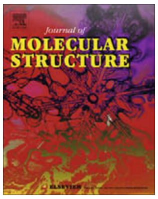
Journal of Molecular Structure 938 (2009) 291–298

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc



Two new one-dimensional luminescent silver(I) and lead(II) coordination polymers containing the flexible ligand 2-(1*H*-imidazole-1-yl)acetic acid

Yong-Tao Wang *, Ting-Xiao Qin, Chao Zhao, Gui-Mei Tang, Tian-Duo Li, Yue-Zhi Cui, Jun-Ying Li

Department of Chemical Engineering, Shandong Institute of Light Industry, Jinan, Shandong 250100, PR China

ARTICLE INFO

Article history:
Received 28 July 2009
Received in revised form 23 September 2009
Accepted 28 September 2009
Available online 6 October 2009

Keywords:
Silver complex
Lead complex
2-(1*H*-Imidazole-1-yl)acetic acid
Dicubane-like
Fluorescence
X-ray

ABSTRACT

The free ligand, 2-(1*H*-imidazole-1-yl)acetate (Hima, **1**), was crystallized from the mixture solution of **1**. Two new coordination polymers, $[Ag(Hima)(NO_3)]$ (**2**) and $\{[Pb(Hima)_2(NO_3)](NO_3)\}_n$ (**3**), are achieved by reaction of a flexible Hima, $AgNO_3$ and $Pb(NO_3)$, respectively. In **2**, the silver(I) atom is coordinated by four oxygen atoms from three carboxylate groups and one nitrate ion in a distorted tetrahedral environment. The free ligand Hima acts as the tridentate coordination mode, which bridges the silver atoms into a zigzag chain featuring a rare $[Ag_2$(carboxylato-O,O′)(carboxylato-$\mu_{1,1}$-O)] six-membered ring. The intradimer Ag···Ag distance is 2.966(1) Å. In **3**, Pb(II) atom exhibits an eight-coordinated dodecahedral coordination geometry, in which a unique 1-D chain structure with dicubane-like can be observed. In two polymers, the ligand Hima exhibits new and unique coordination modes. Solid-state fluorescence spectra reveal that the emission bands of complex **2** center at 462 and 510 nm (λ_{ex} = 280 nm). In **3**, the emission peaks locate at 465 and 547 nm upon excitation at 280 nm. In addition, they have been characterized by IR spectra and TG analysis.

1. Introduction

During the last decades the design and syntheses of metal–organic coordination polymers have been an impetus for supramolecular chemistry and property-oriented crystal engineering, owing to their novel topologies, fascinating structures and their potential applications in optical, electrical, magnetic, catalytic and micro-porous materials [1–6]. The rational design and controllable preparation of metal–organic coordination polymers are highly influenced by several factors, such as the coordination geometry of the central atom, the structural nature of the bridging ligands, the counter anion, the pH values of the reaction solution, the reaction temperature and so on [7–9]. Among these factors, the nature of the bridging ligands and alternation of the geometry of the linker unit take an important role in adjusting the formation of different frameworks with tailored properties and functions.

The ligands containing imidazole and carboxylic groups are excellent bridging blocks for constructing novel functional materials because they combine the coordination modes of imidazole and carboxylic functional groups [10]. In particular, some transition metal coordination polymers containing 2-(1*H*-imidazole-1-yl)acetic acid (Hima) ligand have been obtained, which display fascinating structures and potential applications [11]. Recently, the complexes containing silver(I) carboxylates have been prepared and structurally characterized in many documents owing to their unique structures [12–14]. In addition, the coordination chemistry of lead(II) has been explored extensively because it possesses the large radius, the variable stereochemical activity and the flexible coordination environment, which provide unique opportunities for the construction of novel structures [15–17]. Though many complexes containing silver(I) and lead(II) have been documented, the luminescent silver(I) and lead(II) chains with Hima have not been reported so far. There is still great potential in exploring this area. Meanwhile, as a program of our on-going investigation on constructing novel metal coordination polymers with Hima, herein we wish to report the syntheses, crystal structures and properties of the free ligand Hima (**1**), the complexes $[Ag(Hima)(NO_3)]_n$ (**2**) and $\{[Pb(Hima)_2(NO_3)](NO_3)\}_n$ (**3**). Additionally, the IR spectra and TGA of these compounds have been discussed in details.

2. Experimental

2.1. Materials and general methods

All the starting materials and solvents for syntheses were obtained commercially (ACROS) and used as received. Elemental analyses were performed on a Perkin-Elmer 240 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in range 400–4000 cm^{-1} on a Bruker Tensor 27 spectrometer. Thermogravimetric analysis (TGA) data were collected with a Perkin-Elmer TGS-2 analyzer in N_2 at a heating rate of 10 °C min^{-1}. The

---

* Corresponding author. Tel./fax: +86 0531 89000551.
E-mail address: ceswyt@sohu.com (Y.-T. Wang).

doi:10.1016/j.molstruc.2009.09.045

emission/excitation spectra were recorded on an Edinburgh FLS920 spectrometer equipped with a continuous Xe900 Xenon lamp and an nF900 ns flash lamp.

*2.2. Crystallization of Hima (**1**)*

The product was recrystallized from the water–methanol mixture to give the bar colorless crystals **1**. IR (KBr, cm^{-1}): ν 3130 (br), 3068 (w), 3013 (m), 2956 (w), 2488 (m), 1998 (m), 1618 (s), 1491 (w), 1437 (w), 1375 (s), 1326 (m), 1304 (m), 1291 (m), 1231 (w), 1190 (w), 1087 (w), 1053 (w), 1032 (w), 981 (m), 910 (m), 881 (m), 860 (m), 781 (s), 701 (w), 680 (m), 636 (m), 589 (m), 446 (m), 412 (m).

*2.3. Synthesis of $[Ag(Hima)(NO_3)]_n$ (**2**)*

To a solution of Hima (126 mg, 1 mmol) in water (10 ml), a dilute aqueous solution of $AgNO_3$ (199 mg, 1 mmol) was added dropwise. The mixture was further vigorously stirred *ca.* 30 min at room temperature, and then filtered. The colorless filtrate was allowed to stand at room temperature, and colorless plate single-crystals suitable for X-ray diffraction were obtained by evaporation of water within a week. Total yield: 78% (231 mg). Anal. calcd: for $C_5H_6AgN_3O_5$: C, 20.29; H, 2.04; N, 14.20%. Found: C, 20.18; H, 2.03; N, 14.25%. IR (KBr, cm^{-1}): ν 3425 (br), 2362 (w), 2272 (w), 1612 (s), 1513 (m), 1431 (w), 1390 (s), 1310 (m), 1236 (m), 1108 (m), 1082 (m), 1037 (m), 976 (w), 917 (m), 831 (w), 786 (w), 753 (w), 690 (w), 664 (w), 623 (w), 584 (w), 411 (w).

*2.4. Synthesis of $\{[Pb(Hima)_2(NO_3)](NO_3)\}_n$ (**3**)*

Hima (0.126 g, 1 mmol) was dissolved in water (10 ml) and then a solution of $Pb(NO_3)_2$ (0.166 g, 0.5 mmol) in water (10 ml) was added whilst stirring. The mixture was filtered and kept at ambient temperature for several days. The plate colorless single-crystals suitable for X-ray diffraction were obtained by slow evaporation of water within one week in 80% yield (233 mg). Anal. calcd: for $C_{10}H_{12}N_6O_{10}Pb$: C, 20.59; H, 2.07; N, 14.40%. Found: C, 20.48; H, 2.06; N, 14.45%. IR (KBr, cm^{-1}): ν 3149 (m), 3122 (w), 3109 (w), 3061 (w), 3010 (w), 2964 (w), 2879 (w), 2841 (w), 2767 (w), 2738 (w), 2706 (w), 2613 (w), 2571 (w), 2426 (w), 2324 (w), 2193 (w), 1592 (s), 1570 (s), 1435 (s), 1386 (s), 1313 (m), 1288 (m), 1165 (m), 1082 (m), 1026 (w), 918 (w), 881 (w), 850 (w), 781 (m), 756 (m), 688 (m), 638 (m), 624 (m), 584 (m), 520 (m), 506 (m), 430 (m), 406 (m).

2.5. X-ray crystallography

Single crystal X-ray diffraction measurements of **1**–**3** were carried out with a Bruker APEX II CCD diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection at 298(2) K. The lattice parameters were obtained by least-squares refinement of the diffraction data of reflections, and data collections were performed with Mo-Kα radiation (λ = 0.71073 Å). All the measured independent reflections were used in the structural analysis, and semi-empirical absorption corrections were applied using the SADABS program. The program SAINT [18] was used for integration of the diffraction profiles. All the structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined with SHELXL [19]. Metal atoms were located from the *E*-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full-matrix least-squares methods with anisotropic thermal parameters for all the non-hydrogen atoms based on F^2. All the hydrogen atoms were first found in difference electron density maps, and then placed in the calculated sites and included in the final refinement in the riding model approximation with displacement parameters derived from the parent atoms to which they were bonded. Crystal data as well as details of data collection and refinement for the compounds **1**–**3** are given in Table 1. Selected bond lengths and angles are listed in Table 2.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 651848, 651849 and 695855 for **1**–**3**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

3. Results and discussion

*3.1. Preparation of complexes **2** and **3***

Complexes **2** and **3** were generated from aqueous solutions by reactions of Hima with different metal salts. Compound **2** could also be isolated when using other solvents, such as water, methanol, the mixture of water and ethanol. The products were confirmed by X-ray diffraction, IR spectra and elemental analyses. Similar case was also observed for complex **3**, which indicates that the final products are independent of the solvent. Furthermore, **2** and **3** have the exact 1:1 and 2:1 ligand/metal compositions, respectively. Higher yields of the products were observed when increasing the metal-to-ligand ratio, thus indicating that the products are obviously independent on the ligand-to-metal ratio.

3.2. IR spectra

The IR spectrum of **2** shows characteristic bands of the carboxylate group in the usual region at 1612 cm^{-1} for the asymmetric

Table 1
Crystal and structure refinement for compounds **1**–**3**.

	1	**2**	**3**
Empirical formula	$C_5H_6N_2O_2$	$C_5H_6AgN_3O_5$	$C_{10}H_{12}N_6O_{10}Pb$
Formula weight	126.12	296.00	583.46
T/K	298	298	296
Wavelength/Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a/Å	4.6116(13)	12.226(3)	4.3852(11)
b/Å	8.571(2)	4.9247(13)	11.548(3)
c/Å	14.306(4)	14.914(4)	16.509(4)
α/°	90	90	90.961(3)
β/°	98.718(4)	113.118(3)	91.721(3)
γ/°	90	90	91.883(3)
V/Å^3	558.9(3)	825.9(4)	835.1(4)
Z	4	4	2
μ/mm^{-1}	0.118	2.442	10.170
Crystal size(mm)	0.20 × 0.20 × 0.50	0.08 × 0.16 × 0.35	0.20 × 0.20 × 0.40
ρ/g cm^{-3}	1.499	2.381	2.320
Reflections collected	2877	4233	7047
Independent reflections	1095	1820	3720
reflections [$I > 2\sigma(I)$]	980	1638	3573
$F(0\,0\,0)$	264	576	552
R_{int}	0.036	0.082	0.030
θ range	2.8/26.0	2.8/28.0	1.8/27.7
Goodness of fit on F^2	1.03	1.04	1.20
Largest hole and peak[e Å^{-3}]	−0.29/0.24	−0.98/1.27	−8.35/6.57
R_1[a]/wR_2[b]	0.0461/0.1316	0.0450/0.1288	0.0803/0.2278

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

Table 2
Selected bond lengths (Å) and angles (°) for complexes **2** and **3**.

2			
Ag1–O2	2.281(3)	Ag1–O2^a	2.575(3)
Ag1–O3	2.516(4)	Ag1–O1^b	2.293(3)
Ag1–Ag1^a	2.9664(9)		
O2–Ag1–O3	119.78(10)	Ag1^a–Ag1–O2	78.68(7)
O2^a–Ag1–O3	80.43(9)	Ag1^b–Ag1–O2	57.00(7)
O2–Ag1–O2^a	125.56(9)	Ag1^b–Ag1–O3	149.75(7)
O1^b–Ag1–O3	85.23(11)	Ag1^a–Ag1–O3	94.96(7)
O1^b–Ag1–O2	135.47(11)		
3			
Pb1–O1	2.50(2)	Pb1–O6	2.72(2)
Pb1–O2	2.983(18)	Pb1–O2^a	2.567(18)
Pb1–O4	2.551(14)	Pb1–O3^a	2.535(15)
Pb1–O5	2.915(18)	Pb1–O4^b	2.930(15)
O1–Pb1–O2	46.8(6)	O4–Pb1–O5	74.6(5)
O1–Pb1–O4	82.1(5)	O2^a–Pb1–O4	156.3(5)
O1–Pb1–O5	106.6(6)	O3^a–Pb1–O4	80.1(5)
O1–Pb1–O6	98.2(7)	O4–Pb1–O4^b	74.4(4)
O1–Pb1–O2^a	79.7(6)	O5–Pb1–O6	45.0(6)
O1–Pb1–O3^a	71.3(6)	O2^a–Pb1–O5	125.3(5)
O1–Pb1–O4^b	156.0(5)	O3^a–Pb1–O5	154.7(5)
O2–Pb1–O4	73.3(5)	O4^b–Pb1–O5	71.9(4)
O2–Pb1–O5	59.9(5)	O3^a–Pb1–O6	158.9(6)
O2–Pb1–O6	64.1(6)	O2^a–Pb1–O3^a	79.7(5)
O2–Pb1–O2^a	104.2(5)	O2^a–Pb1–O4^b	121.4(5)
O2–Pb1–O3^a	114.4(5)	O4^b–Pb1–O6	96.8(6)
O2–Pb1–O4^b	127.2(4)	O2^a–Pb1–O6	80.4(6)
O4–Pb1–O6	117.4(6)	O3^a–Pb1–O4^b	99.6(5)

Symmetry codes: ^{a}3/2 − *x*, −1/2 + *y*, 1/2 − *z*; ^{b}3/2 − *x*, 1/2 + *y*, 1/2 − *z* for **2**. ^{a}−1 + *x*, *y*, *z*; 1 + *x*, *y*, *z*; ^{b}−*x*, 1 − *y*, 1 − *z* for **3**.

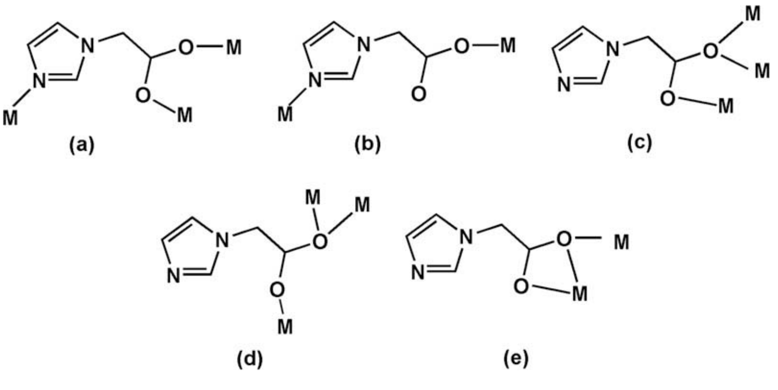
stretching and at 1390 cm^{-1} for the symmetric stretching. The separation (Δ) between $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$, 222 cm^{-1}, is slightly smaller than that in the free ligand Hima [$\nu(CO_2)$ 1618, 1375 cm^{-1}; Δ = 243 cm^{-1}], revealing the existence of bridging modes of the carboxylate groups (Scheme 1a) [20]. For **3**, the asymmetric and the symmetric stretching bands are at 1592 and 1386 cm^{-1}, respectively. The Δ is at 206 cm^{-1}, being significantly smaller than that found in Hima, which can be assigned to the existence of both bridging modes and chelating ones of the carboxylate groups (Scheme 1b). The Pb–O stretching frequencies in **3** are observed in the far-infrared region at 520 and 506 cm^{-1}, which are similar to those found in other Pb(II) complexes [15c,16b]. The IR spectra indicate that the Hima carboxylate groups display in different coordination modes, being in agreement with the crystal structures of **2** and **3**, respectively.

3.3. Crystal structure of **1**

Single X-ray analysis for compound **1** reveals that there exists one molecule of Hima in asymmetric unit (Fig. 1a). It is obviously observed that the molecule of the free ligand Hima adopts the molecular zwitterions, partly because of being in favor of forming the hydrogen bonds. A pair of Hima, each using the imidazole nitrogen atom and carboxylic oxygen one, forms one kind of hydrogen bonds (N2–H1···O1, Table 3) in the head–tail form [21]. Additionally, each Hima making use of imidazole carbon atom and carboxylic oxygen one, forms another kind of hydrogen bonds (C3–H3A···O1 Å and C4–H4A· · ·O2, Table 3) in the same formation. It is interestingly observed in this 2-D array, which are three types of hydrogen-bonded patterns A–D, notated as $R_4^2(10)$ (Fig. 1b(A)), $R_3^3(13)$ (Fig. 1b(B)) and $R_2^2(14)$ (Fig. 1b(C)), respectively. These chains formed by N2–H1···O1 lie parallel to each other, resulting in a two-dimensional hydrogen-bonded layer along the *bc* plane (Fig. 1b). The layers are further extended into a three-dimensional supramolecular array through two kinds of supramolecular interactions, which are offset π–π aromatic stacking interactions with the face-to-face distance of *ca.* 3.31 Å between imidazole rings, and the weak hydrogen-bonded interactions (C2–H2B· · ·O2 3.386(2) Å and C5–H5A· · ·O23.268(2) Å) (Fig. S1 and Table 3).

3.4. Crystal structure of **2**

Single X-ray analysis reveals that compound **2** has 1-D chains structure. In **2**, each Ag(I) center is coordinated by three carboxylic oxygen atoms from three Hima ligands and one nitrate oxygen one, as shown in Fig. 2a. The bond Ag–O lengths fall in the range of 2.281(3) and 2.575(3) Å (see Table 2), being in agreement with related Ag–O coordination bonds [12–14]. The coordination geometry of the four-coordinated Ag(I) center is distorted (the bond angles of O–Ag–O range from 80.43(9) to 135.47(11)°). The three metal–ligand bonds involving different carboxylato groups of Hima ligands are slightly longer than those found in other silver carboxylates [12d], and the fourth bond linked to a nitrate group is slightly smaller those of axially bonded nitrate groups in the dimeric structure of betaine silver(I) nitrate [12f]. Thus, it is observed that (carboxylato-O,O′)- and (carboxylato-$\mu_{1,1}$-O)-bridged centrosymmetric Ag_2(Hima)$_2$ dimers with the carboxylato group of Hima serving in the symmetric *syn–syn* bridging mode, resulting into forming a rare [Ag_2(carboxylato-O,O′)(carboxylato-$\mu_{1,1}$-O)] six-membered ring, which is significantly distinct from those found the related silver(I) carboxylates [12–14]. The Ag···Ag separation of 2.966(1) Å in the six-membered rings is slightly larger than the average value (2.89 Å) in metallic silver, thus indicating a weak or negligible metal–metal interaction. The intra-dimer Ag–O distances and O–Ag–O angles fall in the range of 2.281(3)–2.293(3) Å and 125.56(9)–135.47(11)°, respectively, which are comparable to those found in the other dimeric structures of several known silver(I) carboxylates [12–14]. The present structure is extended into a zigzag polymeric chain running parallel to the *b* axis (Fig. 2b). These chains are further extended to a supramolecular layer along the *ac* plane by weak



Scheme 1. Coordination modes of Hima.

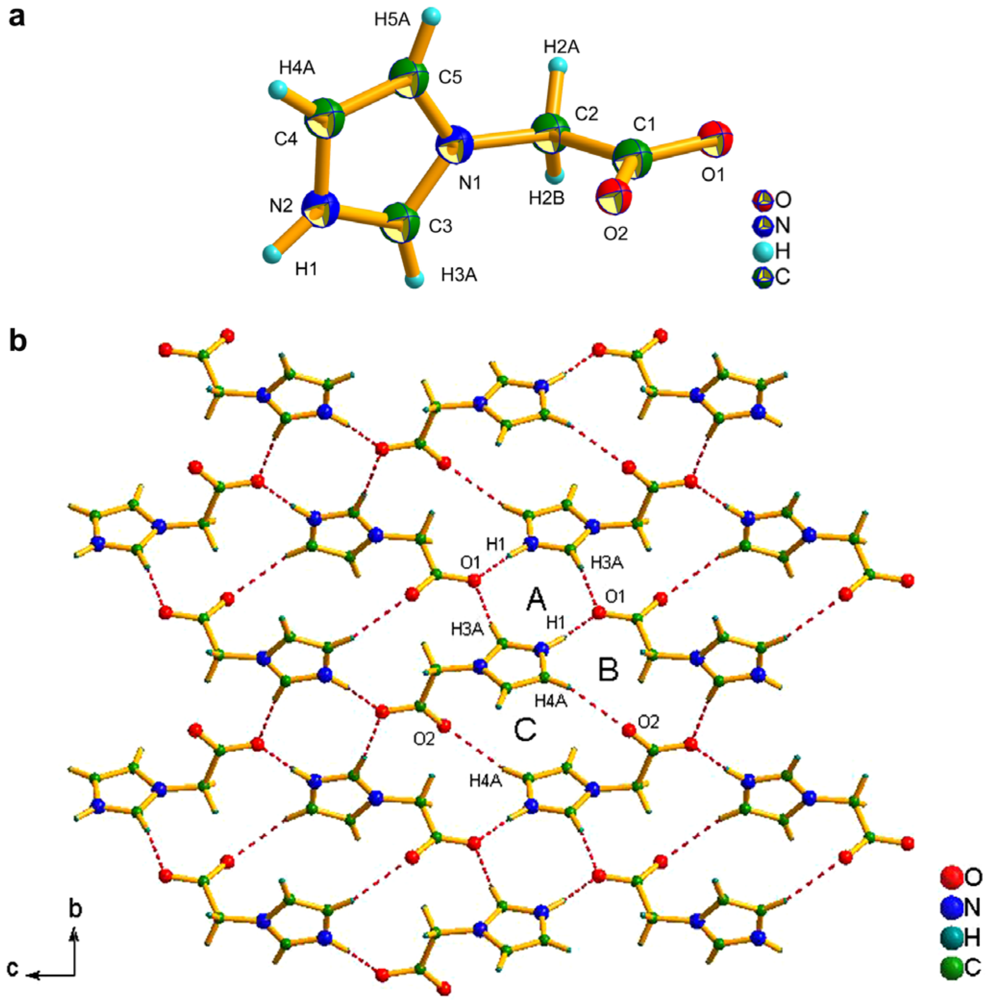


Fig. 1. (a) View of the structure of Hima (**1**). (b) 2-D supramolecular network extended by hydrogen bonds along the *bc* plane in **1**. The red dashed-lines stand for hydrogen bonds. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)

Table 3
Hydrogen bond geometries in the crystal structure of **1–3**.

Compounds	D–H···A	H···A [Å]	D···A [Å]	D–H···A [°]
1				
	N2–H1···O1^{a}	1.72(2)	2.647(2)	173(2)
	C2–H2B···O2^{b}	2.4900	3.386(2)	153.00
	C3–H3A···O1^{b}	2.2200	3.143(2)	174.00
	C4–H4A···O2^{c}	2.4400	3.321(2)	158.00
	C5–H5A···O2^{d}	2.4600	3.268(2)	145.00
2	N2–H2···O5^{a}	2.58(9)	3.117(6)	114(6)
	N2–H2···O5^{b}	1.91(7)	2.854(6)	157(6)
	C2–H2A···O1^{c}	2.3600	3.270(5)	156.00
	C4–H4A···O3^{a}	2.3500	3.242(6)	162.00
3	N2–H2···O8^{a}	2.4800	3.05(4)	124.00
	N2–H2···O9^{a}	2.0500	2.87(3)	159.00
	N4–H4···O8^{b}	2.4700	3.02(4)	122.00
	N4–H4···O10^{b}	1.9300	2.78(3)	172.00
	C2–H2A···O6^{c}	2.3900	3.31(3)	159.00
	C2–H2B···O1^{b}	2.5400	3.25(3)	130.00
	C3–H3A···O7^{c}	2.5600	3.45(4)	161.00
	C4–H4A···O9^{d}	2.4800	3.32(4)	151.00
	C7–H7B···O3^{e}	2.3700	3.22(3)	146.00
	C9–H9A···O10^{d}	2.5100	3.28(4)	141.00
	C10–H10A···O7^{f}	2.2200	3.10(3)	158.00

Symmetry codes: $^{a}-1/2+x$, $1/2-y$, $-1/2+z$; $^{b}-1/2-x$, $-1/2+y$, $1/2-z$; $^{c}-x$, $1-y$, $-z$; $^{d}1+x$, y, z for **1**. $^{a}-1+x$, y, z; $^{b}1-x$, $-1-y$, $-z$; ^{c}x, $1+y$, z for **2**. ^{a}x, $1+y$, z; $^{b}1+x$, y, z; $^{c}-x$, $2-y$, $1-z$; $^{d}1-x$, $1-y$, $-z$; $^{e}-1+x$, y, z; $^{f}1-x$, $1-y$, $1-z$ for **3**.

hydrogen-bonding interactions (C4–H4A···O3^{a} 3.242(6) Å, $a=-1+x$, y, z) (Fig. S2) [21]. A 3-D supramolecular framework is constructed by interlayer weak hydrogen-bonding interactions (N2–H2···O5^{b}, C2–H2A···O1^{c} and N2–H2···O5^{a} 2.854(6), 3.270(5) and 3.117(6) Å, respectively. $a=-1+x$, y, z; $b=1-x$, $-1-y$, $-z$; $c=x$, $1+y$, z) (Fig. S2 and Table 3).

It is worthy of note that in complex **2**, the Hima ligand is a neutral molecule and adopts the zwitterionic formation, be significantly different from those found previously in related complexes containing Hima [11]. Compared to the previously reported coordination modes of Hima (Scheme 1a and b) [11], it is observed that there exists new type of coordination mode for the free ligand Hima in **2** (Scheme 1c).

3.5. Crystal structure of 3

X-ray single-crystal structure determination reveals that **3** crystallizes in the triclinic system space group $P\bar{1}$. Complex **3** possesses one-dimensional (1-D) chain constructed by Pb(II) centers, Hima ligands and nitrate ions. Pb1 is coordinated by two oxygen atoms (O5 and O6) from one nitrate ion, and six carboxylate oxygen atoms (O1, O2, O2A, O3A, O4 and O4B) from four different Hima molecules, forming an eight-coordinated dodecahedral coordination geometry (Fig. 3a). The distances between Pb and O atoms

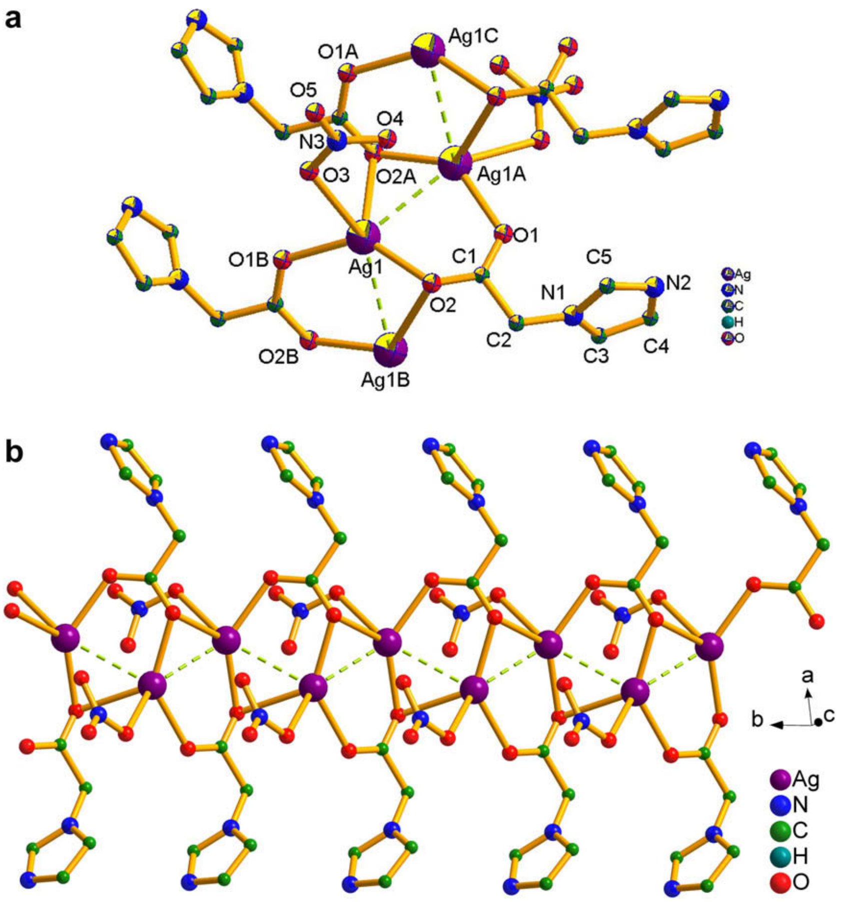


Fig. 2. (a) View of coordination environments of the metal atom in **2** (hydrogen atoms are omitted for clarity). The pale-green dashed-lines denote the silver–silver interactions. (b) View of 1-D chain along the *c* axis in **2**. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)

(ranging from 2.50(2) to 2.98(2) Å) fall in the range of Pb–O covalent bonds (ranging from 2.46 to 2.96 Å) (Fig. 3b) [15,17]. Longer distance is observed between Pb and one oxygen atoms (O2) from Hima molecule (2.98(2) Å), being shorter than Pb–O bonds (3.11 Å) [17]. All Hima ligands act as two- and three-connectors to link four lead centers through bis- and tridentate carboxylate oxygen atoms (Scheme 1d and e). A holodirected geometry in **3** is observed due to the absence of clear gap in the coordination sphere of the Pb(II) ion [22]. As shown in Fig. 3c, in **3** structure, two kinds of separations of Pb···Pb can be found, for example, Pb1 and Pb1A are bridged by a carboxyl O atom with a Pb···Pb distance of 4.385(2) Å. The distance between Pb1 and Pb1C separated by two O atoms of carboxyl groups is 4.970(1) Å. Pb1 and Pb1B are also bridged by another carboxyl O atom, forming a Pb_2O_2 unit with a Pb···Pb distance of 4.372(1) Å, which is too long to include metal–metal interaction [22b,23]. Interestingly, along the *c* axis, four Pb(II) atoms are located at the four corners of a defective double cubane (two cubanes sharing one face and each missing one vertex) and bridged by means of two carboxylic O atoms and two μ_2-O atoms. It is noted that only a limited number of dicubane-like structures constructed through Pb–O bond and bridging O atoms of carboxylate group were observed [24]. By sharing the Pb_2O_2 planes, the kind of dicubane was further extended to a 1-D dicubane-like chain along the *c* axis (Fig. 3c). The diagram of simplified 1-D chain structure is illustrated in Fig. S3.

The structure of compound **3** is expanded into a two-dimensional layer structure along the crystallographic *bc* plane through N–H···O hydrogen bonds interactions from uncoordinated nitrate anions and imidazole groups (D···A distances range from 2.78(3) to 3.05(4) Å, Fig. S2 and Table 3). The thickness of 2-D layer is 1.3 nm and the distance of Pb···Pb in two neighboring chains is 7.618(2) Å (Fig. S4). For **3**, neighboring 2-D layers stack in *AAA* way (Fig. S5). The interlayer distance is 16.509(2) Å (Pb···Pb separation in two neighboring layers). These 2-D layers are further extended to a 3-D supramolecular structure by weak C–H···O supramolecular interactions (D···A distances fall in the range of 3.10(3) to 3.45(4) Å) (Fig. S5 and Table 3).

Being similar to complex **2**, the ligand Hima is also a neutral molecule in **3**. It is interestingly observed that there exist other two kinds of coordination modes for Hima in **3** (Scheme 1d and e), being significantly distinct from that in both complex **2** and those found in the previous documents [11].

3.6. Thermogravimetric analysis (TGA)

TGA measurements were conducted to determine the thermal stability of **2** and **3**. The TGA curve reveals that compound **2** remains intact until one consecutive weight loss occurs from 280 to 350 °C, being ascribed to the loss of ligands (found: 60.49%; calcd: 60.86%). The remaining product weight is 39.51% when further heating at the range of 350–700 °C, which can be ascribed to Ag_2O residue (calcd: 39.14%). TGA of complex **3** indicates that the weight is unchanged until the temperature increases to 310 °C, indicating that the thermal stability of **3** is higher than **2**. The first weight loss of 61.08% (calcd: 61.75%) occurs at the range of 310–390 °C, corresponding to the release of the ligands. The final decomposed product hardly loses any weight (38.92%) upon fur-

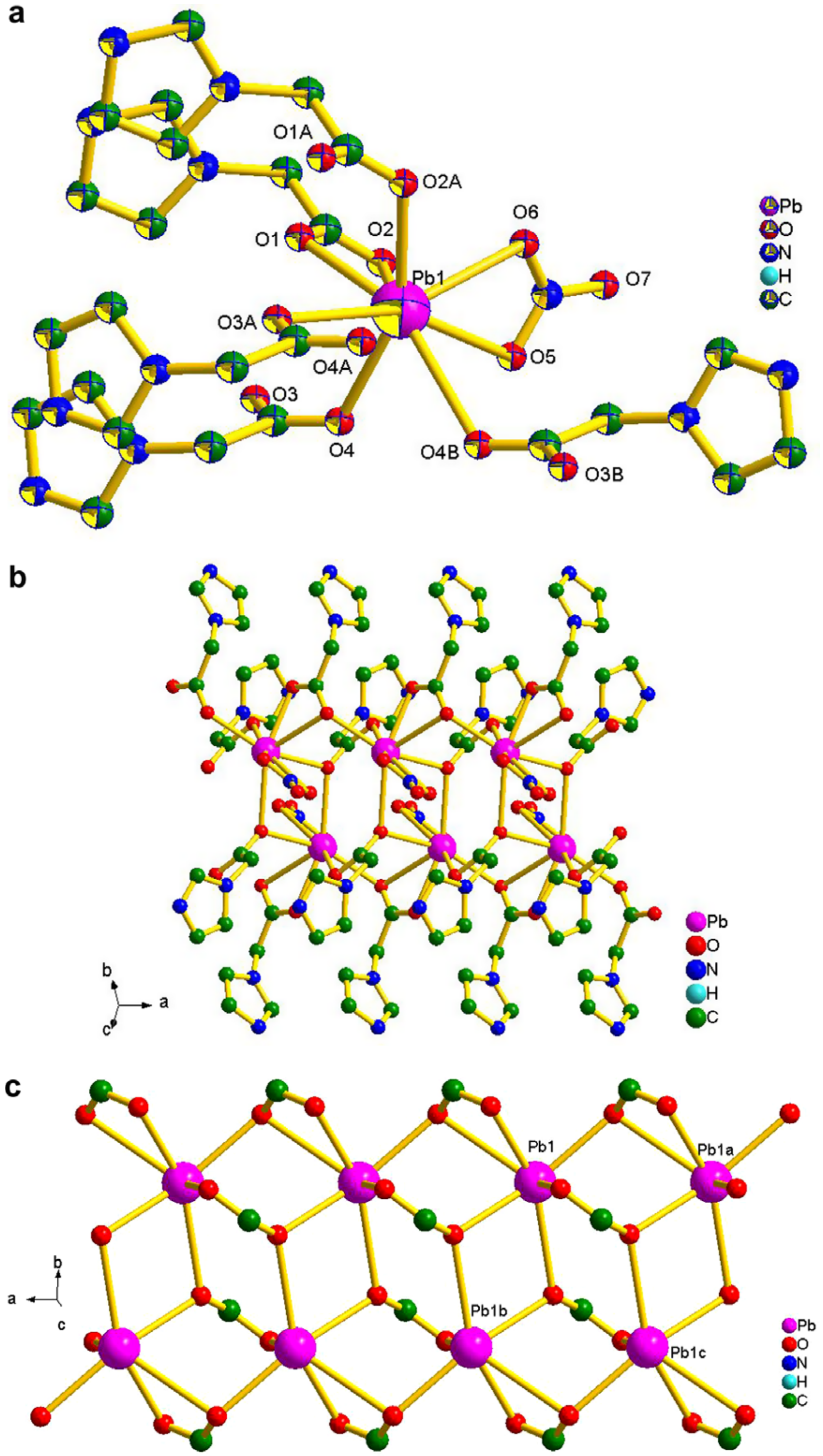


Fig. 3. (a) Perspective view showing the coordination environment around the metal atom in **3** (hydrogen atoms and nitrate ion are omitted for clarity). (b) The 1-D chain of **3**. Partial of nitrate anions are omitted for clarity. (c) The 1-D incomplete-cubane chain of **3**. Partial of carbon and hydrogen atoms are omitted for clarity. Symmetry codes: (a) $-1 + x, y, z$; (b) $-x, 1 - y, 1 - z$; (c) $-1 - x, 1 - y, 1 - z$.

ther heating from 390 to 700 °C, which can be ascribed to PbO residue (calcd: 38.25%).

3.7. Luminescent properties

As illustrated Fig. 4, the solid-state room temperature photoluminescence of **2** exhibits the emission peak at 462 and 510 nm upon an excitation maximum at 280 nm. The solid-state photoluminescence spectrum of **3** at room temperature is observed with the main emission at 465 and 547 nm ($\lambda_{ex} = 280$ nm). To further study the relative luminescence of between the free ligand and its complexes, the photoluminescent spectrum of free ligand Hima was also investigated in solid state at room temperature (Fig. 4). The free ligand Hima shows the fluorescent emission centers on

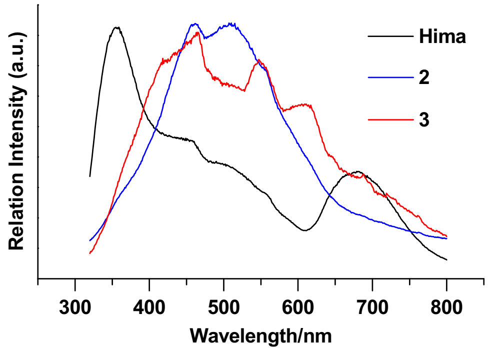


Fig. 4. Solid-state emission spectra of the ligand Hima (**1**) and its complexes (**2**, **3**) at room temperature.

356 and 682 nm with an excitation maximum at 280 nm. In comparison to the free ligand Hima, the main emission peaks of **2** and **3** are red-shifted about 106 and 109 nm, respectively. Apparently, for **2**, the discrepancy of luminescent profiles is tentatively assigned to the ligand-to-metal charge transfer (LMCT). For **3**, these strong fluorescence emissions may be attributed to the Pb^{2+} lone pair to ligand charge transfer [25], and the red-shifted effect may be due to an excited metal-perturbed intraligand state.

4. Conclusions

Using a flexible ligand Hima we isolated two new silver and lead coordination polymers possessing the unique 1-D chains, which were characterized by single crystal X-ray diffraction, IR spectra, elemental analysis, photoluminescence as well as thermal analysis. The present study shows that Hima displays three new kinds of coordination modes and can be used as an excellent bridging ligand to construct novel metal coordination polymers. Efforts to further investigate other coordination polymers based on this kind of flexible organic ligands are in progress in our laboratory.

Acknowledgments

This work was financially supported by the Project of Shandong Province Higher Educational Science and Technology Program (J09LB03), and the Starting Funding of Shandong Institute of Light Industry (to Dr. Yong-Tao Wang). We are indebted to Prof. Xiao-Ming Chen at Sun Yat-Sen University for helpful discussion.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2009.09.045.

References

[1] For examples: (a) N.W. Ockwig, O. Delgado-Friedrichs, M. O'Keeffe, O.M. Yaghi, Acc. Chem. Res. 38 (2005) 176;
(b) B. Kesanli, W. Lin, Coord. Chem. Rev. 246 (2003) 305;
(c) J.-P. Zhang, S.-L. Zheng, X.-C. Huang, X.-M. Chen, Angew. Chem. Int. Ed. 43 (2004) 206.
[2] For examples: (a) S.R. Seidel, P.J. Stang, Acc. Chem. Res. 35 (2002) 972;
(b) N.L. Rosi, J. Kim, M. Eddaoudi, B. Chen, M. O'Keeffe, O.M. Yaghi, J. Am. Chem. Soc. 127 (2005) 1504;
(c) J. Wang, Y.-H. Zhang, M.-L. Tong, Chem. Commun. (2006) 3166.
[3] For examples: (a) S.R. Batten, R. Robson, Angew. Chem. Int. Ed. 37 (1998) 1460;
(b) R. Cao, D.F. Sun, Y.C. Liang, M.C. Hong, K. Tatsumi, Q. Shi, Inorg. Chem. 41 (2002) 2087;
(c) M.L. Tong, Y.M. Wu, J. Ru, X.M. Chen, H.C. Chang, S. Kitagawa, Inorg. Chem. 41 (2002) 4846.
[4] (a) A.Y. Robin, K.M. Fromm, Coord. Chem. Rev. 250 (2006) 2127;
(b) W.-G. Lu, C.-Y. Su, T.-B. Lu, L. Jiang, J.-M. Chen, J. Am. Chem. Soc. 128 (2006) 34;
(c) X.-D. Chen, T.C.W. Mak, J. Chem. Soc. Dalton Trans. (2005) 3646;
(d) I.S. Lee, D.M. Shin, Y.K. Chung, Chem. Eur. J. 10 (2004) 3158.
[5] (a) C.-Y. Su, M.D. Smith, A.M. Goforth, H.-C. zur Loye, Inorg. Chem. 43 (2004) 6881;
(b) X.-Q. Lu, J.-J. Jiang, L. Zhang, C.-L. Chen, C.-Y. Su, B.-S. Kang, Cryst. Growth Des. 5 (2005) 419;
(c) O.R. Evans, W.B. Lin, Acc. Chem. Res. 35 (2002) 511;
(d) C.-D. Wu, A. Hu, L. Zhang, W. Lin, J. Am. Chem. Soc. 127 (2005) 8940.
[6] (a) Y.-P. Ren, X.-J. Kong, L.-S. Long, R.-B. Huang, L.-S. Zheng, Cryst. Growth Des. 6 (2006) 572;
(b) C.-M. Liu, D.-Q. Zhang, D.-B. Zhu, Cryst. Growth Des. 6 (2006) 524;
(c) K. Uemura, S. Kitagawa, K. Fukui, K. Saito, J. Am. Chem. Soc. 126 (2004) 3817;
(d) A.N. Khlobystov, M.T. Brett, A.J. Blake, N.R. Champness, P.M.W. Gill, D.P. O'Neill, S.J. Teat, C. Wilson, M. Schröder, J. Am. Chem. Soc. 125 (2003) 6753.
[7] (a) X.-Y. Wang, L. Wang, Z.-M. Wang, S. Gao, J. Am. Chem. Soc. 128 (2006) 674;
(b) Y.-T. Wang, M.-L. Tong, H.-H. Fan, H.-Z. Wang, X.-M. Chen, J. Chem. Soc. Dalton Trans. (2005) 424;
(c) Y.-T. Wang, H.-H. Fan, H.-Z. Wang, X.-M. Chen, Inorg. Chem. 44 (2005) 4148;
(d) Y.-T. Wang, H.-H. Fan, H.-Z. Wang, X.-M. Chen, J. Mol. Struct. 740 (2005) 61;
(e) L.-F. Ma, L.-Y. Wang, D.-H. Lu, S.R. Batten, J.-G. Wang, Cryst. Growth Des. 9 (2009) 1741.
[8] (a) D.N. Dybtsev, A.L. Nuzhdin, H. Chun, K.P. Bryliakov, E.P. Talsi, V.P. Fedin, K. Kim, Angew. Chem. Int. Ed. 45 (2006) 916;
(b) S.-H. Cho, B. Ma, S.T. Nguyen, J.T. Hupp, T.E. Albrecht-Schmitt, Chem. Commun. (2006) 2563;
(c) C.-Y. Su, X.-P. Yang, B.-S. Kang, T.C.W. Mak, Angew. Chem. Int. Ed. 40 (2001) 1725;
(d) Q. Wang, R. Yang, C.-F. Zhuang, J.-Y. Zhang, B.-S. Kang, C.-Y. Su, Eur. J. Inorg. Chem. (2008) 1702.
[9] (a) A.C. Sudik, A.P. Côté, A.G. Wong-Foy, M. O'Keeffe, O.M. Yaghi, Angew. Chem. Int. Ed. 45 (2006) 2528;
(b) Y. Bai, G.-J. He, Y.-G. Zhao, C.-Y. Duan, D.-B. Dang, Q.-J. Meng, Chem. Commun. (2006) 1530;
(c) P.D.C. Dietzel, B. Panella, M. Hirscher, R. Bloma, H. Fjellvåg, Chem. Commun. (2006) 959;
(d) S.A. Barnett, N.R. Champness, Coord. Chem. Rev. 246 (2003) 145.
[10] For examples: (a) Z.-F. Fei, D.-B. Zhao, T.J. Geldbach, R. Scopelliti, P.J. Dyson, S. Antonijevic, G. Bodenhausen, Angew. Chem. Int. Ed. Engl. 44 (2005) 5720;
(b) J.-D. Lin, J.-W. Cheng, S.-W. Du, Cryst. Growth Des. 8 (2008) 3345;
(c) Q. Xu, R.-Q. Zou, R.-Q. Zhong, C. Kachi-Terajima, S. Takamizawa, Cryst. Growth Des. 8 (2008) 2458;
(d) C.L. Cahill, D.T. de Lill, M. Frisch, Cryst. Eng. Commun. 9 (2007) 15;
(e) Y.-T. Wang, G.-M. Tang, Z.-M. Liu, X.-H. Yi, Cryst. Growth Des. 7 (2007) 2272.
[11] (a) Y.-T. Wang, G.-M. Tang, D.-W. Qin, Aust. J. Chem. 59 (2006) 647;
(b) Y.-T. Wang, G.-M. Tang, Y. Wu, X.-Y. Qin, D.-W. Qin, J. Mol. Struct. 831 (2007) 61;
(c) T.L. Hu, W.P. Du, B.W. Hu, J.R. Li, X.H. Bu, R. Cao, Cryst. Eng. Commun. 10 (2008) 1037.
[12] For examples: (a) M.-L. Tong, S.-L. Zheng, X.-M. Chen, Chem. Eur. J. 6 (2000) 3729;
(b) Q.-M. Wang, T.C.W. Mak, Chem. Commun. (2000) 1435;
(c) J. Powell, M.J. Horvath, A. Lough, A. Phillips, J. Brunet, J. Chem. Soc. Dalton Trans. (1998) 637;
(d) X.-M. Chen, T.C.W. Mak, J. Chem. Soc. Dalton Trans. (1991) 1219;
(e) G. Smith, D.S. Sagatys, C.A. Campbell, D.E. Lynch, C.H.L. Kennard, Aust. J. Chem. 43 (1990) 1707;
(f) W.-Y. Huang, L. Lu, X.-M. Chen, T.C.W. Mak, Polyhedron 10 (1991) 2687.
[13] (a) P.-R. Wei, Q. Li, B.-M. Wu, T.C.W. Mak, Polyhedron 16 (1997) 153;
(b) G. Smith, A.N. Reddy, K.A. Byriel, C.H.L. Kennard, Aust. J. Chem. 47 (1994) 1179;
(c) F. Jaber, F. Charbonnier, R. Faure, Polyhedron 15 (1996) 2909.
[14] (a) X.-M. Chen, T.C.W. Mak, Aust. J. Chem. 44 (1991) 1783;
(b) W.-K. Wong, L. Zhang, W.-T. Wong, Chem. Commun. (1998) 673;
(c) Q.-M. Wang, T.C.W. Mak, J. Am. Chem. Soc. 123 (2001) 1501;
(d) T.G. Appleton, K.A. Byriel, J.R. Hall, C.H.L. Kennard, D.E. Lynch, J.A. Sinkinson, G. Smith, Inorg. Chem. 33 (1994) 444.
[15] (a) Y.-H. Zhao, H.-B. Xu, Y.-M. Fu, K.-Z. Shao, S.-Y. Yang, Z.-M. Su, X.-R. Hao, D.-X. Zhu, E.-B. Wang, Cryst. Growth Des. 8 (2008) 3566;
(b) K.-L. Zhang, W. Liang, Y. Chang, L.-M. Yuan, S.W. Ng, Polyhedron 28 (2009) 647;
(c) H. Yin, S.-X. Liu, Inorg. Chem. Commun. 12 (2009) 187;
(d) B. Ding, E.-C. Yang, J.-H. Guo, X.-J. Zhao, X.-G. Wang, Inorg. Chem. Commun. 11 (2008) 509.
[16] (a) R.L. Davidovich, V. Stavila, D.V. Marinin, E.I. Voit, K.H. Whitmire, Coord. Chem. Rev. 253 (2009) 1316;
(b) K. Lyczko, W. Starosta, I. Persson, Inorg. Chem. 46 (2007) 4402;
(c) J. Yang, J.-F. Ma, Y.-Y. Liu, J.-C. Ma, S.R. Batten, Cryst. Growth Des. 9 (2009) 1894.
[17] (a) C.E. Holloway, M. Melnik, Main Group Met. Chem. 20 (1997) 399;
(b) F.H. Allen, Acta Crystallogr. B58 (2002) 380.
[18] Bruker AXS, SAINT Software Reference Manual, Madison, WI, 1998.

[19] G.M. Sheldrick, SHELXTL NT Version 5.1. Program for Solution and Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
[20] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, John Wiley & Sons, New York, 1986.
[21] G.R. Desiraju, T. Steiner, The Weak Hydrogen Bond in Structural Chemistry and Biology, Oxford University Press, 1999.
[22] (a) J.M. Harrowfield, H. Miyamae, B.W. Skelton, A.A. Soudi, A.H. White, Aust. J. Chem. 49 (1996) 1121;
(b) J.M. Harrowfield, B.W. Skelton, A.H. White, J. Chem. Soc. Dalton Trans. (1993) 2011.
[23] S.-R. Fan, L.-G. Zhu, Inorg. Chem. 45 (2006) 7935.
[24] (a) G.S. Papaefstathiou, A. Escuer, C.P. Raptopoulou, A. Terzis, S.P. Perlepes, R. Vicente, Eur. J. Inorg. Chem. (2001) 1567;
(b) Y.-J. Zhu, Z.-G. Ren, W.-H. Zhang, Y. Chen, H.-X. Li, Y. Zhang, J.-P. Lang, Inorg. Chem. Commun. 10 (2007) 485.
[25] H.G. Zhu, Y. Xu, Z. Yu, Q.J. Wu, H.K. Fun, X.Z. You, Polyhedron 18 (1999) 3491.