

Unusual one-dimensional branched-chain structures assembled by a novel imidazole-containing tripodal ligand with cadmium(II) salts and their fluorescent property

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Abstract

Three novel coordination polymers $[\text{Cd}_3(\text{L})_2(\mu\text{-Br})(\mu\text{-Cl})\text{Br}_3\text{Cl}]$ (**1**), $[\text{Cd}_3(\text{L})_2(\mu\text{-Cl})_2\text{Cl}_4]$ (**2**) and $[\text{Cd}(\text{L})\text{Cl}]_2[\text{CdCl}_4] \cdot \text{H}_2\text{O}$ (**3**) were obtained by reactions of an imidazole-containing tripodal ligand N^1 -(2-aminoethyl)- N^1 -(2-imidazoylethyl)-ethane-1,2-diamine (L) with Cd(II) salts. Their structures were determined by X-ray crystallography. Crystal data for **1**, monoclinic system, $P2_1/c$, $a = 7.752(4) \text{ \AA}$, $b = 31.70(2) \text{ \AA}$, $c = 14.012(7) \text{ \AA}$, $\beta = 109.439(7)^\circ$, $V = 3247(3) \text{ \AA}^3$, $Z = 4$. **2**, monoclinic system, $P2_1/c$, $a = 7.6564(15) \text{ \AA}$, $b = 31.433(6) \text{ \AA}$, $c = 13.925(3) \text{ \AA}$, $\beta = 109.89(3)^\circ$, $V = 3151.1(11) \text{ \AA}^3$, $Z = 4$. **3**, orthorhombic system, $Pbcn$, $a = 22.950(2) \text{ \AA}$, $b = 8.435(7) \text{ \AA}$, $c = 17.360(2) \text{ \AA}$, $V = 3360.3(51) \text{ \AA}^3$, $Z = 4$. Complexes **1** and **2** have similar one-dimensional (1D) branched-chain structure while complex **3** features a 1D zigzag cationic chain with $[\text{CdCl}_4]^{2-}$ serving as counter anion. The photoluminescent measurements reveal that all the complexes exhibit blue fluorescence at room temperature in the solid state.

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Keywords: Tripodal polyamine ligand; Cadmium(II) complex; Branched chain structure; Fluorescence

1. Introduction

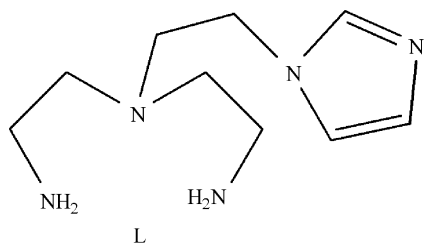
It has been established that the rational design and syntheses of certain desired supramolecular architectures are mainly based on the combination of the pre-designed organic building blocks and the well-defined metal centers with specific coordination geometry [1,2]. Obviously the nature of the coordination sites, conformation, flexibility of organic ligands as well as the geometric preferences, potential properties of the metal centers affected the structure and property of the final assemblies greatly. Except for these, the other factors such as the crystallization

conditions, solvent system, pH value as well as the counter ions should also be considered [3,4]. Among the reported building blocks, the tripodal ligands have been widely used in modeling the active site of metalloproteins and metalloenzymes [5], as well as in the construction of metal–organic frameworks (MOFs) with possible applications in ion recognition, guest inclusion, etc [6]. For example, Zn(II) complex with a tripodal polyamine ligand 2-[bis(2-aminoethyl)amino]ethanol was studied as model compound for Zn-containing hydrolase [5a].

We focused our attention on the reactions of imidazole-containing tripodal ligand with an arene core, e.g., 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene with a variety of metal salts to give complexes with interesting structures and properties [6]. Following such research work, recently we prepared a new imidazole-containing

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Scheme 1.

tripodal polyamine ligand, N^1 -(2-aminoethyl)- N^1 -(2-imidazolethyl)-ethane-1,2-diamine (L) (Scheme 1) and assembled it with $M(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ [$M = \text{Cu}(\text{II}), \text{Zn}(\text{II})$] to give complexes with simultaneously absorption and hydration of atmospheric carbon dioxide [7].

On the other hand, the complexes with Cd(II) centers have drawn growing interest due to the varied frameworks and potential photoluminescent, and non-linear optical (NLO) properties [8,9]. The d^{10} configuration makes the Cd(II) complexes adopt varied coordination geometries, e.g., tetrahedron, trigonal bipyramid, square pyramid or octahedron and also distorted ideal polyhedrons [8]. Therefore, the Cd(II) salt is particularly suitable for the assembly of coordination frameworks. Herein, we reported the syntheses, structural characterizations and fluorescent properties of three new coordination polymers, namely $[\text{Cd}_3(\text{L})_2(\mu\text{-Br})(\mu\text{-Cl})\text{Br}_3\text{Cl}]$ (**1**), $[\text{Cd}_3\text{L}_2(\mu\text{-Cl})_2\text{Cl}_4]$ (**2**), $[\text{Cd}(\text{L})\text{Cl}_2[\text{CdCl}_4] \cdot \text{H}_2\text{O}$ (**3**) obtained by the reactions of ligand L·4HCl with CdBr_2 , $\text{Cd}(\text{BF}_4)_2$, $\text{Cd}(\text{NO}_3)_2$, respectively.

2. Experimental section

All commercially available chemicals were purchased from Aldrich Chemical Company and used as received without further purification. The ligand N^1 -(2-aminoethyl)- N^1 -(2-imidazolethyl)-ethane-1,2-diamine (L) was synthesized by procedures reported previously [7]. Solvents were purified according to standard methods. Elemental analyses for C, H and N were made on a Perkin-Elmer 240C elemental analyzer at the Analysis Center of Nanjing University. The luminescent spectra for the powdered solid samples were recorded at room temperature on an Aminco Bowman Series 2 spectrofluorometer with a xenon arc lamp as the light source. In the measurements of emission and excitation spectra the pass width is 5.0 nm.

2.1. Preparation of $[\text{Cd}_3(\text{L})_2(\mu\text{-Br})(\mu\text{-Cl})\text{Br}_3\text{Cl}]$ (**1**)

An aqueous solution (4 mL) of $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$ (0.0344 g, 0.1 mmol) was added slowly to L·4HCl (0.0343 g, 0.1 mmol) in water (2 mL) with stirring. While the pH of the solution was adjusted to 8 by dropwise addition of 0.5 M NaOH, white precipitate appeared. Then 4 mL CH_3CN was added. After stirring for 30 min at room

temperature, the mixture was sealed into a bomb equipped with a Teflon liner and then heated at 110 °C for 24 h. Colorless prism crystals were obtained by cooling the reaction mixture to room temperature in 50% yield. Calcd. elem. anal. for $\text{C}_{18}\text{H}_{38}\text{Cd}_3\text{Br}_4\text{Cl}_2\text{N}_{10}$: C, 19.26; H, 3.41; N, 12.48. Found: C, 19.30; H, 3.41; N, 12.45.

2.2. Preparation of $[\text{Cd}_3(\text{L})_2(\mu\text{-Cl})_2\text{Cl}_4]$ (**2**)

L·4HCl (0.0343 g, 0.1 mmol) and $\text{Cd}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.0396 g, 0.1 mmol) were mixed in 5 mL water and 0.5 M NaOH solution was added dropwisely to adjust the pH value of the solution to 8. After the mixture was stirred for 2 h at room temperature, it was filtered. Colorless block crystals were obtained by slow diffusion of ethanol into the filtrate after about 7 days. Yield: 60%. Calcd. elem. anal. for $\text{C}_{18}\text{H}_{38}\text{Cd}_3\text{Cl}_6\text{N}_{10}$: C 22.89; H 4.05; N 14.83. Found: C 22.53; H 4.34; N 14.63.

2.3. Preparation of $[\text{Cd}(\text{L})\text{Cl}_2[\text{CdCl}_4] \cdot \text{H}_2\text{O}$ (**3**)

The titled complex was prepared by the similar method as used for complex **2** using $\text{Cd}(\text{NO}_3)_2$ instead of $\text{Cd}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$. Yield: 80%. Calcd. elem. anal. for $\text{C}_{18}\text{H}_{40}\text{Cd}_3\text{Cl}_6\text{N}_{10}\text{O}$: C, 22.46; H, 4.19; N, 14.55. Found: C, 22.42; H, 4.36; N, 14.53.

2.4. X-ray crystal structure determinations

The data collections for complexes **1**, **3** were carried out on a Rigaku Mercury CCD area detector with graphite monochromated Mo- $K\alpha$ ($\lambda = 0.71070 \text{ \AA}$) at 173 K. The structure of complex **1** was solved by direct method (SHELXS 97) [10]. All non-hydrogen atoms were refined anisotropically on F^2 by full-matrix least-squares techniques (SHELXS 97). The structure of complex **3** was solved by direct method with SIR92 [11] and expanded using Fourier techniques [12]. The non-hydrogen atoms in **1**, **3** were refined anisotropically, except the uncoordinated water O atom in **3** refined isotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using the CrystalStructure crystallographic software package [13,14]. Diffraction data for complex **2** were carried out on a Bruker SMART CCD system equipped with monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. The data integration and empirical absorption corrections were carried out by SAINT programs [15]. The structure was solved by direct method (SHELXS 97) [10]. All non-hydrogen atoms were refined anisotropically on F^2 by full-matrix least-squares techniques (SHELXS 97). The hydrogen atoms were generated geometrically. Details of the crystal parameters, data collection and refinements for complexes **1–3** are summarized in Table 1, and selected bond lengths and angles with their estimated standard deviations are given in Table 2. Further

Table 1
Crystallographic data for complexes 1–3

Complex	1	2	3
Empirical formula	C ₁₈ H ₃₈ Cd ₃ Br ₄ Cl ₂ N ₁₀	C ₁₈ H ₃₈ Cd ₃ Cl ₆ N ₁₀	C ₁₈ H ₄₀ Cd ₃ Cl ₆ N ₁₀ O
Formula weight	1122.32	944.48	962.53
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> ben
<i>a</i> (Å)	7.752(4)	7.6564(15)	22.95(2)
<i>b</i> (Å)	31.70(2)	31.433(6)	8.435(7)
<i>c</i> (Å)	14.012(7)	13.925(3)	17.36(2)
β (deg)	109.439(7)	109.89(3)	90.00
<i>V</i> (Å ³)	3247(3)	3151.1(11)	3360.3(51)
<i>Z</i>	4	4	4
<i>D_c</i> (g cm ⁻³)	2.296	1.991	1.902
μ (mm ⁻¹)	7.062	2.543	2.391
2 θ max (deg)	55.0	56.0	55.0
Reflns. collected	25626	18714	50688
Independent reflns.	7415	7170	4317
Obsd. reflns. (<i>I</i> > 2 σ (<i>I</i>))	5986	5895	2854
Parameters refined	334	344	192
<i>R</i> _{int}	0.0493	0.0409	0.104
<i>R</i> (obsd. Data)	0.0883	0.0524	0.0790
<i>R</i> (all data)	0.1141	0.0667	0.1190
<i>WR</i> ₂ (all data)	0.2387	0.1167	0.2430

details are provided in the Supporting Information in Appendix A.

3. Results and discussion

3.1. Crystal structure of [Cd₃(L)₂(μ-Br)(μ-Cl)Br₃Cl] (1) and [Cd₃(L)₂(μ-Cl)₂Cl₄] (2)

Complexes **1** and **2** were obtained by reactions of L·4HCl with CdBr₂·4H₂O and Cd(BF₄)₂·6H₂O, respectively. Complex **1** was prepared by a hydrothermal process (see experimental section), however, it can also be obtained by a diffusion method like the preparation of complex **2**. When the pH of the reaction solution of L·4HCl and CdBr₂·4H₂O was adjusted to ca. 7, no precipitate appeared. After the mixture was stirred for 2 h at room temperature, it was filtered. Colorless crystals were obtained by slow diffusion of ethanol into the filtrate after about 7 days. The cell parameters of *a* = 7.756, *b* = 31.71, *c* = 14.031 Å, β = 109.37°, *V* = 3249 Å³ indicate that the crystal structure of the complex obtained by diffusion method was the same as complex **1**. It is noteworthy that chlorides from L·4HCl were found in both complexes. There are bromides from CdBr₂·4H₂O in **1**, however, no BF₄⁻ anions were found in **2**. As summarized in Table 1, complexes **1** and **2** crystallize in the same space group with similar cell parameters and the structure analysis revealed that they are isomorphous. Thus we just describe the structure of **1** as an example.

As shown in Fig. 1(a), there are three crystallographically independent Cd(II) ions, namely Cd1, Cd2, Cd3. Among the three different Cd(II) centers, Cd1 center is

Table 2
Selected bond distances (Å) and angles (deg) for complexes 1–3

[Cd ₃ (L) ₂ (μ-Br)(μ-Cl)Br ₃ Cl] (1)			
Cd1-Br1	2.485(3)	Cd1-Br2	2.532(2)
Cd1-Br3	2.541(2)	Cd1-N1	2.234(9)
Cd2-Br4	2.637(2)	Cd2-Cl2	2.989(13)
Cd2-N3	2.263(12)	Cd2-N5	2.315(14)
Cd2-N4	2.610(10)	Cd2-Cl1	2.581(4)
Cd3-Cl2	2.538(3)	Cd3-Br4	2.985(2)
Cd3-N8	2.404(13)	Cd3-N6A ^a	2.308(10)
Cd3-N10	2.293(12)	Cd3-N9	2.509(10)
Br1-Cd1-Br2	113.82(9)	Br1-Cd1-Br3	109.03(8)
N1-Cd1-Br1	107.8(3)	Br2-Cd1-Br3	117.39(8)
N1-Cd1-Br2	105.0(3)	N1-Cd1-Br3	102.8(3)
Cl1-Cd2-Br4	109.11(14)	N3-Cd2-Br4	143.8(3)
N4-Cd2-Br4	96.1(2)	N5-Cd2-Br4	100.4(3)
N3-Cd2-Cl1	94.8(3)	Cl1-Cd2-N4	149.4(2)
N5-Cd2-Cl1	86.1(3)	N3-Cd2-N4	72.7(3)
N3-Cd2-N5	108.1(5)	N5-Cd2-N4	72.2(4)
N3-Cd2-Cl2	76.167(17)	N4-Cd2-Cl2	117.867(21)
N5-Cd2-Cl2	169.911(19)	Cl1-Cd2-Cl2	84.428(15)
Br4-Cd2-Cl2	79.507(15)	Cd2-Cl2-Cd3	100.736(18)
Cl2-Cd3-Br4	81.13(8)	Br4-Cd3-N6	91.50(3)
N6A ^a -Cd3-Cl2	100.1(3)	Cd2-Br4-Cd3	98.55(7)
N8-Cd3-Br4	167.6(4)	N9-Cd3-Br4	106.7(2)
N10-Cd3-Br4	80.4(4)	N8-Cd3-Cl2	86.5(4)
N9-Cd3-Cl2	96.1(2)	N10-Cd3-Cl2	156.1(4)
N6A ^a -Cd3-N8	90.9(4)	N6A ^a -Cd3-N9	157.1(4)
N10-Cd3-N6A ^a	95.6(4)	N8-Cd3-N9	73.8(4)
N10-Cd3-N8	111.3(6)	N10-Cd3-N9	75.0(4)
[Cd ₃ (L) ₂ (μ-Cl) ₂ Cl ₄] (2)			
Cd1-N5	2.224(4)	Cd1-Cl1	2.4121(17)
Cd1-Cl2	2.4296(16)	Cd1-Cl3	2.4297(17)
Cd2-N2	2.269(5)	Cd2-N1	2.293(6)
Cd2-N3	2.608(4)	Cd2-Cl6	2.519(2)
Cd2-Cl5	2.5265(16)	Cd2-Cl4	2.9740(18)
Cd3-N7	2.253(6)	Cd3-N10 ^b	2.279(5)
Cd3-N6	2.367(6)	Cd3-N8	2.493(4)
Cd3-Cl4	2.4984(17)	Cd3-Cl5	2.9486(18)
N5-Cd1-Cl1	105.85(12)	N5-Cd1-Cl2	106.67(12)
Cl1-Cd1-Cl2	113.78(7)	N5-Cd1-Cl3	103.06(12)
Cl1-Cd1-Cl3	116.25(7)	Cl2-Cd1-Cl3	110.10(6)
N2-Cd2-N1	107.6(2)	N2-Cd2-Cl6	99.04(15)
N1-Cd2-Cl6	86.23(15)	N2-Cd2-Cl5	141.63(15)
N1-Cd2-Cl5	102.41(15)	Cl6-Cd2-Cl5	106.31(9)
N2-Cd2-N3	72.56(15)	N1-Cd2-N3	72.24(16)
Cl6-Cd2-N3	152.53(11)	Cl5-Cd2-N3	95.07(10)
N2-Cd2-Cl4	75.50(14)	N1-Cd2-Cl4	170.67(14)
Cl6-Cd2-Cl4	84.58(8)	Cl5-Cd2-Cl4	78.71(5)
N3-Cd2-Cl4	117.01(10)	N7-Cd3-N10 ^b	95.88(18)
N7-Cd3-N6	111.1(2)	N10-Cd3-N6 ^b	90.05(19)
N7-Cd3-N8	74.71(17)	N10-Cd3-N8 ^b	156.01(15)
N6-Cd3-N8	73.58(17)	N7-Cd3-Cl4	153.29(17)
N10-Cd3-Cl4 ^b	100.87(13)	N6-Cd3-Cl4	89.67(18)
N8-Cd3-Cl4	96.53(11)	N7-Cd3-Cl5	79.29(17)
N10-Cd3-Cl5 ^b	91.41(13)	N6-Cd3-Cl5	169.30(18)
N8-Cd3-Cl5	107.97(11)	Cl4-Cd3-Cl5	79.64(5)
Cd3-Cl4-Cd2	100.75(6)	Cd2-Cl5-Cd3	100.76(6)
[Cd(L)Cl] ₂ [CdCl ₄]·H ₂ O (3)			
Cd1-Cl1	2.490(3)	Cd1-N1	2.280(1)
Cd1-N2	2.493(9)	Cd1-N3	2.270(9)
Cd2-Cl2	2.454(4)	Cd2-Cl3	2.439(4)
Cl1-Cd1-N1	113.90(3)	Cl1-Cd1-N2	97.50(2)
Cl1-Cd1-N3	132.80(2)	N1-Cd1-N2	76.00(3)
N1-Cd1-N3	109.30(3)	N2-Cd1-N3	75.00(3)
Cl2-Cd2-Cl3	108.30(1)	C1-N1-Cd1	110.20(8)

Symmetry transformations are used to generate equivalent atoms: ^a*x*+1, -*y*+1/2, *z*+1/2; ^b*x*-1, -*y*+1/2, *z*-1/2.

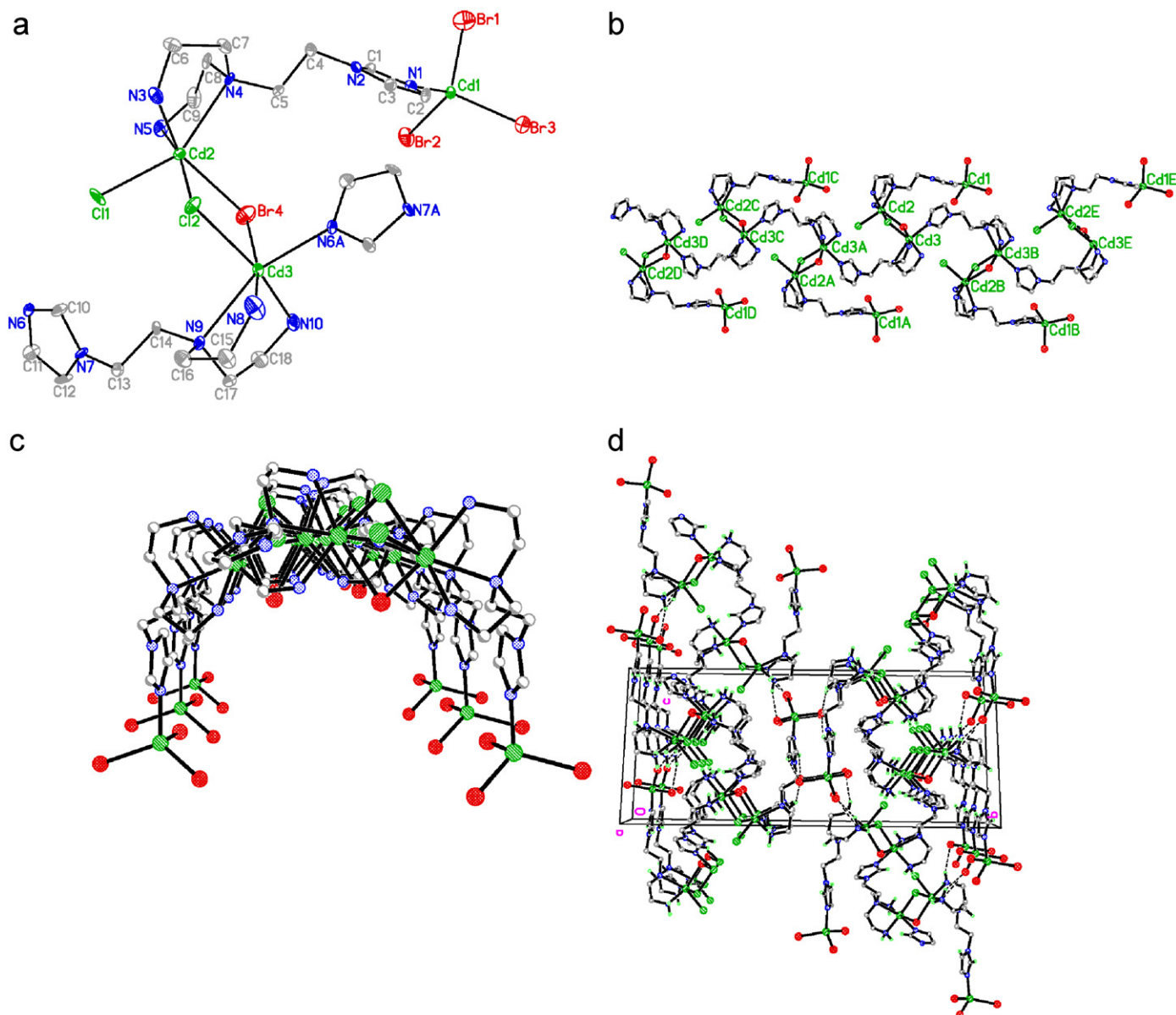


Fig. 1. (a) ORTEP drawing of complex **1**, showing the coordination environments of Cd(II) centers with 30% probability ellipsoids, hydrogen atoms were omitted for clarity. (b) 1D branched chain structure of complex **1**. (c) The side view of the branched chain structure. (d) 3D network of complex **1** linked by hydrogen bonding shown by dashed line viewed along the *a*-axis.

four-coordinated by three terminal Br⁻ anions and one imidazole N atom from L ligand in a slightly distorted tetrahedral geometry with an average coordination angle of 109°. The average Cd–Br_{terminal} bond length of 2.519 Å is similar to that observed in the reported complex [$\{Cd(m-2,5\text{-bis(pyridinio)adipate)Br}_2\}_n$] [Cd–Br = 2.509(2) Å] [16]. While Cd2 center is six-coordinated by three amine N atoms from the same ligand coordinated to the Cd1 center and one terminal, one bridging Cl⁻ anions (originated from L·4HCl) together with one bridging Br⁻ anion in a distorted octahedral geometry with the coordination angle in the range of 72.2(4)–169.911(19)°. It is interesting to find that the ligand L links Cd1 and Cd2 centers together to

serve as the pendant of the branched 1D chain as clearly shown in Figs. 1(b) and (c). The Cd3 center is six-coordinated in a distorted octahedral geometry by four N atoms from two L ligands, one bridging Cl⁻ anion and one bridging Br⁻ anion and the coordination angles around the Cd3 are in the range of 73.8(4)–167.4(4)°. The ligands L connect the Cd3 centers to form 1D infinite zigzag chain serving as the backbone of the branched 1D chain framework (Fig. 1(b)). Just due to the significant connection of double-bridged Cl⁻ and Br⁻ anions (two double-bridged Cl⁻ anions in complex **2**) between the Cd2 and Cd3 centers with Cd2–Cl2–Cd3 = 100.736(18)° and Cd2–Br4–Cd3 = 98.55(7)° in complex **1** [Cd2–Cl4–Cd3 = 100.75(6)°

Table 3
Hydrogen bonds data for the complexes 1–3

D–H...A	Distance of D...A (Å)	Angle of D–H–A (°)
[Cd₃(L)₂(μ-Br)(μ-Cl)Br₃Cl] (1)		
N3–H3A...Br2 ^a	3.576(12)	159
N5–H5A...Cl2 ^b	3.389(14)	148
N5–H5D...Br3 ^c	3.406(13)	153
N10–H10C...Cl1 ^d	3.347(16)	147
C1–H1A...Br1 ^e	3.719(14)	147
C3–H3B...Br1 ^f	3.632(14)	141
C8–H8B...Br1 ^e	3.633(13)	134
C10–H10B...Cl1	3.334(14)	138
[Cd₃(L)₂(μ-Cl)₂Cl₄] (2)		
N2–H2A...Cl1 ^g	3.477(6)	157
N1–H1A...Cl4 ^h	3.347(6)	149
N1–H1D...Cl3 ⁱ	3.367(6)	153
N7–H7C...Cl6 ^j	3.296(7)	149
C16–H16A...Cl6	3.324(7)	126
[Cd(L)Cl]₂[CdCl₄]·H₂O (3)		
N1–H1...Cl3 ^k	3.380(1)	119
N1–H1...O1 ^k	3.150(3)	152
N1–H2...Cl1 ^l	3.469(1)	164
N3–H11...Cl1 ^m	3.324(1)	131
N3–H12...Cl2 ⁿ	3.344(1)	162
C9–H19...Cl1	3.608(2)	144

Symmetry transformations are used to generate equivalent atoms: ^ax, y, –1+z; ^b–1+x, y, z; ^c–1+x, y, –1+z; ^d1+x, 1/2–y, 1/2+z; ^e–1–x, –y, 2–z; ^f–x, –y, 2–z; ^gx, y, 1+z; ^h1+x, y, z; ⁱ1+x, y, 1+z; ^j–1+x, 1/2–y, 1/2+z; ^k–x, 1–y, 1–z; ^m1/2–x, –1/2+y, z; ⁿ–x, –y, 1–z.

and Cd2–Cl5–Cd3 = 100.76(6)° in complex **2**] (Table 2), the branches are incorporated into the 1D chain backbone up and down in the same direction as shown in Fig. 1(b) and (c). It should be noted that the chloride and bromide bridges are asymmetric since the bond lengths of Cd3–Cl2 and Cd2–Br4 are 2.538(3) and 2.637(2) Å, respectively, while the ones of Cd2–Cl2 and Cd3–Br4 are 2.989(13) and 2.985(2) Å (Table 2). Such bridge mode has been observed in complex [Cd(TzHy)Cl₂]·nH₂O [TzHy = (2-thiazolin-2-yl)hydrazine] [17]. The Cd2–Cl2 and Cd3–Br4 bond distances are longer than the ones in complexes [Cd(TzHy)Cl₂]·nH₂O [17] and [Cd(L¹)Cl(μ-Cl)]₂ [L¹ = 2,6-bis(methylthiomethyl)pyridine] [18a] with chloride bridges, and [Cd(μ-pyrazine)(μ-Br)₂]_n with bromide bridges [18b], but comparable with the distance found in complex [{Cd₂(Cl₂CP₂O₆)(H₂O)₄]·H₂O]_n [Cl₂CP₂O₆ = (dichloromethylene)bis(phosphonate)] with Cd–Cl bond distance of 2.940(1) Å [19]. Furthermore, in the solid state the 1D chains are further linked by N–H...Br, N–H...Cl, C–H...Br, C–H...Cl hydrogen bonds between the chains to generate 3D framework (Fig. 1(d)). The hydrogen bonding data are summarized in Table 3.

3.2. Crystal structure of [Cd(L)Cl]₂[CdCl₄]·H₂O (3)

To further investigate the anion effect on the structure of complexes, Cd(NO₃)₂ instead of Cd(BF₄)₂ was used to

react with L by the similar procedures as for **2** to give complex **3**. The single crystal structure analysis revealed that **3** features a 1D undulating chain structure which is made up of infinite cationic chain [Cd(L)Cl]₂²⁺, isolated [CdCl₄]^{2–} anions and lattice water molecule (Fig. 2(a)). In the cationic chain, each Cd(II) ion is five-coordinated by four N atoms from two different L ligands, and one terminal Cl[–] anion (originated from L·4HCl) to extend to an infinite zigzag chain which is just similar to the backbone chain of complexes **1** and **2**. The coordination geometry around the Cd(II) center is a distorted square pyramid given by a τ value of 0.32 according to the Addison's definition (τ = 0, for an ideal square pyramid, and τ = 1, for a perfect trigonal bipyramid) [20]. It is interesting that complex **3** contained isolated [CdCl₄]^{2–} anions serving as counter anions. [CdCl₄]^{2–} was in a slightly distorted tetrahedron with an average bond angle of 108.8° which is similar to that in the previously reported complex R₂[CdCl₄]·EtOH·H₂O [R = 9-(2-ethoxy-carboxylphenyl)-3, 6-bis(ethylamino)-2,7-dimethylxanthylum] [21]. In the solid state, two 1D zigzag chains adopting opposite directions were packed together but not intertwist and stabilized by inter-chain C–H...Cl, N–H...Cl hydrogen bonds to give a 2D layered structure (Fig. 2(b)). Furthermore, [CdCl₄]^{2–} anions and water molecules were fixed between the 2D layers by N–H...Cl (from [CdCl₄]^{2–} anions), and N–H...O hydrogen bonds. As a result of such hydrogen bond linkages, the Cd–Cl bond lengths in [CdCl₄]^{2–} are 2.439(4), 2.454(4) Å which are similar to those in complexes R₂[CdCl₄]·EtOH·H₂O (2.444–2.455 Å), and (cinchonineH₂)[CdCl₄]·2H₂O (2.420–2.493 Å) which have similar hydrogen bonding interactions [22] but shorter than those in complex (2meptH₂)[CdCl₄] (2meptH₂ = 2-methylpentane-1,5-diamine dication) (2.554–2.693 Å and 2.522–2.707 Å) without such hydrogen bonding [23]. In addition, just as in complex **2**, although nitrate salt was used in preparation, no NO₃[–] anion but Cl[–] anion from L·4HCl was found in the complex. The result revealed that the anions in the solution affected the self-assembly product greatly.

3.3. Fluorescence properties of the complexes

It has been reported that Cd(II) complexes showed striking fluorescence property and could serve as good candidates for potential photoactive materials [8c,24,25]. Therefore, the solid-state fluorescent measurements for these three complexes were carried out. The emission spectra for complexes **1–3** and the ligand L are shown in Fig. 3 and their excitation spectra are given in the supporting information in Fig. S1. Complex **1** exhibited broad blue photoluminescence with the maximum emission at 431 nm upon excitation at 340 nm. Complexes **2** and **3** showed similar broad light blue emission with almost the same maximum at 401 nm upon excitation at 340 nm under the same condition. And these fluorescent emissions may be assigned to the intraligand fluorescence since the free

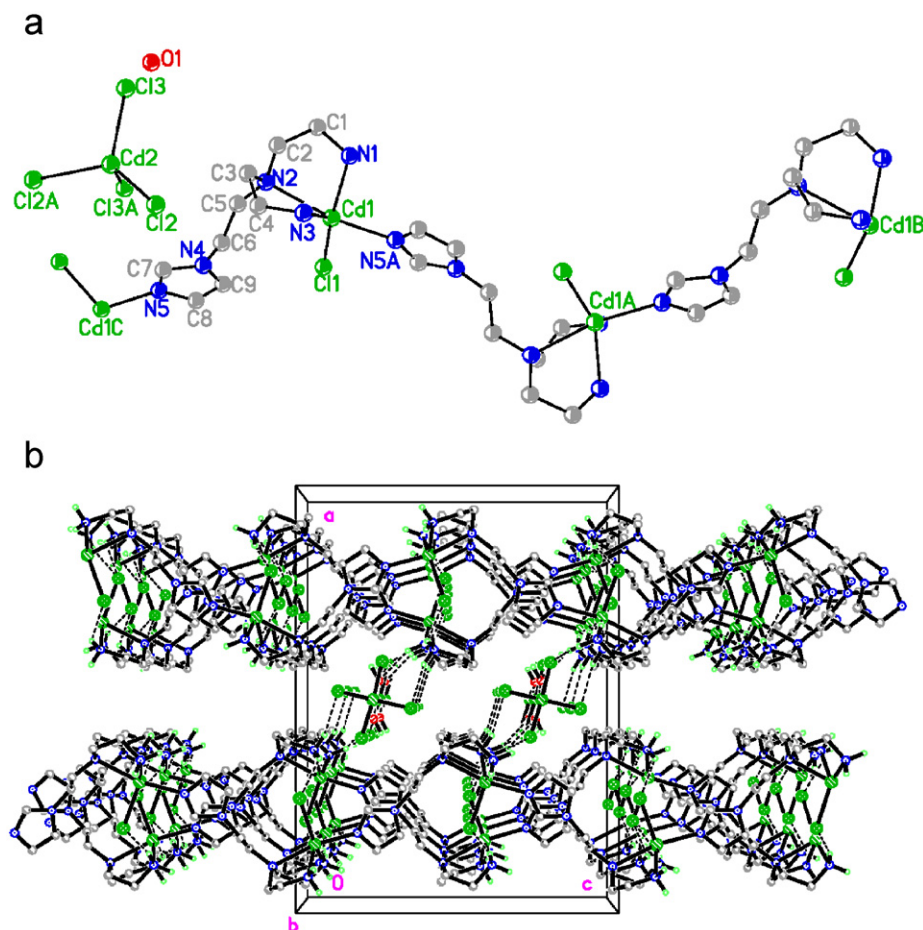


Fig. 2. (a) ORTEP representation of **3**, showing the coordination environment of Cd(II), thermal ellipsoids are shown in 30% probability, hydrogen atoms were omitted for clarity. (b) The crystal packing structure of **3** along the *b*-axis with hydrogen bonding indicated by dashed line.

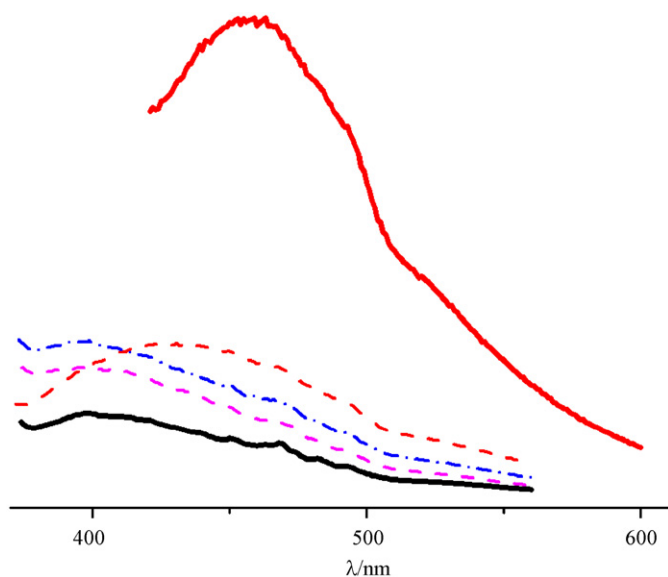


Fig. 3. The emission spectra of the free ligand **L** (solid line, black), complex **1** (dashed line, red), complex **2** (dotted line, magenta), complex **3** (dashed and dotted line, blue) with the excitation at 340 nm, complex **1** (thick solid line, red) upon the excitation at 394 nm.

ligand exhibited a similar broad weak emission at 403 nm upon excitation at 340 nm under the same condition. Just as that found in other coordination complexes with d^{10} configuration metal centers (e.g., Cd(II), Zn(II), Ag(I)) [25], the enhancement of luminescence for **1**, **2**, **3** compared with the free ligand under the same conditions may be attributed to the bridge connection of the ligand to Cd(II) centers, which enhanced its conformational rigidity and then decreased the non-radiative energy loss [24,25]. Emission spectra were also measured with excitation at 360 and 394 nm, and the data excited at 394 nm are exhibited in the supporting information in Fig. S2. It is interesting that complex **1** showed strong blue emission upon excitation at 360 or 394 nm, however no distinct emissions were observed for complexes **2** and **3** under these excitation wavelengths (Fig. S2). The emission band with maximum at 459 nm observed in **1** upon excitation at 394 nm could be tentatively assigned to ligand–metal charge transfer (LMCT). Similar fluorescent property has been reported for complex $[\text{Cd}_2(\mu_5\text{-oxalate})(\mu_3\text{-OH})_2]$ [24a]. The results showed that complex **1** behaved different fluorescent property from complexes **2** and **3**. And the

results suggest that both the coordination atoms (Br^- and Cl^- anions in **1**, only Cl^- anions in **2** and **3**) and structures could affect the fluorescent property greatly. And complex **1** is better candidate for potential blue fluorescent materials than **2**, **3**.

4. Conclusions

An imidazole-containing tripodal polyamine ligand N^1 -(2-aminoethyl)- N^1 -(2-imidazoleethyl)-ethane-1,2-diamine (**L**) was used to react with different Cd(II) salts and three new complexes were obtained. Complexes **1** and **2** have similar branched chain structure while complex **3** features a 1D zigzag chain structure. In complexes **1**, **2**, Cd(II) centers have two different geometries (tetrahedron, distorted octahedron), while in complex **3** Cd(II) centers are in distorted square pyramidal geometry. In all the three complexes, the **L** serves as bridge ligand as reported previously [7]. The results of present study reveal that although no BF_4^- , NO_3^- anions were found in the structure of complexes **2** and **3**, they do impact the self-assembly process and the structure of the final framework greatly. The solid state fluorescent measurements reveal that all the complexes exhibit blue fluorescent at room temperature.

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Appendix A. Supporting information

CCDC <609537(1), 609538 (2), 609539 (3)> contains the supplementary crystallographic data for <SHELXS 97>. 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.

References

- [1] [a] S. Leininger, B. Olenyuk, P.J. Stang, Chem. Rev. 100 (2000) 853;
[b] L. Brammer, Chem. Soc. Rev. 33 (2004) 476.
- [2] [a] S.L. James, Chem. Soc. Rev. 32 (2003) 276;
[b] S. Kitagawa, K. Uemura, Chem. Soc. Rev. 34 (2005) 109.
- [3] [a] J.S. Fleming, K.L.V. Mann, C.A. Carra, Z.E. Psillakis, J.C. Jeffery, J.A. McCleverty, M.D. Ward, Angew. Chem. Int. Ed. 37 (1998) 1279;
[b] L. Carlucci, G. Ciani, D.W.v. Gudenberg, D.M. Proserpio, A. Sironi, Chem. Commun. (1997) 631.
- [4] [a] P. Díaz, J. Benet-Buchholz, R. Vilar, A.J.P. White, Inorg. Chem. 45 (2006) 1617;
[b] S. Torelli, C. Belle, I. Gautier-Luneau, J.L. Pierre, E. Saint-Aman, J.M. Latour, L. Le Pape, D. Luneau, Inorg. Chem. 39 (2000) 3526;
[c] L.-Y. Kong, Z.-H. Zhang, T.-a. Okamura, M.-J. Fei, W.-Y. Sun, N. Ueyama, Chem. Lett. 33 (2004) 1572.
- [5] [a] J. Xia, Y. Xu, S.-A. Li, W.-Y. Sun, K.-B. Yu, W.-X. Tang, Inorg. Chem. 40 (2001) 2394;
[b] J. Xia, Y.-B. Shi, Y. Zhang, Q. Miao, W.-X. Tang, Inorg. Chem. 42 (2003) 70;
[c] J. Parkin, Chem. Commun. (2000) 1971.
- [6] [a] H.J. Choi, M.P. Suh, J. Am. Chem. Soc. 126 (2004) 15844;
[b] J. Fan, W.-Y. Sun, T.-a. Okamura, W.-X. Tang, N. Ueyama, Inorg. Chem. 42 (2003) 3168;
[c] J. Fan, H.-F. Zhu, T.-a. Okamura, W.-X. Tang, N. Ueyama, Chem. Eur. J. 9 (2003) 4724.
- [7] L.-Y. Kong, Z.-H. Zhang, H.-F. Zhu, H. Kawaguchi, T.-a. Okamura, M. Doi, Q. Chu, W.-Y. Sun, N. Ueyama, Angew. Chem. Int. Ed. 44 (2005) 4352.
- [8] [a] R.-H. Wang, M.-C. Hong, J.-H. Luo, R. Cao, Q. Shi, J.B. Weng, Eur. J. Inorg. Chem. (2002) 2904;
[b] A. Erxleben, Coord. Chem. Rev. 246 (2003) 203;
[c] Y.-Q. Gong, R.-H. Wang, Y.-F. Zhou, D.-Q. Yuan, M.-C. Hong, J. Mol. Struct. 705 (2004) 29.
- [9] [a] H. Fleischer, Coord. Chem. Rev. 249 (2005) 799;
[b] W.-B. Lin, Z.-Y. Wang, L. Ma, J. Am. Chem. Soc. 121 (1999) 11249;
[c] H.-Y. Hou, Y.-L. Song, H. Xu, Y.-L. Wei, Y.-Y. Fan, Y. Zhu, L.-K. Li, C.-X. Du, Macromolecules 36 (2003) 999.
- [10] G.M. Sheldrick, SHELXS 97, Program for Refinement of Crystal Structures.
- [11] A. Altomare, M.C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Guagliardi, G. Polidori, SIR92, J. Appl. Crystallogr. 26 (1993) 343.
- [12] P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, R. de Gelder, R. Israel, J.M.M. Smits, DIRDIF99, The DIRDIF-99 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1999.
- [13] CrystalStructure 3.5.1: Crystal Structure Analysis Package, Rigaku and Rigaku/MS (2000–2003). 9009 New Trails Dr. The Woodlands, TX 77381, USA.
- [14] CRYSTALS Issue 10: D. J. Watkin, C. K. Prout, J. R. Carruthers, P. W. Betteridge, Chemical Crystallography Laboratory, Oxford, UK, 1996.
- [15] SAINT, Program for Data Extraction and Reduction, Bruker AXS, Inc., Madison, WI, 2001.
- [16] D.-D. Wu, T.C.W. Mak, Polyhedron 15 (1996) 1775.
- [17] A. B.-García, M.A. D.-Diez, F.J. G.-Barros, F.J. H.-Rolando, A.M. P.-Galán, J.D. M.-Ramos, C. V.-Calahorra, Polyhedron 16 (1997) 297.
- [18] [a] W. Lai, S.M. Berry, D.C. Bebout, R.J. Butcher, Inorg. Chem. 45 (2006) 571;
[b] R.D. Bailey, W.T. Pennington, Polyhedron 16 (1997) 417.
- [19] M. Kontturi, E. Laurila, R. Mattsson, S. Peräniemi, J.J. Vepsäläinen, M. Ahlgrén, Inorg. Chem. 44 (2005) 2400.
- [20] A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn, G.C. Verschoor, J. Chem. Soc. Dalton Trans. (1984) 1349.
- [21] H. Wang, R.-G. Xiong, C.-M. Liu, H.-Y. Chen, X.-Z. You, W. Chen, Inorg. Chim. Acta 254 (1997) 183.
- [22] A. W.-Birczyńska, B.J. Oleksyn, J. Śliwiński, J. Goslar, W. Hilczer, S.K. Hoffmann, J. Mol. Struct. 751 (2005) 109.
- [23] A.B. Corradi, M.R. Cramarossa, M. Saladini, J. Giusti, A. Saccani, F. Sandrolini, Inorg. Chim. Acta 233 (1995) 85.
- [24] [a] J. Lu, Y. Li, K. Zhao, J.-Q. Xu, J.-H. Yu, G.-H. Li, X. Zhang, H.-Y. Bie, T.-G. Wang, Inorg. Chem. Commun. 7 (2004) 1154;

- [b] H.-F. Zhu, W. Zhao, T.-a. Okamura, J. Fan, W.-Y. Sun, N. Ueyama, *New J. Chem.* 28 (2004) 1010;
- [c] R.L. Sang, L. Xu, *Inorg. Chem.* 44 (2005) 3731;
- [d] J.H. Luo, F.L. Jiang, R.H. Wang, L. Han, Z.Z. Lin, R. Cao, M.C. Hong, *J. Mol. Struct.* 707 (2004) 211.
- [25] [a] S.-L. Zheng, M.-L. Tong, S.-D. Tan, Y. Wang, J.-X. Shi, Y.-X. Tong, H.K. Lee, X.-M. Chen, *Organometallics* 20 (2001) 5319;
- [b] S.-L. Zheng, J.-H. Yang, X.-L. Yu, X.-M. Chen, W.-T. Wong, *Inorg. Chem.* 43 (2004) 830.