

This article was downloaded by: [Renmin University of China]

On: 13 October 2013, At: 10:33

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gcoo20>

Synthesis, crystal structure and thermal analysis of two transition metal coordination compounds based on flexible 2-nitro-benzene-1,4-dioxyacetic acid (NBDOA)

Zhi-Min Li^a, Tong-Lai Zhang^a, Wei Yu^b, Jian-Guo Zhang^a, Li Yang^a & Zun-Ning Zhou^a

^a State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing 100081, China

^b School of Urban Development and Environmental Engineering, Shanghai Second Polytechnic University, Shanghai 201209, China

Published online: 26 Apr 2011.

To cite this article: Zhi-Min Li, Tong-Lai Zhang, Wei Yu, Jian-Guo Zhang, Li Yang & Zun-Ning Zhou (2011) Synthesis, crystal structure and thermal analysis of two transition metal coordination compounds based on flexible 2-nitro-benzene-1,4-dioxyacetic acid (NBDOA), *Journal of Coordination Chemistry*, 64:9, 1513-1524, DOI: [10.1080/00958972.2011.574285](https://doi.org/10.1080/00958972.2011.574285)

To link to this article: <http://dx.doi.org/10.1080/00958972.2011.574285>

PLEASE SCROLL DOWN FOR ARTICLE

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

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing,

systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

Synthesis, crystal structure and thermal analysis of two transition metal coordination compounds based on flexible 2-nitro-benzene-1,4-dioxyacetic acid (NBDOA)

ZHI-MIN LI[†], TONG-LAI ZHANG^{*†}, WEI YU[‡], JIAN-GUO ZHANG[†],
LI YANG[†] and ZUN-NING ZHOU[†]

[†]State Key Laboratory of Explosion Science and Technology,
Beijing Institute of Technology, Beijing 100081, China

[‡]School of Urban Development and Environmental Engineering, Shanghai Second
Polytechnic University, Shanghai 201209, China

(Received 8 October 2010; in final form 23 February 2011)

Two transition metal coordination compounds, $[\text{Cd}(\text{NBDOA}) \cdot (\text{H}_2\text{O})_2]_n$ and $[\text{Co}(\text{phen}) \cdot (\text{H}_2\text{O})_4](\text{NBDOA}) \cdot 2\text{H}_2\text{O}$, were synthesized and characterized by elemental analysis and infrared (IR) spectroscopy. The structures investigated by X-ray single crystal diffraction reveal that the coordination polymer $[\text{Cd}(\text{NBDOA}) \cdot (\text{H}_2\text{O})_2]_n$ possesses two kinds of microporous channels which are bridged by five kinds of hydrogen bonds to generate a 3-D supramolecular network. $[\text{Co}(\text{phen})(\text{H}_2\text{O})_4](\text{NBDOA}) \cdot 2\text{H}_2\text{O}$ was constructed by $[\text{Co}(\text{phen}) \cdot (\text{H}_2\text{O})_4]^{2+}$ and NBDOA^{2-} through electrostatic attraction and many kinds of hydrogen-bonding interactions. The thermal stabilities of the compounds were studied by differential scanning calorimeter (DSC) and thermogravimetry–differential thermogravimetric (TG–DTG) measurements, which shows that cadmium(II) and cobalt(II) complexes begin exothermic decomposition at 540 K and 529 K with final residues of CdO and CoO, respectively.

Keywords: Cadmium(II); Cobalt(II); 2-Nitro-benzene-1,4-dioxyacetic acid; Crystal structure; Thermal analysis

1. Introduction

Metal-organic networks (coordination polymers) attract much attention because of topology design and potential properties in adsorption, catalysis, luminescence, magnetism, *etc.* [1–10]. Aromatic di- or multicarboxylates are good candidates for the assembly of cavity-containing metal-organic architectures derived from two characteristics. First, they show various coordination geometries using completely or partially deprotonated carboxylic groups; second, they can act as both hydrogen-bond donors and acceptors depending on the number of deprotonated carboxylic groups.

*Corresponding author. Email: ztlibit@bit.edu.cn

During the past decade, many frameworks have been synthesized and characterized by using rigid multicarboxylate ligands such as 1,4-benzenedicarboxylate [11], 1,3,5-benzenetricarboxylate [12], 1,2,4,5-benzenetetracarboxylate [13, 14] or 1,2,4-benzenetricarboxylate [15, 16]. But flexible multicarboxylate ligands have been less studied [17–19], possibly due to the difficulties in predicting the resulting framework structures.

Benzene-1,4-dioxyacetic acid (BDOAH₂) as an excellent flexible multicarboxylate ligand received interest due to the presence of the –OCH₂– group. Gao and co-workers have reported the structures of some transition metal (Cd(II), Zn(II), Cu(II), Co(II)) coordination polymers based on BDOA^{2–}, most have a fascinating 1-D helical or zigzag chain [1, 17, 20–23]. In 2006, Yang *et al.* [24] investigated 3-D hybrid frameworks and properties of alkaline earth metal complexes of BDOA^{2–}, demonstrating BDOAH₂ has characteristics of both flexibility and rigidity to be a new building block in construction of novel 3-D networks. Some lanthanide coordination polymers containing BDOA^{2–} were reported by Li *et al.* [25] and Deng *et al.* [26]. In these complexes, BDOA^{2–} adopts various coordination modes to connect to lanthanides and constructed different networks. To obtain more new compounds with excellent properties and fascinating architecture based on flexible benzene-1,4-dioxyacetic acid, 2-nitro-benzene-1,4-dioxyacetic acid (NBDOAH₂) was chosen.

NBDOAH₂ is a multidentate flexible ligand with versatile coordination modes, which can be regarded as an excellent candidate for the construction of supramolecular complexes [27, 28]. In our recent work, a series of coordination polymers using NBDOA anion as ligand were prepared, focused on transition metal and alkaline earth metal including Co(II), Cu(II), Mn(II), Zn(II), and Ca(II) [28–32]. To explore such compounds, we have undertaken the synthesis, crystal structure and thermal analysis of a Cd(II) polymer complex [Cd(NBDOA)·(H₂O)₂]_n.

Furthermore, 2-nitro-benzene-1,4-dioxyacetic acid as a dibasic phenoxyacetic acid can construct structures with various cations. Hence, a Co(II) complex, [Co(phen)·(H₂O)₄](NBDOA)·2H₂O, was synthesized using phenanthroline as the neutral ligand and NBDOA as counter anions. Although, NBDOA has constructed a large number of complexes in our previous work as ligand [29–31], as an outer anion is reported for the first time. Co(II) coordinated with phenanthroline has been reported a lot [33–36], but only a few reports on [Co(phen)(H₂O)₄]²⁺ [37–39].

The metal chelating property aspects of 1,10-phenanthroline have been widely utilized in all aspects of coordination chemistry [40–45]. Great interest has focused on Co(II) coordination compounds based on phenanthroline. In these compounds, various anions were coordinated with the central Co(II). There are three Co(II) coordination cations with phenanthroline and water, Co(phen)₃²⁺ [46–49], Co(phen)₂(H₂O)₂²⁺ [24, 50–52], and Co(phen)(H₂O)₄²⁺ [37–39, 53]. In 2004, Lu did structures of a layered vanadium oxide with an interlayer metal coordination complex [Co(phen)₃][V₁₀O₂₆]H₂O, and in 1999, Geraghty reported the structures of two cobalt(II) complexes of octanedioic acid (odaH₂) and nonanedioic acid (ndaH₂), [Co(phen)₃]oda·14H₂O, and [Co(phen)₃]nda·11.5H₂O. Sha described the structure of Co(phen)₂(H₂O)₂²⁺ in 2007, Yesilel synthesized and characterized phenanthroline complexes of Co(II) orotates and studied the thermal stability. Recently, the complexes formed by Co(phen)(H₂O)₄²⁺ and sulfuric acid, adipic acid, and suberic acid were synthesized and characterized, all showing a fantastic 3-D structure.

In this study, two coordination compounds, $[\text{Cd}(\text{NBDOA}) \cdot (\text{H}_2\text{O})_2]_n$ and $[\text{Co}(\text{phen}) \cdot (\text{H}_2\text{O})_4](\text{NBDOA}) \cdot 2\text{H}_2\text{O}$, were synthesized and the crystal structures and thermal decomposition properties were studied.

2. Experimental

2.1. Physical measurements

Elemental analyses were performed on the Carlo Erba 1106 full-automatic trace organic elemental analyzer. Fourier transform infrared spectroscopy (FT-IR) spectra were recorded with a Bruker Equinox 55 FT-IR spectrometer in dry KBr pellets from 400–4000 cm^{-1} with a resolution of 4 cm^{-1} . A Perkin Elmer Pyris1 differential scanning calorimeter (DSC) (sample mass: about 1.0 mg; self-generating atmosphere; heating rate, 10 K min^{-1}) was used for DSC measurement. A Perkin Elmer Pyris1 thermogravimetry–differential thermogravimetric (TG–DTG) analyzer (sample mass: about 1.0 mg; atmosphere, flowing dry, oxygen-free nitrogen with a flowing rate of 20 mL min^{-1} ; heating rate, 10 K min^{-1}) was used for TG analysis.

2.2. Synthesis of $[\text{Cd}(\text{NBDOA}) \cdot (\text{H}_2\text{O})_2]_n$

NBDOAH₂ was prepared by nitration of benzene-1,4-dioxyacetic acid, which was synthesized by reaction of hydroquinone with chloroacetic acid in a molar ratio of 1 : 2 at 373 K [54]. A mixture of 0.3 mmol $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 0.3 mmol NBDOAH₂, 0.6 mmol NaOH, and 15 mL H₂O was sealed in a 25 mL Teflon-lined autoclave and kept at 373 K for 72 h under autogenous pressure. After cooling slowly to room temperature, yellow crystals were collected in 76% yield (based on Cd). Anal. Calcd for $[\text{Cd}(\text{NBDOA}) \cdot (\text{H}_2\text{O})_2]_n$: C, 28.76%; H, 2.65%; N, 3.35%. Found: C, 28.84%; H, 2.56%; N, 3.41%. IR (KBr pellet) data (νcm^{-1}): 3556, 3389, 2941, 1578, 1530, 1425, 1343, 1286, 1223, 1158, 1063, 952, 859, 818, 757.

2.3. Synthesis of $[\text{Co}(\text{phen}) \cdot (\text{H}_2\text{O})_4](\text{NBDOA}) \cdot 2\text{H}_2\text{O}$

$[\text{Co}(\text{phen}) \cdot (\text{H}_2\text{O})_4](\text{NBDOA}) \cdot 2\text{H}_2\text{O}$ was prepared by addition of 0.5 mmol 1,10-phenanthroline, 1.0 mmol NaOH, and 0.5 mmol $\text{Co}(\text{NO}_3)_2$ to a hot aqueous solution of 0.5 mmol NBDOAH₂ with subsequent filtration. Pink block crystals were obtained from the filtered solution at room temperature over several days, yield 72% (based on NBDOAH₂). Anal. Calcd for $[\text{Co}(\text{phen}) \cdot (\text{H}_2\text{O})_4](\text{NBDOA}) \cdot 2\text{H}_2\text{O}$: C, 42.86%; H, 4.38%; N, 6.82%. Found: C, 42.45%; H, 4.29%; N, 6.75%. IR (KBr pellet) data (νcm^{-1}): 3458, 3369, 3085, 2964, 1672, 1658, 1605, 1533, 1421, 1362, 1274, 1265, 1158, 1082, 862, 757, 726, 621.

2.4. X-ray crystallography

A suitable blue block crystal of $[\text{Cd}(\text{NBDOA}) \cdot (\text{H}_2\text{O})_2]_n$ with dimensions of 0.22 × 0.20 × 0.14 mm was mounted on a glass fiber and the data were collected on a

Table 1. Crystallographic data and structure refinement for the complexes.

	[Cd(NBDOA)·(H ₂ O) ₂] _n	[Co(phen)·(H ₂ O) ₄](NBDOA)·2H ₂ O
Empirical formula	C ₁₀ H ₁₁ CdNO ₁₀	C ₂₂ H ₂₇ CoN ₃ O ₁₄
Formula weight	417.60	616.40
Temperature (K)	294(2)	153(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2(1)/ <i>c</i>
Unit cell dimensions (Å, °)		
<i>a</i>	7.793(2)	7.3815(2)
<i>b</i>	8.043(2)	14.5750(4)
<i>c</i>	11.235(3)	24.0014(5)
α	95.818(4)	
β	91.440(5)	93.249(1)
γ	107.805(4)	
Volume (Å ³), <i>Z</i>	665.9(3), 2	2578.05(11), 4
Calculated density (g cm ⁻³)	2.083	1.588
Absorption coefficient (mm ⁻¹)	1.696	0.744
<i>F</i> (000)	412	1276
Crystal size (mm ³)	0.22 × 0.20 × 0.14	0.52 × 0.44 × 0.09
θ range for data collection (°)	2.68–26.41	3.10–27.48
Limiting indices	−8 ≤ <i>h</i> ≤ 9; −9 ≤ <i>k</i> ≤ 9; −11 ≤ <i>l</i> ≤ 13	−9 ≤ <i>h</i> ≤ 9; −18 ≤ <i>k</i> ≤ 18; −31 ≤ <i>l</i> ≤ 31
Reflections collected	3375	25051
Independent reflections	2338 [<i>R</i> _{int} = 0.0226]	5897 [<i>R</i> _{int} = 0.0257]
Data/restraints/parameters	2338/6/199	5897/12/410
Goodness-of-fit on <i>F</i> ²	1.047	1.008
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0323, <i>wR</i> ₂ = 0.0761	<i>R</i> ₁ = 0.0313, <i>wR</i> ₂ = 0.0915
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0425, <i>wR</i> ₂ = 0.0817	<i>R</i> ₁ = 0.0333, <i>wR</i> ₂ = 0.0929
Largest difference peak and hole (e Å ⁻³)	0.755 and −0.703	0.548 and −0.546

Bruker Smart CCD diffractometer with a Mo-K α radiation ($\lambda = 0.71073$ Å) at 294(2) K by using an ω scan mode in the range of $1.83 < \theta < 25.02^\circ$. A total of 3375 reflections were collected, of which 2338 were unique with $R_{\text{int}} = 0.0226$. All non-hydrogen atoms were located by direct methods and subsequent difference Fourier syntheses. The hydrogens bound to carbon were located by geometric calculations, and their positions and thermal parameters were fixed during the structure refinement. All calculations were performed by the SHELXTL-97 program [55].

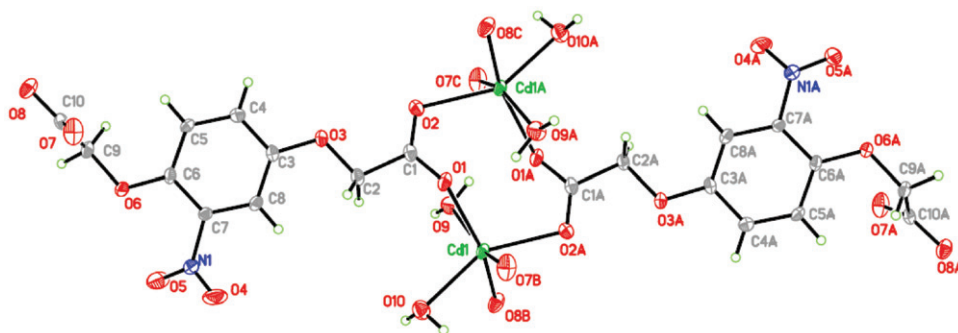
The X-ray single data collection of [Co(phen)·(H₂O)₄](NBDOA)·2H₂O was carried on a Rigaku RAXIS-RAPID diffractometer using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at 153(2) K. The structure was solved by direct methods by using SHELXS-97 program [56] and refined by full-matrix least squares techniques based on *F*² with the SHELXTL-97 program package [55]. All non-hydrogen atoms were located by direct methods and subsequent difference Fourier syntheses. Hydrogens bound to carbon were located by geometrical calculations, and their positions and thermal parameters were fixed during the structure refinement.

Crystallographic data and experimental details for structure analyses are summarized in table 1. Further information concerning the crystal-structure determinations in crystallographic information file format is available in the Supporting Information.

Table 2. Selected bond lengths (Å) and angles (°) for $[\text{Cd}(\text{NBDOA}) \cdot (\text{H}_2\text{O})_2]_n$ and $[\text{Co}(\text{phen}) \cdot (\text{H}_2\text{O})_4](\text{NBDOA}) \cdot 2\text{H}_2\text{O}$.

$[\text{Cd}(\text{NBDOA}) \cdot (\text{H}_2\text{O})_2]_n$		$[\text{Co}(\text{phen}) \cdot (\text{H}_2\text{O})_4](\text{NBDOA}) \cdot 2\text{H}_2\text{O}$	
Cd(1)–O(8)#1	2.277(3)	Co–O(9)	2.059(1)
Cd(1)–O(2)#2	2.296(3)	Co–O(12)	2.145(1)
Cd(1)–O(1)	2.319(3)	Co–O(10)	2.070(1)
Cd(1)–O(9)	2.426(3)	Co–N(2)	2.146(1)
O(7)–Cd(1)#3	2.347(3)	Co–O(11)	2.028(1)
Cd(1)–O(10)	2.329(3)	Co–N(3)	2.148(1)
O(8)#1–Cd(1)–O(2)#2	87.98(12)	O(11)–Co–O(9)	175.34(5)
O(2)#2–Cd(1)–O(1)	104.31(11)	O(11)–Co–O(12)	89.51(4)
O(2)#2–Cd(1)–O(10)	147.55(12)	O(11)–Co–N(2)	96.25(6)
O(8)#1–Cd(1)–O(7)#3	125.17(13)	O(12)–Co–N(2)	90.87(5)
O(1)–Cd(1)–O(7)#3	79.64(13)	O(10)–Co–N(3)	98.77(5)
O(8)#1–Cd(1)–O(9)	78.63(12)	O(11)–Co–O(10)	91.81(6)
O(1)–Cd(1)–O(9)	76.83(11)	O(9)–Co–O(12)	87.62(4)
O(7)#3–Cd(1)–O(9)	156.19(13)	O(9)–Co–N(2)	87.46(5)
O(8)#1–Cd(1)–O(1)	154.38(12)	O(11)–Co–N(3)	87.58(5)
O(8)#1–Cd(1)–O(10)	84.44(12)	O(12)–Co–N(3)	168.16(5)
O(1)–Cd(1)–O(10)	95.75(12)	O(9)–Co–O(10)	84.67(6)
O(2)#2–Cd(1)–O(7)#3	80.00(12)	O(10)–Co–O(12)	92.80(5)
O(10)–Cd(1)–O(7)#3	78.84(13)	O(10)–Co–N(2)	171.17(6)
O(2)#2–Cd(1)–O(9)	102.32(12)	O(9)–Co–N(3)	95.96(5)
O(10)–Cd(1)–O(9)	106.97(12)	N(2)–Co–N(3)	78.05(5)

Symmetry transformations used to generate equivalent atoms for $[\text{Cd}(\text{NBDOA}) \cdot (\text{H}_2\text{O})_2]_n$: #1: $x+1, y, z-1$; #2: $-x+1, -y+2, -z+1$; #3: $-x+1, -y+2, -z+2$.

Figure 1. Coordination environment of cadmium in $[\text{Cd}(\text{NBDOA}) \cdot (\text{H}_2\text{O})_2]_n$.

3. Results and discussion

3.1. Crystal structure of $[\text{Cd}(\text{NBDOA}) \cdot (\text{H}_2\text{O})_2]_n$

The molecular structure of $[\text{Cd}(\text{NBDOA}) \cdot (\text{H}_2\text{O})_2]_n$ consists of one Cd(II), one 2-nitrobenzene-1,4-dioxyacetic, and two coordinated waters. Selected bond distances and angles are given in table 2. The coordination environment of the central Cd(II) is shown in figure 1 as a six-coordinate distorted octahedral geometry defined by four carboxylate oxygens from four NBDOA²⁻ ligands and two oxygens from two

coordinated waters. O7, O8, O9, and O1 form the equatorial plane, and O2 and O10 are axial.

The Cd–O distances (carboxylate) [2.277(3)–2.347(3) Å] lie within the range of the corresponding bond distances [2.251–2.879 Å] reported for normal Cd-carboxylate complexes [57], [2.347(4), 2.364(5)] of $[\text{Cd}(\text{BDOA}) \cdot 2\text{H}_2\text{O}]_n$ [20]. Contrast to the distances of Cu–O (carboxylate) [1.951(2)–1.978(2) Å] of $\{[\text{Cu}_2(\text{NBDOA})_2 \cdot (\text{H}_2\text{O})_2] \cdot 2(\text{H}_2\text{O})\}_n$ [31] and Ca–O (carboxylate) [2.328(8)–2.489(4) Å] of $[\text{Ca}(\text{nbdo}) (\text{H}_2\text{O})_2]_n$ [32], the distances of Cd–O (carboxylate) is about 0.3 Å longer than Cu–O and 0.1 Å shorter than Ca–O. The angles O–Cd(1)–O in the title compound are from 76.83(11) to 156.19(13)°, and the torsion angles of C(3)–O(3)–C(2)–C(1) and C(6)–O(6)–C(9)–C(10) are $-179.6(3)$ and $-78.3(5)$ °, respectively, displaying the flexible character of the ligand. The coordination mode of the complex is shown in figure 2. Each NBDOA²⁻ binds to four Cd ions, and both of the carboxylates adopt skew-skew bidentate bridging coordination, which means the Cd ions are not coplanar to carboxylate and the torsion angles of C–C–O–Cd are quite different. For C1 carboxylate the two coordinated Cd ions are at the same side of the carboxylate

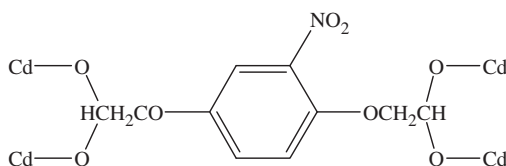


Figure 2. Coordination mode of 2-nitro-benzene-1,4-dioxyacetic in $[\text{Cd}(\text{NBDOA}) \cdot (\text{H}_2\text{O})_2]_n$.

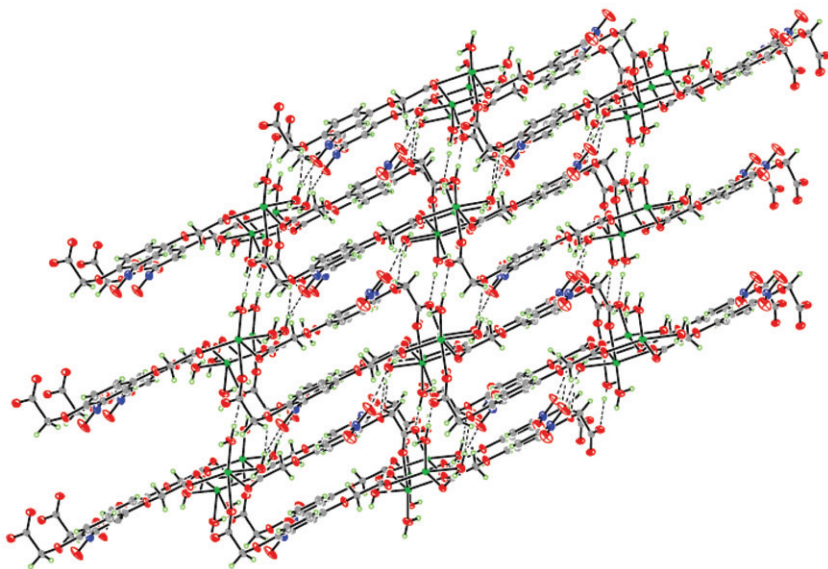


Figure 3. The 1-D channel viewed along the *a* axis of $[\text{Cd}(\text{NBDOA}) \cdot (\text{H}_2\text{O})_2]_n$.

plane, while for C10 carboxylate, the two coordinated Cd ions are at opposite sides of the carboxylate plane.

As shown in figure 3, there exists a 1-D microporous channel along the a axis, constructed by two NBDOA²⁻ ligands and two Cd ions with the cavity about $10.855 \times 5.061 \text{ \AA}^2$, also shown in figure 4 (bore A), with Cd \cdots Cd distance in the unit of 13.081 \AA . Along the b axis there are two kinds of eight-membered rings (bore C and bore D shown in figure 4), constructed by two carboxylates and two Cd ions; the distances of Cd \cdots Cd in the two rings are 4.243 and 4.378 \AA , respectively. The two rings are almost vertical to each other, forming an infinite chain along the b axis, which connects the 1-D channel into a 2-D channel, with another kind of channel (bore B in figure 4) formed with a cavity of $9.657 \times 4.710 \text{ \AA}^2$, and Cd \cdots Cd distance in the unit is 11.087 \AA . The two kinds of channels intersect each other.

In the complex, there are five kinds of intermolecular hydrogen bonds (given in Table 3), three of which are between coordinated water and carboxylate; the other two exist between coordinated water and nitro and oxyacetic groups. The intermolecular hydrogen bonds connect the 2-D structure to a 3-D supramolecular network.

3.2. Crystal structure of $[\text{Co}(\text{phen}) \cdot (\text{H}_2\text{O})_4](\text{NBDOA}) \cdot 2\text{H}_2\text{O}$

X-ray structure analysis shows that this complex is composed of one $[\text{Co}(\text{phen}) \cdot (\text{H}_2\text{O})_4]^{2+}$, one NBDOA²⁻, and two crystal waters, as illustrated in figure 5. In the structure of $[\text{Co}(\text{phen}) \cdot (\text{H}_2\text{O})_4]^{2+}$, the cobalt is six-coordinate by two nitrogens from a chelating phen and four oxygens from four coordinated waters in a distorted octahedral geometry. Its equatorial plane is defined by N(2), O(9), O(10), and O(11) with mean

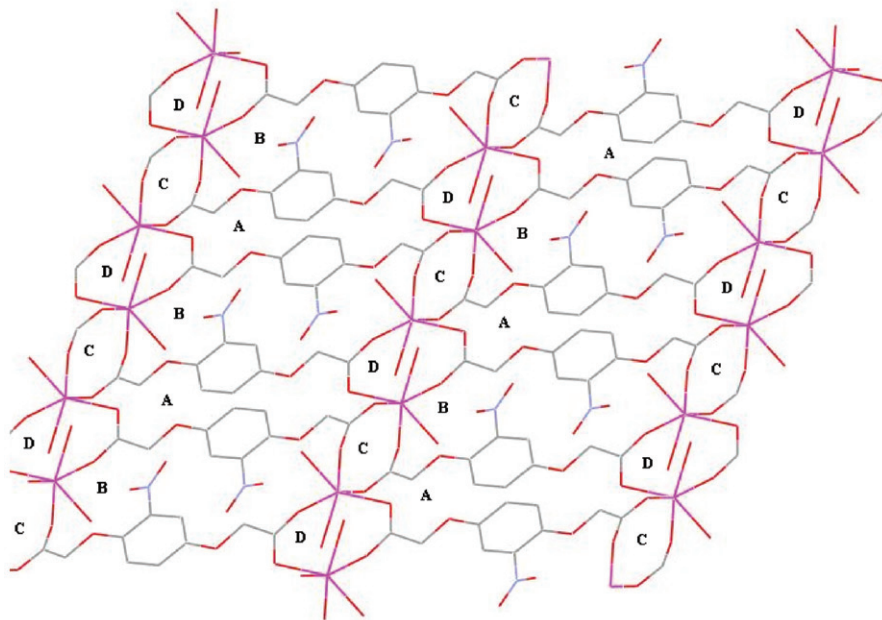
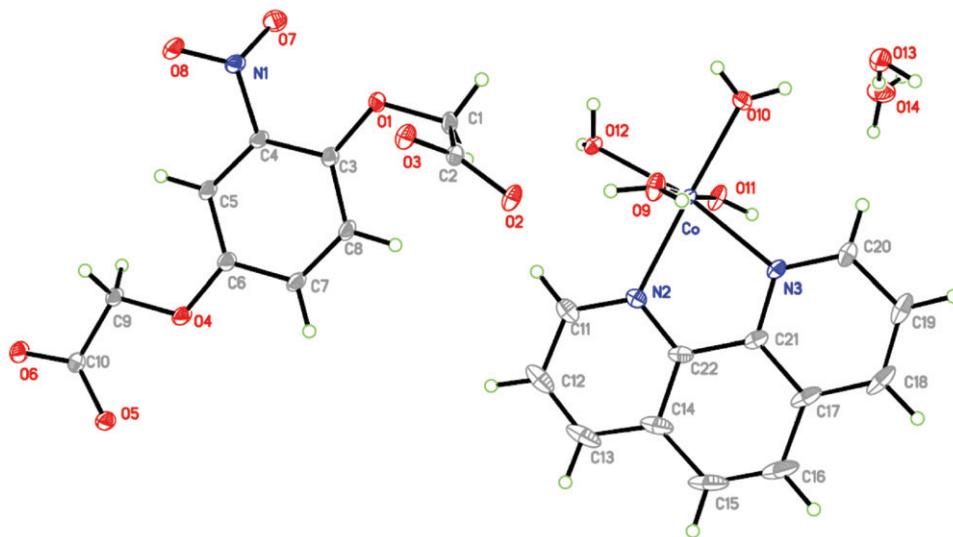


Figure 4. The perspective view of the microporous channels of $[\text{Cd}(\text{NBDOA}) \cdot (\text{H}_2\text{O})_2]_n$.

Table 3. Hydrogen bond lengths (Å) and angles (°) for $[\text{Cd}(\text{NBDOA}) \cdot (\text{H}_2\text{O})_2]_n$ and $[\text{Co}(\text{phen}) \cdot (\text{H}_2\text{O})_4](\text{NBDOA}) \cdot 2\text{H}_2\text{O}$.

D–H···A	$d(\text{D–H})$	$d(\text{H···A})$	$d(\text{D···A})$	$\angle(\text{D–H···A})$
$[\text{Cd}(\text{NBDOA}) \cdot (\text{H}_2\text{O})_2]_n$				
O9–H9C···O8#5	0.853	2.000	2.811	158.57
O9–H9D···O1#2	0.856	2.234	2.879	132.05
O10–H10A···O2#6	0.850	2.123	2.964	170.32
O10–H10B···O5#7	0.848	2.245	2.909	135.25
O10–H10B···O6#7	0.848	2.454	3.248	156.26
$[\text{Co}(\text{phen}) \cdot (\text{H}_2\text{O})_4](\text{NBDOA}) \cdot 2\text{H}_2\text{O}$				
O(10)–H(10B)···O(6)#2	0.820(2)	2.114(17)	2.8302(18)	146(3)
O(11)–H(11A)···O(2)#3	0.820(2)	1.822(4)	2.6381(16)	173(2)
O(11)–H(11B)···O(5)#4	0.820(2)	2.035(9)	2.8231(16)	161(2)
O(12)–H(12A)···O(3)#3	0.820(2)	1.989(3)	2.8074(16)	176(2)
O(12)–H(12B)···O(6)#2	0.820(2)	1.877(7)	2.6774(16)	165(2)
O(13)–H(13A)···O(14)	0.823(2)	1.896(8)	2.663(2)	154.6(17)
O(13)–H(13B)···O(3)#5	0.821(2)	2.043(8)	2.8561(17)	171(5)
O(14)–H(14B)···O(5)#4	0.821(2)	1.905(12)	2.7164(19)	169(6)
O(14)–H(14A)···O(1)#6	0.821(2)	2.22(2)	2.9417(18)	147(3)
O(14)–H(14A)···O(7)#6	0.821(2)	2.31(2)	2.974(2)	139(3)

Symmetry transformations used to generate equivalent atoms for $[\text{Cd}(\text{NBDOA}) \cdot (\text{H}_2\text{O})_2]_n$: #2: $-x+1, -y+2, -z+1$; #5: $-x, -y+1, -z+2$; #6: $x+1, y, z$; #7: $-x+1, -y+1, -z+2$; for $[\text{Co}(\text{phen}) \cdot (\text{H}_2\text{O})_4](\text{NBDOA}) \cdot 2\text{H}_2\text{O}$: #2: $x-1/2, -y+3/2, z-1/2$; #3: $x-1, y, z$; #4: $-x+1, -y+1, -z+1$; #5: $-x+3/2, y-1/2, -z+1/2$; #6: $-x+1/2, y-1/2, -z+1/2$.

Figure 5. Molecular structure of $[\text{Co}(\text{phen}) \cdot (\text{H}_2\text{O})_4](\text{NBDOA}) \cdot 2\text{H}_2\text{O}$.

deviation of 0.061 Å; the Co(II) is away from the mean basal plane by 0.009 Å. N(3) and O(12) occupy apical sites with the N(3)–Co–O(12) angle of 168.16(5)°. For NBDOA²⁻ the O1, N1, and O4 are almost coplanar to the benzene ring, with mean deviation of 0.0085 Å for the plane defined by O1, N1, O4, and carbons of the benzene ring, while for C1, C2, C9, and C10 the deviations are larger and they are not coplanar to the

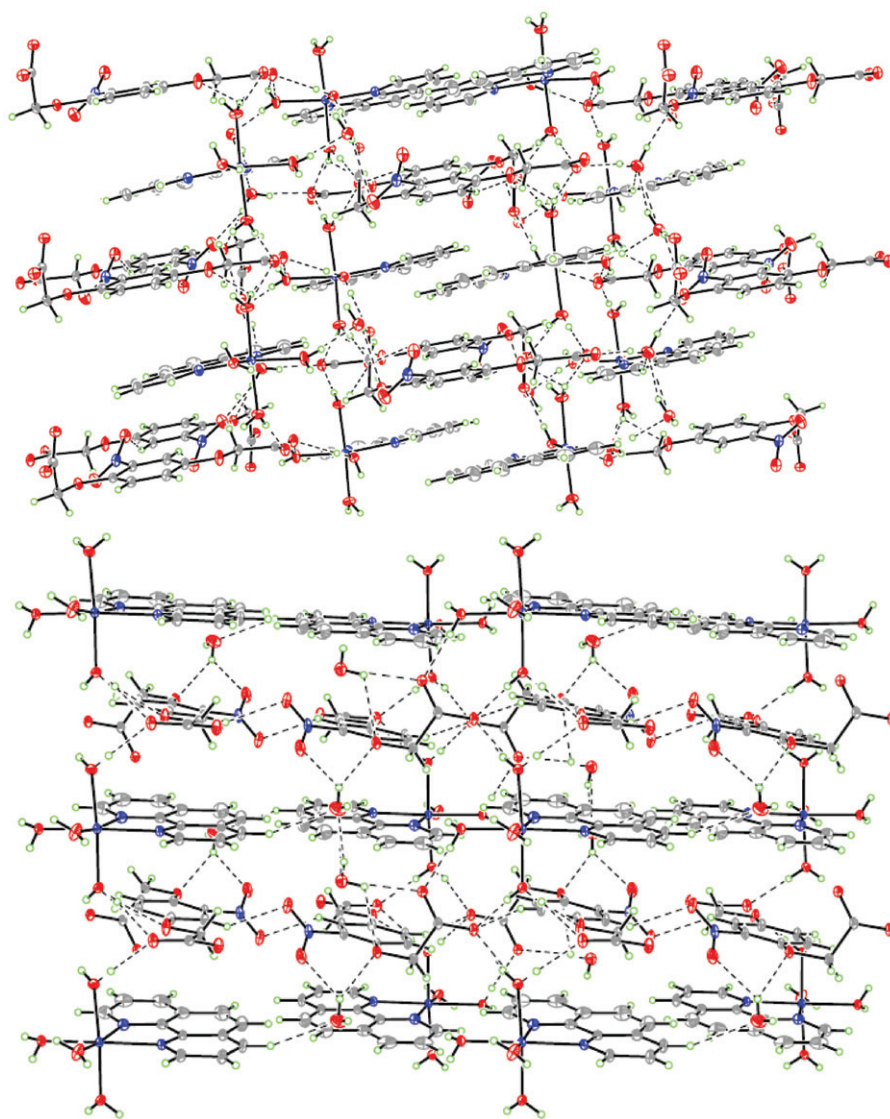


Figure 6. Packing diagram of $[\text{Co}(\text{phen}) \cdot (\text{H}_2\text{O})_4](\text{NBDOA}) \cdot 2\text{H}_2\text{O}$ along b axis (above) and c axis (below).

former plane, especially for C2 the deviation is 1.4877 \AA . Selected bond distances and angles are given in table 2. The torsion angles of C6–O4–C9–C10 and C3–O1–C1–C2 are $176.6(1)$ and $-70.8(1)^\circ$, respectively, which displays the flexibility of 2-nitrobenzene-1,4-dioxyacetate acid.

Besides the electrostatic attraction between $[\text{Co}(\text{phen}) \cdot (\text{H}_2\text{O})_4]^{2+}$ and NBDOA^{2-} , there are many kinds of hydrogen-bonding interactions, table 3. Each $[\text{Co}(\text{phen}) \cdot (\text{H}_2\text{O})_4]^{2+}$ connects five NBDOA^{2-} and one crystal water through eight kinds of hydrogen-bonds, in which seven are between coordinated water and oxygen of carboxyl, and the other is between coordinated water and one crystal water. NBDOA^{2-}

displays versatile hydrogen-bonds, offering oxygen to form 11 kinds of hydrogen-bonds with five $[\text{Co}(\text{phen}) \cdot (\text{H}_2\text{O})_4]^{2+}$ cations and three crystal waters, in which not only two carboxyl groups take part in hydrogen-bonds, but also O1 and O7 from oxyacetate and nitro form $\text{O}(14)\text{--H}(14\text{A}) \cdots \text{O}(1)$ and $\text{O}(14)\text{--H}(14\text{A}) \cdots \text{O}(7)$ hydrogen-bonds.

The supramolecular layers along b and c axes in the complex are shown in figure 6. $[\text{Co}(\text{phen}) \cdot (\text{H}_2\text{O})_4]^{2+}$ and NBDOA^{2-} are alternately arranged along $b \times c$ plane, which was bridged by hydrogen-bonds among the coordinated waters and carboxyl groups resulting in a 2-D layer; the angle of the neighboring phen ring and benzene ring of NBDOA is 7.7° , and the distance of adjacent Co(II) is 7.382 \AA . The 2-D layer is connected through hydrogen-bonds to form a 3-D supramolecular structure.

3.3. Thermal analysis

In the DSC curve (Supplementary material) of $[\text{Cd}(\text{NBDOA}) \cdot (\text{H}_2\text{O})_2]_n$ there are one endothermic and two exothermic processes. The TG–DTG curves (Supplementary material) demonstrate that there exist three main mass loss stages: from 420 to 482 K, 8.43%; from 540 to 618 K, 24.87%; and from 618 to 761 K, 46.95%. The first mass loss is attributed to loss of coordinated water (Calcd 8.62%), an endothermic process in the DSC curve. The second mass loss stage is the loss of the nitro group and two phenoxyacetate radicals (OCH_2) (Calcd 25.40%). There is no distinguishing heat effect during this stage in the DSC curve. When the temperature is 692 K, the coordination polymer decomposes rapidly, with large mass loss in TG curve and the intensive exothermic peak in the DSC curve. The final residue for $[\text{Cd}(\text{NBDOA}) \cdot (\text{H}_2\text{O})_2]_n$ at 873.2 K is 19.92% of which coincides with the calculated value of CdO, 19.49%.

The DSC and TG–DTG curves of $[\text{Co}(\text{phen}) \cdot (\text{H}_2\text{O})_4](\text{NBDOA}) \cdot 2\text{H}_2\text{O}$ are shown in the “Supplementary material” provided. There are three mass loss stages. The first one with 16.62% occurs between 320.0–390.4 K, reaching largest rate at 370.6 K in DTG curve related to the endothermic peak observed in DSC curve, which corresponds to loss of the two lattice waters and four coordinated waters (Calcd 17.53%); the second with 23.35% occurs in the range of 529.7–604.1 K, reaching its largest rate at 541.2 K in the DTG curve, corresponding to the first exothermic peaks observed in the DSC curve. This stage may be classified to loss of phenoxyacetate radical $(-\text{OCH}_2\text{COO})_2$ (Calcd 24.03%); the third mass loss process with 47.47% occurs, reaching largest rate at 696.4 K in DTG curve, corresponding to loss of phenanthroline and combustion of the organic groups, giving the broad exothermic peak observed in the DSC curve. When the temperature is 766.8 K, the residue is constant with 12.56%, which coincides with the calculated value of CoO, 12.15%.

4. Conclusions

NBDOAH₂ as a multidentate flexible ligand and dibasic phenoxyacetic acid were used to construct two transition metal complexes. The central Cd(II) of $[\text{Cd}(\text{NBDOA}) \cdot (\text{H}_2\text{O})_2]_n$ were coordinated by tetradentate NBDOA and two waters, and form a 2-D microporous channel, which connected to a 3-D supramolecular structure through five kinds of hydrogen bonds. In $[\text{Co}(\text{phen}) \cdot (\text{H}_2\text{O})_4](\text{NBDOA}) \cdot 2\text{H}_2\text{O}$, 1,10-phenanthroline

coordinates with Co(II) making NBDOA out of the coordination sphere. $[\text{Co}(\text{phen}) \cdot (\text{H}_2\text{O})_4]^{2+}$ and NBDOA^{2-} were connected by electrostatic attraction and various hydrogen-bonding interactions to construct the structure. Thermal analyses for the two compounds reveal that both release considerable heat when decomposed and large volumes of gas were produced. NBDOA as a multidentate flexible ligand or dibasic acid construct coordination or ionic compounds as a new building block in design and construction of multifunctional materials.

Supplementary Material

CCDC 631932 and 276076 contain the supplementary crystallographic data of two compounds for this article. These data can also be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44 1223 336033; Email: deposit@ccdc.cam.ac.uk or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)]).

Acknowledgments

The authors gratefully acknowledge the financial support from the National Natural Science Foundation of China (no. 20471008) and the Excellent Young Scholars Research Fund of Beijing Institute of Technology (no. 000Y02-8).

References

- [1] X.J. Zheng, L.C. Li, S. Gao, L.P. Jin. *Polyhedron*, **23**, 1257 (2004).
- [2] N.L. Rosi, J. Eckert, M. Eddaoudi, D.T. Vodak, J. Kim, M. O'Keeffe, O.M. Yaghi. *Science*, **300**, 1127 (2003).
- [3] H. Xu, J. Liang, J. Zhuang, H. Kou, R. Wang, Y. Li. *J. Mol. Struct.*, **689**, 177 (2004).
- [4] N.L. Rosi, J. Kim, M. Eddaoudi, B. Chen, M. O'Keeffe, O.M. Yaghi. *J. Am. Chem. Soc.*, **127**, 1504 (2005).
- [5] N.Z. Logar, V. Kaučič. *Acta Chim. Slov.*, **53**, 117 (2006).
- [6] M.J. Rosseinsky. *Microporous Mesoporous Mater.*, **73**, 15 (2004).
- [7] G.S. Papaefstathiou, L.R. MacGillivray. *Coord. Chem. Rev.*, **246**, 169 (2003).
- [8] D.T. Vodak, M.B. Braun, J. Kim, M. Eddaoudi, O.M. Yaghi. *Chem. Commun.*, **24**, 2534 (2011).
- [9] T.K. Maji, W. Kaneko, M. Ohba, S. Kitagawa. *Chem. Commun.*, **36**, 4613 (2005).
- [10] R.F. Wu, T.L. Zhang, X.J. Qiao, J.G. Zhang, L. Yang, W. Yu. *Chin. J. Struct. Chem.*, **25**, 849 (2006).
- [11] Z.Q. Zhang, R.D. Huang, Y.Q. Xu, L.Q. Yu, Z.W. Jiao, Q.L. Zhu, C.W. Hu. *Inorg. Chim. Acta*, **362**, 5183 (2009).
- [12] L.J. Murray, M. Dinca, J. Yano, S. Chavan, S. Bordiga, C.M. Brown, J.R. Long. *J. Am. Chem. Soc.*, **132**, 7856 (2010).
- [13] L.M. Zhao, B. Zhai, D.L. Gao, W. Shi, B. Zhao, P. Cheng. *Inorg. Chem. Commun.*, **13**, 1014 (2010).
- [14] O. Fabelo, J. Pasan, L. Canadillas-Delgado, F.S. Delgado, A. Labrador, F. Lloret, M. Julve, C. Ruiz-Perez. *Cryst. Growth Des.*, **8**, 3984 (2008).
- [15] J.X. Chen, S.X. Liu, E.Q. Gao. *Polyhedron*, **23**, 1877 (2004).
- [16] J.Y. Baeg, S.W. Lee. *Inorg. Chem. Commun.*, **6**, 313 (2003).
- [17] J.W. Liu, S. Gao, L.H. Huo. *Chin. J. Inorg. Chem.*, **20**, 707 (2004).
- [18] H.F. Zhu, W.Y. Sun, T.A. Okamura, N. Ueyama. *Inorg. Chem. Commun.*, **6**, 168 (2003).

- [19] Y. Yang, G.Q. Jiang, Y.Z. Li, J.F. Bai, Y. Pan, X.Z. You. *Inorg. Chim. Acta*, **359**, 3257 (2006).
- [20] S. Gao, L.H. Huo, J.W. Liu, Y.M. Xu, H. Zhao. *Chin. J. Inorg. Chem.*, **21**, 1081 (2005).
- [21] S. Gao, J.W. Liu, L.H. Huo, H. Zhao. *Chin. J. Inorg. Chem.*, **21**, 1349 (2005).
- [22] J.W. Liu, L.H. Huo, S. Gao, H. Zhao, Z.B. Zhu, J.G. Zhao. *Chin. J. Inorg. Chem.*, **20**, 707 (2004).
- [23] S. Gao, J.W. Liu, L.H. Huo, H. Zhao, S.W. Ng. *Appl. Organomet. Chem.*, **19**, 169 (2005).
- [24] Y. Yang, G.Q. Jiang, Y.Z. Li, J.F. Bai, Y. Pan, X.Z. You. *Inorg. Chim. Acta*, **359**, 3257 (2006).
- [25] X.F. Li, Z.B. Han, X.N. Cheng, X.M. Chen. *Inorg. Chem. Commun.*, **9**, 1091 (2006).
- [26] H. Deng, Y.C. Qiu, Y.H. Li, Z.H. Liu, O. Guillou. *Inorg. Chim. Acta*, **362**, 1797 (2009).
- [27] W. Yu, L. Yang, T.L. Zhang, J.G. Zhang, Z.H. Liu, F.J. Ren, X.C. Hu, R.F. Wu. *Chin. J. Struct. Chem.*, **26**, 1135 (2007).
- [28] Z.M. Li, T.L. Zhang, L. Yang, W. Yu, J.G. Zhang. *Chem. Res.*, **21**, 10 (2010).
- [29] L. Yang, W. Yu, T.L. Zhang, J.G. Zhang, S.Z. Wang, R.F. Wu. *Z. Anorg. Allg. Chem.*, **633**, 2046 (2007).
- [30] W. Yu, T.L. Zhang, J.G. Zhang, L. Yang, S.Z. Wang, R.F. Wu. *Z. Anorg. Allg. Chem.*, **634**, 754 (2008).
- [31] W. Yu, L. Yang, T.L. Zhang, J.G. Zhang, Z.H. Liu, F.J. Ren, X.C. Hu, R.F. Wu. *Chin. J. Struct. Chem.*, **26**, 1135 (2007).
- [32] L. Yang, W. Yu, T.L. Zhang, J.G. Zhang, X.C. Hu, Z.H. Lu, S.Z. Wang. *Chin. J. Chem.*, **26**, 645 (2008).
- [33] F. Chen, W.M. Lu, Y. Zhu, B. Wu, X.M. Zheng. *J. Coord. Chem.*, **62**, 808 (2009).
- [34] Y.F. Yu, Y.Q. Wei, R. Broer, R.J. Sa, K.C. Wu. *J. Solid State Chem.*, **181**, 539 (2008).
- [35] M. Wang, C.B. Ma, C.N. Chen, Q.T. Liu. *J. Mol. Struct.*, **891**, 292 (2008).
- [36] M. Yuan, Y.G. Li, E.B. Wang, Y. Lu, C.W. Hu, N.H. Hu, H.Q. Jia. *J. Chem. Soc., Dalton Trans.*, 2916 (2002).
- [37] H.L. Zhu, Y.J. Pan, X.J. Wang, K.B. Yu. *J. Chem. Crystallogr.*, **34**, 199 (2004).
- [38] S.R. Fan, L.G. Zhu. *Chin. J. Chem.*, **23**, 1292 (2005).
- [39] Y.Q. Zheng, Z.P. Kong, J.L. Lin. *J. Coord. Chem.*, **55**, 1249 (2002).
- [40] M. Moghimi, R. Alizadeh, A. Shokrollahi, H. Aghabozorg, M. Shamsipur, A. Shokravi. *Inorg. Chem.*, **42**, 1616 (2003).
- [41] M.S. Goodman, A.D. Hamilton, J. Weiss. *J. Am. Chem. Soc.*, **117**, 8447 (1995).
- [42] Y.Q. Zheng, Z.P. Kong. *Inorg. Chem. Commun.*, **6**, 478 (2003).
- [43] Q.F. Xie, Y.M. Chen. *J. Quanzhou Normal Univ.*, **23**, 42 (2005).
- [44] Y.M. Chen, Q.F. Xie. *Chem. Res.*, **16**, 28 (2005).
- [45] Y.F. Wang, R.F. Li, Q.L. Wang, L.H. Yu, G.M. Yang, D.Z. Liao. *Transition Met. Chem.*, **29**, 728 (2004).
- [46] Y. Lu, E.B. Wang, J.T. Chen, Y.F. Qi, C.W. Hu, L. Xu, J. Peng. *J. Solid State Chem.*, **177**, 946 (2004).
- [47] M. Geraghty, M. McCann, M. Devereux, V. McKee. *Inorg. Chim. Acta*, **293**, 160 (1999).
- [48] Z.Y. Shi, X.J. Gu, J. Peng, E.B. Wang. *J. Mol. Struct.*, **737**, 147 (2005).
- [49] L. Žůrková, R. Kucsera, R. Gyepes, M. Sivák. *Monatsh. Chem.*, **134**, 1071 (2003).
- [50] O.Z. Yesileli, H. Ölmez. *J. Therm. Anal. Calorim.*, **86**, 211 (2006).
- [51] J.Q. Sha, J. Peng, J. Chen, H.S. Liu, A.X. Tian, P.P. Zhang. *Solid State Sci.*, **9**, 1012 (2007).
- [52] Y.M. Chen, Q.F. Xie. *Chem. Res.*, **16**, 28 (2005).
- [53] Y. Zheng, Z.P. Kong. *Inorg. Chem. Commun.*, **6**, 478 (2003).
- [54] W. Yu, T.L. Zhang, L. Yang, J.G. Zhang, R.F. Wu, F.J. Ren, J.Y. Guo, L.H. Liu. *Z. Kristallogr. NCS*, **221**, 229 (2006).
- [55] G.M. Sheldrick. *SHELXL-97, Program for X-ray Crystal Structure Refinement*, University of Göttingen, Germany (1997).
- [56] G.M. Sheldrick. *SHELXS-97, Program for X-ray Crystal Structure Solution*, University of Göttingen, Germany (1997).
- [57] Y.Q. Xu, Y.F. Zhou, D.Q. Yuan, M.C. Hong. *Chin. J. Struct. Chem.*, **25**, 704 (2006).