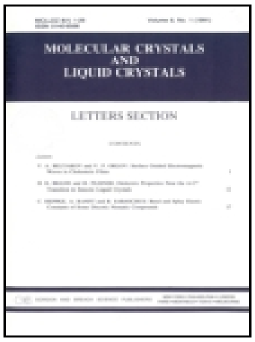

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Structural Variation of Two Low-Dimensional Cd(II) Coordination Polymers Decorated by Isomeric Organic Linkers

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*Two new two-dimensional (2D) Cd(II) coordination compounds constructed from two isomeric thiophenedicarboxylic acid, namely, $[Cd(3,4\text{-}tdc)]_n$ (**1**), $[Cd(2,3\text{-}tdc)(H_2O)]_n$ (**2**) (3,4-tdc = 3,4-thiophenedicarboxylate; 2,3-tdc = 2,3-thiophenedicarboxylate), were obtained by the hydrothermal reaction and structurally determined by single-crystal X-ray diffraction. Structural analyses reveal both of them display 2D-layered network, but their detailed structures are clearly different from each other.* ***1*** *exhibits a 2D-layered network with a uninodal 4-connected SP 2-periodic (6,3)Id topology, while* ***2*** *features a 2D network with 4-connected sql topology. The results indicate the isomeric effect of thiophenedicarboxylates may lead to diverse architectures in the absence of N-donor auxiliary ligands.*

Keywords Cadmium; crystal structure; thermal stability; 3,4-thiophenedicarboxylic acid; 2,3-thiophenedicarboxylic acid

Introduction

Primarily driven by their potential applications as function materials as well as their structural diversities and intriguing variety of topologies, recently, there is tremendous interest in the chemistry of coordination compounds (CPs) constructed from polycarboxylic ligands with multiple coordination sites [1–3]. Relying on the well-designed carboxylate-group binding preferences, a variety of structural topologies within these crystalline materials can be obtained. Among them, commercially available "V-shaped" 2,5-thiophenedicarboxylic acid as an effective organic rigid linker to construct CPs with diverse network topologies has been well developed [4–8]. However, the numble of thiophene-based CPs is rather limited as compared with the above-mentioned CPs.

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Very recently our group has been investigating the CPs of 3,4-thiophenedicarboxylic acid (3,4-H_2tdc) and 2,3-thiophenedicarboxylic acid (2,3-H_2tdc), endowed with two carboxylate groups and a thiophene ring. Moreover, multiple coordinate sites involving carboxylate oxygen atoms make them good bridging linkers for constructing multi-dimensional CPs with intriguing network topologies [9–12]. For instance, $\{[Cd(3,4\text{-}tdc)(bpe)(H_2O)]\cdot 2H_2O\}_n$ (bpe = 1,2-bis(4-pyridyl)ethylene) shows 4-connected **irl** topology, $[Cd(3,4\text{-}tdc)(bpp)]_n$ (bpp = 1,3-bis(4-pyridyl)propane) exhibits 5-connected **lpx1** topology, while $[Cd(3,4\text{-}Htdc)_2(bipy)]_n$ (bipy = 4,4′-bipyridine) displays 6-connected ($5^{10}.6^4.7$) topology. Furthermore, effects of isomeric thiophene skeleton of H_2tdc on the frameworks incorporating N-donor auxiliary ligands are also observed in ours previous reports, where structural diversities indicate that both N-donor auxiliary ligands and isomeric effect of the thiophene skeleton play dominating roles in modulating the resulted crystalline materials. However, may be the isomeric effect of thiophenedicarboxylates influence the formation of different topological structures in the absence of N-donor auxiliary ligands? which is useful in crystal engineering and supramolecular chemistry.

We thus attempted to prepare Cd(II) CPs in the absence of N-donor auxiliary ligands not only to extend ours work about the isomeric effect of thiophenedicarboxylates, but to offer the possibility of controlling the desired network structures. In this contribution, two two-dimensional (2D) CPs with different net topologies were successfully synthesized by hydrothermal reactions of employing isomeric thiophenedicarboxylic acid to assembly with Cd^{2+} ions. we report the single-crystal structural determinations and thermogravimetric analysis (TGA) properties of both crystalline materials.

Experimental

Materials and Physical Measurements

3,4-Thiophenedicarboxylic acid and 2,3-thiophenedicarboxylic acid were synthesized in accordance with the procedure reported, repectively [13, 14]. Other chemicals and solvents were in analytical grade and used without further purification. The hydrothermal reaction was performed in a 25 mL Teflon-lined stainless steel autoclave under autogenous pressure. The IR spectra were recorded as KBr pellets on a Nicolet Avatar-360 spectrometer in the range of 4000–400 cm^{-1}. Elemental analyses for C, H, and N were carried out on a Perkin-Elmer 2400II analyzer. Thermogravimetric analyses were carried out on a SDTQ600 thermogravimetric analyzer. A platinum pan was used for heating the sample with a heating rate of 10°C/min under a N_2 atmosphere.

Preparation of $[Cd(3,4\text{-}tdc)]_n$ (1) and $[Cd(2,3\text{-}tdc)(H_2O)]_n$ (2)

Complexes **1–2** were synthesized by a similar procedure. A mixture of H_2tdc (17.2 mg, 0.1 mmol), $Cd(OAc)_2\cdot 2H_2O$ (26.7 mg, 0.1 mmol), piperazine (3.5 mg, 0.1 mmol), and 8 mL deionized water was sealed in a 25 mL Teflon-lined stainless steel vessel and heated at 140°C for 5 days under autogenous pressure, followed by cooling to room temperature at a rate of 5°C/hr. Block crystals were collected and washed with distilled water several times. Complex **1**, yellow crystals, yield: 33% (based on Cd). Elemental analysis calcd (%) for $C_6H_2CdO_4S$: C, 25.48; H, 0.71. Found: C, 25.50; H, 0.76. IR (cm^{-1}): 1525(s), 1479(s), 1378(s), 1340(m), 1143(m), 1063(m), 890(w), 877(m), 859(m), 838(m), 806(s), 759(vs), 673(m). Complex **2**, colorless crystals, yield: 23% (based on Cd). Elemental analysis calcd

Table 1. Crystallographic data

Empirical formula	$C_6H_2CdO_4S$	$C_6H_4CdO_5S$
Formula weight	282.54	300.55
Crystal system	Monoclinic	Monoclinic
Space group	$P2(1)/c$	$P2(1)/c$
Unit cell dimensions	$a = 12.606(12)$ (Å), $b = 7.142(7)$ (Å), $c = 7.686(7)$ (Å), $\beta = 94.753(13)°$	$a = 11.187(3)$ (Å), $b = 9.592(4)$(Å), $c = 7.387(3)$(Å), $\beta = 101.171(2)°$
Volume (Å^3), Z	689.6(11), 4	777.6(5), 2
Calculated density (Kg/m^3)	2.721	2.567
μ (mm^{-1})	3.430	3.058
Reflections collected/unique	2941/1248	3292/1424
F(000)	536	576
R (int)	0.0364	0.0159
GOF on F^2	1.010	1.034
Final R indices [$I > 2\sigma (I)$]	$R_1 = 0.0365$, $wR_2 = 0.0923$	$R_1 = 0.0214$, $wR_2 = 0.0575$
Final R indices (all data)	$R_1 = 0.0404$, $wR_2 = 0.0962$	$R_1 = 0.0221$, $wR_2 = 0.0582$

(%) for $C_6H_4CdO_5S$: C, 23.96; H, 1.33. Found: C, 23.98; H, 1.38. IR (cm^{-1}): 3407 (br), 1528(s), 1482(s), 1379(s), 1341(m), 1144(m), 1062(m), 891(w), 878(m), 838(m), 805(s), 753(vs), 670(m).

Crystallographic Data Collection and Refinement

The single crystals of **1**–**2** were mounted on a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromated Mo *K*a radiation (λ = 0.71073 Å) at 296(2) K. An empirical absorption correction was applied using the SADABS program [15]. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXL-97 program package [16]. All nonhydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms on water molecules were located from difference Fourier maps and were refined using riding model. Other hydrogen atoms were placed at the calculation positions. S atoms of **2** are in positional disorder, respectively, and has been resolved in terms of their occupancy. A summary of the crystallographic data, selected bond lengths, and of **1**–**2** and hydrogen bond parameters of **2** are listed in Tables 1 and 2, respectively.

Results and Discussion

The hydrothermal reaction of corresponding H_2tdc, cadmium acetate dihydrate, and piperazine in the H_2O at 140°C afforded the two complexes. The reaction temperature should be carefully controlled to form suitable single-crystals for X-ray diffraction. Note that piperazine not only serves as a templating agent but also acts as an organic base in the reaction system, since only precipitates or microcrystalline products unsuitable for single crystal X-ray diffraction analysis were formed if equal amount of triethylamine, potassium

Table 2. Selected bond lengths (Å) and bond angles (°) for **1** and **2**. (Symmetry code for **1**: #1 x, $-y+1/2$, $z-1/2$; #2 x, $y-1$, z; #3 $-x+2$, $-y+1$, $-z+2$; #4 x, $-y+1/2$, $z+1/2$; for **2**: #1 $-x$, $y+1/2$, $-z+1/2$; #2 x, $-y+3/2$, $z+1/2$; #3 $-x$, $-y+1$, $-z+1$)

Compound **1**					
Cd(1)-O(1)	2.297(4)	Cd(1)-O(2)	2.335(4)	Cd(1)-O(3)#1	2.265(4)
Cd(1)-O(4)#2	2.380(4)	Cd(1)-O(4)#3	2.406(4)	Cd(1)-O(3)#3	2.451(4)
Cd(1)-O(1)#4	2.452(4)				
O(3)#1-Cd(1)-O(1)	77.54(12)	O(3)#1-Cd(1)-O(2)	122.37(14)	O(1)-Cd(1)-O(2)	85.92(13)
O(3)#1-Cd(1)-O(4)#2	78.57(14)	O(1)-Cd(1)-O(4)#2	151.89(12)	O(2)-Cd(1)-O(4)#2	94.56(13)
O(3)#1-Cd(1)-O(4)#3	82.84(12)	O(1)-Cd(1)-O(4)#3	119.55(13)	O(2)-Cd(1)-O(4)#3	149.01(12)
O(4)#2-Cd(1)-O(4)#3	71.46(15)	O(3)#1-Cd(1)-O(3)#3	118.69(8)	O(1)-Cd(1)-O(3)#3	88.69(12)
O(2)-Cd(1)-O(3)#3	115.60(15)	O(4)#2-Cd(1)-O(3)#3	115.90(12)	O(4)#3-Cd(1)-O(3)#3	53.31(12)
O(3)#1-Cd(1)-O(1)#4	155.04(13)	O(1)-Cd(1)-O(1)#4	124.00(9)	O(2)-Cd(1)-O(1)#4	54.72(12)
O(4)#2-Cd(1)-O(1)#4	77.11(14)	O(4)#3-Cd(1)-O(1)#4	94.64(12)	O(3)#3-Cd(1)-O(1)#4	77.60(13)
Compound **2**					
Cd(1)-O(1)	2.320(2)	Cd(1)-O(1)#2	2.338(2)	Cd(1)-O(2)#2	2.529(2)
Cd(1)-O(3)	2.339(2)	Cd(1)-O(3)#3	2.5215(19)	Cd(1)-O(4)#1	2.2672(19)
Cd(1)-O(5)	2.322(2)				
O(4)#1-Cd(1)-O(5)	157.42(7)	O(4)#1-Cd(1)-O(1)	80.77(8)	O(5)-Cd(1)-O(1)	116.77(7)
O(4)#1-Cd(1)-O(1)#2	94.00(8)	O(5)-Cd(1)-O(1)#2	88.08(8)	O(1)-Cd(1)-O(1)#2	122.69(6)
O(4)#1-Cd(1)-O(3)	91.55(7)	O(5)-Cd(1)-O(3)	79.20(7)	O(1)-Cd(1)-O(3)	78.33(7)
O(1)#2-Cd(1)-O(3)	158.87(7)	O(4)#1-Cd(1)-O(3)#3	76.55(7)	O(5)-Cd(1)-O(3)#3	81.49(7)
O(1)-Cd(1)-O(3)#3	147.58(7)	O(1)#2-Cd(1)-O(3)#3	82.06(7)	O(3)-Cd(1)-O(3)#3	79.43(7)
O(4)#1-Cd(1)-O(2)#2	118.29(7)	O(5)-Cd(1)-O(2)#2	80.77(8)	O(1)-Cd(1)-O(2)#2	78.91(7)
O(1)#2-Cd(1)-O(2)#2	53.70(7)	O(3)-Cd(1)-O(2)#2	138.49(7)	O(3)#3-Cd(1)-O(2)#2	132.51(7)

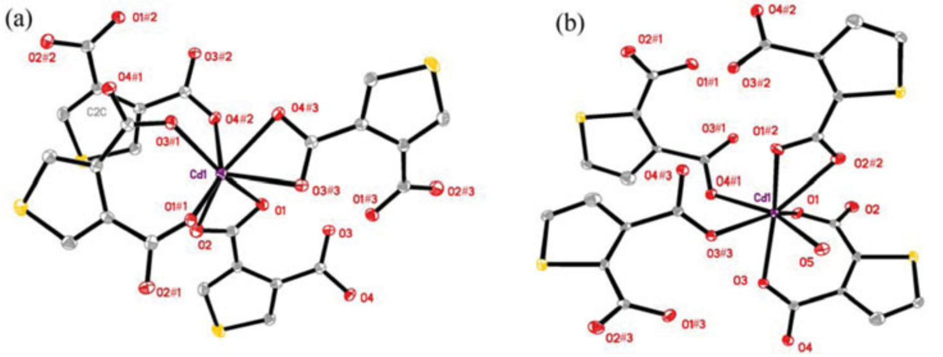

Figure 1. View of the coordination environment of Cd^{2+} ions of **1**–**2**. (Symmetry code for **1**: #1 x, $-y+1/2$, $z-1/2$; #2 x, $y-1$, z; #3 $-x+2$, $-y+1$, $-z+2$; for 2: #1 $-x$, $y+1/2$, $-z+1/2$; #2 x, $-y+3/2$, $z+1/2$; #3 $-x$, $-y+1$, $-z+1$)

hydroxide, or sodium hydroxide is used as a starting base. **1**–**2** are stable at room temperature and not soluble in water and common organic solvents. The elemental analysis results match well with the composition of crystal structure determination.

The results of crystallographic analysis reveal that compounds **1** and **2** crystallize in the monoclinic space group $P2(1)/c$ and feature 2D neutral layer structures, but there are some interesting differences observed. As shown in Fig. 1, the unit of **1** contains one unique Cd^{2+} ion, one fully deprotonated 3,4-tdc^{2-} anion. The Cd^{2+} ion with a distorted capped trigonal prism geometry defined by two chelating carboxylate groups (O1, O2, O3#3, and O4#3) and three carboxylate oxygen atoms (O1#1, O3#1, and O4#2) from four 3,4-tdc^{2-} anions. In **2**, the asymmetric unit consists of one unique Cd^{2+} ion, one fully deprotonated 2,3-tdc^{2-} anion, and one coordinated water molecule. Each Cd^{2+} ion also takes a distorted capped trigonal prism geometry and is bonded by one chelating carboxylate groups (O1#2 and O2#2), four carboxylate oxygen atoms (O1, O3, O3#3, and O4#1) coming from different 2,3-tdc^{2-} anions and one water molecule oxygen atom (O5). In **1** and **2**, the Cd–O bond lengths range from 2.264 (4) to 2.529(2) Å, which are expected as those observed in reported Cd^{2+} complexes [17]. The bond angles of O–Cd–O are in the range of 53.34 (12)° to 158.86(7)°. Bond lengths and angles within the coordination sphere are given in Table 2.

In **1**, all the carboxylic groups are deprotonated and adopt a μ_4-κ^2,κ^2,κ^2,κ^1 coordination mode, in which one carboxyl group is twisted to the thiophene ring plane by 22.84°(O1–C1–O2) and another is 40.60° (O3–C6–O4), respectively. Interestingly, neighboring Cd centers are linked by O1 atoms from carboxyl groups (O1–C1–O2) to give rise to a cadmium carboxylate chain along c axis. The cadmium carboxylate chains are further bridged by another carboxyl groups (O3–C6–O4) to form a 2D layer (Fig. 2a). Different from **1**, 2,3-tdc^{2-} anion assumes a μ_4-κ^1,κ^1,κ^2,κ^2 binding mode in **2**, and the thiophene ring and carboxyl groups are twisted by 27.28° (O1–C5–O2) and 58.81° (O3–C6–O4), respectively. Similar to in **1**, carboxyl groups (O1–C5–O2) of 2,3-tdc^{2-} anions connect neighboring Cd centers leading to a 1D cadmium carboxylate chain running along c axis, and which is further linked *via* another carboxyl groups (O3–C6–O4) to generate a 2D architecture (Fig. 2b). Obviously, the 2D architecture is strengthened by hydrogen bonds between the coordinated water molecule and two carboxylate oxygen atoms of two 2,3-tdc^{2-} anions.

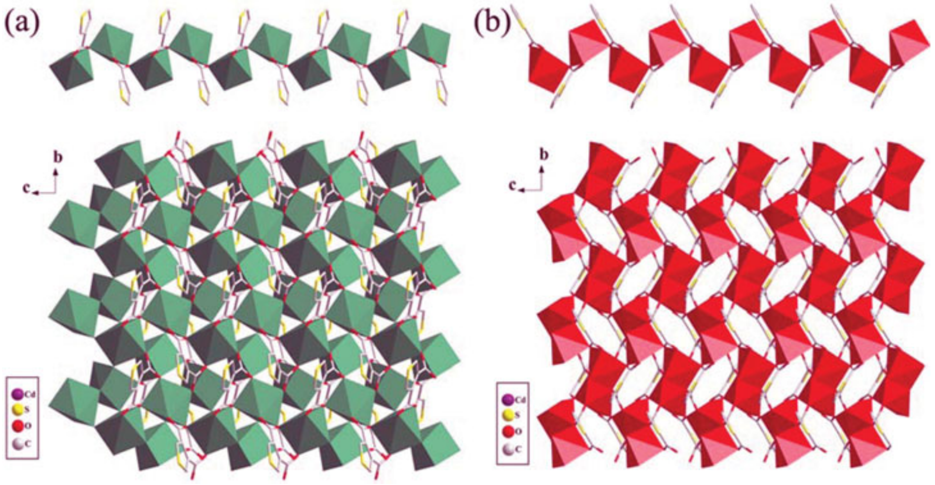

Figure 2. View of the cadmium carboxylate chain and 2D layered network. (a) Compound **1**. (b) Compound **2**.

To achieve better insight into the two compounds, 3,4-tdc^{2-} anion, operating in μ_4-coordination mode to bridge four Cd atoms, may be reduced to a 4-connected node. While, each Cd atom connects four 3,4-tdc^{2-} anions and may therefore be considered as a 4-connected node. Thus, topology analysis by the TOPOS software indicates **1** is

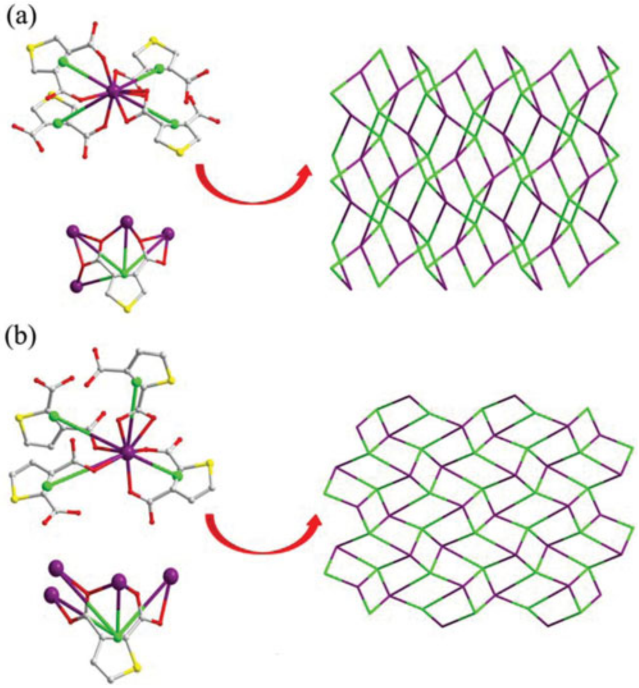

Figure 3. Ball-and-stick and schematic representations of 4-connected nodes and crossponding topology. (a) Compound **1**. (b) Compound **2**.

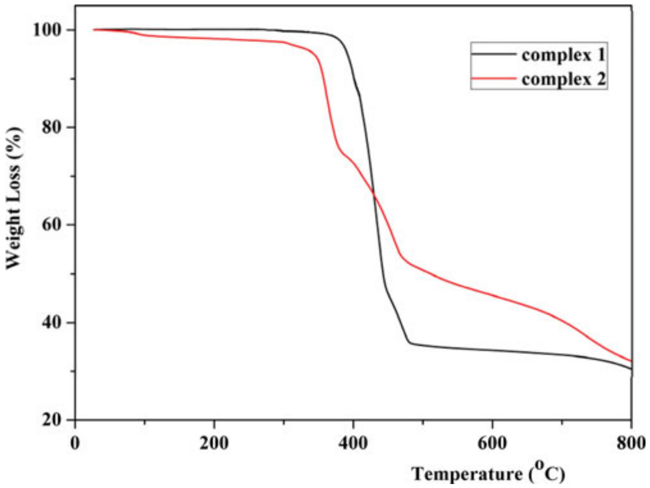

Figure 4. TGA curve for **1** and **2**.

a relatively rare 4-connected SP 2-periodic net (6,3)Id (Fig. 3(a)) with a Schläfli symbol of $4^2.6^4$. Comparatively, 2,3-tdc^{2-} anions and Cd atoms also serve as 4-connected nodes, and can be regarded as two kinds of 4-connected nodes in **2**. Thus, The resulting structure can be described as a familiar 4-connected sql/Shubnikov tetragonal plane net with a Schläfli symbol of $4^4.6^2$ (Fig. 3(b)). Notably, all 4-connecting nodes in **1** and **2** take the tetrahedral geometries and thus, result in a nonplanar feature of the two 2D layers.

It is worth emphasizing that 3,4-H_2tdc and 2,3-H_2tdc are completely deprotonated by piperazine and exhibit superior efficiency as all carboxylate groups participate in coordination of Cd^{2+} ions. Howerer, subtle different coordination modes of the tdc^{2-} anions significantly contribute to the diverse structures of **1**–**2.** This fact shows that the isomeric effect of thiophenedicarboxylates may result in the formation of CPs with different topological structures in the absence of N-donor auxiliary ligands. To examine the thermal stability of **1**–**2**, TGA experiments were performed on powder samples with a heating rate of 10°C/min. Complex **1** is stable under 380°C, and then it decomposed at higher temperatures. For **2**, the initial weight loss of 6.06% in the TGA curve from 80°C to 120°C suggests the release of coordination water molecules (calcd: 5.99%). The host framework starts to decompose beyond 340°C.

Conclusion

In summary, we have successfully synthesized two thiophenedicarboxylate CPs in the absence of N-donor auxiliary ligands. Complex **1** exhibits a 2D layered network with a uninodal 4-connected SP 2-periodic (6,3)Id topology, and complex **2** features a 2D network with a 4-connected sql topology. The structural difference of **1** and **2** may be attributed to the isomeric effect of thiophenedicarboxylates. We are presently exploring the other CPs based on the two isomeric thiophenedicarboxylates and studying the relationship between their structures and properties.

Acknowledgments

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Supplementary Materials

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center with registration number CCDC 945058 (**1**) and 945059 (**2**). Copies of this information can be obtained free of charge *via* http: //www.ccdc.cam.ac.uk/conts/ retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033.

References

[1] Ockwig, N. W., Delgado-friedrichs, O., O'Keeffe, M., & Yaghi, O. M. (2005). *Acc. Chem. Res.*, *38*, 176.
[2] Adarsh, N. N., & Dastidar, P. (2012). *Chem. Soc. Rev.*, *41*, 3039.
[3] Li, D., Wu, Y., Zhao, J., Zhang, J., & Lu, J. Y. (2014). *Coord. Chem. Rev.*, *261*, 1.
[4] Chen, B., Mok, K., Ng, S., & Drew, M. G. B. (1999). *New J. Chem.*, *23*, 877.
[5] Yang, J., Lutz, M., Grzech, A., Mulder, F. M., & Dingemans, T. J. (2014). *Cryst. Eng. Comm.*, *16*, 5121.
[6] Kettner, F., Worch, C., Moellmer, J., Gläser, R., Staudt, R., & Krautscheid, H. (2013). *Inorg. Chem.*, *52*, 8738.
[7] Zhou, L., Wang, C., Zheng, X., Tian, Z., Wen, Li., Qu, H., & Li, D. (2013). *Dalton Trans.*, *42*, 16375.
[8] Zhang, J., Chen, S., Wu, T., Feng, P., & Bu, X. (2008). *J. Am. Chem. Soc.*, *130*, 12882.
[9] Li, Z., Xue, L., Li, S., Wang, J., Zhao, B., Kan, J., & Su, W. (2013). *Cryst. Eng. Comm.*, *15*, 2745.
[10] Li, Z., Zhang, T., Xue, L., Miao, S., Zhao, B., Kan, J., & Su, W., (2013). *Cryst. Eng. Comm.*, *15*, 7423.
[11] Zhang, T., Wang, G., & Xue, L. (2014). *Cryst. Res. Technol.*, *49*, 257.
[12] Xue, L., Chang, X., Li, S., Ma, L., & Wang, L. (2014). *Dalton Trans.*, *43*, 7219.
[13] Tserng, K., & Bauer, L. (1975). *J. Org. Chem.*, *40*, 172.
[14] Chao,Y., Kuo, S., Ku, K., Chiu, I., Wu, C., Mauger, A., Wang, H., & Lee, K. (1999). *Bioorg. Med. Chem.*, *7*, 1025.
[15] Sheldrick, G. M. (1997). *SADABS*, University of Göttingen: Göttingen.
[16] Sheldrick, G. M. (1997). *SHELXTL97: Program for Refining Crystal Structure Refinement*, University of Göttingen: Göttingen.
[17] Liu, F., Hao, H., Sun, C., Lin, X., Chen, H., Huang, R., & Zheng, L. (2012). *Cryst. Growth Des.*, *12*, 2004.