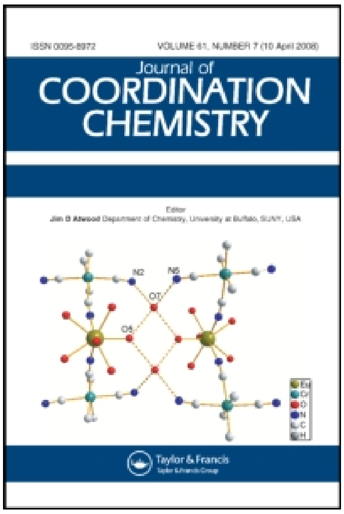

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Two new Pb(II) coordination polymers, $[Pb_2$(μ-4,4'-bipy) (μ-2-$sb)_2(DMF)]$<i>_n and $\{[Pb_2$(μ-4,4'-bipy) (μ-2-$sb)_2(H_2O)_2] \cdot H_2O\}$<i>_n (4,4'-bipy = 4,4'-bipyridine and 2-H_2sb = 2-sufobenzoic acid)

Hong-Ping Xiao[a]; Jia-Guo Wang[a]; Ali Morsali[b]; Wei-Bing Zhang[a]; Xin-Hua Li[a]
[a] School of Chemistry and Materials Science Engineering, Wenzhou University, Wenzhou, China [b] Department of Chemistry, School of Science, Tarbiat Modares University, Tehran, Iran

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Two new Pb(II) coordination polymers, $[Pb_2(\mu\text{-}4,4'\text{-bipy})(\mu\text{-}2\text{-sb})_2(DMF)]_n$ and $\{[Pb_2(\mu\text{-}4,4'\text{-bipy})(\mu\text{-}2\text{-sb})_2(H_2O)_2]\cdot H_2O\}_n$ (4,4′-bipy = 4,4′-bipyridine and 2-H_2sb = 2-sufobenzoic acid)

HONG-PING XIAO*†, JIA-GUO WANG†, ALI MORSALI*‡,
WEI-BING ZHANG† and XIN-HUA LI†

†School of Chemistry and Materials Science Engineering, Wenzhou University,
Wenzhou, China
‡Department of Chemistry, School of Science, Tarbiat Modares University,
P.O. Box 14155-4838, Tehran, Iran

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Two new 2D $Pb_2(\mu\text{-}4,4'\text{-bipy})(\mu\text{-}2\text{-sb})_2$ coordination polymers, $[Pb_2(\mu\text{-}4,4'\text{-bipy})(\mu\text{-}2\text{-sb})_2(DMF)]_n$ (**1**) and $\{[Pb_2(\mu\text{-}4,4'\text{-bipy})(\mu\text{-}2\text{-sb})_2(H_2O)_2]\cdot H_2O\}_n$ (**2**), have been synthesized, characterized and studied by X-ray crystallography. The structural studies show the Pb atoms to have seven- and eight-coordinate holodirected geometries.

Keywords: Lead(II); 4,4′-Bipyridine; 2-Sufobenzoic acid; Coordination polymer

1. Introduction

Control of molecular arrangements of coordination polymers has attracted much attention [1, 2], with extended systems of a variety of metals providing information about supramolecular isomerism. Lead(II) complexes are frequently discussed in coordination and stereo-activity of heavy metals [3–16].

2-Sufobenzoic acid (2-H_2sb), with both carboxylate and sulfonate available as coordinating groups, forms polynuclear complexes and may also be a candidate for investigation of "stereo-chemical activity" of valence shell electron lone pairs in polymeric and supramolecular compounds.

The sulfonate group has very different coordination ability than carboxylate; 2-sulfobenzoate has been useful for constructing diverse networks [17–23]. The present, determination of structures of 2-sufobenzoate (2-sb) Pb(II) complexes with 4,4′-bipyridine (4,4′-bipy) provides two-dimensional coordination polymers with the less-common holodirected lead(II) coordination spheres.

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*Corresponding authors. Email: morsali_a@yahoo.com; hp-xiao@yahoo.com.cn

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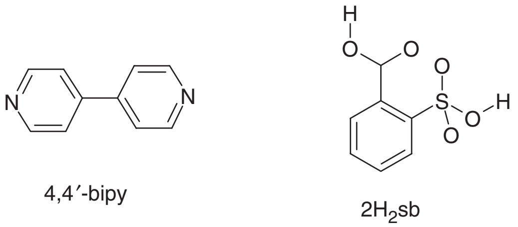


Scheme 1. Ligands used in the construction of lead(II) coordination polymer frameworks.

2. Experimental

2.1. *Physical property measurements*

All reagents and solvents were commercially available and used as received. IR spectra were recorded using Perkin–Elmer 597 and Nicolet 510P spectrophotometers. Microanalyses were carried out using a Heraeus CHN–O– Rapid analyzer.

2.2. *Synthesis of [Pb_2(μ-4,4′-bipy)(μ-2-sb)$_2$(DMF)]$_n$ (1)*

DMF solution (10 mL) containing 4,4′-bipyridine (0.20 mmol) and 2-sufobenzoic acid (0.20 mmol) was added slowly to a water solution (10 mL) containing $Pb(CH_3COO)_2 \cdot 3H_2O$ (0.20 mmol). The mixture was left to stand at room temperature and in about two months colorless crystals were obtained, m.p. > 300°C. $C_{15}H_{15}N_2O_6PbS$: Calcd C, 32.26; H, 2.71; N, 5.02. Found: C, 32.07; H, 2.63; N, 4.94. FT-IR (KBr, cm^{-1}) selected bonds: $\nu = 3069$w, 2931m, 1633s, 1695s, 1534s, 15440s, 1393s, 1319s, 1236s, 1104w, 1079s, 1062s, 1006s, 845m, 815m, 755m, 739m, 724m, 656m, 621m, 548m.

2.3. *Synthesis of {[Pb_2(μ-4,4′-bipy)(μ-2-sb)$_2$(H_2O)$_2$] • H_2O}$_n$ (2)*

An ethanol solution (10 mL) containing 4,4′-bipyridine (0.20 mmol) and 2-sufobenzoic acid (0.20 mmol) was added slowly to a water solution (10 mL) containing $Pb(NO_3)_2$ (0.20 mmol). The mixture stood at room temperature about one month giving colorless crystals, m.p. > 300°C. $C_{12}H_{14}NO_8PbS$: Calcd C, 26.72; H, 2.62; N, 2.60. Found: C, 26.59; H, 2.48; N, 2.51. IR (KBr, cm^{-1}) selected bonds: $\nu = 3328$m, 1607s, 1595vs, 1541s, 1441m, 1393vs, 1144w, 1061w, 1008w, 847m, 756m, 726m, 623m, 549m.

2.4. *Crystallography*

X-ray measurements were made at 298(2) and 273(2) K using a Siemens R3 m/V diffractometer for **1** and **2**, respectively. The intensity data were collected within the theta range 1.76 to 25.98 and 1.92 to 25.29° using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) for **1** and **2**, respectively. Accurate unit cell parameters and an orientation matrix for data collection were obtained from least-squares refinement. The structures were solved by direct methods and refined by full-matrix least-squares on F^2. Crystal data and refinement parameters are given in table 1 and selected bond lengths and angles in table 2. ORTEP diagrams and perspective views of the packing are shown in figures 1–4.

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

Identification code	**1**	**2**
Empirical formula	$C_{15}H_{15}N_2O_6PbS$	$C_{12}H_{14}NO_8PbS$
Formula weight	558.54	539.49
Temperature (T)	273(2)	298(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	Pc
Unit cell dimensions (Å, °)		
a	7.0710(8)	11.5879(9)
b	11.5024(13)	7.0970(6)
c	11.7815(13)	18.7300(15)
α	114.740(2)	
β	91.511(2)	92.8210(10)
γ	101.920(2)	
V (Å^3)	844.62(16)	1538.5(2)
Z	2	4
D_{Calcd} (g cm^{-3})	2.196	2.329
Absorption coefficient (mm^{-1})	10.146	11.143
$F(000)$	530	1020
Crystal size (mm^3)	$0.49 \times 0.24 \times 0.20$	$0.21 \times 0.20 \times 0.13$
θ range for data collection (°)	1.92–25.29	1.76–25.98
Index ranges	$-8 \le h \le 8$	$-14 \le h \le 12$
	$-13 \le k \le 13$	$-6 \le k \le 8$
	$-13 \le l \le 14$	$-22 \le l \le 22$
Reflections collected	6135	8341
Independent reflections	3049	3013
Absorption correction	Multi-scan	None
Max. and min. transmission	0.2361 and 0.0827	0.3252 and 0.2031
Refinement method	Full-matrix	Full-matrix
	Least-squares on F^2	Least-squares on F^2
Data/restraints/parameters	3049/0/228	3013/0/208
Goodness-of-fit on F^2	1.025	1.099
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0290$	$R_1 = 0.0249$
	$wR_2 = 0.0743$	$wR_2 = 0.0616$
R indices (all data)	$R_1 = 0.0306$	$R_1 = 0.0272$
	$wR_2 = 0.0752$	$wR_2 = 0.0624$
Largest diff. peak, hole (e Å^{-3})	1.889 and −1.711	0.701 and −1.498

3. Results and discussion

Reaction between 4,4′-bipyridine lead(II) acetate trihydrate and 2-sufobenzoic acid in DMF/water and between 4,4′-bipyridine, lead(II) nitrate and 2-sufobenzoic acid in water provided crystalline materials analyzing as $[Pb_2(\mu\text{-}4,4'\text{-bipy})(\mu\text{-}2\text{-sb})_2(DMF)]_n$ (**1**) and $\{[Pb_2(\mu\text{-}4,4'\text{-bipy})(\mu\text{-}2\text{-sb})_2(H_2O)_2] \cdot H_2O\}_n$ (**2**). Single X-ray crystal analysis reveals that **1** and **2** crystallize monoclinic and triclinic with space group $P\bar{1}$ and Pc, respectively. The structure of these complexes are two-dimensional polymers bridged by both 4,4′-bipy and 2-sb^{2-} ligands. The coordination number in these complexes is seven and eight in **1** and **2**, respectively. In **1**, the Pb atoms are coordinated by one nitrogen from 4,4′-bipy, five O atoms of 2-sb^{2-} and one O atom of DMF, while in **2** by one nitrogen from 4,4′-bipy ligand, five O atoms of 2-sb^{2-} and two oxygens of water.

The structures are one-dimensional linear chains, running parallel to the a axis, with a building block of [Pb-2-sb]. The 2-sb^{2-} anions bridge lead(II) ions. Intrachain Pb⋯Pb distances are 4.411(2) and 4.807(2) Å in **1** and 3.962(2) and 4.620(2) Å in **2**. Individual polymeric chains are almost parallel and further bridged

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

1		**2**	
Pb(1)–O(2)#1	2.477(5)	Pb(1)–N(1)	2.545(4)
Pb(1)–O(1)	2.561(4)	Pb(1)–O(1)	2.575(3)
Pb(1)–N(1)	2.610(4)	Pb(1)–O(6)	2.594(3)
Pb(1)–O(6)	2.610(4)	Pb(1)–O(4)	2.632(3)
Pb(1)–O(3)	2.670(4)	Pb(1)–O(7)	2.651(4)
O(2)#1–Pb(1)–O(1)	106.08(16)	Pb(1)–O(3)#1	2.720(3)
O(2)#1–Pb(1)–N(1)	76.95(16)	N(1)–Pb(1)–O(1)	96.74(10)
O(1)–Pb(1)–N(1)	79.22(14)	N(1)–Pb(1)–O(6)	82.02(12)
O(2)#1–Pb(1)–O(6)	84.34(16)	O(1)–Pb(1)–O(6)	70.19(10)
O(1)–Pb(1)–O(6)	151.13(15)	N(1)–Pb(1)–O(4)	77.51(10)
N(1)–Pb(1)–O(6)	77.06(14)	O(1)–Pb(1)–O(4)	68.85(9)
O(2)#1–Pb(1)–O(3)	159.37(16)	O(6)–Pb(1)–O(4)	131.14(10)
O(1)–Pb(1)–O(3)	73.69(13)	N(1)–Pb(1)–O(7)	83.15(13)
N(1)–Pb(1)–O(3)	82.85(15)	O(1)–Pb(1)–O(7)	139.09(10)
O(6)–Pb(1)–O(3)	87.19(14)	O(6)–Pb(1)–O(7)	148.73(11)
		O(4)–Pb(1)–O(7)	71.26(9)
		N(1)–Pb(1)–O(3)#1	82.52(9)
		O(1)–Pb(1)–O(3)#1	147.86(9)
		O(6)–Pb(1)–O(3)#1	77.93(10)
		O(4)–Pb(1)–O(3)#1	140.62(8)
		O(7)–Pb(1)–O(3)#1	72.94(9)

Symmetric codes 1: #1 $-x$, $-y$, $-z$; 2: #1 $-x$, y, $-z+1/2$

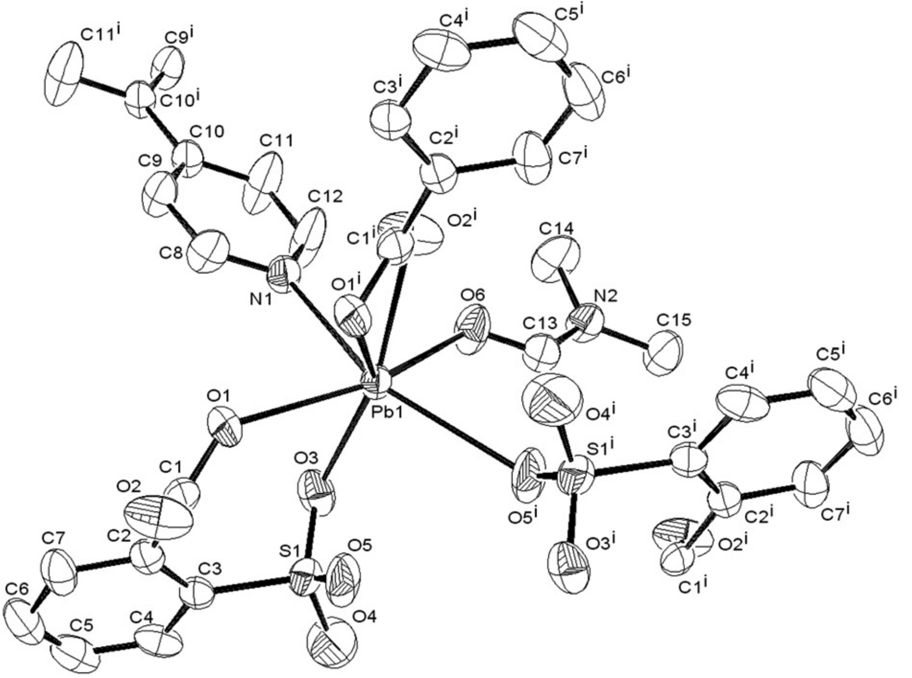


Figure 1. The ORTEP diagram of $[Pb_2(\mu\text{-}4,4'\text{-bipy})(\mu\text{-}2\text{-sb})_2(DMF)]_n$ (**1**), showing the coordination of Pb(II). i: $-x$, $-y$, $-z$.

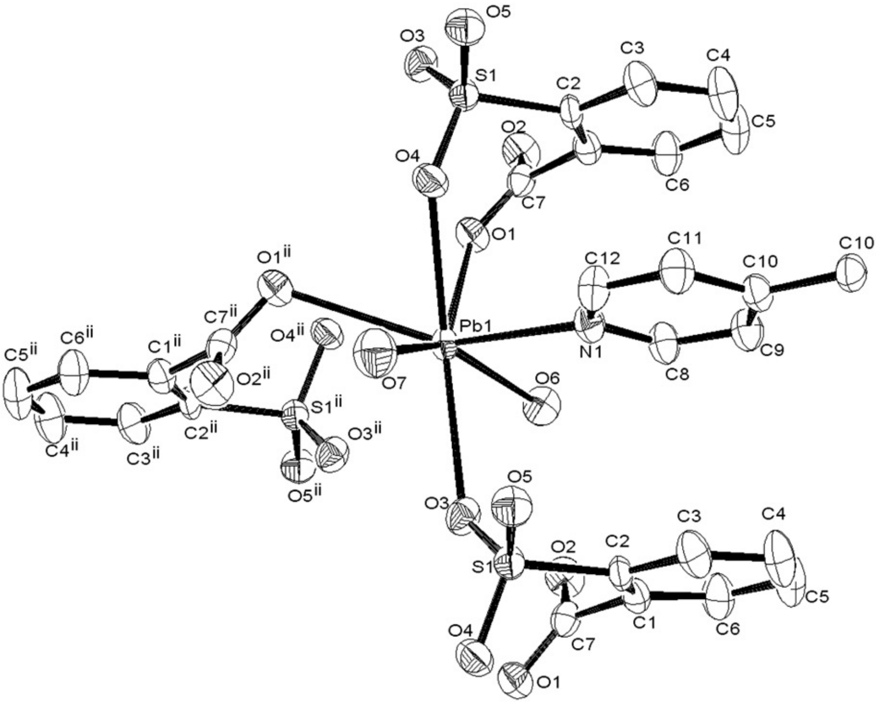


Figure 2. The ORTEP diagram of $[Pb_2(\mu\text{-}4,4'\text{-bipy})(\mu\text{-}2\text{-sb})_2(H_2O)_2]_n$ (**2**), showing coordination of Pb^{II}. i: $-x, y, -z+1/2$; ii: $-x, -y, -z$.

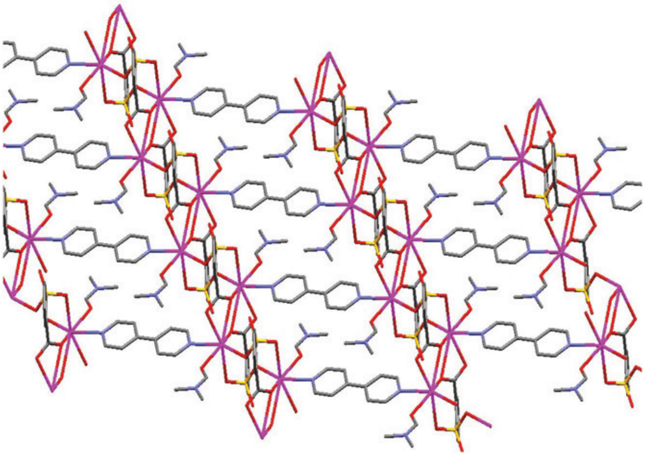


Figure 3. A perspective view of the two-dimensional layers in **1**.

by bidentate 4,4′-bipy, resulting in two-dimensional frameworks, as shown in figures 3 and 4.

Each 2-sb^{2-} is a five donor ligand, connecting four and five Pb^{+2} ions in **1** and **2**, respectively. In **1** the carboxylate of 2-sb^{2-} is bidentate bridging group (totally tridentate), where two oxygen atoms of the carboxylate group coordinate to a lead(II) and one also bridges two adjacent lead(II) ions. The $-SO_3$ is bidentate

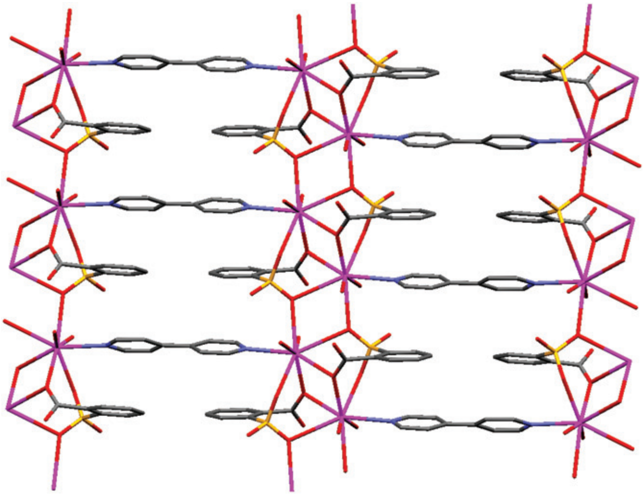
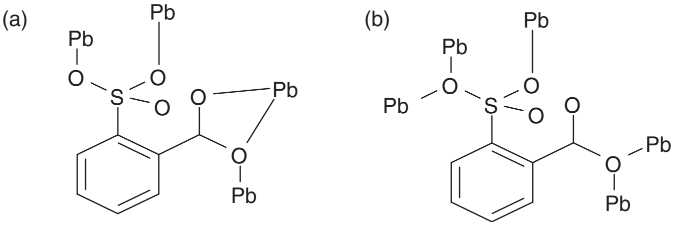


Figure 4. A perspective view of the two-dimensional layers in **2**.



Scheme 2. The coordination modes of ligand 2-sb^{2-}.

bridging [scheme 2(a)]. In **2** the carboxylate of the 2-sb^{2-} is only bridging, coordinating with one oxygen at one lead and two at the other lead [scheme 2(b)].

Stereo-chemical activity of the lone pair in divalent lead compounds has been discussed by Shimoni–Livny *et al.* based on a thorough review of crystal data available in the Cambridge Structural Database (CSD) [4]. They classify lead coordination as holodirected which refers to complexes in which the bonds to ligand atoms are directed throughout the surface of encompassing sphere, while hemidirected refers to those cases in which the bonds to ligand atoms are directed only to a part of the coordination sphere, leaving a gap in the distribution of bonds to the ligand (chart 1).

The 4,4′-bipy and 2-sb^{2-} ligands do not leave any gap in the coordination sphere around lead(II) in **1** and **2**, indicating that the lone pair of electrons on lead(II) is inactive, probably due to the ability of both 4,4′-bpy and 2-sb^{2-} to bridge, forming the two-dimensional coordination polymer.

One water in $\{[Pb_2(\mu\text{-}4,4'\text{-bipy})(\mu\text{-}2\text{-sb})_2(H_2O)_2]\cdot H_2O\}_n$ is involved in a hydrogen-bonding network (figure 5) as hydrogen bond donors towards the uncoordinated oxygens of 2-sb (table 3). Consequently, the 2D structure is grown by hydrogen bonds into a three-dimensional network. As the guest waters are tightly hydrogen bonded, their removal does not create any significant voids within the structure of this compound [24].

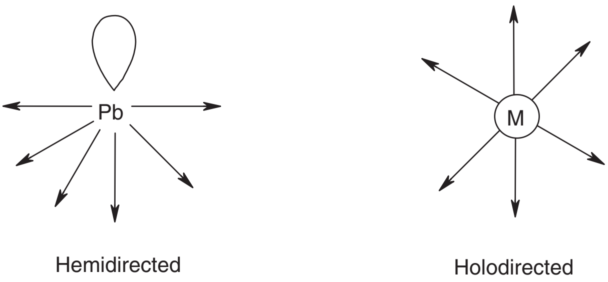


Chart 1. The two different geometries of Pb(II).

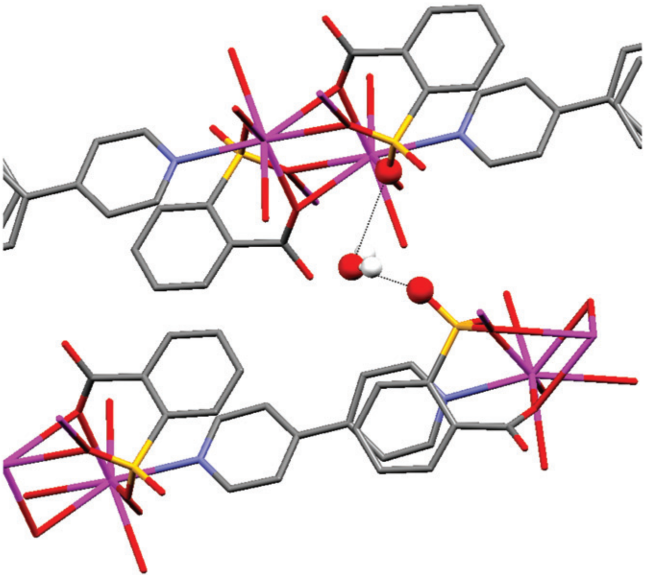


Figure 5. Hydrogen bonding of free water in **2**.

Table 3. Hydrogen bonds for $\{[Pb_2(\mu\text{-}4,4'\text{-bipy})(\mu\text{-}2\text{-sb})_2(H_2O)_2]\cdot H_2O\}_n$ (**2**) [Å and °].

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
O(8)–H(8B)···O(4)#1	0.85	2.41	3.003(5)	126.9
O(8)–H(8A)···O(5)#4	0.85	2.12	2.939(4)	162.6
O(7)–H(7B)···O(2)#5	0.85	1.98	2.771(5)	154.7
O(7)–H(7A)···O(5)#1	0.85	2.26	3.005(5)	146.4
O(6)–H(6A)···O(8)#6	0.85	1.93	2.782(4)	175.3
O(6)–H(6B)···O(2)#1	0.85	1.96	2.774(4)	159.1

Symmetry transformations used to generate equivalent atoms:
#1: $x, y-1, z$; #2: $x, y+1, z$; #3: $-x+2, y, -z+1/2$; #4: $-x+1, y-1, -z+1/2$; #5: $-x+1, -y+2, -z$; #6: $-x+1, -y+1, -z$.

Supplementary material

Crystallographic data for the structures reported in the article has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-659594 for **1** and CCDC-659591 for **2**. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: + 44–1223/336033; E-mail: deposit@ccdc.cam.ac.uk].

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