Polyhedron 42 (2012) 216-226

Contents lists available at SciVerse ScienceDirect

Polyhedron



journal homepage: www.elsevier.com/locate/poly

Metal–organic coordination architectures of condensed heterocyclic based 1,2,4-triazole: Syntheses, structures and emission properties

Duo-Zhi Wang^{a,*}, Qin Zhang^a, Jian-Bin Zhang^b, Yuan-Gao Wu^a, Ling-Hua Cao^a, Peng-Yuan Ma^a

^a Xinjiang Laboratory of Advanced Functional Materials, Chemistry and Chemical Engineering School of Xinjiang University, Urumqi 830046, PR China ^b Physics and Chemistry Test Center of Xinjiang University, Urumqi 830046, PR China

ARTICLE INFO

Article history: Received 12 April 2012 Accepted 17 May 2012 Available online 9 June 2012

Keywords: Triazole ligands Metal complexes Crystal structure Emission properties

ABSTRACT

In efforts to explore the effects of metal ions, ligand structures, counteranions on the structures and properties of metal-organic complexes, seven d¹⁰ metals (Zn and Cd) and transition metals (Cu and Co) coordination compounds with condensed heterocyclic based 1,2,4-triazole 4,7-diphenyl-1,2,4-triazolo[3,4-b]-1,3,4-thiadiazole (L¹), 4-phenyl-7-(pyridine-3-yl)-1,2,4-triazolo[3,4-b]-1,3,4-thiadiazole (L²), 4-phenyl-7-(pyridine-4-yl)-1,2,4-triazolo[3,4-b]-1,3,4-thiadiazole (L³), and 4-(pyridine-3-yl)-7-(pyridine-4-yl)-1,2,4-triazolo[3,4-b]-1,3,4-thiadiazole (L^4), $Zn(L^1)_2Cl_2$ (1), $Co(L^1)_2Cl_2$ (2), {[$Cd(L^2)_2(H_2O)_2$]. $(ClO_4)_2\}_{\infty} (\textbf{3}), Cd(\textbf{L}^2)_2(NO_3)_2(H_2O)_2 (\textbf{4}), \{[Cu(\textbf{L}^3)_2(NO_3)_2] \cdot (CH_2Cl_2)\}_{\infty} (\textbf{5}), \{[Cu(\textbf{L}^3)_2(OH)(MeOH)] \cdot (MeOH)_2 \cdot (Me$ BF_4 _{[∞} (**6**) and $[Cd(L^4)_2(NO_3)_2]_{\infty}$ (**7**) were synthesized and structurally characterized by elemental analyses, IR spectroscopy and single-crystal X-ray diffraction. Complexes 1, 2 and 4 have a mononuclear structure, **1** and **2** have similar structure, **3** and **6** have a neutral rhombohedral grid with a(4, 4) topology, the coordination network of **3** further assembled into a three-dimensional framework by O-H···O hydrogenbonding interactions, 5 reveals a coordination chain structures consisting of a neutral chain $\{[Cu(L^3)_2(NO_3)_2]\cdot (CH_2Cl_2)\}_{\infty}$ with the Cu^{II} centers, and **7** has a coordination chain. Obviously, the structural differences among them are attributable to the difference of metal ions, counter-anions, the locality and amount of coordination atoms in ligands framework. All the complexes are air stable at room temperature. Furthermore, the fluorescent properties of complexes 1, 3, 4, 7 and corresponding ligands have been investigated and discussed.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Metal-organic frameworks (MOFs) have received much interest due to their various potential applications such as optical nonlinearity, luminescence, magnetism, conductivity, catalytic activity, selective adsorption/separation, and their topological features [1]. In recent years, polydentate aromatic nitrogen heterocyclic ligands with five-membered rings (azoles) have been well used in the construction of supramolecular structures [2]. Among polyazoles, imidazoles and triazoles ligands have been extensively used to construct various coordination networks with diverse topologies and interesting properties [3]. The structure and properties of metal complexes depend on the metal ion and the donor atoms. as well as the structure of the ligand and the metal-ligand interactions [4]. However, the construction of the coordination polymers with desired topologies and specific properties still remains a far-reaching challenge since there are so many factors influencing the formation and structure of the complexes such as the geometric requirements of metal ions, the character of the ligands,

counter-ions, the reaction solvent and temperature, pH value etc. A careful choice or design of organic ligands coupled with suitable metal ions may lead to new complexes with specific structures and properties [5–9].

Great efforts have been focused on ligands based on azole heterocycles, which have both good coordination ability and diverse coordination modes [10]. As the simple small molecular ligands, 1,2,4-triazole and its derivatives are very interesting not only because they can be used as spin crossover materials which has the potential application in information storage but also they can form a variety of novel structural motifs [11]. Until now, 1,2,4-triazole, especially its derivatives, gains more interest as ligands to bridge different metal ions to form functional coordination polymers because of their potential bridging fashions [3c,12]. For example, some complexes containing 1,4-bis(triazol-1-ylmethyl)benzene with the third order NLO (nonlinear optics) properties and the fluorescence properties have been documented [13]. Previously, we reported a series of bis-triazole ligands, 9,10-bis(triazol-1ylmethyl)anthracene with d¹⁰ metal coordination polymers with better luminescence properties [14]; and some transition metalorganic coordination complexes with 1,4-bis(1,2,4-triazol-1ylmethyl)naphthalene/4,4'-bis(1,2,4-triazol-1-ylmethyl)biphenyl



^{0277-5387/\$ -} see front matter © 2012 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.poly.2012.05.028

have been investigated [8b]. However, there are still only rare reports of ligands based on condensed heterocyclic based 1,2,4-triazole as building blocks for the construction of coordination complexes.

In this work, four ligands of condensed heterocyclic based 1,2,4triazole: 4,7-diphenyl-1,2,4-triazolo[3,4-b]-1,3,4-thiadiazole (L¹), 4-phenyl-7-(pyridine-3-yl)-1,2,4-triazolo[3,4-b]-1,3,4-thiadiazole (L²), 4-phenyl-7-(pyridine-4-yl)-1,2,4-triazolo[3,4-b]-1,3,4-thiadiazole (L³), and 4-(pyridine-3-yl)-7-(pyridine-4-yl)-1,2,4-triazolo[3,4-b]-1,3,4-thiadiazole (L⁴), (Chart 1), have been designed and synthesized. The reactions of these ligands with the corresponding metal salts lead to the formation of seven new metal-organic complexes with 0-D, 1-D and 2-D network structures. Herein, we report the syntheses, crystal structures and emission properties of these complexes. The influences of the locality and amount of coordination atoms in the same ligands' framework and counteranions on the resultant structures of their metal complexes are briefly discussed. In addition, the emission properties of part of these complexes have also been investigated in the solid state at room temperature.

2. Experimental

2.1. Materials and general methods

All the other reagents used for the syntheses were commercially available and employed without further purification. The intermediate of 3-phenyl-4-amino-5-sulfhydryl-1,2,4-triazole (**a**) was prepared according to reported procedures [15]. IR spectra were measured on a Brucker Equinox 55 FT-IR spectrometer with KBr Pellets in the range of 4000–400 cm⁻¹. Elemental analyses of C, H and N were performed on a Thermo Flash EA 1112-NCHS-O analyzer. ¹H NMR data were collected using an INOVA-400 NMR spectrometer. Chemical shifts are reported in relative to TMS. Solid-state emission and excitation spectra of compounds were measured using a Cary Eclips fluorescence spectrophotometer.

2.2. Synthesis of L^1-L^4

2.2.1. 4,7-diphenyl-1,2,4-triazolo[3,4-b]-1,3,4-thiadiazole (L¹)

The route of synthesis is shown in Chart 2, the intermediate of 3-phenyl-4-amino-5-sulfhydryl-1,2,4-triazole (**a**) (5 mmol) and benzoic acid (5 mmol) was added to freshly distilled POCl₃ (20 mL). After heating in an oil bath at 120° for 8 h, then removing excess POCl₃ under depress pressure. Poured reactor into cold water, neutralized with NaOH to give ligand **L**¹, recrystallized from absolute ethanol to give ligand **L**¹ as white crystals. Yield: ~65%. m.p. 209–211 °C. ¹H NMR (CDCl₃): δ : 7.50–8.44(m, 10H, phenyl); *Anal.* Calc. for C₁₅H₁₀N₄S: C, 64.73; H, 3.62; N, 20.13; Found: C, 64.92; H, 3.54; N, 20.24%. IR (cm⁻¹, KBr pellets): 3061w, 3028w, 2895w, 1971w, 1903w, 1809w, 1774w, 1685w, 1655w, 1595w, 1578w, 1512m, 1469s, 1436m, 1380m, 1358m, 1311m, 1289m, 1268m, 1238m, 1175w, 1155w, 1108w, 1075m, 1022w, 1000m, 975s, 954m, 919m, 798w, 772s, 765s, 714w, 683s, 651m, 617m, 606m.



2.2.2. 4-phenyl-7-(pyridine-3-yl)-1,2,4-triazolo[3,4-b]-1,3,4-thiadiazole(**L**²)

Ligand L² were obtained by the similar method described for L¹. Yield: ~60%. m.p. 239–240 °C. ¹H NMR (CDCl₃): δ : 9.21(d, 1H, *J* = 2 Hz, pyridine-2), 8.86(dd, 1H, *J* = 1.6, 5.2 Hz, phenyl-4), 8.39–8.42(m, 2H, pyridine-4,6), 8.25–8.28(m, 1H, pyridine-5), 7.52–7.605(m, 4H, phenyl-2, 3, 5, 6); *Anal.* Calc. for C₁₄H₉N₅S: C, 60.2; H, 3.25; N, 25.07; Found: C, 60.63; H, 3.22; N, 24.95%. IR (cm⁻¹, KBr pellets): 3325w, 3049w, 2998w, 1992w, 1916w, 1887w, 1809w, 1765w, 1732w, 1693w, 1651w, 1586m, 1571m, 1533w, 1514w, 1480s, 1460s, 1420s, 1380m, 1357m, 1335m, 1308w, 1290m, 1270m, 1244m, 1192m, 1172m, 1123m, 1096w, 1074w, 1049w, 1026m, 998w, 975s, 955s, 922m, 812s, 770s, 721w, 701s, 684s, 672s, 621m, 600m.

2.2.3. 4-phenyl-7-(pyridine-4-yl)-1,2,4-triazolo[3,4-b]-1,3,4-thiadiazole(**L**³)

Ligand L³ were obtained by the similar method described for L¹. Yield: ~55%. m.p. 234–236 °C. ¹H NMR (CDCl₃): δ : 8.90(d, 2H, J = 4.4 Hz, pyridine-2,6), 7.86(d, 2H, J = 4.4 Hz, pyridine-3,5), 8.40(dd, 2H, J = 1.6, 6.8 Hz phenyl-2, 6), 7.55–7.61(m, 3H, phenyl-3, 4, 5); *Anal.* Calc. for C₁₄H₉N₅S: C, 60.2; H, 3.25; N, 25.07; Found: C, 60.63; H, 3.22; N, 24.95%. IR (cm⁻¹, KBr pellets): 3429m, 3074w, 3038w, 2897w, 2552w, 2447w, 1974w, 1944w, 1825w, 1779w, 1708w, 1677w, 1625w, 1597s, 1560w, 1513w, 1491w, 1467s, 1438s, 1415s, 1380m, 1359m, 1330m, 1311m, 1292m, 1268m, 1245m, 1217m, 1184m, 975s, 959s, 856w, 820s, 774s, 699s, 685s,651m, 610s, 597s.

2.2.4. 4-(pyridine-3-yl)-7-(pyridine-4-yl)-1,2,4-triazolo[3,4-b]-1,3,4-thiadiazole(**L**⁴)

Ligand L⁴ were obtained by the similar method described for L¹. Yield: ~45%. m.p. 231–232 °C. ¹H NMR (CDCl₃): δ : 7.26–9.67(m, 8H, pyridine); *Anal.* Calc. for C₁₃H₈N₆S: C, 55.70; H, 2.88; N, 29.98; Found: C, 55.64; H, 2.93; N, 28.95%. IR (cm⁻¹, KBr pellets): 3030m, 2894w, 2433w, 1942w, 1698w, 1629w, 1595s, 1571s, 1523s, 1510s, 1486s, 1470s, 1455s, 1409s, 1379s, 1332m, 1310m, 1278s, 1248s, 1220m, 1191s, 1119m, 1095m, 1066m, 1028m, 979s, 962s, 825s, 807s, 723m, 703s, 692s, 653s, 614s, 600s, 497m, 408m.



Table 1

Crystal data and structure refinement summary for complexes 1-7.

	1	2	3	4
Formula	$C_{30}H_{20}Cl_2N_8S_2Zn$	$C_{30}H_{20}Cl_2N_8S_2Co$	$C_{28}H_{22}Cl_2N_{10}O_{10}S_2Cd$	C ₂₈ H ₂₄ N ₁₂ O ₈ S ₂ Cd
Formula weight	692.93	686.49	905.98	833.13
Crystal system	triclinic	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	ΡĪ	P21/c	ΡĪ
T/K	293(2)	293(2)	293(2)	293(2)
a (Å)	8.9844(18)	9.0111(18)	9.2872(19)	7.7599(16)
b (Å)	11.136(2)	11.096(2)	11.644(2)	9.5188(19)
<i>c</i> (Å)	16.275(3)	16.269(3)	16.208(3)	12.220(2)
α (°)	92.85(3)	92.58(3)	90.00	71.06(3)
β(°)	99.72(3) deg	99.92(3)	101.70(3)	86.03(3)
γ (°)	112.03(3)	112.12(3)	90.00	68.84(3)
V (A ³)	1476.5(5)	1473.6(5)	1716.4(7)	795.0(3)
Z	2	2	2	1
$D (g \text{ cm}^{-3})$	1.559	1.547	1.629	1.736
μ (mm ⁻¹)	1.191	0.942	0.970	0.890
F(000)	704	698	844	418
Measured reflections	14612	14562	12592	6133
Observed reflections	6697	6697	3927	2804
R ^a /wR ^b	0.0330/0.1284	0.0370/0.1581	0.0539/0.1782	0.0354/0.1124
	5		6	7
Formula	$C_{29}H_{20}Cl_2N_{12}O_6S_2Cu$		$C_{31}H_{32}BF_4N_{10}O_4S_2Cu$	C ₂₆ H ₁₆ N ₁₄ O ₆ S ₂ Cd
Formula weight	831.12		823.03	797.06
Crystal system	triclinic		monoclinic	triclinic
Space group	P1		P2(1)/c	ΡĪ
T (K)	293(2)		293(2)	293(2)
a (Å)	7.3047(15)		12.724(3)	7.5156(15)
b (Å)	10.152(2)		14.129(3)	8.6668(17)
<i>c</i> (Å)	11.641(2)		20.078(4)	13.067(3)
α (°)	91.98(3)		90	104.01(3)
β(°)	105.00(3)		100.01(3)	101.00(3)
γ (°)	105.94(3)		90	102.68(3)
$V(A^3)$	796.6(3)		3554.5(12)	778.4(3)
Z	1		4	1
$D (g \text{ cm}^{-3})$	1.730		1.514	1.700
μ (mm ⁻¹)	1.051		0.805	0.902
F(000)	420		1636	398
Measured reflections	7876		27885	7671
Observed reflections	5943		6575	3536
K"/WK"	0.0431/0.1211		0.0773/0.2729	0.0358/0.1028

^a $R = \sum (||F_0| - |F_C||) / \sum |F_0|.$

^b $wR = [\sum w(|F_0|^2 - |F_c|^2)^2 / \sum w(F_0^2)]^{1/2}.$

2.3. Synthesis of complexes 1-7

2.3.1. $Zn(L^1)_2Cl_2(1)$

Complex **1** was prepared by dissolving ZnCl_2 ·4H₂O (0.3 mmol) and **L**¹ (0.3 mmol) in ethanol solution (15 mL). Colorless plateshaped crystals were formed after several days with the evaporation of the solvent (ca. 40% yield based on **L**¹). Anal. Calc. for $C_{30}H_{20}\text{ZnCl}_2N_8S_2$: C, 52.00; H, 2.91; N, 16.17. Found: C, 51.89; H, 2.79; N, 16.26%. IR (cm⁻¹, KBr pellets): 3433w, 3049w, 2576w, 1965w, 1892w, 1809w, 1761w, 1685w, 1594w, 1533w, 1516w, 1473s, 1440s, 1370m, 1336m, 1314m, 1290m, 1270s, 1236m, 1187m, 1158m, 1126m, 1098m, 1072m, 1044m, 1012m, 961m, 922m, 850w, 811w, 764s, 687s, 651m, 604s, 501m, 470m, 412m.

2.3.2. Co(L¹)₂Cl₂ (2)

Blue crystals of **2** suitable for X-ray analysis were obtained by the similar method described for **1**, except for using $CoCl_2 \cdot 6H_2O$ instead of $ZnCl_2 \cdot 4H_2O$ (ca. 30% yield based on L^1). Anal. Calc. for $C_{30}H_{20}CoCl_2N_8S_2$: C, 52.49; H, 2.94; N, 16.32. Found: C, 52.37; H, 2.87; N, 16.29%. IR (cm⁻¹, KBr pellets): 3422w, 3049w, 1964w, 1892w, 1809w, 1762w, 1686w, 1594w, 1532w, 1516m, 1491m, 1473s, 1440s, 1370m, 1346m, 1335m, 1315m, 1292m, 1270s, 1239m, 1214m, 1188m, 1159m, 1126m, 1099m, 1073m, 1041m, 1024m, 1014s, 962s, 924m, 850w, 813m, 764s, 713m, 688s, 673m, 653m, 606s, 504m, 472m, 418m.

2.3.3. { $[Cd(\mathbf{L}^2)_2(H_2O)_2] \cdot (ClO_4)_2$ }_{∞} (**3**)

Complex **3** was obtained by a procedure similar to that for **1** except for using Cd(ClO₄)₂·6H₂O instead of ZnCl₂·4H₂O and **L**² instead of **L**¹ (ca. 25% yield based on **L**²). Anal. Calc. for C₂₈H₂₂CdCl₂N₁₀O₁₀S₂: C, 37.12; H, 2.45; N, 15.46. Found: C, 37.36; H, 2.49; N, 15.41%. IR (cm⁻¹, KBr pellets): 3386s, 3083m, 2495w, 2165w, 1973w, 1907w, 1826w, 1777w, 1629m, 1603m, 1576m, 1527m, 1472s, 1422s, 1380m, 1342m, 1317m, 1296m, 1279m, 1254m, 1199m, 1182m, 1092s, 1029s, 994s, 958s, 925m, 818m, 772m, 720m, 691s, 624s, 502m, 414m.

2.3.4. $Cd(\mathbf{L}^2)_2(NO_3)_2(H_2O)_2(\mathbf{4})$

Colorless crystals of **4** suitable for X-ray analysis were obtained by the similar method described for **3**, except for using Cd(NO₃)₂·6H₂O instead of Cd(ClO₄)₂·6H₂O (ca. 35% yield based on **L**²). Anal. Calc. for C₂₈H₂₂CdN₁₂O₈S₂: C, 40.46; H, 2.67; N, 20.22. Found: C, 40.22; H, 2.69; N, 20.17%. IR (cm⁻¹, KBr pellets): 3181m, 3067m, 2449w, 2337w, 1893w, 1811w, 1748w, 1653m, 1597m, 1535w, 1514w, 1465s, 1422s, 1350m, 1301s, 1199m, 1133m, 1036m, 982m, 961m, 813m, 765m, 690s, 638m, 609m, 500m, 411m.

2.3.5. { $[Cu(L^3)_2(NO_3)_2] \cdot (CH_2Cl_2)$ }_{∞} (**5**)

A solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.10 mmol) in methanol solution (8 mL) was layered onto a solution of L^3 (0.10 mmol) in CH_2Cl_2 (8 mL). Blue plate-shaped crystals of complex **5** were formed after

several days with the evaporation of the solvent (ca. 30% yield based on L^3). Anal. Calc. for $C_{29}H_{20}Cl_2N_{12}O_6S_2Cu$: C, 41.91; H, 2.42; N, 20.22. Found: C, 41.79; H, 2.69; N, 20.12%. IR (cm⁻¹, KBr pellets): 3499m, 3069w, 2926w, 2426w, 1764w, 1614m, 1599w, 1535w, 521m, 1502s, 1476s, 1445s, 1420s, 1384s, 1284s, 1221w, 1183w, 1131w, 1062w, 1025m, 977m, 921w, 866w, 835m, 816m, 769m, 716m, 691s, 667w, 610m.

2.3.6. { $[Cu(L^3)_2(OH)(MeOH)] \cdot (MeOH)_2 \cdot BF_4\}_{\infty}$ (6)

Blue crystals of 6 suitable for X-ray analysis were obtained by the similar method described for **5**, except for using $Cu(BF_4)_2 \cdot H_2O$ instead of $Cu(NO_3)_2 \cdot 3H_2O$ (ca. 30% yield based on L^3). Anal. Calc. for $C_{31}H_{32}BF_4N_{10}O_4S_2Cu$: C, 45.23; H, 3.92; N, 17.02. Found: C, 45.29; H, 3.87; N, 17.14%. IR (cm⁻¹, KBr pellets): 3589m, 3337m, 3108m, 1654w, 1615m, 1531w, 1499m, 1474s, 1422s, 1378w, 1332m, 1293m, 1272m, 1221w, 1055s, 1012s, 973s, 877w, 837m, 823m, 767s, 691s, 674m, 608s.

2.3.7. $[Cd(L^4)_2(NO_3)_2]_{\infty}$ (7)

Complex **7** was obtained by a procedure similar to that for **1** except for using Cd(NO₃)₂·6H₂O instead of ZnCl₂·4H₂O and **L**⁴ instead of **L**¹ (ca. 35% yield based on **L**⁴). *Anal.* Calc. for C₂₆H₁₆CdN₁₄O₆S₂: C, 39.18; H, 2.02; N, 24.60. Found: 38.98; H, 2.03; N, 24.63%. IR (cm⁻¹, KBr pellets): 3664w, 3445w, 3102w, 3071m, 3032w, 2833w, 2456w, 2322w, 1955w, 1738w, 1600s, 1586m, 1534w, 1518m, 1477s, 1427s, 1302s, 1251s, 1217m, 1194m, 1121m, 1099m, 1050m, 1032s, 1004s, 970s, 947m, 862m, 818s, 732m, 704s, 655m, 635s, 608s, 527w, 501w, 473w, 427m, 406m.

Caution! Perchlorate complexes of metal ions in the presence of organic ligands are potentially explosive. Only a small amount of material should be used and handled with care.

2.4. X-Ray crystallography

Single-crystal X-ray diffraction measurements for complexes 1-7 were carried out on a R-AXIS SPIDER diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection at 293(2) K. The determinations of unit cell parameters and data collections were performed with MoKa radiation (k = 0.71073) and unit cell dimensions were obtained with least-squares refinements. The program SAINT [16] was used for integration of the diffraction profiles. All the structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL [17]. Semi-empirical absorption corrections were carried out using sadabs program [18]. Metal atoms in the complexes were located from the E-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^2 . The hydrogen atoms of the ligand were generated geometrically; and the hydrogen atoms of the water molecules were located from difference maps and refined with isotropic temperature factors. Crystal data and structure refinement parameters details for complexes 1-7 are given in Table 1.

3. Results and discussion

3.1. Synthesis and general characterization

 L^1-L^4 was prepared in higher yield as white crystalline solid by the reaction of 3-phenyl-4-amino-5-sulfhydryl-1,2,4-triazole (**a**) with different aromatic carboxylic acid. The structures of L^1-L^4 were determined by ¹H NMR, IR, elemental analysis. All the complexes **1–7** are air stable at room temperature.

Table 2

Selected bond distances (Å) and Angles (°) for complexes 1-7.

Complex 1			
Zn(1)-N(5)	2.020(2)	Zn(1)-N(1)	2.033(3)
Zn(1)-Cl(2)	2.220(1)	Zn(1)-Cl(1)	2.228(1)
N(5) - Zn(1) - N(1)	115 6(1)	N(5) - Zn(1) - Cl(2)	101 1(9)
$N(1) T_{p}(1) C(2)$	1102(0)	N(5) Zn(1) Cl(1)	100 6(9)
N(1) = ZII(1) = CI(2)	110.3(9)	N(3) = ZII(1) = CI(1)	109.0(8)
N(1) - 2n(1) - CI(1)	101.2(9)	CI(2) - Zn(1) - CI(1)	119.8(5)
Complex 2			
$C_0(1) = N(5)$	2,006(3)	$C_0(1) = N(1)$	2009(2)
$C_{0}(1) = C_{0}(1)$	2.000(3)	$C_{0}(1) = C_{1}(2)$	2.005(2)
CO(1) - CI(1)	2.220(1)	CO(1) = CI(2)	2.255(1)
N(5) - Co(1) - N(1)	117.4(1)	N(5) - Co(1) - CI(1)	110.8(9)
N(1)-Co(1)-Cl(1)	100.5(9)	N(5)-Co(1)-Cl(2)	100.6(9)
N(1)-Co(1)-Cl(2)	109.5(8)	Cl(1)-Co(1)-Cl(2)	119.1(5)
Complex 2			
Complex 3			
Cd(1) - O(1W)	2.289(4)	Cd(1) - N(1)	2.330(4)
$Cd(1)-N(5)^{#2}$	2.353(4)		
$N(1)^{\#1}-Cd(1)-N(5)^{\#2}$	86.4(2)	$O(1W)^{\#1}-Cd(1)-N(1)$	92.3(2)
O(1W) - Cd(1) - N(1)	87.7(2)	$N(1)-Cd(1)-N(5)^{#2}$	93.6(2)
$O(1W)^{\#1} - Cd(1) - N(5)^{\#2}$	869(2)	$O(1W) - Cd(1) - N(5)^{\#2}$	93 1(2)
O(100) = Cd(1) = N(3)	80.5(2)	O(100) - CO(1) - IO(3)	55.1(2)
Complex 4			
Cd(1) - O(1W)	2.289(3)	Cd(1) - O(2)	2.323(3)
Cd(1) = N(1)	2 337(3)		
O(2) Cd(1) N(1)	2.557(5)	$O(1W)$ $Cd(1)$ $O(2)^{\#1}$	01 1(1)
O(2) = Cu(1) = N(1)	89.7(T)	O(1 v v) - C d(1) - O(2)	01.1(1)
$O(1W)^{m} - Cd(1) - O(2)^{m}$	98.9(1)	$O(2) - Cd(1) - N(1)^{m}$	90.3(1)
$O(1W)^{\#1}-Cd(1)-N(1)$	90.7(1)	O(1W) - Cd(1) - N(1)	89.29(1)
Complex 5			
$C_{\rm rel}(1)$ N(8)	1 059(4)	$C_{\rm rel}(1)$ N(1)	1.070(4)
Cu(1) = N(8)	1.958(4)	Cu(1) = N(1)	1.976(4)
$Cu(1) - N(12)^{m}$	2.029(3)	Cu(1) - O(6)	2.167(3)
Cu(1)–O(3)	2.184(4)		
$N(8)-Cu(1)-N(12)^{\#1}$	97.71(1)	$N(1)-Cu(1)-N(12)^{\#1}$	89.5(1)
N(8) - Cu(1) - O(6)	89.4(1)	N(1)-Cu(1)-O(6)	88.9(1)
$N(12)^{\#1}$ -Cu(1)-O(6)	129 7(1)	N(8) = Cu(1) = O(3)	86 2(1)
$N(1) C_{1}(1) O(2)$	$9E_{C}(1)$	$N(12)^{\#1}$ (y(1) (2)	151 7(1)
N(1) - Cu(1) - O(3)	85.6(1)	$N(12)^{-1} - Cu(1) - O(3)$	151.7(1)
O(6) - Cu(1) - O(3)	/8.2(1)		
Complex 6			
$C_{\mu} = O(1)$	1002(3)	Cu = N(1)	1 088(6)
Cu = O(1)	1.007(0)	$Cu = N(\Gamma)^{\#1}$	1.008(5)
Cu = N(6)	1.997(6)	Cu-N(5)	1.998(5)
Cu–O(1)**2	2.303(4)		
O(1) - Cu - N(1)	85.7(2)	O(1)-Cu-N(6)	84.7(2)
$N(1)-Cu-N(5)^{\#1}$	94.1(2)	N(6)-Cu-N(5) ^{#1}	95.9(2)
$O(1)-Cu-O(1)^{\#2}$	84.9(2)	$N(1)-Cu-O(1)^{\#2}$	95.2(2)
$N(6) = C_{11} = O(1)^{\#2}$	96 5(2)	$N(5)^{\#1} - Cu = O(1)^{\#2}$	934(2)
	50.5(2)		55.1(2)
Complex 7			
Cd(1)-N(1)	2.289(1)	Cd(1) - N(7)	2.326(7)
Cd(1) - O(1)	2.361(8)	Cd(1) - O(4)	2.353(7)
$Cd(1) = N(5)^{\#1}$	2 390(9)	$Cd(1) = N(12)^{\#2}$	2437(8)
$N(7) Cd(1) N(10)^{\#2}$	2.330(3)	N(7) Cd(1) O(1)	100 7(2)
$N(1) = Cu(1) = N(12)^{-1}$	00.0(3)	N(7) = CU(1) = O(1)	100.7(3)
N(1) - Cd(1) - O(1)	80.1(3)	N(7) - Cd(1) - O(4)	81.8(3)
N(1)-Cd(1)-O(4)	97.5(3)	$N(1)-Cd(1)-N(12)^{#2}$	93.6(3)
$N(1)-Cd(1)-N(5)^{\#1}$	86.7(3)	$N(7)-Cd(1)-N(5)^{\#1}$	91.1(3)
$O(1)-Cd(1)-N(5)^{\#1}$	73.9(3)	$O(4)-Cd(1)-N(5)^{\#1}$	106.3(3)
· · · · · · · · · · · · · · · · · · ·			

Symmetry code for **3**: #1 -x + 1, -y, -z; #2 x - 1/2, -y + 1/2, z - 1/2; #3 -x + 3/2, y - 1/2, -z + 1/2. for **4**: #1 -x, -y, -z + 2. for **5**: #1 x - 1, y - 1, z. for **6**: #1 x, -y + 3/2, z + 1/2; #2 -x + 1, -y + 1, -z + 1. for **7**: #1 x, y + 1, z; #2 x, y - 1, z.

The infrared spectra of **1–7** exhibits characteristic absorptions for corresponding ligands with a slight shift due to coordination. The absorption band at about 1350 cm^{-1} , 1384 cm^{-1} and 1302 cm^{-1} indicates the existence of the NO₃⁻ anion in **4**, **5** and **7**. The characteristic bands of the free perchlorate ion appear at 1092 cm^{-1} and 624 cm^{-1} in **3**. The absorption band at 1055 cm^{-1} indicates the existence of the BF₄⁻ anion in **6**. L¹–L⁴ and **1–7** all exhibited absorptions corresponding to the framework vibrations of aromatic rings at about $1420-1650 \text{ cm}^{-1}$.

3.2. Description of the crystal structure

3.2.1. $Zn(L^1)_2Cl_2(1)$ and $Co(L^1)_2Cl_2(2)$

Structural analyses were carried out and similar cell parameters of complexes 1 and 2 (Table 1) indicate that they have similar structure. Compounds 1 and 2 have the general formula of $M(L^1)_2Cl_2$



Fig. 1. View of (a) the coordination environment of Zn^{II} ions in **1** (b) the 1-D chain by inter-plane $\pi \pi$ stacking interactions of **1** (c) the 1-D chain formed by the C-H Cl and C-H N weak interactions of **1** (H atoms omitted for clarity).

[M = Zn (1), M = Co (2)]. In 1, the coordination environment of Zn^{II} ion is also the same as that of Co^{II} ion in 2. Therefore, we just describe structure of complex 1 later in this text in detail relatively.

Complex **1** crystallizes in $P\overline{1}$ space group and the selected bond distances and angles were listed in Table 2. The X-ray diffraction analysis shows that **1** has a mononuclear structure (see Fig. 1a). The Zn^{II} center features a distorted tetrahedral geometry, and

linked to two distinct triazole N donors of two L^1 ligands and two chlorine atoms, the Zn(1)–N(5) and Zn(1)–N(1) bond distances are 2.020(2) and 2.033(3) Å, respectively, which are in the normal range [19]. Two L^1 ligands all adopt monodentate coordination mode. All the atoms of each ligand L^1 are almost in the same plane, the mean deviations from the planes of two ligands are ca. 0.0649 and 0.0497 Å, the dihedral angles between planes of two ligands L^1



Fig. 2. View of the coordination environment of Co^{II} ions in 2 (H atoms omitted for clarity).

is 104.9°. It should be pointed out that two planes of ligands from the adjacent mononuclear structure are almost parallel to each other, these mononuclear structure were further extended into 1-D chain by inter-plane $\pi \pi$ stacking interactions between the ligands planes from adjacent mononuclear structure. The centroid-centroid separations are 3.378 and 3.290 Å, respectively (Fig. 1**b**).

In addition, the C–H Cl and C–H N weak interactions were observed between adjacent mononuclear structures. The distance of C(4) Cl(2) is 3.404 Å with the angle C(4)–H(4B) Cl(2) being 101.46°, the distance of C(7) N(2) is 3.494 Å with the angle C(7)–H(7A) N(6) being 156.55°, Therefore, mononuclear structures were further assembled by the C–H Cl and C–H N weak interactions into an infinite a supramolecular chain along the other direction (Fig. 1c).

The mononuclear structure of complex **2** shows in Fig. 2. The mean deviations from the planes of two ligands in **2** are ca. 0.0505 and 0.0620 Å, the dihedral angles between planes of two ligands **L**¹ is 104.2°. Similarly, inter-plane π π stacking interactions and the C–H Cl and C–H N weak interactions were observed in **2**, the centroid–centroid separations are 3.369 and 3.278 Å, respectively. The distance of C(19) Cl(2) is 3.404 Å with the angle C(19)–H(19A) Cl(1) being 100.79°, the distance of C(22) N(2) is 3.489 Å with the angle C(22)–H(22A) N(2) being 156.60°. The



Fig. 3. View of (a) the coordination environment of Cd^{II} ions in **3** (b) 2-D (4,4) network structure of **3** (c) the 3-D supramolecular network by O-H…O hydrogen-bonding interactions (H atoms omitted for clarity).



Fig. 4. View of (a) the coordination environment of Cd^{II} ions in **4** (b) the 1-D chain by O-H...O hydrogen bonding interactions of **4** (c) the 2-D supramolecular sheet formed by the O-H...O and O-H N weak interactions of **4** (H atoms omitted for clarity).

mononuclear structure were further extended into a chain along different directions by inter-plane π π stacking interactions and the C-H Cl and C-H N weak interactions.

3.2.2. { $[Cd(L^2)_2(H_2O)_2] \cdot (ClO_4)_2$ }_{∞} (**3**)

Complex **3** is a neutral rhombohedral grid with (Fig. 3b) a (4, 4) topology (Fig. 3c). The centrosymmetric unit contains a Cd^{II} center, two **L**² ligands and two water molecules. The Cd^{II} center is coordinated to two N atoms of 1,2,4-triazolo[3,4-b]-1,3,4-thiadiazole from distinct **L**² ligands [Cd(1)–N(1) = 2.333(5) Å], two N atoms of pyridine from distinct **L**² ligands [Cd(1)–N(5) = 2.356(5) Å] in

the equatorial plane and two O atoms from water molecules [Cd(1)-O(1W) = 2.288(5) Å] at the axial positions to complete its distorted octahedron coordination geometry with the coordination angles varying from $86.36(15)^{\circ}$ to 180.00° (Fig. 3a and Table 2).

Each \mathbf{L}^2 ligand links two Cd^{II} ions and in turn each Cd^{II} ion connects four ligands forming a layer structure with (4, 4) grid units, in which all the Cd^{II} ions are located in one plane (Fig. 3**b**). From Fig. 3**b**, each (4, 4) grid unit is constructed by four ligands acting as four edges and four Cd^{II} ions as four vertexs. All the lengths of the edges are equal (the edges are 10.289 Å) and the orthogonal distances are 11.644 and 16.968 Å, respectively. The uncoordinated



Fig. 5. View of (a) the coordination environment of Cu^{II} ions in 5 (b) the 1-D supramolecular chain (H atoms omitted for clarity).

 ClO_4^- anions serving as counteranion, and locate at the cavities of the sheets and form O–H···O hydrogen-bonding with the coordinated water molecules of the complex to give a three-dimensional framework [O···O separations are 2.65 and 2.81 Å, respectively]. The hydrogen-bonding parameters (Å, °) were listed in Table 2.

3.2.3. $Cd(L^2)_2(NO_3)_2(H_2O)_2$ (4)

The structure of 4 consists of a centrosymmetric mononuclear neutral molecule $Cd(L^2)_2(NO_3)_2(H_2O)_2$ (Fig. 4a). In the mononuclear unit, the six-coordinated environment of Cd(II) ion is as follows in detail: two oxygen atoms from two water molecules and two nitrogen atoms of pyridine from two distinct ligands L² [adopting N-terminal coordination mode] are coordinated to the Cd(II) ion; meanwhile, the last two coordination sites are occupied by two oxygen atoms from two different NO₃⁻ anions, respectively. The L^2 ligand adopts monodentate coordination mode. All the atoms of the ligand L^2 are amost (almost) in the same plane, the mean deviations from the planes of the ligand is ca. 0.0783 Å. It should be noted that an 1-D structure along *a* direction is formed through intermolecular O-H...O hydrogen bonding interactions. As shown in Fig. 4b, the O(3) atom of the NO_3^- anions serves as the acceptors to form O(1w)-H(1)...O(3) intermolecular hydrogen bonds with coordinated water molecules. The O...O distance of 2.806 Å fall into the normal range of hydrogen bond interactions.

In addition, the O–H N hydrogen bonding interactions were observed between adjacent a supramolecular chain formed by the O–H...O hydrogen bonding interactions (Fig. 4**b**). The distance of O(1W) N(5) is 2.834 Å, Therefore, the supramolecular chain were further assembled by the O–H N hydrogen bonding interactions into an infinite 2-D supramolecular network structure (Fig. 4**c**).

Obviously, the structural difference of **3** and **4** is attributable to the difference of counter anions, namely, ClO_4^- for **3** and NO_3^- for **4**.

3.2.4. {[$Cu(L^3)_2(NO_3)_2$]·(CH_2Cl_2)} $_{\infty}$ (**5**)

The structure of **5** is a 1-D neutral coordination chain. As shown in Fig. 5b, the six-coordinated environment of Cu^{II} (Fig. 5a) center is as follows in detail: three nitrogen atoms belonging to three distinct **L**³ ligands [the Cu–N lengths are all within normal range and at the range of from 1.958(4) to 2.029(3) Å] and three oxygen atoms from two distinct NO₃⁻ anions [one NO₃⁻ anion adopted bidentate chelating coordination mode, Cu–O lengths of 2.184(4) and 2.506 Å, respectively, another NO₃⁻ anion adopted monodentate coordination mode, Cu–O lengths of 2.167(3) Å] are coordinated to the Cu^{II} center. The selected bond distances and angles were listed in Table 2. In **5**, two unequivalent **L**³ were observed, one **L**³ adopted bidentate bridge coordination mode, and link the complex **5** into a supramolecular chain, another monodentate coordination mode. The distance of the two Cu^{II} center was 10.756 Å.

3.2.5. { $[Cu(L^3)_2(OH)(MeOH)] \cdot (MeOH)_2 \cdot BF_4$ }_{\pi} (6)

To investigate the influence of counter-anions in constructing coordination frameworks, **6** was obtained by the reaction of L^3 with Cu(BF₄)₂·H₂O instead of Cu(NO₃)₂·3H₂O used for **5**. Complex **6** crystallizes in the monoclinic system space group, *P*2(1)/*c*. Selected bond lengths and angles were shown in Table 2. X-ray single-crystal diffraction analyses revealed that **6** have an infinite square grid structure consisting of the dinuclear Cu₂O₂ units, Cu-O₂-Cu (*C_i* symmetry), and **L**³ ligands. The Cu^{II} center has a distorted



Fig. 6. View of (a) the coordination environment of Cu^{II} ions in 6 (b) the binuclear structure unit of 6 (c) 2-D (4,4) network structure of 6 (H atoms omitted for clarity).

octahedron coordination geometry, which is formed by three nitrogen donor atoms of distinct ligands L^3 , two symmetrical O atoms from OH⁻ anions and one O atom of MeOH molecules (Fig. 6a). The Cu^{II} donor bond distances are all within normal range [Cu-N(1) = 1.988(6) Å, Cu-N(6) = 1.997(6) Å, Cu-N(5) = 1.998(5) Å, Cu-O(1) = 1.902(3) Å, Cu-O(1)#2 = 2.303(4) Å, Cu-O(3)#2 = 2.567 Å] (symmetry code: #2 -x + 1,-y + 1,-z + 1) (Table 2). The bond angles around the Cu^{II} ions are in the range of 84.67(19)-178.2(2)°. The Cu^{II} centers bridged by two OH⁻ anions are separated by a relatively short distance of 3.113 Å. It is well below the summed Van der Waals radii of two copper atoms (2.8 Å), this distance is longer than 2.8 Å, indicating there is no Cu⁻⁻Cu interaction. Two O atoms link two Cu^{II} ions to form a dinuclear unit Cu₂O₂ (Fig. 6b). At the same time, the dinuclear Cu₂O₂ units are interconnected by four **L**³ ligands via copper-nitrogen bonds to form a 2-D layer with (4, 4) topology (Fig. 6c). The resulting 2-D layers are packed parallel to complete the final 3-D structure. No obvious π - π interactions are found between the layers.

3.2.6. $[Cd(L^4)_2(NO_3)_2]_{\infty}$ (7)

As shown in Fig. 7, complex **7** crystallizes in P1 space group, as shown in Fig. 7 and **7** has 1-D neutral coordination chain. The Cd^{II}



Fig. 7. View of (a) the coordination environment of Cd^{II} ions in 7 (b) the 1-D supramolecular chain (H atoms omitted for clarity).

ion is six-coordinated to two oxygen atoms of two distinct nitrate anions [adopting monodentate coordination mode, Cd(1)–O(1) = 2.361(8) Å, Cd(1)–O(4) = 2.353(7) Å], two N donors of pyridine from two distinct ligands L^4 [Cd(1)–N(5) = 2.390(9) Å, Cd(1)–N(12) = 2.437(8) Å] and two N donors of triazoles ring from two distinct L^4 ligands [Cd(1)–N(1) = 2.289(10) Å, Cd(1)–N(7) = 2.326(7) Å] to form a distorted octahedral geometry. The selected bond distances and angles were listed in Table 2. In 7, all L^4 ligands are unequivalent, and adopt a bidentate bridged coordination mode. The distance of the two N atoms coordinated to Cd^{II} center was unequal, 5.656 and 5.580 Å, respectively, and the adjacent Cd^{II} centers are linked by two bridging L^4 in two different directions to form 1-D chain [the non-bonding Cd/Cd distances are 8.667 Å].

3.3. Luminescent properties

Aromatic organic molecules and mixed inorganic–organic hybrid coordination polymers are promising luminescent materials for their potential applications, such as light-emitting materials (LEDs) [20]. The emission spectra of L^1 , L^2 , L^4 and complexes 1, 3, 4 and 7 in the solid state at room temperature were investigated (see Supplementary 1). L^1 exhibits an intense blue fluorescent emission band at 422 nm upon excitation at 370 nm. Complex 1 exhibits weak blue fluorescent emission bands at 397 nm upon excitation at 350 nm. L^2 exhibits an intense blue fluorescent emission band at 450 nm upon excitation at 396 nm. Complexes 4 display strong fluorescent emission bands at 427 nm upon excitation

at 372 nm. Difference from **4**, complex **3** exhibits two intense emission bands at 411 and 435 nm upon excitation at 380 nm. L^4 exhibits an intense blue fluorescent emission band at 439 nm upon excitation at 370 nm. Complex **7** exhibits two intense emission bands at 406 and 461 nm upon excitation at 375 nm. Compared with that of the free ligand, complexes in the solid state have a similar blue shift. This blue shift was respect to the free ligands may be caused by the coordination or the changes of conformation of ligands [21].

3.4. Conclusion

A series of new d¹⁰ metals (Zn and Cd) and transition metals (Cu and Co) metal-organic complexes with 4,7-diphenyl-1,2,4-triazolo[3,4-b]-1,3,4-thiadiazole (L¹), 4-phenyl-7-(pyridine-3-yl)-1,2, 4-triazolo[3,4-b]-1,3,4-thiadiazole (L²), 4-phenyl-7-(pyridine-4yl)-1,2,4-triazolo[3,4-b]-1,3,4-thiadiazole (L³) and 4-(pyridine-3-yl)-7-(pyridine-4-yl)-1,2,4-triazolo[3,4-b]-1,3,4-thiadiazole (L⁴) have been synthesized and structurally characterized. The influences of the locality and amount of coordination atoms in the same ligands' framework and counteranions on the resultant structures of their metal complexes are briefly discussed. Some intra-molecular and/or inter-molecular weak interactions, such as hydrogen bonding, also play important roles in the formation of these complexes, especially in the aspects of linking the discrete subunits and low-dimensional entities into high-dimensional supramolecular networks. Moreover, the fluorescence properties of ligands L^1 , L^2 , L^4 and corresponding Zn^{II}/Cd^{II} complexes display strong blue fluorescent emission at room temperature. This approach may be useful for the construction of a variety of new transition metal complexes and luminescent coordination polymers with novel structures that have the potential of leading to new fluorescent materials.

Acknowledgments

This work was financially supported by the National Natural Science Funds of XinJiang, China (No. 2011211A009) and supported by the Open Project Program of Xinjiang Laboratory of Advanced Functional Materials, China (XJDX0902-2010-02).

Appendix A. Supplementary data

CCDC 853771-853777 contains the supplementary crystallographic data for complexes $1 Zn(L^1)_2Cl_2$, $2 Co(L^1)_2Cl_2$, $3 \{ Cd(L^2)_2 \}$ $(H_2O)_2 \cdot (ClO_4)_2 \in \mathbf{4} \cdot Cd(\mathbf{L}^2)_2 (NO_3)_2 (H_2O)_2, \quad \mathbf{5} \cdot \{ Cu(\mathbf{L}^3)_2 (NO_3)_2 \in \mathbf{5} \cdot (Cu(\mathbf{L}^3)_2 (NO_3)_2) = \mathbf{5} \cdot (Cu(\mathbf{L}^3)_2 (NO_3)_2 (NO_3)_2 = \mathbf{5} \cdot (Cu(\mathbf{L}^3)_2 (NO_3)_2) = \mathbf{5} \cdot (Cu(\mathbf{L}^3)_2 (NO_3)_2 (NO_3)_2 = \mathbf{5} \cdot (Cu(\mathbf{L}^3)_2 (NO_3)$ (CH_2Cl_2) , **6** { $[Cu(L^3)_2(OH)(MeOH)]$ (MeOH)₂ BF₄} and 7 { $[Cd(L^4)_2]$ $(NO_3)_2]_{\infty}$, respectively. These data 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; or e-mail: deposit@ccdc. cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/ j.poly.2012.05.028.

References

- [1] (a) O.K. Farha, A.M. Spokoyny, K.L. Mulfort, S. Galli, J.T. Hupp, C.A. Mirkin, Small 5 (2009) 1727;
 - (b) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O.M. Yaghi, Science 295 (2002) 469:
 - (c) X.H. Bu, M.L. Tong, H.C. Chang, S. Kitagawa, S.R. Batten, Angew. Chem., Int. Ed. 43 (2004) 192:
 - (d) J.R. Li, D.J. Timmons, H.C. Zhou, J. Am. Chem. Soc. 131 (2009) 6368;
 - (e) X.M. Zhang, Z.M. Hao, W.X. Zhang, X.M. Chen, Angew. Chem., Int. Ed. 46 (2007) 3456

(f) P. Horcajada, C. Serre, G. Maurin, N.A. Ramsahye, F. Balas, M. Vallet-Regí, M.

- Sebban, F. Taulelle, G. Ferey, J. Am. Chem. Soc. 130 (2008) 6774; (g) Y.F. Zeng, X. Hu, F.C. Liu, X.H. Bu, Chem. Soc. Rev. 38 (2009) 469;
- (h) Q. Yu, Y.F. Zeng, J.P. Zhao, Q. Yang, X.H. Bu, Cryst. Growth Des. 10 (2010) 1878
- [2] (a) U. Beckmann, S. Brooker, Coord. Chem. Rev. 245 (2003) 17;
 - (b) R. Bronisz, Inorg. Chem. 46 (2007) 6733;
 (c) R. Bronisz, Inorg. Chem. 44 (2005) 4463;

 - (d) J. Fan, G.T. Yee, G. Wang, B.E. Hanson, Inorg. Chem. 45 (2006) 599.
- [3] (a) X. Zhu, H.Y. Ge, Y.M. Zhang, B.L. Li, Y. Zhang, Polyhedron 25 (2006) 1875; (b) N. Masciocchi, G.A. Ardizzoia, S. Brenna, F. Castelli, S. Galli, A. Maspero, A. Sironi, Chem. Commun. (2003) 2018;
 - (c) M.H. Klingele, S. Brooker, Coord. Chem. Rev. 241 (2003) 119:
 - (d) Q.W. Zhai, X.Y. Wu, S.M. Chen, C.Z. Lu, W.B. Yang, Cryst. Growth Des. 6

(2006) 2126;

- (e) X.L. Tong, D.Z. Wang, T.L. Hu, W.C. Song, Y. Tao, X.H. Bu, Cryst. Growth Des. 9 (2009) 2280:
- (f) T.L. Hu, J.R. Li, C.S. Liu, X.S. Shi, J.N. Zhou, X.H. Bu, J. Ribas, Inorg. Chem. 45 (2006) 162
- [4] N.A. Negm, M.F. Zaki, Colloids Surf., B 64 (2008) 179.
- [5] (a) P. Sood, A. Chandrasekaran, R.O. Day, R.R. Holms, Inorg. Chem. 37 (1998) 3747.
 - (b) D.F. Weng, W.H. Mu, X.J. Zheng, D.C. Fang, L.P. Jin, Inorg. Chem. 47 (2008) 1249.
- [6] D. Braga, F. Grepioni, Coord. Chem. Rev. 183 (1999) 19.
- (a) A.J. Blake, N.R. Champness, P. Hubberstey, W.S. Li, M.A. Withersby, M. Schröder, Coord. Chem. Rev. 183 (1999) 139; (b) L. Carlucci, G. Ciani, P. Macchi, D.M. Proserpio, Chem. Commun. (1998) 1837.
- (c) H.P. Wu, C. Janiak, G. Rheinwald, H. Lang, J. Chem. Soc., Dalton Trans. (1999) 183;
- (d) D.K. Cao, Y.Z. Li, Y. Song, L.M. Zheng, Inorg. Chem. 44 (2005) 3599.
- [8] (a) M.J. Zaworotko, Chem. Commun. (2001) 1;
- (b) D.Z. Wang, T.L. Hu, J.P. Zhao, X.H. Bu, CrystEngComm 12 (2010) 3587. (a) A. Mishra, W. Wernsdorfer, K.A. Abboud, G. Christou, J. Am. Chem. Soc. 126 (2004) 15648;
 - (b) F.A.A. Paz, J. Klinowski, Inorg. Chem. 43 (2004) 3948;
 - (c) J.R. Li, X.H. Bu, R.H. Zhang, Inorg. Chem. 43 (2004) 237.
- [10] (a) J. Fan, W.Y. Sun, T. Okamura, Y.Q. Zheng, B. Sui, W.X. Tang, N. Ueyama, Cryst. Growth Des. 4 (2004) 579;
- (b) C.Y. Sun, X.J. Zheng, S. Gao, L.C. Li, L.P. Jin, Eur. J. Inorg. Chem. (2005) 4150. [11] B. Ding, Y.Y. Liu, Y.Q. Huang, W. Shi, P. Cheng, D.Z. Liao, S.P. Yan, Cryst. Growth Des. 9 (2009) 593.
- [12] (a) S. Ferrer, J.G. Haasnoot, J. Reedijk, E. Müller, M.B.M.A. Cingi, M. Lanfranchi, M. Lanfredi, J. Ribas, Inorg. Chem. 39 (2000) 1859; (b) L. Yi, B. Ding, B. Zhao, P. Cheng, D.Z. Liao, S.P. Yan, Z.H. Jiang, Inorg. Chem.
 - 43 (2004) 33: (c) J.P. Zhang, X.M. Chen, Chem. Commun. (2006) 1689;

 - (d) Q.G. Zhai, X.Y. Wu, S.M. Chen, C.Z. Lu, W.B. Yang, Cryst. Growth Des. 6 (2006) 2126.
- [13] (a) X.R. Meng, Y.L. Song, H.W. Hou, H.Y. Han, B. Xiao, Y.T. Fan, Y. Zhu, Inorg. Chem. 43 (2004) 3528;
 - (b) X.R. Meng, Y.R. Liu, Y.L. Song, H.W. Hou, Y.T. Fan, Y. Zhu, Inorg. Chim. Acta 358 (2005) 3024;
 - (c) B.L. Li, Y.F. Peng, B.Z. Li, Y. Zhang, Chem. Commun. (2005) 2333;
 - (d) B.Z. Li, Y.F. Peng, X.G. Liu, B.L. Li, Y. Zhang, J. Mol. Struct. 741 (2005) 235; (e) Y.F. Peng, H.Y. Ge, B.Z. Li, B.L. Li, Y. Zhang, Cryst. Growth Des. 6 (2006) 994.
- [14] D.Z. Wang, C.S. Liu, J.R. Li, L. Li, Y.F. Zeng, X.H. Bu, CrystEngComm 9 (2007) 287.
- [15] N.D. Obushak, N.T. Pokhodylo, I.I. Krupa, V.S. Matiichuk, Russ. J. Org. Chem. 43 (8) (2007) 1223.
- [16] Bruker AXS, SAINT Software Reference Manual, Madison, WI, USA, 1998.
- G.M. Sheldrick, SHELXTL NT Version 5.1. Program for Solution and Refinement of [17] Crystal Structures, University of Göttingen, Germany, 1997.
- [18] G.M. Sheldrick, sadabs, Siemens Area Detestor Absorption Correction Program, University of Gottingen, Gottingen, Germany, 1994.
- [19] X.W. Wang, J.Z. Chen, J.H. Liu, Cryst. Growth Des. 7 (2007) 1227.
 [20] (a) For examples: M. Altmann, U.H.F. Bunz, Angew. Chem., Int. Ed. 34 (1995) 569:
 - (b) U.H.F. Bunz, Chem. Rev. 100 (2000) 1605;
 - (c) R.L. Sang, L. Xu, Inorg. Chem. 44 (2005) 3731;
 - (d) D.M. Ciurtin, N.G. Pschirer, M.D. Smith, U.H.F. Bunz, H.C. Zur Loye, Chem. Mater. 13 (2001) 2743:
 - (e) F Würthner A Sautter Chem Commun (2000) 445
- [21] K.J. Wei, Y.S. Xie, J. Ni, M. Zhang, Q.L. Liu, Cryst. Growth Des. 6 (2006) 1341.