, bridging two Pb(II) centers, and the Pb(II) is five-coordinate with hemidirected geometry [11].

The structure of **1** is stabilized by face-to-face $\pi\cdots\pi$ interactions between the imidazole rings of benzimidazole with centroid separation of 3.604 Å and the dihedral angle of 0.02°. Also, the centroid distance is 3.864 Å between parallel phenyl rings adjoining to the tetrazole. C–H···π interactions are present between the ethyl and adjacent tetrazole as well as the phenyl of benzimidazole. Further, adjacent 1-D chains are stabilized by strong hydrogen bonds (C···O 2.78 Å for C14–H14a···O6, C···O 3.034 Å for C14–H14b···O1, and C···N 2.92 Å for C10–H10···N5) and $\pi\cdots\pi$

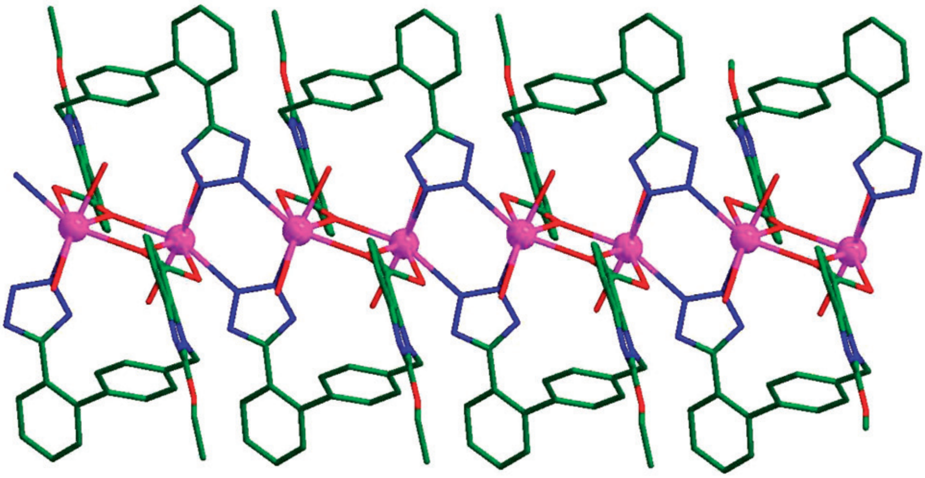


Figure 2. The 1-D chain of Pb(II) complex running along the *a*-axis.

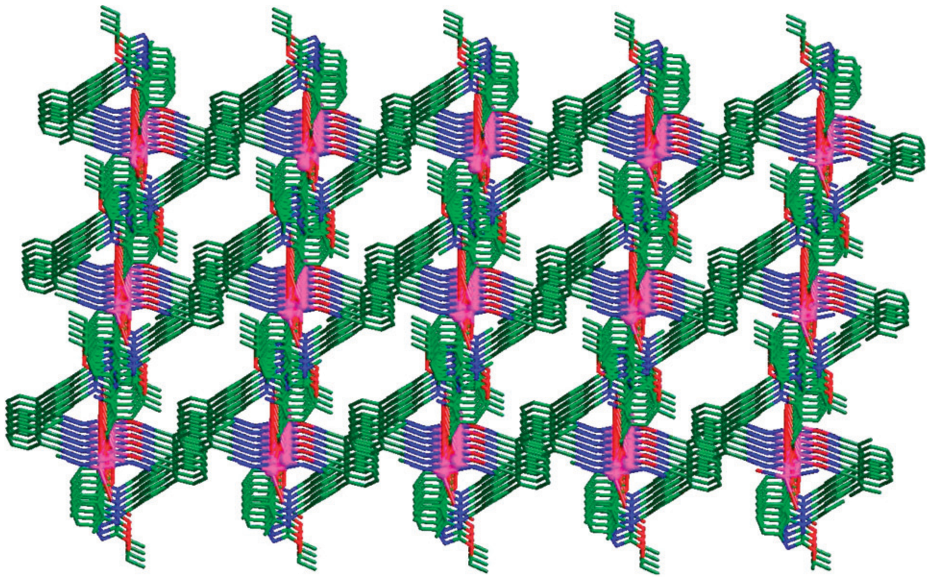


Figure 3. A 3-D supramolecular packing diagram of **1**.

interactions, which extend the chain motifs into a 3-D supramolecular architecture (figure 3). Besides, the chain-to-chain strong H-bonding, $\pi\cdots\pi$ interactions play an important role in formation and stabilization of the supramolecular network.

Complex **1** is air-stable and retains crystalline integrity at ambient temperature. The thermogravimetric analysis curve (figure S1) shows that the weight loss of 10.9% for **1** from 45°C to 170°C (Calcd 10.1%) corresponds to loss of four-coordinated water molecules and one DMF per formula. The dehydrated complex is stable to 285°C.

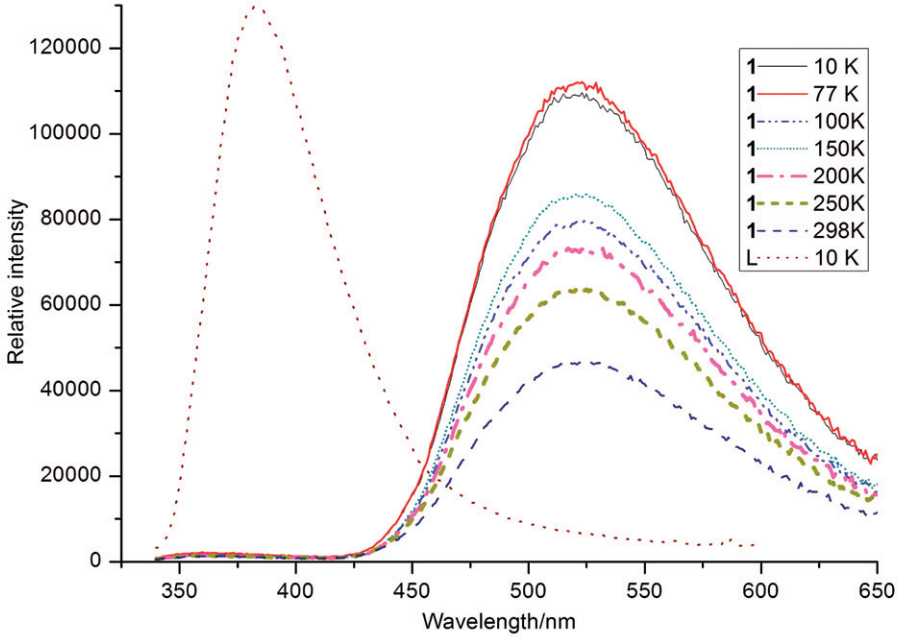


Figure 4. The photoluminescence of **1** and tppbc at 298 K and low temperatures.

3.2. *Luminescence properties*

The photoluminescence of **1** (figure 4) and tppbc (figure S2) at 298 K, as well as low temperatures, were determined in the solid state. At 298 K, the emission spectrum of **1** results in a low-energy strong emission with $\lambda_{max} = 522$ nm upon excitation at 310 nm, whereas tppbc emits fluorescence at $\lambda_{max} = 383$ nm with excitation wavelength of 333 nm, indicating structure-dependent photoluminescence of the coordination framework. Luminescence originates from the radiation of singlet and triplet excited states. As heavy atom, Pb(II) can effectively enhance the rate of intersystem crossing, which reduces the fluorescence emission and increases the rate of triplet excited state formation [12]. At room temperature, the nonradiative rate constant is very large, which is not conducive to observe phosphorescence. Thus, the intensity of phosphorescence is enhanced after cooling.

The lifetimes for tppbc at 298 K, 250 K, 200 K, 150 K, 100 K, 77 K, and 10 K yield $\tau = 1.498 \pm 0.024$, 1.655 ± 0.024, 1.830 ± 0.029, 1.979 ± 0.033, 2.056 ± 0.034, 2.101 ± 0.035, and 2.058 ± 0.030 *ns,* respectively. Again, the values indicate that the tppbc are single-state emissions. The lifetimes for solid **1** yield $\tau = 2.131 \pm 0.095$, 2.787 ± 0.059, 3.387 ± 0.124, 3.962 ± 0.965, 3.728 ± 0.433, 3.877 ± 0.587, and 3.991 ± 0.241 *ms* at series corresponding temperatures like tppbc, respectively, showing that emissions are triplet-state radiation. At low temperature, the phosphorescence intensity of **1** increases. The luminescence lifetimes in the microsecond range or even longer, together with the large Stokes shift from the excitation maximum to the low-energy emission maximum of **1**, are in accord with the fact that low-energy emissions are typical of emission origins for triplets [13].

4. Summary

A new 1-D Pb(II) complex $\{[Pb_2(H_2O)_4(tppbc)_2]\cdot(CH_3)_2NCHO\}_n$ (**1**) based on the tetrazole-carboxylate bifunctional ligand has been achieved and characterized. Additionally, inhibition of nonradiative decay of the emitting triplet state and vibronic resolution upon cooling is favorable to enhancement of phosphorescence.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference number 848838. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033).

Acknowledgments

We gratefully acknowledge the financial support by the Talent Supporting Plan of He'nan Scientific and Technological Innovation (No. 2010HASTIT016) and the He'nan Key Science and Technology Research (Nos. 102102310079 and 112102310084).

References

[1] (a) A. Corma, H. Garcia, F.X.L. Xamena. *Chem. Rev.*, **110**, 4606 (2010); (b) J. Long, E. Chelebaeva, J. Larionova, Y. Guari, R.A.S. Ferreira, L.D. Carlos, F.A. Almeida Paz, A. Trifonov, C. Guérin. *Inorg. Chem.*, **50**, 9924 (2011); (c) K.S. Lovejoy, S.J. Lippard. *Dalton Trans.*, 10651 (2009); (d) M.D. Allendorf, C.A. Bauer, R.K. Bhakta, R.J.T. Houk. *Chem. Soc. Rev.*, **38**, 1330 (2009); (e) A.U. Czaja, N. Trukhan, U. Muller. *Chem. Soc. Rev.*, **38**, 1284 (2009).

[2] (a) J.-J. Jiang, S.-R. Zheng, Y. Liu, M. Pan, W. Wang, C.-Y. Su. *Inorg. Chem.*, **47**, 10692 (2008); (b) K. Binnemans. *Chem. Rev.*, **109**, 4283 (2009).

[3] N. Noshiranzadeh, A. Ramazani, A. Morsali, A.D. Hunter, M. Zeller. *Inorg. Chem. Commun.*, **10**, 738 (2007).

[4] (a) S. Stagni, E. Orselli, A. Palazzi, L. De Cola, S. Zacchini, C. Femoni, M. Marcaccio, F. Paolucci, S. Zanarini. *Inorg. Chem.*, **46**, 9126 (2007); (b) Y. Qiu, Y. Li, G. Peng, J. Cai, L. Jin, L. Ma, H. Deng. *Cryst. Growth Des.*, **10**, 1332 (2010); (c) P.-P. Liu, A.-L. Cheng, Q. Yue, N. Liu, W.-W. Sun, E.-Q. Gao. *Cryst. Growth Des.*, **8**, 1668 (2008); (d) P. Pachfule, R. Das, P. Poddar, R. Banerjee. *Cryst. Growth Des.*, **10**, 2475 (2010).

[5] (a) V. Hartdegen, T.M. Klapotke, S.M. Sproll. *Inorg. Chem.*, **48**, 9549 (2009); (b) S.M. Zhang, Z. Chang, T.L. Hu, X.H. Bu. *Inorg. Chem.*, **49**, 11581 (2010).

[6] (a) B. Ding, E.-C. Yang, J.-H. Guo, X.-J. Zhao, X.-G. Wang. *Inorg. Chem. Commun.*, **11**, 1481 (2008); (b) M.L. Hu, A. Morsali, L. Aboutorabi. *Coord. Chem. Rev.*, **255**, 2821 (2011).

[7] (a) G.M. Sheldrick. *SHELXTL-97, Program for Refining Crystal Structure Refinement*, University of Göttingen, Germany (1997); (b) G.M. Sheldrick. *SHELXS-97, Program for Crystal Structure Solution*, University of Göttingen, Germany (1997); (c) G.M. Sheldrick. *Acta Cryst.*, **A64**, 112 (2008).

[8] (a) F. Marandi, R. Rutvand, M. Rafiee, J.H. Goh, H.K. Fun. *Inorg. Chim. Acta*, **363**, 4000 (2010); (b) H. Yin, S.X. Liu. *Inorg. Chem. Commun.*, **12**, 187 (2009).

[9] (a) H. Xu, Z. Chao, Y. Sang, H. Hou, Y. Fan. *Inorg. Chem. Commun.*, **11**, 1436 (2008); (b) M. Rafizadefa, V. Amania, B. Neumuller. *Z. Anorg. Allg. Chem.*, **632**, 2383 (2006).
[10] A.L. Spek. *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands (2003).
[11] J.F. Kou, M. Su, Y.H. Zhang, Z.D. Huang, S.W. Ng, G. Yang. *Z. Naturforsch.*, **65b**, 1467 (2010).
[12] (a) K.M. C. Wong, L.L. Hong, W.H. Lam, N. Zhu, V.W.W. Yam. *J. Am. Chem. Soc.*, **129**, 4350 (2007); (b) H.Y. Chao, W. Lu, Y. Li, M.C.W. Chan, C.M. Che, K.K. Cheung, N. Zhu. *J. Am. Chem. Soc.*, **124**, 14696 (2002).
[13] M.A. Omary, H.H. Patterson. *Inorg. Chem.*, **39**, 1060 (1998).