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

Syntheses, structures, and properties of seven-coordinate calcium(II) and five-coordinate lead(II) complexes with 1-D structures

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Accepted author version posted online: 14 Aug 2012.Published online: 06 Sep 2012.

To cite this article: Xiao-Jian Kong , Xiao-Zeng Li , Shi Ren & Li-Na Zhu (2012) Syntheses, structures, and properties of seven-coordinate calcium(II) and five-coordinate lead(II) complexes with 1-D structures, Journal of Coordination Chemistry, 65:20, 3641-3652, DOI: 10.1080/00958972.2012.721128

To link to this article: http://dx.doi.org/10.1080/00958972.2012.721128

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Journal of Coordination Chemistry
Vol. 65, No. 20, 20 October 2012, 3641–3652

Syntheses, structures, and properties of seven-coordinate calcium(II) and five-coordinate lead(II) complexes with 1-D structures

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(*Received 8 April 2012; in final form 24 July 2012*)

Two new 1-D heterometallic coordination polymers (CPs), $\{[Ca(NiL)(H_2O)_4]\cdot 3H_2O\}_n$ (**1**) and $\{[Pb(NiL)(H_2O)_2]\cdot 3H_2O)\}_n$ (**2**), have been prepared by reactions of $CaCl_2$ and NiL and $Pb(NO_3)_2$ and NiL in CH_2Cl_2–H_2O. H_2L denotes dimethyl 5,6,7,8,15,16-hexahydro-6,7-dioxodibenzo-9,10-benzo-[1,4,8,11]tetraazacyclotetradecine-13,18-dicarboxylate. Single-crystal X-ray diffraction studies show that the coordination geometries around Ni(II) in both **1** and **2** are similar distorted N_4 square planar. All Ni–N bonds are short. Complex **1** has 1-D zigzag chain, while **2** shows 1-D "head-to-tail" structure. In crystals **1** and **2**, 1-D CP chains were parallel-packed and 3-D supramolecular networks were formed *via* weak hydrogen bond interactions between aqua ligands and lattice water. The effects of water on the assemblies of the two CPs are discussed. Coordinated water plays an important role on the assembly procedure.

Keywords: synthesis; crystal structure; macrocyclic complex; coordination polymer

1. Introduction

The large number of crystal structures reported has transformed coordination chemistry [1, 2]. Coordination polymers (CPs) for gas storage [3–5], nonlinear optics [6, 7], catalysis [8], and nanomedicine [9] have been reported. Carboxylate is a versatile ligand for adopting different binding modes and favors the formation of polymeric complexes [10–12]. Schiff base ligands containing N and O can easily coordinate metal ions and because of their facile syntheses, tunable steric and electronic properties [13–17] have been extensively studied in coordination chemistry. Calcium(II) may coordinate between five and nine donors, displaying irregular geometries, prefers oxygen donors, and tends to form polynuclear structures [18–21]. Lead complexes through coordination in biological systems attract attention [22]. Lead(II) with a large radius and flexible coordination environment provides opportunities for construction of CPs [23, 24]. Hydrogen bonding is involved in the generation of supramolecular assemblies in calcium(II) and lead(II) complexes [25, 26].

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2012 Taylor & Francis
http://dx.doi.org/10.1080/00958972.2012.721128

Herein, we report the preparation of NiL as a new precursor macrocyclic complex containing carboxylate and Schiff base groups. H_2L denotes dimethyl 5,6,7,8,15,16-hexahydro-6,7-dioxodibenzo-9,10-benzo-[1, 4, 8, 11]tetraazacyclotetradecine-13,18-dicarboxylate. We chose $CaCl_2$ and $Pb(NO_3)_2$ in the same mixed solvent of CH_2Cl_2–H_2O to react with NiL and isolated two new metal-organic CPs, $\{[Ca(NiL)(H_2O)_4]\cdot 3H_2O\}_n$ (**1**) and $\{[Pb(NiL)(H_2O)_2]\cdot 3H_2O)\}_n$ (**2**). We report here the syntheses and crystal structures of **1** and **2**. We also discuss hydrogen bonding and the effects of water on the coordination assemblies.

2. Experimental

2.1. *Materials and measurements*

All starting materials, solvents, and reagents were obtained from commercial suppliers and used without purification. 1,1′-Oxalylbisisatin was prepared according to the literature method [27]. FT-IR spectra were recorded using a BIO-RAD 3000 infrared spectrophotometer from 4000 to 400 cm^{-1} using KBr pellets. The single-crystal structure was determined on a Bruker SMART 1000 CCD diffractometer. Elemental analyses for C, H, and N were performed on a Perkin-Elmer 240 analyzer. Thermogravimetric analyses (TGA) were carried out in a nitrogen stream using STA-409PC equipment at a heating rate of 10°C min^{-1}. Elemental analyses of Ca, Pb, and Ni in the two compounds were performed using Inductive Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) (Varian Vista-MPX) at a high frequency emission power of 1.5 kW and a plasma airflow of 15.0 L min^{-1}. ^1H and ^{13}C NMR spectra were measured on a Bruker AC-P500 Instrument (400 MHz) with DMSO-d_6 as the solvent and TMS as the internal standard. Mass spectra were recorded on a Thermo Finnigan Trace DSQ mass detector.

2.2. *Synthesis of the complexes*

2.2.1. Synthesis of NiL. A mixture of 1,1′-oxalylbisisatin (3.4835 g, 0.010 mol) and solution of 0.8000 g (0.020 mol) NaOH in 100 mL of water was stirred below 40°C for 90 min to afford a yellow solution. To the solution, $Ni(OAc)_2\cdot 4H_2O$ (2.8860 g, 0.010 mol) and 0.8000 g (0.020 mol) NaOH (in dropwise) was added. To the above solution, a solution of 1,2-benzenediamine (1.085 g, 0.010 mol) in 20 mL of water was then carefully added drop-wise under stirring at 80°C for 3 h, and the solution was kept stirring at 80°C for additional 10 h. The reaction mixture was then cooled to room temperature and filtered. The filtrate was evaporated by heating on a water bath of 55°C to obtain a dark red paste. The mixture of the paste and 15 mL of ethanol was stirred for 40 min and then filtered. The solid was dried under vacuum to afford a dark red powder. Yield: 52% (2.9085 g). Anal. found (Calcd for $C_{24}H_{12}N_4NiO_6Na_2$) (%): C 51.40 (51.75), H 2.28 (2.17), N 10.25 (10.06), Ni 10.35 (10.54). Main IR bands (KBr, cm^{-1}): 1636(s), 1581(s), 1533(s), 1471(m), 1452(m), 1371(s), 1249(m), 1169(m), 1115(m), 991(m), 788(m), 751(m). ^1H NMR (400 MHz, DMSO-d_6) δ, 8.50 (t, $J = 8.4$ Hz, 4H), 7.77 (d, $J = 8.4$ Hz, 2H), 7.36 (t, $J = 7.2$ Hz, 2H), 7.15 (d, $J = 7.6$ Hz, 2H), 6.96 (t, $J = 7.2$ Hz, 2H). EI-MS Calcd for $C_{24}H_{12}N_4NiO_6^{2-}$ $[M+H]^-$ 512.0 found 512.1.

2.2.2. Synthesis of $\{[Ca(NiL)(H_2O)_4]\cdot 3H_2O\}_n$ (1). The mixture of the above dark red powder (0.0365 g, 0.066 mmol), $CaCl_2$ (0.0091 g, 0.082 mmol), CH_2Cl_2 (15 mL) and water (15 mL) was stirred for 30 min at room temperature to give a red solution. The filtrate of the solution was then kept at room temperature for several days, and red crystals suitable for X-ray single crystal analysis were obtained. Yield: 35% (0.0155 g). Anal. found (Calcd for $C_{24}H_{26}CaN_4NiO_{13}$): C 42.76 (42.56), H 3.71 (3.87), N 8.45 (8.27), Ca 5.78 (5.91), Ni 8.78 (8.67)%. IR (KBr cm^{-1}): 3424(m), 1629(s), 1591(s), 1543(s), 1475(m), 1453(m), 1365(s), 1252(m), 1177(m), 1125(m), 989(m), 781(m), 739(m).

2.2.3. Synthesis of $\{[Pb(NiL)(H_2O)_2]\cdot 3H_2O)\}_n$ (2). Red crystals suitable for X-ray single-crystal analysis were obtained by the same method used for preparing **1** except using $Pb(NO_3)_2$ (0.0265 g, 0.080 mmol) instead of $CaCl_2$ (0.0091 g, 0.082 mmol). Yield: 23% (0.0123 g). Anal. found (Calcd for $C_{24}H_{22}N_4NiO_{11}Pb$): C 35.54 (35.66), H 2.92 (2.74), N 7.01 (6.93), Ni 7.38 (7.26), Pb 25.78 (25.63)%. Main IR bands: 3418(m), 1611(s), 1586(s), 1546(s), 1466(m), 1444(m), 1365(s), 1258(m), 1176(m), 1118(m), 979(m), 782(m), 733(m).

2.3. *X-ray structure determinations*

Transparent single crystals of **1** and **2** were selected for X-ray diffraction investigations with the aid of a microscope and mounted on glass fibers for single-crystal X-ray diffraction measurements. Data were collected at 113(2) K for **1** and 295(2) K for **2** on a Bruker Smart-1000-CCD area detector. Measurements were done using monochromatic Mo-Kα radiation ($\lambda = 0.71073$ Å). The absorption correction was based on multiple and symmetry-equivalent reflections in the data set using SADABS based on the method of Blessing. The structures were solved by direct methods and refined with full-matrix least-squares using the SHELXL97 [28] and SHELX-TL [29] package. Table 1 summarizes crystal data and other pertinent information of **1** and **2**.

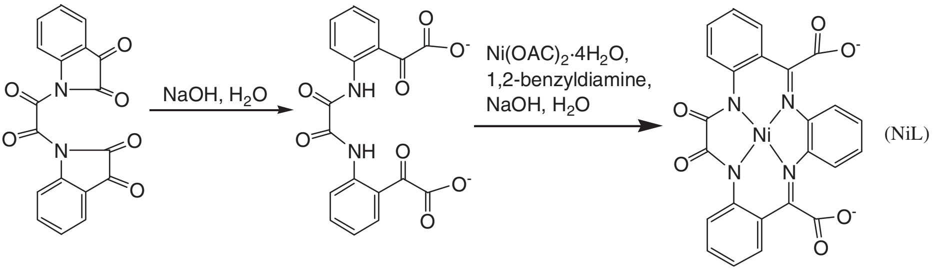
3. Results and discussion

3.1. *Syntheses*

NiL was initially prepared following scheme 1, a similar approach to those in the syntheses of analogous macrocyclic oxamide complexes [27]. Excess $CaCl_2$, $Pb(NO_3)_2$ and solvent (including H_2O/CH_2CH_2) were required for the formation of crystalline **1** and **2** as in other reported cases by our group [30].

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

Empirical formula	$C_{48}H_{44}Ca_2N_8Ni_2O_{25}$	$C_{24}H_{22}N_4NiO_{11}Pb$
Formula weight	1330.45	808.36
Temperature (K)	113(2)	295(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	$P2_1/n$
Unit cell dimensions (Å, °)		
a	7.873(3)	15.698(10)
b	25.541(10)	8.738(6)
c	26.092(10)	18.973(13)
α	90	90
β	90	90.209(7)
γ	90	90
Volume (Å^3), *Z*	5247(4), 4	2602(3), 4
Calculated density (Mg m^{-3})	1.684	2.063
Absorption coefficient (mm^{-1})	1.012	7.254
F(000)	2736	1568
Crystal size (mm^3)	0.20 × 0.18 × 0.12	0.20 × 0.20 × 0.20
θ range for data collection (°)	1.56–25.25	3.17–25.01
Limiting indices	$-9 \le h \le 9$; $-30 \le k \le 25$; $-31 \le l \le 31$	$-19 \le h \le 19$; $-10 \le k \le 10$; $-22 \le l \le 22$
Reflections collected/unique	37,557	21,518
Independent reflection	4754 [*R*(int) = 0.0797]	4563 [*R*(int) = 0.1180]
Completeness to θ	25.25 (99.9%)	25.01 (99.3%)
Correction	Semi-empirical	Semi-empirical
Max. and min. transmission	0.8880 and 0.8229	0.4092 and 0.2643
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4654/0/396	4863/12/374
Goodness-of-fit on F^2	1.234	1.060
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0970$, $wR_2 = 0.1766$	$R_1 = 0.0691$, $wR_2 = 0.1725$
R indices (all data)	$R_1 = 0.0987$, $wR_2 = 0.1774$	$R_1 = 0.0775$, $wR_2 = 0.1816$
Largest difference peak and hole (e Å^{-3})	1.388 and −0.923	1.827 and −2.399



Scheme 1. Synthesis of NiL.

3.2. *Descriptions of the structures*

3.2.1. Crystal structure of 1. X-ray diffraction reveals that **1** crystallizes in the orthorhombic space group *Pbca* and has an infinite 1-D zigzag chain (figure 1a). The asymmetric unit is composed of Ca(NiL)(H_2O)$_4$ (figure 1b) and three lattice water molecules. In the binuclear entity of **1**, calcium(II) and nickel(II) are bridged by an

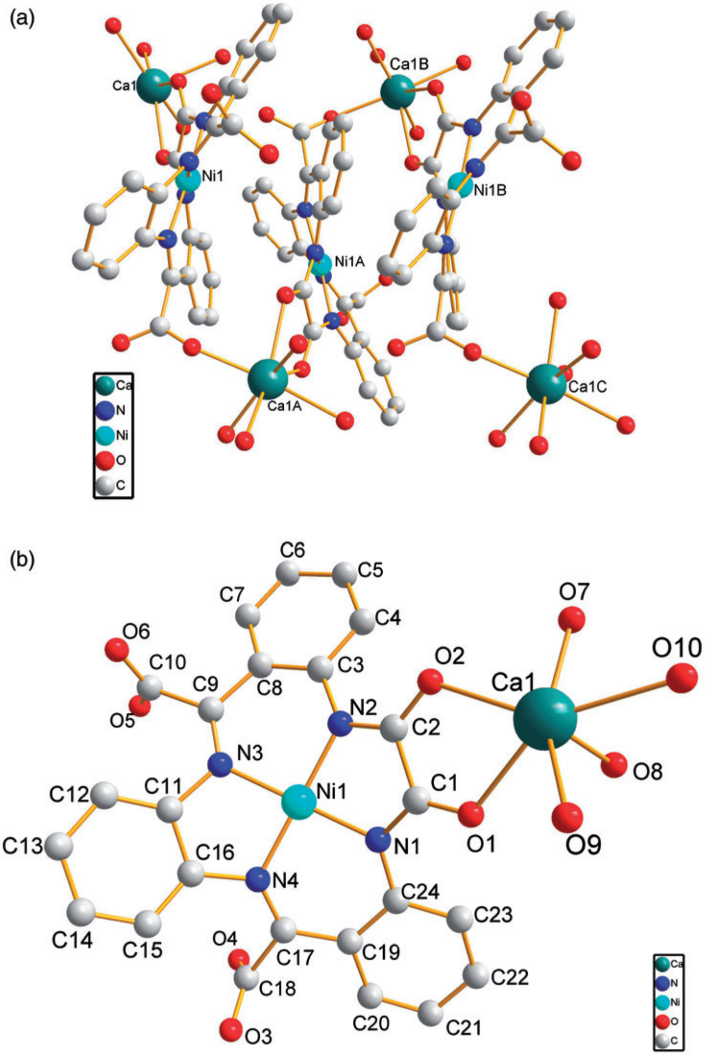


Figure 1. (a) 1-D zigzag chain structure of **1**. (b) The asymmetric unit of **1**. Hydrogen atoms have been omitted for clarity.

oxamido group from the macrocyclic ligand. Nickel(II) is coordinated by four nitrogen atoms and forms a slightly distorted square-planar configuration. Deviations of the four nitrogen atoms from the corresponding NiN_4 least square plane are 0.0183–0.0463 Å while nickel deviates 0.0033 Å. All Ni–N bonds are quite short (1.8566–1.8828 Å), consistent with the strong donor ability of two deprotonated oxamido nitrogen atoms and two imino nitrogen atoms. Each calcium(II) coordinates two oxygens from oxamido of one NiL, one oxygen from carboxyl of another NiL and four oxygens from water, forming a slightly distorted pentagonal-bipyramidal coordination geometry. The Ca–O (water) distances are 2.345(6) and 2.457(8) Å and the Ca–O (oxygen of carboxyl) bond is significantly shorter [2.311(6) Å]. The other Ca–O (oxygen of oxamido) distances are 2.383(5) and 2.496(5) Å. The seven-coordination of calcium has been observed in related metal complexes [18]. Calcium(II) is not located at a crystallographic center of symmetry because of seven-coordination and why calcium(II) is linked by two kinds of oxygen atoms (belonging to carboxyl group and oxamido group) from two NiL molecules in **1**. In each dinuclear entity, the Ni···Ca distance is 5.619(3) Å. In **1**, the N(1)–C(1) and N(2)–C(2) bond lengths in oxamido groups are 1.339(8) Å and 1.330(8) Å, respectively, longer than N=C double bonds (N(3)–C(9) (1.298(8) Å) and N(4)–C(17) (1.302(9) Å), but much shorter than N–C single bonds N(3)–C(11) (1.442(8) Å) and N(4)–C(16) (1.426(8) Å). The sum of the three bond angles around each amidate nitrogen (C(1)–N(1)–C(24) or C(2)–N(2)–C(3), C(9)–N(3)–C(11) and C(17)–N(4)–C(16)) is close to 360° (370.6–372.1°). Thus, the amidate nitrogen atoms are sp^2-hybridized and the π-electrons are delocalized into carbonyl. The delocalized system provides a thermodynamic stabilization.

3.2.2. Crystal structure of 2. X-ray diffraction reveals that **2** crystallizes in the monoclinic space group $P2_1/n$ and shows a 1-D "head-to-tail" chain (figure 2a). The asymmetric unit contains Pb(NiL)$(H_2O)_2$ (figure 2b) and three lattice water molecules. In the binuclear entity of **2**, lead(II) is linked to nickel(II) *via* the exo–cis oxygen atoms of the oxamido macrocyclic ligand. Four nitrogen atoms bond to nickel(II) in a slightly distorted square-plane, in the range of 0.0075–0.0586 Å; deviation of nickel is quite small, only 0.0030 Å. All Ni–N bonds are quite short (1.8629–1.8762 Å), consistent with coordinating abilities of deprotonated oxamido and imino nitrogen atoms. Lead(II) coordinates with two oxygen atoms from oxamido of one NiL, one oxygen from carboxyl of another NiL and two oxygen atoms from water, forming a slightly distorted trigonal bipyramidal coordination geometry. The Pb–O (water) distances are 2.497(11) and 2.703(14) Å and the Pb–O (oxygen of carboxyl) bond is significantly shorter [2.371(6) Å]. The other Pb–O (oxygen of oxamido) distances are 2.383(7) and 2.435(7) Å. Five-coordination of lead(II) is observed in related complexes [31–36]. In each dinuclear entity, the Ni···Pb distance is 5.525(3) Å. In **2**, the N(1)–C(4) and N(2)–C(9) bond lengths in the oxamido groups are 1.339(13) Å and 1.336(11) Å, respectively, a little longer than N=C double bonds (N(3)–C(12) (1.317(10) Å) and N(4)–C(3) (1.296(10) Å), but much shorter than N–C single bonds N(3)–C(1) (1.458(9) Å) and N(4)–C(10) (1.434(11) Å). The sum of the three bond angles around each amidate nitrogen [(C(4)–N(1)–C(15) or C(9)–N(2)–C(6), C(12)–N(3)–C(1) and C(3)–N(4)–C(10)] is close to 360° (369.7–370.2°). Thus, amidate nitrogen atoms are sp^2-hybridized and delocalization of the π-electrons into carbonyl is stabilized.

3.3. $\pi\cdots\pi$ *Interactions and hydrogen bonds*

Each NiL fragment of every binuclear entity of **1** and **2** overlaps with NiL fragments of adjacent binuclear entities of **1** and **2**. Many intermolecular atom to atom distances between the two NiL ligands binding to the same metal center are shorter than 3.80 Å, revealing that $\pi\cdots\pi$ interactions strengthen the structure of the two complexes [37, 38]. These $\pi\cdots\pi$ interactions play a crucial role in self-complementary for the NiL ligand [38]. Intermolecular hydrogen bonds, O–H···O and C–H···O, were formed in **1** and **2**. Hydrogen bond parameters are given in tables 2 and 3. 3-D supramolecular network was formed *via* intermolecular hydrogen bond interactions between metal-complex and free water molecules. The molecular units are linked into infinite chains, which lie

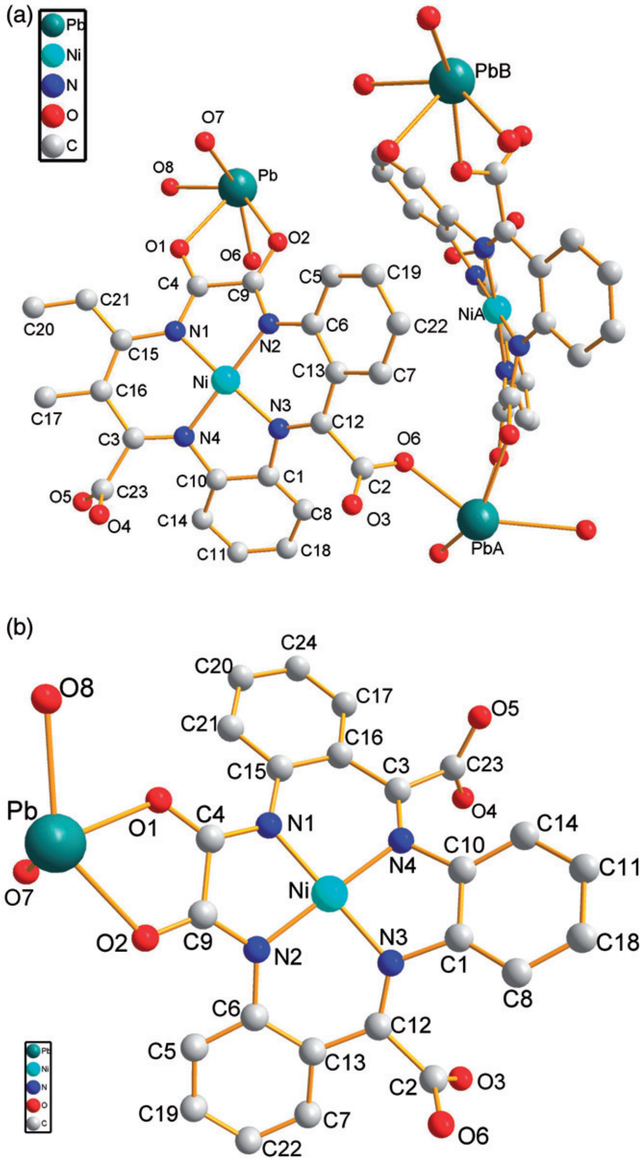


Figure 2. (a) 1-D "head-to-tail" structure of **2**. (b) The asymmetric unit of **2**. Hydrogen atoms have been omitted for clarity.

parallel in the crystals of the two complexes with different packing mode. The packing diagrams (figures 3 and 4) of the polymers show the presence of infinite arrays of molecular units in **1** and **2**.

3.4. *Water effects*

Obviously, water plays a significant role in supramolecular self-assembly. The coordination ability and steric effect of water may play an important role as both

Table 2. Hydrogen bonding parameters of **1**.

Donor–H···acceptor	D–H (Å)	D···A (Å)	H···A (Å)*	D–H···A (°)
O9–H9A···O13	0.85	2.14	2.45	101
O9– H9B···O8[a]	0.85	2.6	3.338	147
O7–H7A···O4[b]	0.85	2.42	2.782	106
O7–H7B···O11[f]	0.85	2.21	2.672	114
O8–H8A···O13[c]	0.85	2.1	2.74	131
O8–H8B···O6[d]	0.85	2.05	2.712	134
O10–H10A···O12[f]	0.85	1.98	2.776	155
O10–H10B···O4[b]	0.85	2.03	2.858	163
O11–H11A···O2[g]	0.85	2.08	2.855	151
O11–H11B···O4[e]	0.85	2.02	2.844	163
O12–H12A···O3	0.85	2.09	2.828	145
O12–H12B···O3[a]	0.85	2.3	3.047	147
O13–H13A···O9	0.85	2.15	2.45	100
O13–H13A···O12[f]	0.85	2.16	2.79	131
O13–H13B···O9	0.85	2.09	2.45	105
C4–H4···O2	0.95	2.36	2.925	117
C12–H12···O6	0.95	2.33	3.157	146
C13–H13···O11	0.95	2.55	3.394	149
C14–H14···O5[e]	0.95	2.54	3.42	155
C15–H15···O3	0.95	2.31	3.118	143
C20–H20···O3	0.95	2.54	3.14	121
C22–H22···O1[h]	0.95	2.57	3.506	170
C23–H23···O1	0.95	2.28	2.859	119

*The esd's are 0.002–0.011A for H···A (Å).
Symmetry codes: [a]−1/2 + *x*,*y*,1/2−*z*; [b]3/2−*x*,1/2 + *y*,*z*; [c]1 + *x*,*y*,*z*; [d]1/2 + *x*,1/2−*y*,−*z*; [e]1−*x*,−*y*,−*z*; [f]3/2−*x*,1/2 + *y*,*z*; [g]3/2−*x*,−1/2 + *y*,*z*; [h]1/2 + *x*,*y*,1/2−*z*.

Table 3. Hydrogen bonding parameters of **2**.

Donor–H···acceptor	D–H (Å)	D···A (Å)	H···A (Å)*	D–H···A (°)
O7–H7A···O11[a]	0.85	2.33	3.18	175
O7–H7B···O4[b]	0.85	2.53	2.872	106
O8–H8B···O11[c]	0.85	2.38	2.7	103
O8–H8B···O4[d]	0.85	2.5	2.826	104
O9–H9B···O3	0.85	1.85	2.702	174
O10–H10A···O7[e]	0.85	1.92	2.74	162
O10–H10B···O4[f]	0.85	2.4	2.827	112
O11–H11A···O8[e]	0.85	1.94	2.7	148
C5–H5···O2	0.93	2.29	2.851	119
C8–H8···O6	0.93	2.42	3.225	145
C11–H11···O3[g]	0.93	2.54	3.377	149
C14–H14···O5	0.93	2.36	3.171	146
C17–H17···O5	0.93	2.46	3.033	120
C19–H19···O6[h]	0.93	2.44	3.267	147
C21–H21···O1	0.93	2.18	2.805	124

*The esd's are 0.002–0.019A for H···A (Å).
Symmetry codes: [a]1 + *x*, −1 + *y*, *z*; [b]2−*x*, 1−*y*, 1−*z*; [c]1 + *x*, *y*, *z*; [d]1/2 + *x*, 3/2−*y*,−1/2 + *z*; [e]−1 + *x*, *y*, *z*; [f]−1/2 + *x*, 1/2−*y*, −1/2 + *z*; [g]1−*x*, 1−*y*, 1−*z*; [h]3/2−*x*, −1/2 + *y*, 1/2−*z*.

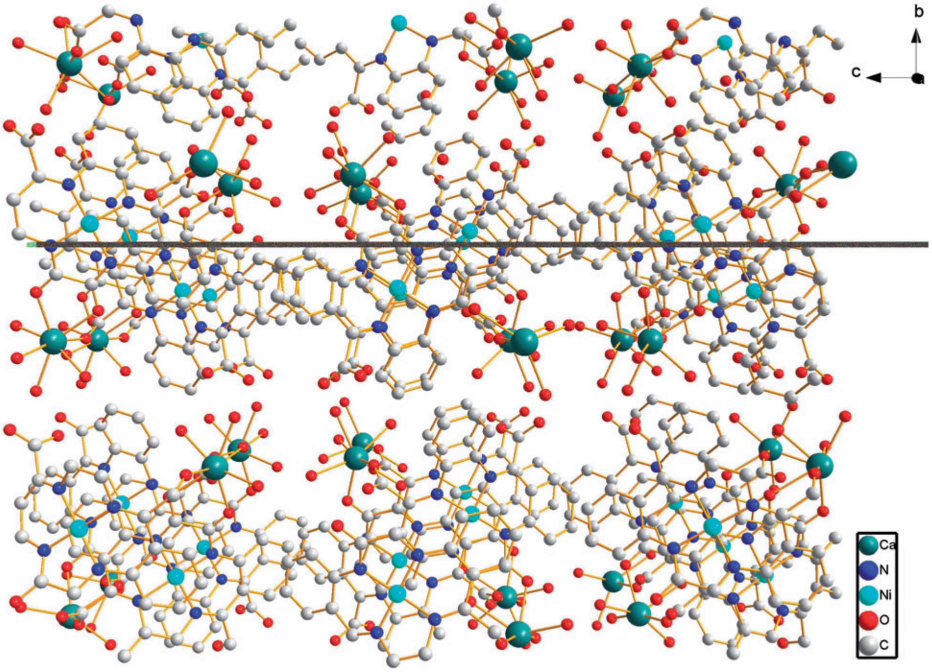


Figure 3. Packing diagram of the infinite molecular structure in the crystal of **1**. Solvent and hydrogen atoms are omitted for clarity.

ligand and guest in the final structures. Water shows affinities to calcium(II) and lead(II), resulting in coordination. Water, as guest, locates in the crystalline frameworks, inducing crystal lattice packing patterns.

3.5. *IR spectroscopic properties*

The IR spectrum of NiL shows an absorption at 1636 cm^{-1} assigned to stretching vibration of oxamido C=O; 1629 cm^{-1} for **1** and 1611 cm^{-1} for **2** are absorptions of the oxamido C=O coordinated to calcium(II) and lead(II). Bands at 1591 cm^{-1} for **1** and 1586 cm^{-1} for **2** are due to ν(C=N).

3.6. *Thermogravimetric measurements*

TGA on polycrystalline samples of **1** and **2** were performed in N_2 from 30–850°C, as shown in Supplementary material. Compound **1** starts to lose weight at *ca* 136°C from solvent water. The weight loss from 136°C to 406°C is in accord with decomposition of five water molecules (found: 15.45%; Calcd: 15.50%). Heating the sample to higher temperatures led to decomposition of the other components. The first weight loss of **2** occurred almost at the beginning of the heating (30°C). Weight loss from 20°C to 298°C is in accord with decomposition of six water molecules (found: 11.09%; Calcd: 11.13%).

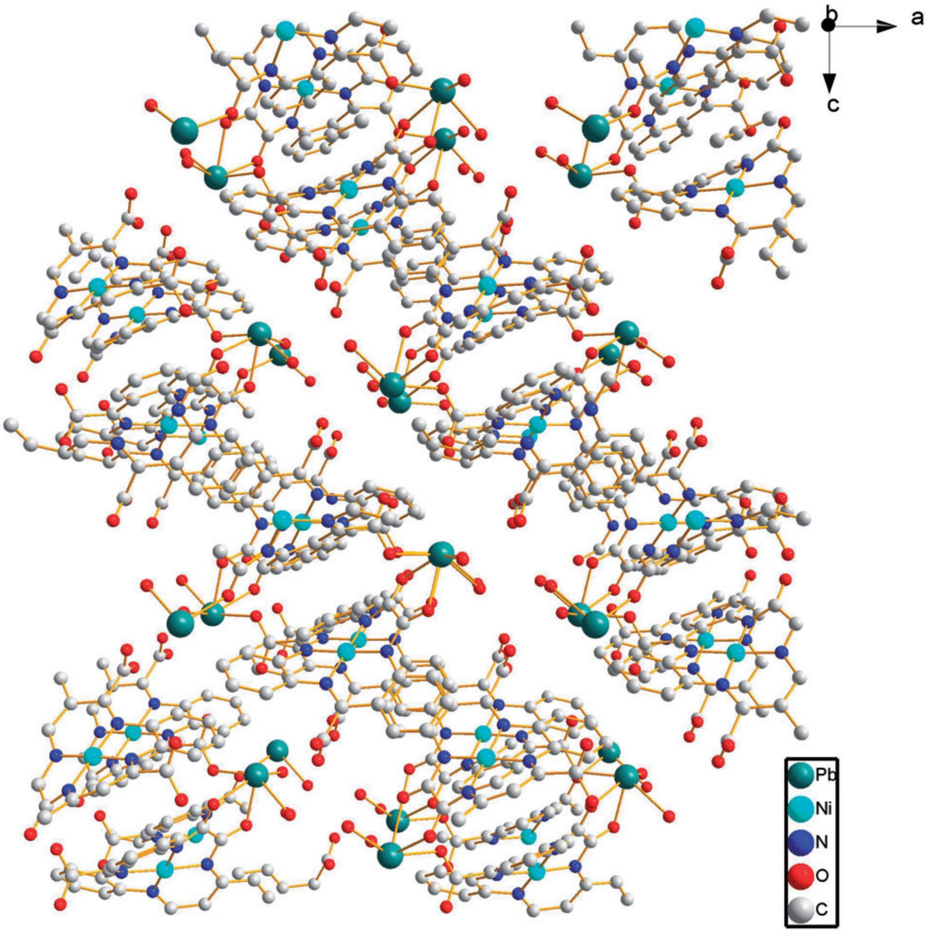


Figure 4. Packing diagram of the infinite molecular structure in the crystal of **2**. Solvent and hydrogen atoms are omitted for clarity.

Heating the sample to higher temperatures (more than 298°C) led to decomposition of the other components.

4. Conclusion

Two new coordination complexes, $\{[Ca(NiL)(H_2O)_4] \cdot 3H_2O\}_n$ (**1**) and $\{[Pb(NiL)(H_2O)_2] \cdot 3H_2O)\}_n$ (**2**), are synthesized and structurally characterized. Complex **1** is a 1-D single zigzag chain while **2** shows a 1-D "head-to-tail" chain. Complexes **1** and **2** were obtained by coordinated-water induced assembly of calcium(II) ion and NiL, and lead(II) ion and NiL, respectively. 3-D supramolecular networks were formed *via* weak hydrogen bond interactions between the coordinated and free water molecules in **1** and **2**. Both **1** and **2** exhibit moderately good stabilities. The results herein will help to construct CPs with desirable structures.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 871024 for **1** and 862870 for **2**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgments

We acknowledge the support by the National Natural Science Foundation of China (No. 20801040).

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