ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2016, Vol. 42, No. 8, pp. 546–556. © Pleiades Publishing, Ltd., 2016.

Two Heterometallic Complexes with a New Macrocyclic Oxamido Complex Ligand[1]

Y. H. Li[a], Z. G. Ma[a], B. Yuan[a], B. B. Ding[a], X. Z. Li[a, b, *], and L. N. Zhu[a]

[a] *Department of Chemistry, School of Science, Tianjin University, and Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin, 300072 P.R. China*

[b] *State Key Laboratory of Crystal Material (Shandong University), Jinan, 250100 P.R. China*

**e-mail: lixiaozeng321@tju.edu.cn*

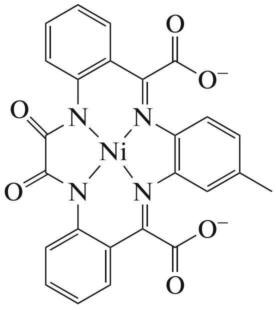
Received September 17, 2016

Abstract—A new macrocyclic oxamido-nickle(II) complex Na_2NiL was synthesized. L denotes the doubly deprotonated forms of (13Z, 19Z)-16-methyl-6,7-dioxo-5,6,7,8-tetrahydrotriben-zo[b,f,l][1,4,8,11]tetra-azacyclotetradecine-13,20-dicarboxylate. Based on the complex ligand $Ni(L^{2-})$, two heterometallic complexes $[Ca_2(NiL)_2(H_2O)_8] \cdot 10H_2O$ (**I**) and $[Co(NiL)_2(H_2O)_2][Co(H_2O)_6] \cdot 2.8H_2O$ (**II**) were prepared. X-ray single crystal analyses (CCDC nos. 914618 (**I**), 914616 (**II**)) revealed that $[Ca_2(NiL)_2(H_2O)_8]$ in **I** is a molecular box and the trinuclear complex anion $[Co(NiL)_2(H_2O)_2]^{2-}$ in **II** is centrosymmetric. Thermogravimetric analyses showed that **I** exhibited moderately good stability and Co(II) catalyzed the thermal decomposition of **II**.

DOI: 10.1134/S1070328416080030

INTRODUCTION

Metalloligands or “complexes-as-ligands” are efficient for the construction of functionalized coordination materials. Such materials have been utilized for many applications including gas storage [1–9] and separation [7–9] as well as heterogeneous catalysis [10, 11] due to the existence of exposed metal centers. Ligands with carboxylate groups are versatile for adopting different binding modes [12–14]. Macrocyclic oxamide mononuclear complexes, in which the exo-cis oxygen donors are active to chelate metal ions, allow one to synthesize heterometallic multinuclear materials with exposed metal centers [15–21]. In this contribution, a new metal complex of a macrocyclic oxamido Schiff base ligand with carboxylate groups $Ni(L^{2-})$ was used as a “complex ligand” to synthesize two new heterometallic complexes, $[Ca_2(NiL)_2(H_2O)_8)] \cdot 10H_2O$ (**I**) and $[Co(NiL)_2(H_2O)_2][Co(H_2O)_6] \cdot 2.8H_2O$ (**II**). The L^{2-} ions denote the doubly deprotonated forms of (13Z,19Z)-16-methyl-6,7-dioxo-5,6,7,8-tetrahydrotribenzo[b,f,l][1,4,8,11]tetraaza-cyclotetradecine-13,20-dicarboxylate. The thermostability of **I** and **II** were also studied via thermogravimetric analysis.



$Ni(L^{2-})$

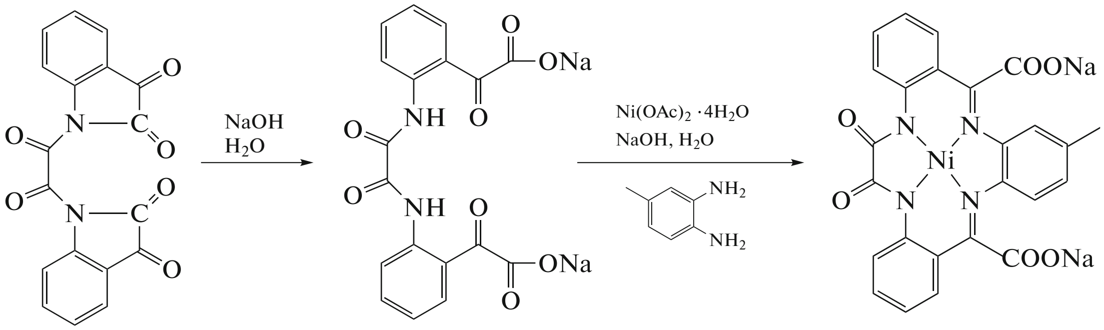
EXPERIMENTAL

Materials and measurements. All reagents and solvents employed were commercially available and used as received without further purification. 1,1'-Oxalylbisisatin was prepared by the literature method [22] and its ring opening in NaOH solution was carried out following the principle mentioned in the same literature. Elemental analyses were performed on a Perkin-Elmer 240 analyzer. IR spectra were recorded as KBr pellets on a BIO-RAD 3000 infrared spectrophotometer from 4000 to 400 cm^{-1}. Thermogravimetric analyses (TGA) were carried out on a STA-409PC equipment at a heating rate of 10°C min^{-1} under nitrogen. Mass spectra (ESI) was recorded on a Thermo Finnigan LCQ Advantage mass spectrometer.

---

[1] The article is published in the original.

Synthesis of Na_2NiL. A mixture of 1.1'-oxalylbisisatin (3.4827 g, 10.0 mmol) and a solution of NaOH (0.8000 g, 20.0 mmol) in 50 mL water was stirred at 40°C for 2 h to form a bright yellow solution. To the above solution was added dropwise another solution of $Ni(OAc)_2 \cdot 4H_2O$ (2.4884 g, 10.0 mmol) and NaOH (0.8000 g, 20.0 mmol) in 10 mL water. To the above solution was then added 3,4-diaminotoluene (1.2466 g, 10.0 mmol) slowly under stirring at 75°C, and the solution was kept stirring for another 6 h at 75°C. The resulting mixture was then cooled to room temperature and filtered. The filtrate was evaporated by heating on a water bath of 60°C to afford a dark red paste, the mixture of the paste and 100 mL ethanol was stirred for 30 min and then filtered under vacuum. The filtrate was dried on a water bath of 60°C to afford a dark red powder. The yield was 4.6828 g (~82.0%, calculated on the amount of 1.1'-oxalylbisisatin). Na_2NiL was prepared according to the following scheme:



For $C_{25}H_{14}N_4O_6Na_2Ni$

anal. calcd., %:	C, 52.58;	H, 2.47;	N, 9.81.
Found, %:	C, 52.19;	H, 2.63;	N, 9.75.

IR (KBr; ν, cm^{-1}): 1627 s, 1577 s, 1534 s, 1474 m, 1439 m, 1401 s, 1251 m, 1251 m, 1220 m, 1204 m, 1168 m, 1048 m, 1017 m, 749 m.

MS (ESI) for Na_2NiL (*m/z*): $[M-H]^-$ calcd. 570.1; found 570.8.

Synthesis of I. A mixture of Na_2NiL (0.0713 g, 0.1248 mmol), $CaCl_2$ (0.0152 g, 0.1370 mmol), water (50 mL) and acetonitrile (150 mL) was stirred to form a red solution. The filtrate of the solution was then stored at room temperature for 3 days, and red crystals suitable for X-ray single crystal analysis were formed. The yield was 0.0759 g (~83.6%, calculated on the amount of Na_2NiL).

For $C_{50}H_{64}N_8O_{30}Ca_2Ni_2$

anal. calcd., %:	C, 41.28;	H, 4.43;	N, 7.70.
Found, %:	C, 41.60;	H, 4.39;	N, 7.81.

IR (KBr; ν, cm^{-1}): 3386 m, 1612 s, 1533 s, 1519 s, 1475 w, 1440 m, 1380 s, 1326 m, 1299 m, 1253 m, 1206 m, 1717 m, 749 m.

Synthesis of II. A mixture of Na_2NiL (0.0690 g, 0.0121 mmol), $CoCl_2 \cdot 6H_2O$ (0.0212 g, 0.0891 mmol), water (60 mL) and acetonitrile (120 mL) was stirred to form a red solution. The filtrate of the solution was then stored at room temperature for 7 days, then deep red crystals suitable for X-ray single crystal analysis were formed. The yield was 0.0431 g (~52.3%, calculated on the amount of Na_2NiL).

For $C_{50}H_{49.6}N_8O_{22.8}Co_2Ni_2$

anal. calcd., %:	C, 44.07;	H, 3.67;	N, 8.22.
Found, %:	C, 44.13;	H, 3.58;	N, 8.31.

IR (KBr; ν, cm^{-1}): 3135 m, 1601 s, 1582 s, 1536 s, 1475 s, 1439 s, 1376 m, 1253 w, 1207 w, 1178 w, 752 m.

X-ray structure determinations. Crystallographic data were collected on a Bruker Apex II CCD area-detector diffractometer (MoK_α, $\lambda = 0.71073$ Å) at 173(2) and 296(2) K for **I** and **II**, respectively. Adsorption correction was applied by using multiscan program SADBS. The structures were solved by direct method and subsequent Fourier difference techniques (SHELXS-97) and refined using full-matrix least-squares procedure on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97) [23]. Hydrogen atoms were added geometrically and refined with the riding model position parameters and fixed isotropic thermal parameters. Crystal data and pertinent information are summarized in Table 1. Selected bond lengths and angles are given in Table 2 for **I** and **II**.

Supplementary material for structures has been deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 914618 (**I**), 914616 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Table 1. Crystallographic data and structure refinements for **I** and **II**

Parameter	Value	
	I	**II**
Mr	1454.63	2725.24
Temperature, K	173(2)	296(2)
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$
a, Å	13.774(3)	17.2036(11)
b, Å	23.298(6)	16.1661(10)
c, Å	19.274(6)	20.9220(13)
β, deg	103.727(4)	107.5170(10)
V, Å^3	6009(3)	5548.9(6),
Z	4	2
ρ_{calcd}, g cm^{-3}	1.608	1.631
μ, mm^{-1}	0.896	1.345
F(000)	3024	2792
Crystal size, mm	0.16 × 0.14 × 0.13	0.15 × 0.14 × 0.13
θ Range for date collection, deg	1.75–25.01	2.52–28.09
Range of reflection indices	$-16 \leqslant h \leqslant 9, -26 \leqslant k \leqslant 27,$ $-20 \leqslant l \leqslant 22$	$-16 \leqslant h \leqslant 20, -17 \leqslant k \leqslant 19,$ $-24 \leqslant l \leqslant 13$
Reflections collected	15069	13922
Unique reflections (R_{int})	5296 (0.0440)	4874 (0.0274)
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Data/restraints/parameters	5296/2/427	4874/8/438
Goodness-of-fit on F^2	1.031	1.071
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0440$, $wR_2 = 0.1071$	$R_1 = 0.0450$, $wR_2 = 0.1390$
R indices (all data)	$R_1 = 0.0570$, $wR_2 = 0.1140$	$R_1 = 0.0579$, $wR_2 = 0.1498$
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.598/–0.602	0.841/–0.525

Table 2. Selected bond lengths and angles for **I** and **II**

Bond	*d*, Å	Bond	*d*, Å
		I	
Ni(1)–N(1)	1.864(3)	O(2)–C(25)	1.238(4)
Ni(1)–N(2)	1.869(3)	O(6)–Ca(1)[a]	2.358(2)
Ni(1)–N(4)	1.869(3)	N(1)–C(1)	1.334(4)
Ni(1)–N(3)	1.887(3)	N(1)–C(2)	1.397(4)
Ca(1)–O(1)	2.335(2)	N(2)–C(8)	1.314(4)
Ca(1)–O(10)	2.347(3)	N(2)–C(10)	1.432(4)
Ca(1)–O(7)	2.348(3)	N(3)–C(17)	1.301(4)
Ca(1)–O(6)[a]	2.358(3)	N(3)–C(15)	1.446(4)
Ca(1)–O(9)	2.362(3)	N(4)–C(25)	1.345(4)
Ca(1)–O(8)	2.443(2)	N(4)–C(20)	1.397(4)
Ca(1)–O(2)	2.643(2)	C(1)–C(25)	1.522(5)
O(1)–C(1)	1.241(4)		
		II	
Co(1)–O(7)	2.086(3)	O(6)–C(1)	1.251(4)
Co(1)–O(6)	2.091(3)	N(1)–C(16)	1.314(5)
Co(1)–O(5)	2.102(2)	N(1)–C(15)	1.431(5)
Co(2)–O(8)	2.064(3)	N(2)–C(24)	1.337(5)
Co(2)–O(10)	2.083(4)	N(2)–C(19)	1.409(5)
Co(2)–O(9)	2.085(3)	N(3)–C(1)	1.329(5)
Ni(1)–N(1)	1.872(3)	N(3)–C(2)	1.410(5)
Ni(1)–N(2)	1.881(3)	N(4)–C(8)	1.295(6)
Ni(1)–N(3)	1.887(3)	N(4)–C(10)	1.448(5)
Ni(1)–N(4)	1.892(3)	C(1)–C(24)	1.525(5)
O(5)–C(24)	1.247(4)		
Angle	ω, deg	Angle	ω, deg
		I	
N(1)Ni(1)N(2)	93.1(1)	O(9)Ca(1)O(8)	72.89(9)
N(1)Ni(1)N(4)	85.9(1)	O(1)Ca(1)O(2)	64.77(8)
N(2)Ni(1)N(4)	176.6(1)	O(10)Ca(1)O(2)	72.82(8)
N(1)Ni(1)N(3)	179.3(1)	O(7)Ca(1)O(2)	82.15(9)
N(2)Ni(1)N(3)	86.7(1)	O(6)[a]Ca(1)O(2)	99.36(8)
N(4)Ni(1)N(3)	94.4(1)	O(9)Ca(1)O(2)	137.72(8)
O(1)Ca(1)O(10)	137.51(9)	O(8)Ca(1)O(2)	149.38(8)
O(1)Ca(1)O(7)	86.11(9)	C(1)O(1)Ca(1)	124.4(2)
O(10)Ca(1)O(7)	85.8(1)	C(1)N(1)C(2)	122.4(3)
O(1)Ca(1)O(6)[a]	83.96(9)	C(1)N(1)Ni(1)	111.1(2)
O(10)Ca(1)O(6)[a]	105.9(1)	C(2)N(1)Ni(1)	126.4(2)

Table 2. (Contd.)

O(7)Ca(1)O(6)^a	168.14(9)	C(8)N(2)C(10)	123.4(3)
O(1)Ca(1)O(9)	74.96(9)	C(8)N(2)Ni(1)	126.4(2)
O(10)Ca(1)O(9)	144.6(1)	C(10)N(2)Ni(1)	110.2(2)
O(7)Ca(1)O(9)	82.8(1)	C(17)N(3)C(15)	124.4(3)
O(6)^{a}Ca(1)O(9)	88.3(1)	C(17)N(3)Ni(1)	125.5(2)
O(1)Ca(1)O(8)	143.95(8)	C(15)N(3)Ni(1)	110.2(2)
O(10)Ca(1)O(8)	78.15(9)	C(25)N(4)C(20)	123.4(3)
O(7)Ca(1)O(8)	105.47(9)	C(25)N(4)Ni(1)	111.0(2)
O(6)^{a}Ca(1)O(8)	79.26(8)	C(20)N(4)Ni(1)	125.5(2)
Angle	ω, deg	Angle	ω, deg
II			
O(7)Co(1)O(6)	86.1(1)	C(16)N(1)Ni(1)	125.2(3)
O(6)Co(1)O(5)	78.92(9)	C(15)N(1)Ni(1)	111.9(3)
O(8)Co(2)O(10)	88.8(1)	C(24)N(2)C(19)	122.5(3)
O(8)Co(2)O(9)	90.1(1)	C(24)N(2)Ni(1)	110.8(2)
O(10)Co(2)O(9)	90.6(2)	C(19)N(2)Ni(1)	126.4(3)
N(1)Ni(1)N(2)	93.12(1)	C(1)N(3)C(2)	122.2(3)
N(1)Ni(1)N(3)	177.8(6)	C(1)N(3)Ni(1)	110.6(3)
N(2)Ni(1)N(3)	86.5(1)	C(2)N(3)Ni(1)	127.1(3)
N(1)Ni(1)N(4)	86.3(1)	C(8)N(4)C(10)	122.3(4)
N(2)Ni(1)N(4)	178.3(2)	C(8)N(4)Ni(1)	126.7(3)
N(3)Ni(1)N(4)	94.01(1)	C(10)N(4)Ni(1)	110.8(3)
C(16)N(1)C(15)	121.8(3)		

* Symmetry codes: ^{a} $-x + 1, y, -z + 3/2$ (**I**).

RESULTS AND DISCUSSION

Compound **I** includes hetero-tetranuclear molecular boxes $[Ca_2(NiL)_2(H_2O)_8]$ (Fig. 1). Each Ni^{2+} ion has a distorted N_4 square-planar coordination geometry with short Ni–N bond lengths (1.869–1.887 Å) (Table 2). Deviations of the four donors and the Ni center from their mean plane are in the range of –0.0507 to +0.0137 Å. The dihedral angles between the NiN_4 plane and three phenyl rings in the $Ni(L^{2-})$ ligand are respectively 24.91°, 26.15° and 23.80°. Distance between the two N_4 planes of the two $Ni(L^{2-})$ ligands in a molecular box is 3.670(6) Å. Each Ca^{2+} ion coordinates two oxamido oxygens (O(1), O(2)) of a $Ni(L^{2-})$, one carboxyl oxygen (O(6*A*)) of another $Ni(L^{2-})$ and four water oxygens (O(7)–O(10)), forming a slightly distorted pentagonal-bipyramidal coordination geometry. The seven-coordination of calcium is very common in related metal complexes [24].

The N–C bonds (1.334–1.345 Å) in the oxamido groups are longer than the N=C double bonds (N(2)–C(8) 1.314 and N(3)–C(17) 1.301 Å), but obviously shorter than N–C single bonds (N(2)–C(10) 1.432 and N(3)–C(15) 1.446 Å). The sum of the three bond angles around each amidate nitrogen is close to 360° (359.9°). These data reveal sp^2-hybridized character of the amidate nitrogens and delocalization of the π-electrons on these atoms and the carbonyls. The C–C bonds in oxamido groups are longer than normal single bonds (see C(1)–C(25) 1.522 Å), indicating that each oxamido group is divided into two π-systems, each of which includes a carbonyl and an amidate nitrogen.

Complex **II** contains centrosymmetric hetero-trinuclear complex anions ($[Co(NiL)_2(H_2O)_2]^{2-}$) and

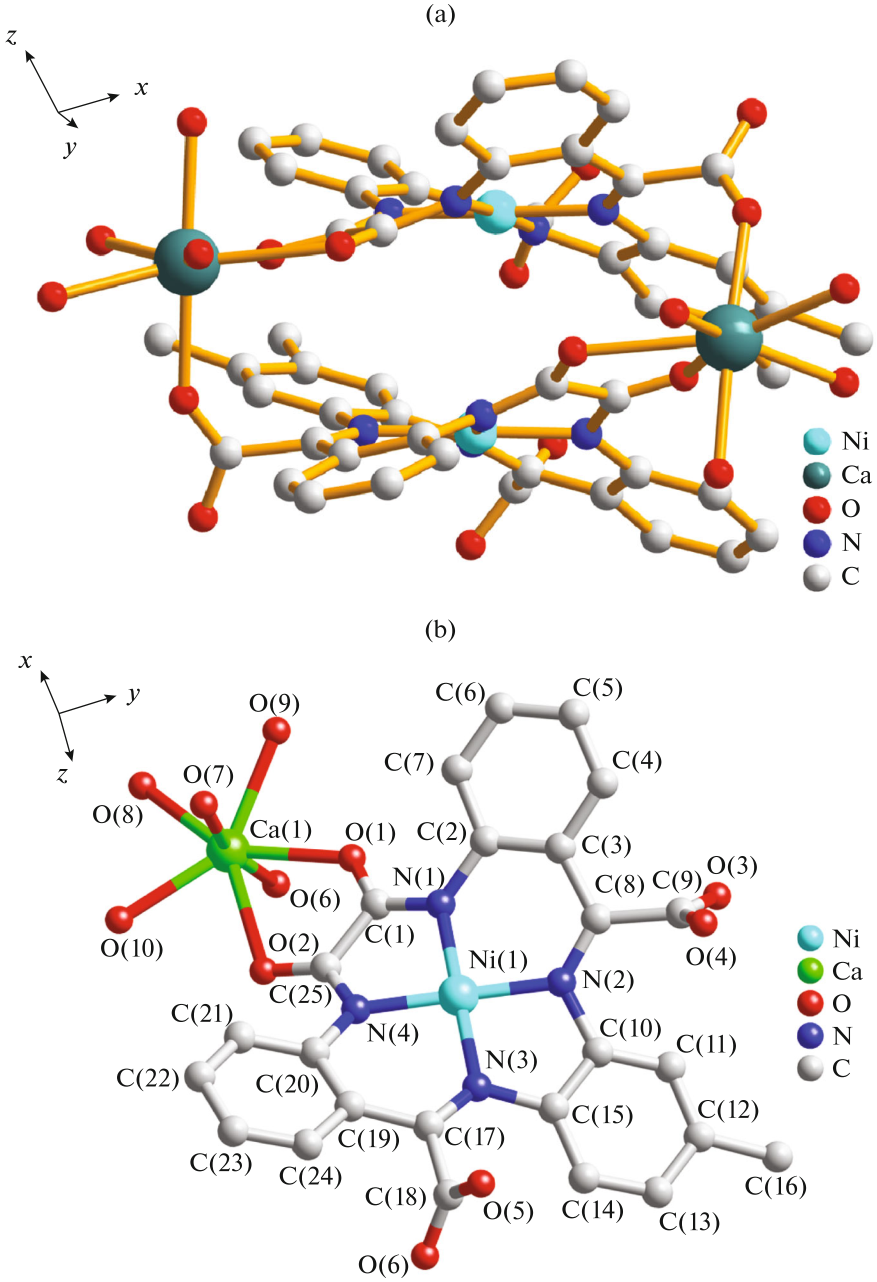


Fig. 1. View of the hetero-tetranuclear molecular box (a) and coordination environments of Ni and Ca (b). Hydrogen atoms were omitted for clarity.

mononuclear complex cations ($[Co(H_2O)_6]^{2+}$, Fig. 2). In the complex anion of **II**, Co(1) has a distorted coordination octahedron with four oxygen atoms (O(5), O(6), O(5*A*), O(6*A*)) from two complex ligands in the equatorial plane and two aqua oxygen atoms (O(7), O(7*A*)) at the two axial positions. The axial Co–O bond distances (2.086(3) Å) are shorter than the equatorial Co–O ones (2.091(3)–2.102(2) Å) (Table 2). The Co and Ni atoms are linked by the oxamido groups from the macrocyclic ligands, the Co···O distance is 5.277(4) Å. The Ni atom in the complex has a slightly distorted N_4 square-planar coordination geometry. The deviations of the four N atoms and the Ni atom from their mean plane are in the range of −0.0300 to +0.0323 Å, and Ni–N bonds are quite short and close (1.872–1.892 Å). The phenyl ring of 3,4-diaminotoluene and the Co(1)–O(5)–O(6) plane tilt on the same side of NiN_4 plane. The dihedral

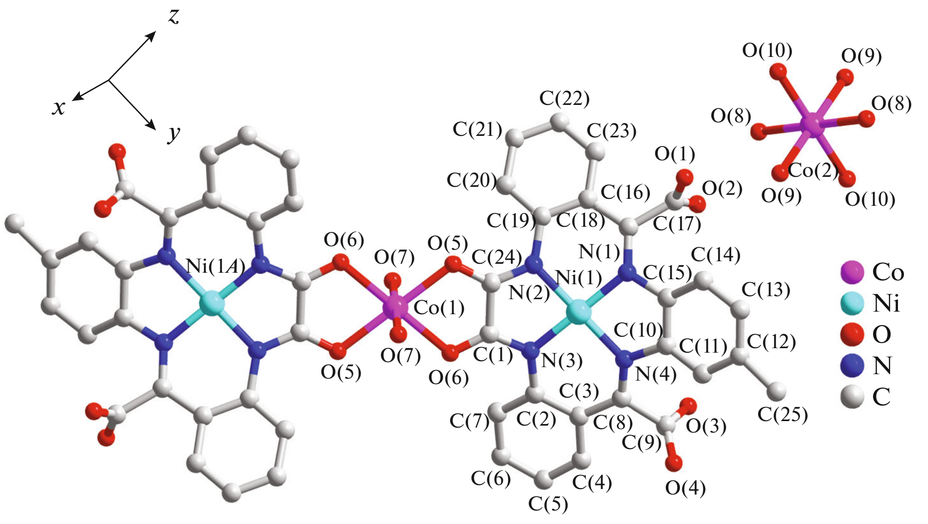


Fig. 2. Structures of $[Co(NiL)_2(H_2O)_2]^{2-}$ and $[Co(H_2O)_6]^{2+}$ in **II**. Hydrogen atoms were omitted for clarity.

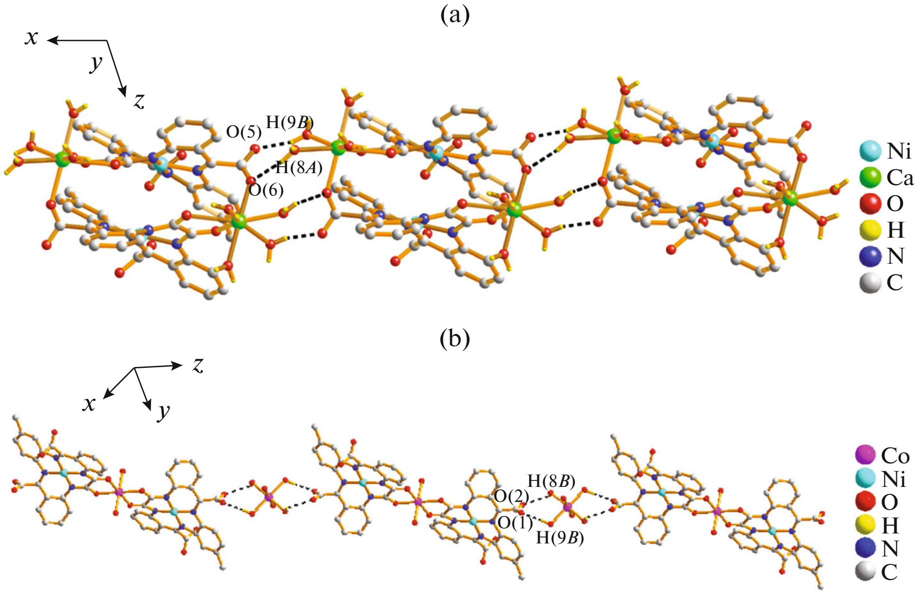


Fig. 3. The infinite 1D hydrogen-bonding chain of **I** (a) and **II** (b).

angles between the NiN_4 plane and the two planes are 18.56° and 12.34°, respectively. The other two phenyl rings of the complex ligand tilt on the other side of the NiN_4 plane with the dihedral angles between the NiN_4 plane and two phenyl rings being 14.25° and 29.97°. In the complex cation of **II**, Co(2) is closely bound to six oxygen atoms of water molecules in octahedral coordination.

The N(2)–C(24) and N(3)–C(1) bond lengths in the oxamido groups are 1.337 and 1.329 Å, respectively, a little longer than N=C double bonds (N(1)–C(16) 1.314, N(4)–C(8) 1.295 Å), but much shorter than N–C single bonds (N(1)–C(15) 1.431, N(4)–C(10) 1.448 Å). The sum of the three bond angles around each amidate nitrogen is close to 360° (359.7°–359.9°). Thus, the amidate nitrogen atoms should be sp^2-hybridized and the *p*-electrons on them should be delocalized into the oxamido carbonyls.

Rich intermolecular hydrogen bonds of O–H···O type were observed in **I** and **II**. Parameters of hydrogen bonds are given in Table 3. Some of the hydrogen bonds generate a 1D chain (Fig. 3) (O(6)···H(8*A*), O(5)···H(9*B*) in **I** and O(1)···H(9*B*), O(2)···H(8*B*) in **II**), then a 2D structure (Fig. 4) is formed with the

Table 3. Geometric parameters of hydrogen bonds in **I*** and **II****

D–H···A	Distance, Å			Angle DHA, deg
	D–H	H···A	D···A	
I				
O(7)–H(7*A*)···O(4)[a]	0.84	2.07	2.890(4)	164
O(7)–H(7*B*)···O(11)[b]	0.84	1.89	2.724(4)	176
O(8)–H(8*A*)···O(6)[c]	0.84	2.29	3.093(4)	161
O(8)–H(8*B*)···O(3)[d]	0.84	1.85	2.689(4)	178
O(9)–H(9*A*)···O(14)[b]	0.84	1.94	2.769(4)	167
O(9)–H(9*B*)···O(5)[c]	0.84	1.90	2.716(4)	164
O(10)–H(10*A*)···O(4)[d]	0.84	1.94	2.780(4)	172
O(10)–H(10*B*)···O(13)	0.84	2.03	2.854(4)	166
O(11)–H(11*A*)···O(15)[b]	0.84	2.04	2.872(5)	170
O(11)–H(11*B*)···O(8)	0.84	2.14	2.946(4)	159
O(12)–H(12*A*)···O(15)[e]	0.84	2.11	2.952(5)	174
O(12)–H(12*B*)···O(5)	0.84	2.15	2.702(4)	123
O(13)–H(13*A*)···O(15)	0.84	2.13	2.877(5)	147
O(13)–H(13*B*)···O(2)	0.84	2.17	2.926(4)	150
O(14)–H(14*A*)···O(12)[d]	0.84	2.07	2.764(4)	139
O(14)–H(14*B*)···O(4)[d]	0.84	1.85	2.672(4)	164
O(15)–H(15*A*)···O(14)	0.84	1.93	2.754(5)	166
O(15)–H(15*B*)···O(12)[e]	0.84	2.21	2.952(5)	147
* Symmetry codes: [a] $-x+1, -y+1, -z+1$; [b] $-x+3/2, -y+1/2, -z+1$; [c] $x+1, y, z$; [d] $x+1/2, y-1/2, z$; [e] $-x+1/2, -y+1/2, -z+1$.				
II				
O(7)–H(7)[a]···O(1)[a]	0.84	1.85	2.671(4)	167
O(7)–H(7*B*)···O(3)[b]	0.84	1.74	2.568(4)	170
O(8)–H(8*A*)···O(4)[c]	0.84	2.00	2.721(5)	144
O(8)–H(8*B*)···O(2)	0.84	2.42	2.742(5)	104
O(9)–H(9*B*)···O(1)	0.84	1.92	2.760(5)	173
O(10)–H(10*B*)···O(7)[d]	0.84	1.96	2.798(6)	174

** Symmetry codes: [a] $-x+2, y, -z+1/2$; [b] $x+1/2, y-1/2, z$; [c] $-x+3/2, y-1/2, -z+1/2$; [d] $x-1/2, -y+1/2, z+1/2$.

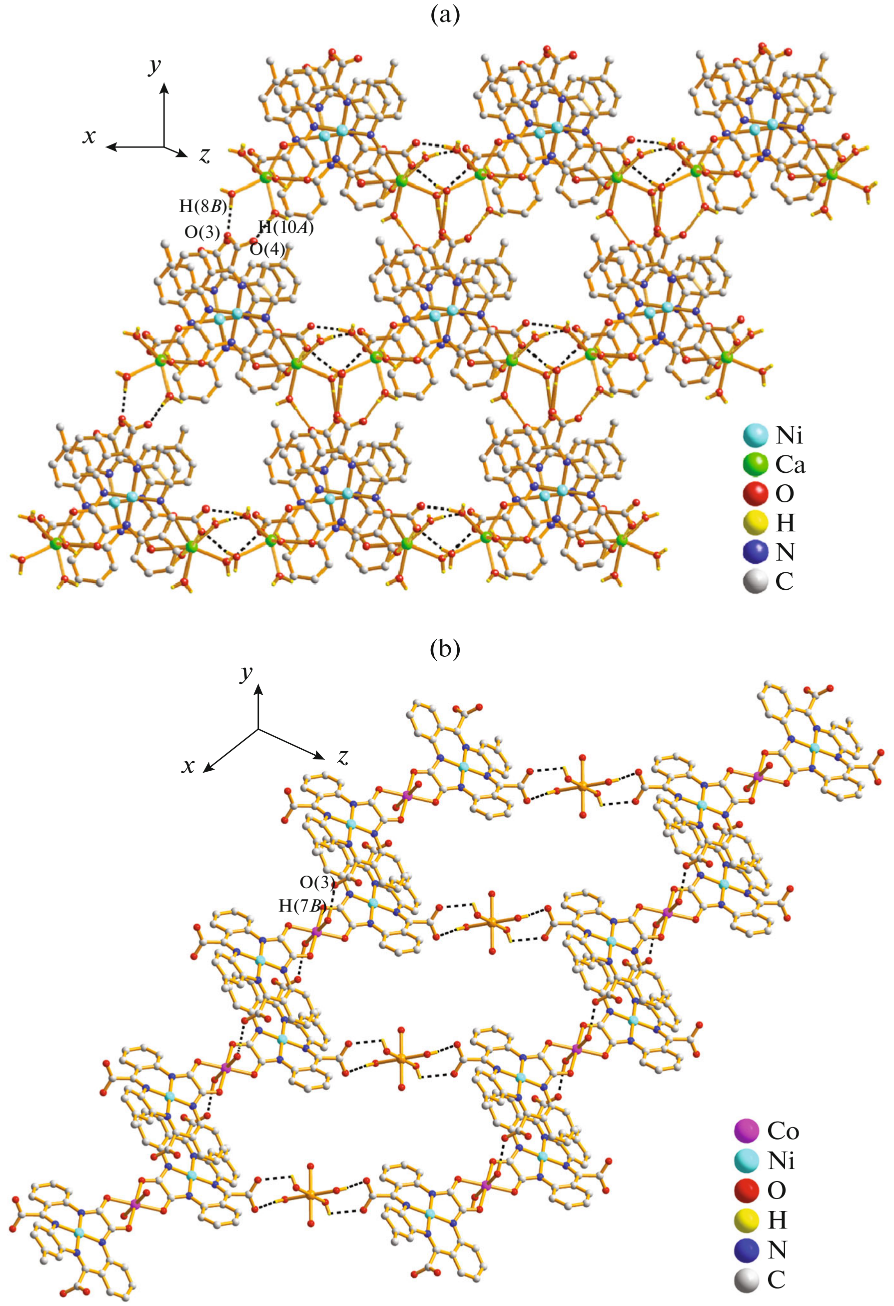


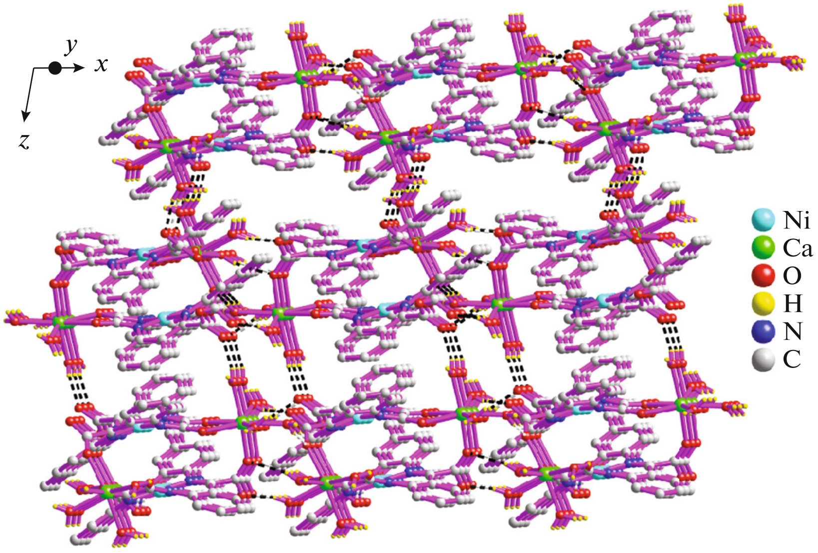
Fig. 4. The 2D layer structure of **I** (a) and **II** (b) connected by hydrogen-bonding.

O(3)···H(8*B*), O(4)···H(10*A*) in **I** and O(3)···H(7*B*) in **II**. The layers are further connected to form 3D networks (Fig. 5) by additional hydrogen bonds (O(4)···H(7*A*) in **I**; O(1)···H(7*A*), O(4)···H(8*A*) in **II**).

The band at 1627 cm^{-1} in the IR spectrum of Na_2NiL is the absorption of ν(C=O) (oxamido), and the corresponding bands for **I** and **II** shifted to 1601 and 1612 cm^{-1}, respectively, due to the stronger coordination of C=O→Ca and C=O→Co than that of C=O→Na. The bands at 1534, pearonding1533 and 1536 cm^{-1} for Na_2NiL, **I** and **II**, respectively, can be assigned to the absorptions of the carboxylate groups coordinating to the Na^+, Co^{2+} and Ca^{2+} ions. The present of water molecules in **I** and **II** were confirmed by the appearance of broad bands at 3500–3300 cm^{-1}.

TGA on polycrystalline samples of **I** and **II** were performed in N_2 atmospheres and the TGA curves are

(a)



(b)

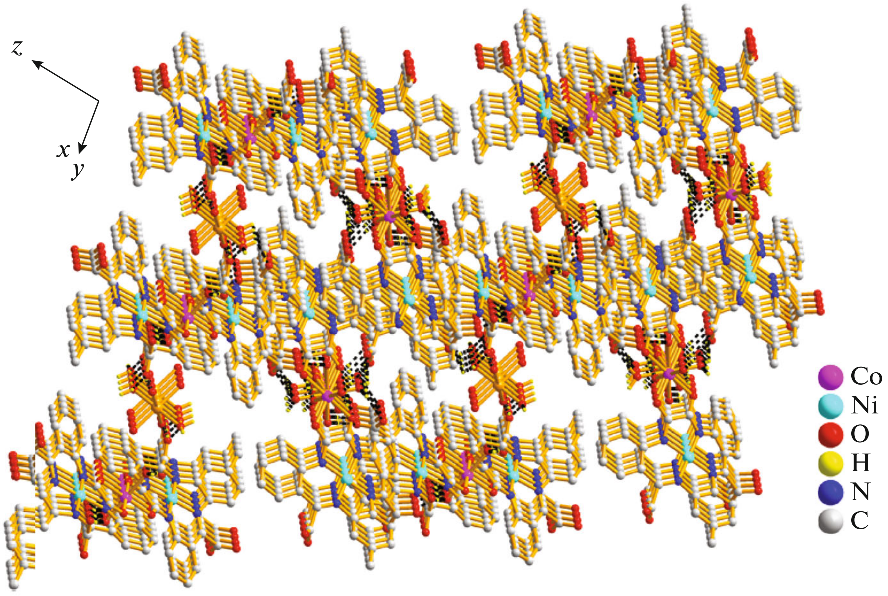


Fig. 5. 3D supramolecular structure via hydrogen-bonding of **I** (a) and **II** (b).

shown in Fig. 6. The first weight loss of **I** started almost at 30°C and completed at ~128°C with a weight loss of 12.69%, corresponding to all the lattice water molecules in **I** (calcd. 12.38%). There was almost no weight loss in the temperature range of ~128–390°C. The observed weight loss (7.14%) in the range 390–451°C for **I** is attributed to the loss of the six coordination water molecules (calcd. 7.43%). Heating the sample to higher temperatures led to decomposition of the other components. Compound **II** started to lose weight at ~50°C. The calculated weight loss percentages consistent with the lattice and coordination water in **II** are 1.85 and 5.29%, respectively. The TGA curve of **II** shows no information near these weight loss percentages and near their sum (7.14%, corresponding to ~115°C) that can help one to identify the temperature at which the lattice and coordination water had been completely lost, and thus the complex ligand Ni(L^{2-}) in **II** should begin to decompose at a temperature lower than 115°C. The result of the TGA implys that Co(II) catalyzed the decomposition of Ni(L^{2-}) in **II**.

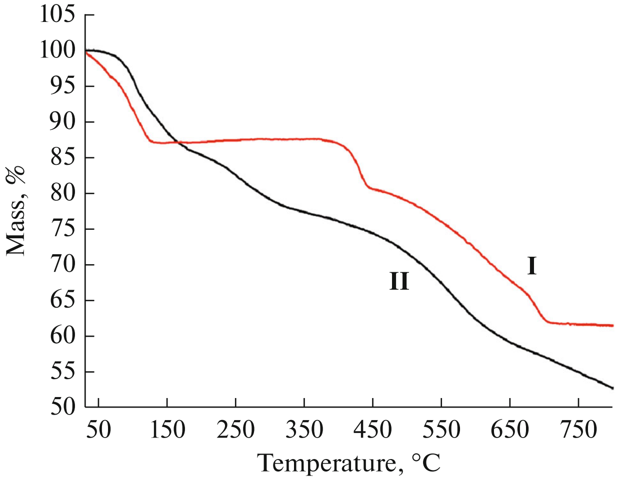


Fig. 6. TG curves of the complexes **I** and **II**.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science foundation of China (grant no. 21371130) and the State Key laboratory of Crystal Material (Shandong University) (grant no. KF1302).

REFERENCES

1. Duriska, M.B., Neville, S.M., Lu, J.Z., et al., *Angew. Chem. Int. Ed.*, 2009, vol. 48, no. 47, p. 8919.
2. Dincă, M. and Long, J.R., *Angew. Chem. Int. Ed.*, 2008, vol. 47, no. 36, p. 6766.
3. Murray, L.J., Dincă, M., and Long, J.R., *Chem. Soc. Rev.*, 2009, vol. 38, no. 5, p. 1294.
4. Chen, B.L., Zhao, X.B., Putkham, A., et al., *J. Am. Chem. Soc.*, 2008, vol. 130, no. 20, p. 6411.
5. Vitillo, J.G., Regli, L., Chavan, S., et al., *J. Am. Chem. Soc.*, 2008, vol. 130, no. 26, p. 8386.
6. Xiang, S.C., Zhou, W., Zhang, Z.J., et al., *Angew. Chem. Int. Ed.*, 2010, vol. 49, no. 27, p. 4615.
7. Britt, D., Furukawa, H., Wang, B., et al., *Proc. Natl. Acad. Sci. U.S.A.*, 2009, vol. 106, no. 49, p. 20637.
8. Dietzel, P.D.C., Besikiotis, V., and Blom, R., *J. Mater. Chem.*, 2009, vol. 19, no. 39, p. 7362.
9. Hou, L., Shi, W.J., Wang, Y.Y., et al., *Chem. Commun.*, 2011, vol. 47, no. 19, p. 5464.
10. Horike, S., Dinca, M., Tamaki, K., and Long, J.R., *J. Am. Chem. Soc.*, 2008, vol. 130, no. 18, p. 5854.
11. Xie, M.H., Yang, X.L., and Wu, C.D., *Chem. Commun.*, 2011, vol. 47, no. 19, p. 5521.
12. Rao, C.N.R., Natarajan, S., and Vaidhyanathan, R., *Angew. Chem. Int. Ed.*, 2004, vol. 43, no. 12, p. 1466.
13. Policar, C., Lambert, F., Cesario, M., and Morgenstern-Badarau, I., *Eur. J. Inorg. Chem.*, 1999, no. 12, p. 2201.
14. Rueff, J.M., Masciocchi, N., Rabu, P., et al., *Eur. J. Inorg. Chem.*, 2001, no. 11, p. 2843.
15. Christodoulou, D., Kanatzidis, M.G., and Coucouvanis, D., *Inorg. Chem.*, 1990, vol. 29, no. 2, p. 191.
16. Sun, Y.Q., Liang, M., Dong, W., et al., *Eur. J. Inorg. Chem.*, 2004, no. 7, p. 1514.
17. Liu, Z.L., Li, L.C., Zhang, L., et al., *New J. Chem.*, 2004, vol. 27, no. 3, p. 583.
18. Wang, S.B., Yang, G.M., Li, R.F., et al., *Eur. J. Inorg. Chem.*, 2004, no. 24, p. 4907.
19. Brewer, G., Brewer, C., Scheidt, W.R., and Shang, M., *Inorg. Chem. Commun.*, 2005, vol. 8, no. 8, p. 676.
20. Li, X.Z., Hao, P.P., Wang, D., et al., *CrystEngComm*, 2012, vol. 14, no. 2, p. 366.
21. Wang, L., Li, X.Z., and Zhu, L.N., *J. Coord. Chem.*, 2011, vol. 64, no. 17, p. 3102.
22. Black, D.S.C. and Moss, G.I., *Aust. J. Chem.*, 1987, vol. 40, no. 1, p. 129.
23. Sheldrick, G.M., *SHELXS-97* and *SHELXL-97, Software for Crystal Structure Analysis,* Madison: Siemens Analytical X-ray Instruments Inc., 1997.
24. Shi, X.M., Li, X.Z., Ding, B.B., and Zhu, L.N., *Z. Anorg. Allg. Chem.*, 2013, vol. 639, nos. 3–4, p. 592.