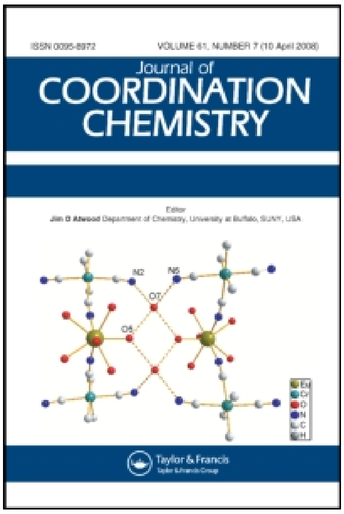

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Synthesis, characterization and crystal structures of two binary acid complexes based on L-glutamate and L-aspartate

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Two amino acid complexes, $[Cd(L\text{-glu})(H_2O)]_n \cdot nH_2O$ (**1**) and $[Co(L\text{-asp})(phen)(N_3)] \cdot 2H_2O$ (**2**) (L-glu = L-glutamate, L-asp = L-aspartate, phen = 1,10-phenanthroline), have been synthesized and characterized by elemental analyses, IR spectra and TG-DSC analysis. Single crystal X-ray structure analyses revealed that each L-glutamate acts as a pentadentate ligand binding to three octahedral Cd(II) atoms through the amino group and two carboxyl groups to form a neutral helical network. Complex **2** is a mononuclear compound in which Co(III) is octahedrally coordinated by tridentate L-aspartate, monodentate azide and chelating phen ligand. Thermal stability and fluorescence of **1** have been investigated. The complex shows strong blue fluorescence in the solid state.

Keywords: L-Glutamic acid; L-Aspartic acid; Cadmium complex; Crystal structure; Thermal stability

1. Introduction

The chemistry of metal carboxylates continues to be an active research field [1]. Numerous complexes with polycarboxylate ligands have been studied [2]. Many polycarboxylate coordination polymers have interesting structural motifs and potential applications to optical, electronic, magnetic, catalytic and porous materials [3]. However, coordination polymers constructed from chiral amino acids are rare. Amino carboxylates possess additional nitrogen donor sites which can result in the formation of metal complexes with novel network structural features. Glutamate and aspartate own two terminal carboxyl groups and an α-amino group, which can display different coordination modes to afford mono- or polynuclear complexes [4–6]. Recently we started to investigate possible coordination polymers assembled by a series of biscarboxylate ligands such as acetylenedicarboxylate and butanedicarboxylate [7, 8].

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When L-glutamate and L-aspartate were employed as biscarboxylate ligands, one interesting helical cadmium coordination polymer $[Cd(L\text{-glu})(H_2O)]_n \cdot nH_2O$ (**1**) and one L-aspartate mononuclear cobalt complex $[Co(L\text{-asp})(phen)(N_3)] \cdot 2H_2O$ (**2**) were prepared. We report here their synthesis, crystal structures, thermal stability and fluorescence property.

2. Experimental

2.1. *Materials and measurements*

All chemicals were of reagent grade and used as received without further purification. C, H and N analyses were performed on a Vario EL III elemental analyzer. Infrared spectra were recorded with a Nicolet A370 FT-IR spectrometer in KBr pellets in the 4000–400 cm^{-1} region. TG-DSC analysis was completed on a Netzsch STA 449C thermal analyzer at a heating rate of 10°C min^{-1} in air. Fluorescence spectrum was recorded on a Shimadzu RF-5301 spectrophotometer.

2.2. *Synthesis*

2.2.1. $[Cd(L\text{-glu})(H_2O)]_n \cdot nH_2O$ (1). A mixture of L-glutamic acid (2.0 mmol) and NaOH (2.0 mmol) in 10 mL water was added dropwise to a 15 mL aqueous solution of $CdCl_2 \cdot 2.5H_2O$ (1.0 mmol) and hexamethylenetetramine (1.0 mmol) with constant stirring. After stirring for 2 h, the mixture was filtered, and the filtrate was set at room temperature for two weeks. Colorless crystals of **1** were harvested with 30% yield based on Cd. Anal. Calcd for $C_5H_{11}CdNO_6$ (%): C, 20.46; H, 3.78; N, 4.77. Found: C, 20.36; H, 3.51; N, 4.24. IR (KBr, cm^{-1}): 3334 m, 2913 w, 1581 s, 1543 s, 1409 s, 1082 m, 1002 m.

2.2.2. $[Co(L\text{-asp})(phen)(N_3)] \cdot 2H_2O$ (2). Sodium azide (0.2 mmol) dissolved in 2 mL water was added to a 5 mL aqueous solution of $CoCl_2 \cdot 6H_2O$ (0.1 mmol). Then 5 mL ethanol solution of L-aspartic acid (0.1 mmol) and piperidine (0.2 mmol) was added to the solution with stirring. Finally, 1,10-phenanthroline (0.2 mmol) was added to the mixture with constant stirring for 6 h. The mixture was filtered to remove the deposit, and the clear wine-colored solution was kept at room temperature for 3 days. Dark-red crystals of **2** were harvested with 39% yield based on Co. Anal. Calcd for $C_{16}H_{17}CoN_6O_6$ (%): C, 42.87; H, 3.82; N, 18.75. Found: C, 44.06; H, 3.78; N, 19.22. IR (KBr, cm^{-1}): 3436 m, 3232 w, 3053 w, 2051 s, 1658 s, 1613 s, 1384 s, 847 m, 721 m.

2.3. *Crystal structure determination*

Single crystal X-ray diffraction measurements of **1** and **2** were carried out on a Bruker Smart Apex-II CCD diffractometer with graphite monochromatic Mo-Kα radiation ($\lambda = 0.71073$ Å) using both φ and ω-scan modes at 273(2) K. Data reductions were made with the SAINT package. Absorption corrections were performed using SADABS.

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

	1	**2**
Empirical formula	$C_5H_{11}CdNO_6$	$C_{32}H_{34}Co_2N_{12}O_{12}$
Formula weight	293.55	896.57
Crystal system	Orthorhombic	Monoclinic
Space group (Å, °)	$P2_12_12_1$	$P2_1$
a	7.2660(2)	9.0504(2)
b	10.7768(2)	18.4554(4)
c	11.5857(2)	10.8753(2)
β	90.00	100.153(1)
V (Å^3)	907.21(3)	1788.04(6)
Z	4	2
D_{Calcd} (Mg m^{-3})	2.149	1.650
Absorption coefficient (mm^{-1})	2.407	1.011
$F(000)$	576	920
Crystal size (mm^3)	$0.35 \times 0.30 \times 0.30$	$0.30 \times 0.20 \times 0.20$
Measured reflections	6845	12234
Independent reflections	1645 [R (int) = 0.0201]	5177 [R (int) = 0.0322]
Data/restraints/parameters	1645/0/135	5177/6/524
Goodness-of fit on F^2	1.070	1.021
R [$I > 2\sigma(I)$]	$R_1 = 0.0122$, $wR_2 = 0.0295$	$R_1 = 0.0470$, $wR_2 = 0.1152$
R (all data)	$R_1 = 0.0123$, $wR_2 = 0.0295$	$R_1 = 0.0559$, $wR_2 = 0.1219$
Largest diff. peak and hole (e Å^{-3})	0.168 and −0.183	0.827 and −0.327

The structures were solved by direct methods with SHELXS-97 and refined on F^2 by full-matrix least-squares with SHELXL-97 [9]. All non-hydrogen atoms were refined anisotropically, and H atoms were treated by a mixture of independent and constrained refinement. The crystal data and structure refinement results are summarized in table 1.

3. Results and discussion

3.1. *Description of crystal structures*

X-ray crystallographic analysis revealed that **1** assumes a coordination polymeric network. As shown in figure 1, the cadmium center is octahedrally coordinated by one N and five O atoms. Cd–N bond length is 2.2886(18) Å, and Cd–O(1w) is 2.248(2) Å. Four carboxyl O–Cd bond lengths are in the range of 2.2528(16)–2.4493(17) Å (table 2). Amino N and three carboxyl O atoms occupy the equatorial positions, whereas carboxyl O(1) atom and coordinated water O(1w) occupy the axial positions, forming a distorted octahedral coordination geometry. Bond angles O(1)–Cd(1)–O(1w), N(1)–Cd(1)–O(3A) and O(2B)–Cd(1)–O(4A) are 160.18(8), 167.31(7), 140.58(6)°, respectively. The α-amino N and carboxyl O(1) coordinate to Cd(II) to form a chelating five-member ring. Other bond lengths and angles are normal [10].

L-Glutamate anion acting as a pentadentate ligand links three Cd(II) centers through two carboxyl groups and an amino group to form a polymeric structure. One carboxylate binds to the central Cd(II) in a bidentate chelating mode, while the other carboxylate links two Cd(II) atoms in a typical bidentate bridging mode. Two Cd(II) atoms are bridged by two carboxyl groups to form a dimer of cadmium (see packing diagram). The structure of **1** is a complicated two-dimensional (4,4) network with nodes of Cd_2 dimer and bridges of L-glutamate anion. Derived from chiral L-glutamic acid, the

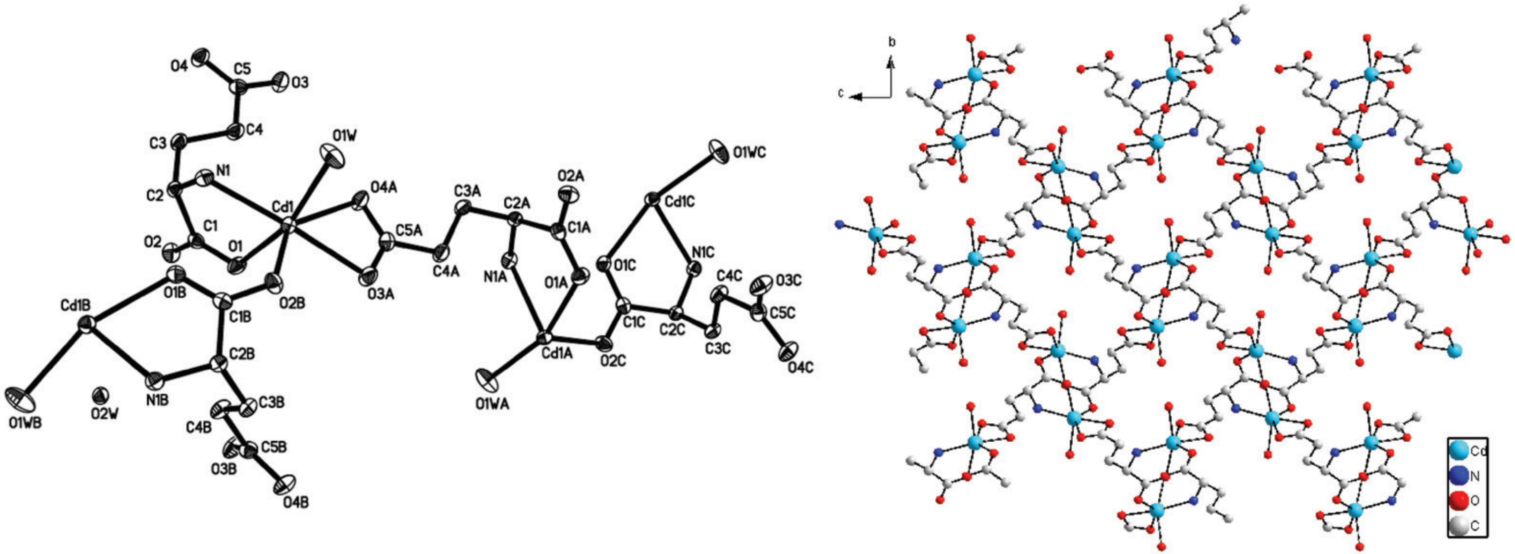

Figure 1. Views of the asymmetric structural unit and packing diagram of **1**.

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

Cd(1)–O(1)	2.2886(18)	Cd(1)–N(1)	2.2890(19)
Cd(1)–O(1w)	2.248(2)	C(1)–O(1)	1.253(3)
Cd(1)–O(2B)	2.2528(16)	C(1)–O(2)	1.252(3)
Cd(1)–O(3A)	2.3098(16)	C(5)–O(3)	1.270(3)
Cd(1)–O(4A)	2.4493(17)	C(5)–O(4)	1.250(3)
O(1w)–Cd(1)–O(2B)	93.47(7)	N(1)–Cd(1)–O(4A)	118.98(6)
O(1)–Cd(1)–N(1)	73.27(6)	N(1)–Cd(1)–O(2B)	100.23(6)
O(2B)–Cd(1)–O(3A)	87.68(6)	N(1)–Cd(1)–O(3A)	167.31(7)
O(3A)–Cd(1)–O(4A)	54.57(6)	O(1w)–Cd(1)–O(1)	160.18(8)
O(2B)–Cd(1)–O(4A)	140.58(6)		
Co(1)–N(1)	1.919(7)	C(13)–O(1)	1.30(5)
Co(1)–N(2)	1.919(6)	C(13)–O(2)	1.26(5)
Co(1)–O(1)	1.905(5)	C(16)–O(3)	1.19(5)
Co(1)–O(4)	1.916(5)	C(16)–O(4)	1.27(5)
Co(l)–N(3)	1.956(6)	N(3)–N(4)	1.20(4)
Co(l)–N(6)	1.938(6)	N(4)–N(5)	1.16(4)
N(1)–Co(1)–O(1)	173.8(13)	N(7)–Co(2)–O(5)	174.3(13)
N(2)–Co(1)–O(4)	175.7(12)	N(8)–Co(2)–O(7)	175.4(12)
N(3)–Co(1)–N(6)	173.5(14)	N(9)–Co(2)–O(12)	176.2(13)
Co(1)–N(3)–N(4)	117(2)	Co(2)–N(9)–N(10)	116(2)

crystal structure of **1** possesses $P2_12_12_1$ chiral space group, so that **1** is a neutral helical coordination polymer [11].

Different from the polymeric structure of **1**, complex **2** is an L-aspartate coordinated mononuclear cobalt compound. As shown in figure 2, the asymmetric structural unit consists of two crystallographically independent $[Co(\text{L-asp})(phen)(N_3)]$ molecules and four water molecules. Each Co(III) center is octahedrally coordinated. Two phen N atoms and two O atoms from two carboxyl groups of L-aspartate are both symmetrically coordinated to the Co(III) center to form the equatorial plane of the coordination octahedron. Bond distances Co(1)–N(1), Co(1)–N(2), Co(1)–O(1) and Co(1)–O(4) are 1.919(7), 1.919(6), 1.905(5), 1.916(5) Å, respectively. Along the axial direction, amino N atom and azide coordinate to Co(III) with bond distances of Co–N(6) 1.938(6) Å and Co–N(3) 1.956(6) Å. The azide group is a monodentate and coordinates nonlinearly to Co(III) atom with a Co(1)–N(3)–N(4) angle of 117(2)°. Other bond lengths and angles are as expected [12].

L-Aspartate as a tridentate ligand coordinates to Co atom, forming a chelating five-membered ring and a six-membered ring. Here, the chelate effect plays an important role in formation of the L-aspartate mononuclear complex. Comparatively, L-glutamate is more favorable to form a polynuclear complex [13]. In addition, there exist hydrogen bond network amongst amino group, carboxylate, azide and lattice water in **2**, which help to consolidate the crystal packing. The distance between adjacent phen aromatic rings is 3.528(18) Å indicating some π–π stacking interactions that lead to a supermolecular architecture.

3.2. *Spectroscopic, thermal and fluorescent properties*

The IR spectra of **1** and **2** display the characteristic vibration bands of glutamate and aspartate. In **1**, the strong absorption bands near 1581 and 1543 cm^{-1} are attributed to the asymmetric stretching vibrations $\nu_{as}(COO^-)$ of two carboxyl groups of glutamate.

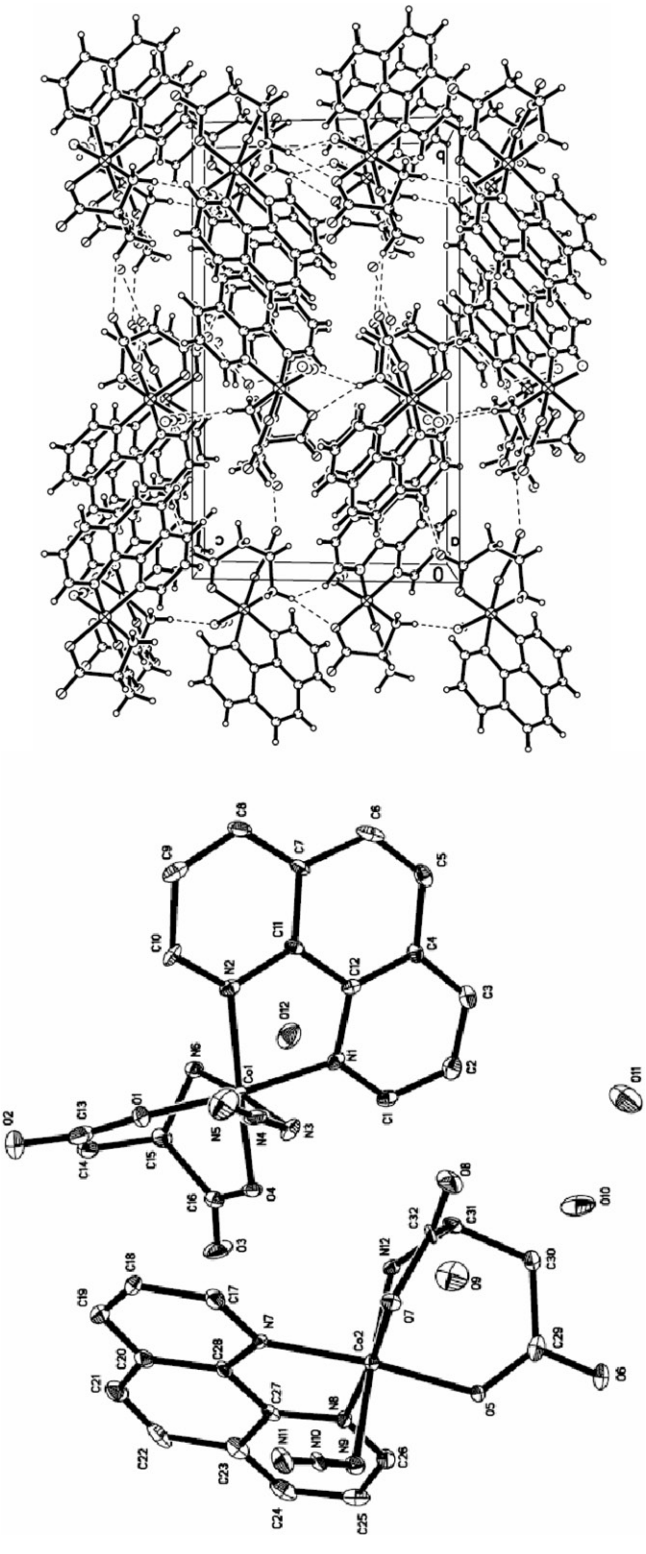

Figure 2. Views of the asymmetric structural unit and packing diagram of **2**.

Both carboxyl groups have similar symmetric stretching vibrations $\nu_s(COO^-)$ near 1409 cm^{-1}. The frequency differences between $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ are 172, 134 cm^{-1} respectively. The former indicates one carboxyl group coordinates to Cd(II) in a bidentate bridging mode, while the latter indicates another carboxyl group coordinates in a bidentate chelating mode [14]. In **2**, the asymmetric stretching vibrations $\nu_{as}(COO^-)$ of two L-aspartate carboxyl groups appear at 1658 and 1613 cm^{-1}, and both symmetric stretching vibrations appear at 1384 cm^{-1}. The frequency differences are 274, 229 cm^{-1} respectively, which are larger and indicate

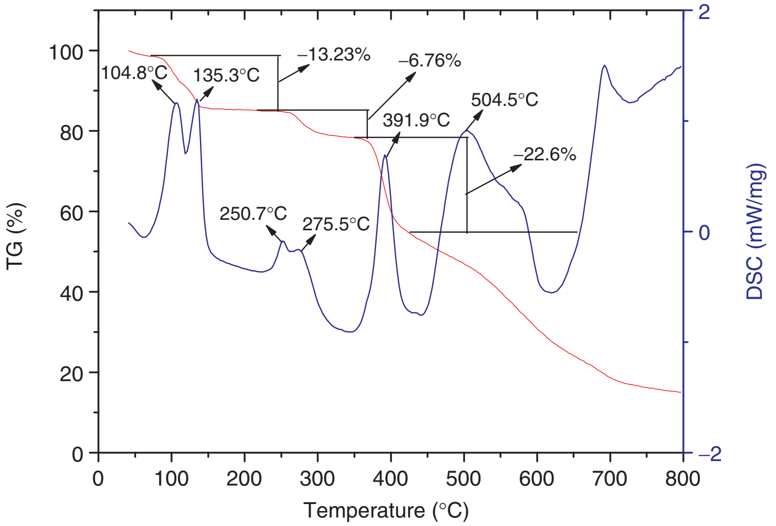

Figure 3. TG-DSC thermal analysis curves of **1**.

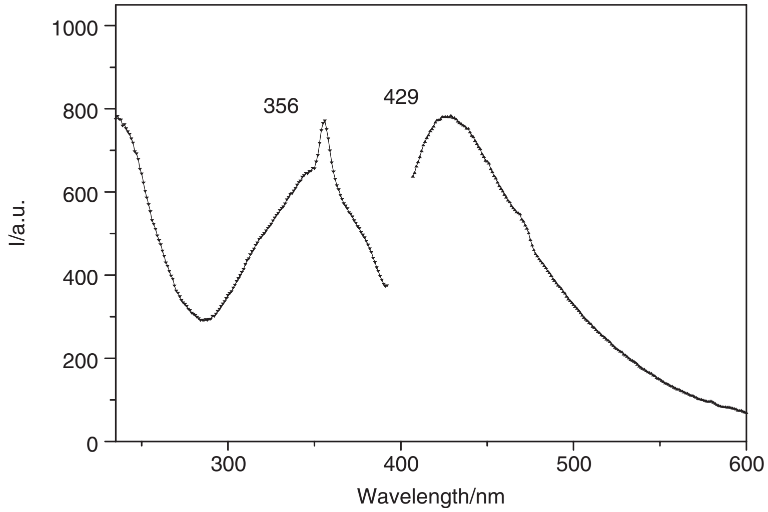

Figure 4. Fluorescence spectrum of **1**, left half is excitation spectrum and right half is emission spectrum.

that both carboxyl groups coordinate to Co(III) in a monodentate mode [14]. The characteristic strong absorption of azide appears at 2051 cm^{-1}.

TG-DSC analysis from 30 to 800°C was performed for **1**. As shown in figure 3, the first weight-loss occurred in the temperature range of 80–140°C with two exothermic peaks at 104.8 and 135.3°C corresponding to the release of lattice and coordinated water molecules (found 13.23%, Calcd 12.27%). The second weight-loss step in the range of 240–300°C may be due to the release of amino group (found 6.76%, Calcd 5.46%). The subsequent weight loss at 380–420°C was a result of decomposition of L-glutamate, which led to residual product $CdCO_3$ (found 57.41%, Calcd 58.74%) [8, 15]. $CdCO_3$ decomposed further to form CdO residue which sublimed at high temperature [16].

The fluorescent spectrum of **1** in the solid state is shown in figure 4. Photoexcitation of **1** with 356 nm light gives a strong emission peak with maximum at 429 nm. This emission band might be attributed to ligand-to-metal charge transfer (LMCT), which has been observed in other polynuclear Cd(II) complexes [17], suggesting that complex **1** may be a good candidate as a blue-light emitter.

Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC-629929 for complex **1** and CCDC-629590 for complex **2**. Copies of the data can be obtained free of charge from CCDC, 12 Union Road, Cambridge, CB2IEZ, UK. Email: deposit@ccdc.cam.ac.uk.

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References

[1] C.N.R. Rao, S. Natarajan, R. Vaidhyanathan. *Angew. Chem. Int. Ed.*, **43**, 1466 (2004).
[2] B.H. Ye, M.L. Tong, X.M. Chen. *Coord. Chem. Rev.*, **249**, 545 (2005).
[3] O.M. Yaghi, M. O'Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi, J. Kim. *Nature*, **423**, 705 (2003).
[4] R.S. Dickins, A.S. Batsanov, J.A.K. Howard, D. Parker, H. Puschmann, S. Salamano. *J. Chem. Soc., Dalton Trans.*, 70 (2004).
[5] L. Gasque, S. Bernes, R. Ferrari, G. Mendoza-Diaz. *Polyhedron*, **21**, 935 (2002).
[6] C.D. Brondino, R. Calvo, A.M. Atria, E. Spodine, O. Pena. *Inorg. Chim. Acta*, **228**, 261 (1995).
[7] M. Shao, M.X. Li, H. Dai, W.C. Lu, B.L. An. *J. Mol. Struct.*, **829**, 155.
[8] M.X. Li, H. Dai, M. Shao, L. Shi, K.H. Lin, Z.X. Cheng, L.H. Weng. *Chin. J. Chem.*, **24**, 487 (2006).
[9] G.M. Sheldrick. *SHELX-97 Program for Crystal Structure Solution and Refinement*, University of Göttingen, Germany (1997).
[10] L.F. Ma, L.Y. Wang, J.G. Wang, Y.F. Wang, X. Feng. *Inorg. Chim. Acta*, **359**, 2241 (2006).

[11] M. Mizutani, N. Maejima, K. Jitsukawa, H. Masuda, H. Einaga. *Inorg. Chim. Acta*, **283**, 105 (1998).
[12] H.J. Zhao, M.X. Li, M. Shao, H.J. Liu. *Acta Cryst.*, **E62**, m965 (2006).
[13] Y.G. Zhang, M.K. Saha, I. Bernal. *Cryst. Eng. Comm.*, 34 (2003).
[14] G.B. Deacon, R.J. Phillips. *Coord. Chem. Rev.*, **33**, 227 (1980).
[15] H.L. Saha, S. Mitra. *Thermochim. Acta*, **116**, 53 (1987).
[16] F.A. Cotton, G. Wilkinson. *Advanced Inorganic Chemistry*, 3rd edn, p. 510, John Wiley & Sons, New York (1972).
[17] E.N. Nfor, W. Liu, J.L. Zuo, X.Z. You. *Transit. Metal Chem.*, **31**, 837 (2006).