Double-Bridged 1-D Chain Polymers of Zinc and Cadmium Constructed by a Flexible Dipyridyl-Type Linking Ligand: {[ML$_{1.5}$(NO$_3$)$_2$]·(CH$_3$OH)}$_∞$ {M = Zn or Cd; L = (3-py)-CH$_2$-NH-(CH$_3$)C$_6$H$_3$-C$_6$H$_3$(CH$_3$)-NH-CH$_2$-(3-py)}

Sung Yol Yun, Young-Keun Lee, and Soon W. Lee[*]

Department of Chemistry (BK21), Sungkyunkwan University, Natural Science Campus, Suwon 440-746, Korea
[*]E-mail: soonwlee@skku.edu

Coordination polymers, also known as metal-organic frameworks (MOFs) or metallosupramolecular networks, continuously gain much attention due to their remarkable properties such as catalysis, nonlinear optical activity, spin crossover, luminescence, long-range magnetism, adsorption-desorption, and gas storage.[1-15] These polymers are generally constructed by exploiting intramolecular metal-ligand covalent bonds, frequently as well as intermolecular interactions such as van der Waals contacts, π-π stacking, hydrogen bonding, and cation-π bonding.

Aromatic multi-carboxylates and dipyridyl derivatives are typically used as linking ligands for the preparation of coordination polymers. Long linking ligands containing terminal pyridyl rings, however, were recently employed to produce intriguing polymers with various topologies.[16-25] We have continually prepared long dipyridyl-, di(furan)-, di(thiophene)-, and di(ether)-type linking ligands and their coordination polymers.[26-37]

We very recently prepared ligand **L3** and its Co, Zn, and Cd coordination polymers (Chart 1).[36] Ligand **L3** is a reduced form of **L2**, and coordination polymers based on ligand **L3** have novel intriguing topologies, consistent with our expectation that free rotations about the Ar-NH, NH-CH$_2$, and CH$_2$-(4-py) bonds may be possible. In other words, our previous work demonstrated that reduced species of diimine ligands possess a greatly enhanced structural flexibility, which may create novel polymers that cannot be obtained from the original rigid diimine ligands. As an extension of that work, we decided to reduce ligand **L1** and to prepare coordination polymers by employing the resulting reduced ligand. It is worth noting that ligand **L1** is a structural isomer of ligand **L2** due to the different nitrogen positions in the terminal pyridyl rings. We report herein the

preparation of ligand **L**, (3-py)-CH$_2$-NH-(CH$_3$)C$_6$H$_3$-C$_6$H$_3$(CH$_3$)-NH-CH$_2$-(3-py), and structures of its zinc and cadmium coordination polymers.

Experimental Section

All solid chemicals were purified by recrystallization, and all solvents were distilled and stored over molecular sieves. ^{1}H and ^{13}C{^{1}H} NMR data were collected on a 500 MHz Varian Inova spectrometer at the Cooperative Center for Research Facilities (CCRF) in Sungkyunkwan University. Infrared (IR) samples were prepared as KBr pellets, and their spectra were obtained in the range 400~4000 cm^{-1} on a Nicolet 320 FTIR spectrophotometer. Elemental analyses were performed with an EA1110 (CE instrument, Italy) at the Korea Basic Science Institute. Ligand **L1** was prepared by the literature method.[28]

Preparation of (3-py)-CH$_2$-NH-(CH$_3$)C$_6$H$_3$-C$_6$H$_3$(CH$_3$)-NH-CH$_2$-(3-py) (L). To compound **L1** (7.0 g, 17.9 mmol) in ethanol (50 mL) was added sodium borohydride (6.78 g, 179 mmol) in small portions with stirring at room temperature. The resulting mixture was stirred for 12 h, and then filtered. The remaining orange solid was extracted with dichloromethane (100 mL), and washed with water (30 mL × 3). The organic phase was dried over MgSO$_4$ and filtered, and the solvent was removed. The resulting yellow solid was washed with hexane (25 mL × 2) and dried under vacuum. Data for ligand **L**: Yield 67%. mp: 189~190 ^{o}C (decomp). IR (cm^{-1}): 3376 (m), 3215 (m), 2920 (m), 2633 (m), 2362 (m), 2078 (m), 1619 (s), 1498 (s), 1063 (m), 813 (m), 493 (m). ^{1}H NMR (CDCl$_3$): δ 8.64 (m, 4H), 7.7-7.25 (m, 8H), 6.58 (dd, 2H), 4.5 (s 4H), 3.8 (br s 2H), 2.2 (s 6H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 154.1, 150.3, 149.3, 148.3, 147.6, 144.4, 131.2-122.3, 110.7, 47.37 (N-CH$_2$), 18.00 (CH$_3$).

Preparation of {[ZnL$_{1.5}$(NO$_3$)$_2$]·(CH$_3$OH)}$_∞$ (1). Ligand **L** (40 mg, 0.101 mmol) was dissolved in tetrahydrofuran (2 mL), and the resulting solution was filtered. A methanol solution (2 mL) containing Zn(NO$_3$)$_2$·6H$_2$O (20 mg, 0.067 mmol) was prepared in the same way. Two solutions were combined, and the combined solution was heated in a sealed vial at 70 ^{o}C for 3 days and then air-cooled to room temperature. The resulting crystals were filtered, washed with ethanol (3 × 5 mL), and air-dried to give polymer **1** (40 mg, 0.049 mmol, 73%). Anal. Calcd. for C$_{40}$H$_{43}$N$_8$O$_7$Zn (M$_r$ = 813.19): C, 59.08; H, 5.33; N, 13.78.

Chart 1
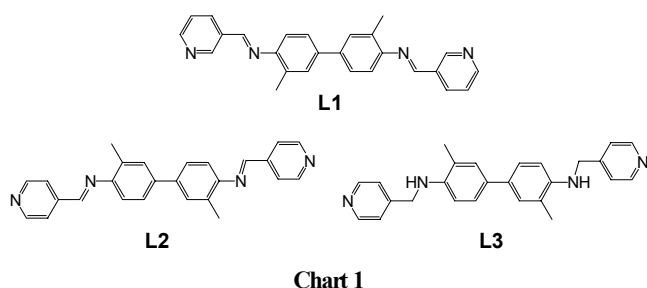
Found: C, 59.24; H, 4.93; N, 13.82. mp: 283~284 °C (decomp).
IR (cm^{-1}): 3418 (m), 3019 (s), 2920 (m), 1720 (m), 1611 (m), 1439 (s), 1193 (s), 1030 (m), 805 (s), 704 (s).

Preparation of {[CdL$_{1.5}$(NO$_3$)$_2$]·(CH$_3$OH)}$_\infty$ (2). Polymer **2** was prepared similarly to polymer **1**. A mixed solution of a dichloromethane solution (2 mL) containing ligand **L** (37 mg, 0.094 mmol) and a methanol solution (2 mL) containing Cd(NO$_3$)$_2$·6H$_2$O (20 mg, 0.064 mmol) was heated for 3 days to produce polymer **2** (29 mg, 0.035 mmol, 55%). Anal. Calcd. for C$_{40}$H$_{43}$N$_8$O$_7$Cd (M_r = 860.22): C, 55.85; H, 5.04; N, 13.03. Found: C, 56.18; H, 4.97; N, 13.12. mp: 235~237 °C (decomp). IR (cm^{-1}): 3421 (m), 3025 (s), 2917 (m), 1506 (m), 1436 (m), 1303 (m), 805 (m), 704 (m).
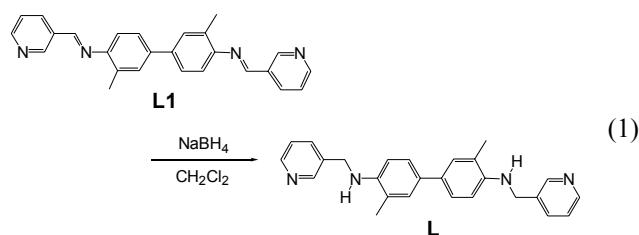
X-ray structure determination. All X-ray data were collected with a Bruker Smart APEX2 diffractometer equipped with a Mo X-ray tube. Absorption corrections were made by SADABS based upon the Laue symmetry of equivalent reflections.[38] All calculations were carried out with SHELXTL programs.[39] Unless otherwise stated, non-hydrogen atoms were refined anisotropically, and hydrogen atoms were generated in idealized positions and refined in a riding model. The methanol guest molecules in both polymers show an extremely high structural disorder. Anisotropic refinements applying several possible site occupation factors for the C and O atoms in them were unstable, and therefore these atoms were refined isotropically. The N-H hydrogen atoms in polymer **1** were located and refined isotropically. Details on crystal data, intensity collection, and refinement details are given in Table 1.

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Center: 732114 (**1**) and 732115 (**2**). Copies of this information may be obtained free of charge from: The director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Results and Discussion

Preparation of ligand L. A long, flexible linking ligand, {(3-py)-CH$_2$-NH-(CH$_3$)C$_6$H$_3$-C$_6$H$_3$(CH$_3$)-NH-CH$_2$-(3-py), **L**}, which possesses two terminal 3-pyridyl rings and an intervening 3,3'-dimethyldiphenyl fragment, was prepared in 67% yield by reducing its parent diimine species {(3py)-CH = N-(CH$_3$)C$_6$H$_3$-C$_6$H$_3$(CH$_3$)-N = CH-(3py), **L1** in Chart 1} with NaBH$_4$ (eq 1). Ligand **L** was characterized by NMR, IR, and elemental analysis data.

Table 1. X-ray Data Collection and Structure Refinement

	Polymer **1**	Polymer **2**
formula	C$_{40}$H$_{43}$N$_8$O$_7$Zn	C$_{40}$H$_{43}$N$_8$O$_7$Cd
crystal color	yellow	yellow
crystal size, mm	0.16 × 0.15 × 0.12	0.20 × 0.16 × 0.08
fw	813.19	860.22
temp, K	296(2)	296(2)
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a, Å	9.9825(4)	10.0466(8)
b, Å	31.876(1)	31.996(3)
c, Å	12.1733(5)	12.229(1)
β, deg	91.102(2)	90.647(4)
V, Å^3	3872.9(3)	3930.8(6)
Z	4	4
D_{calcd}, g cm^{-3}	1.395	1.454
μ, mm^{-1}	0.695	0.616
$F(000)$	1700	1772
T_{min}	0.8969	0.8871
T_{max}	0.9212	0.9526
no. of reflns measured	79587	69414
no. of reflns unique	9418	9493
no. of reflns with $I > 2\sigma (I)$	4707	5686
no. of params refined	508	497
max. in $\Delta\rho$ (e Å^{-3})	1.070	1.024
min. in $\Delta\rho$ (e Å^{-3})	−0.575	−0.571
GOF on F^2	1.009	0.938
$R1^a$	0.0721	0.0450
$wR2^b$	0.1887	0.1032

^{a}$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b}$wR2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$

(1)

Preparation and structures of polymers 1 and 2. A mixture consisting of a THF solution of ligand **L** and a MeOH solution of Zn(NO$_3$)$_2$·6H$_2$O was heated for 3 days in a sealed vial to produce polymer **1**, {[ZnL$_{1.5}$(NO$_3$)$_2$]·(MeOH)}$_\infty$. In a similar way, polymer **2**, {[CdL$_{1.5}$(NO$_3$)$_2$]·(MeOH)}$_\infty$, was prepared from ligand **L** and Cd(NO$_3$)$_2$·6H$_2$O in CH$_2$Cl$_2$-MeOH under solvothermal conditions. Both polymers contain methanol (solvent) guest molecules and were characterized by elemental analysis, IR spectroscopy, and X-ray diffraction.

Polymers **1** and **2** are isostructural, and therefore only polymer **1** is described in detail. The local coordination environment of Zn in polymer **1** is shown in Figure 1. An asymmetric unit consists of one Zn^{2+} ion, two nitrato ligands, and one and half ligands. The Zn^{2+} ion is coordinated by three N atoms from three **L** ligands and three O atoms from two nitrato ligands. The coordination sphere of Zn can be described as a distorted octahedron.

The 6-memebered rings in the ligands have various dihedral angles among them (Table 2). In particular, the terminal pyridyl rings have extremely different dihedral angles: 84.1(2)° (between Planes 1 and 4) and 0° (between Plane 5 and its symmetry-equivalent ring). In other words, one ligand containing the N1-N4 and C1-C26 atoms has practically perpendicular pyridyl rings, and the other has parallel ones. These orientations result in significantly distinct N···N separations (N1···N4 = 16.775(5) Å, a *cisoid* conformation; N5···N5A ($-x + 1, -y + 2, -z + 1$) =

Table 2. Dihedral Angles (deg) among 6-Memeberd Rings in Polymer **1**

Plane 1···Plane 2	88.4(2)	Plane 2···Plane 3	16.8(2)	Plane 3···Plane 1	83.5(1)
Plane 1···Plane 4	84.1(2)	Plane 5···Plane 6	84.4(1)		

Plane 1: N1, C1-C5; Plane 2: C7-C12; Plane 3: C14-C19; Plane 4: N4, C22-C26; Plane 5: N5, C27-C31; Plane 6: C33-C38.

13.645(6) Å, a *transoid* conformation), which in turn give significantly different Zn···Zn separations (19.062(1) and 14.961(1) Å).
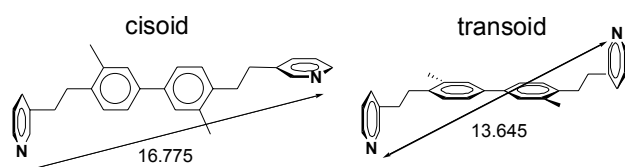
The projection of polymer **1** clearly shows a 1-D chain (Figure 2), in which a repeating unit is a loop (metallacycle) consisting of two Zn^{2+} ions and two ligands with two methanol guest molecules. This polymer has two distinct ligands; one (N1-N4 and C1-C26) participates in the loop formation, and the other links the loops approximately in the [100] direction to complete a 1-D polymer. The methanol guests are located off the loop planes. 1-Dimensional coordination polymers are

Figure 1. Local coordination environment around Zn in polymer **1**, with 30% probability thermal ellipsoids. Selected bond lengths (Å) and angles (°): Zn1-N4#1 2.125(3), Zn1-N5 2.126(3), Zn1-O5 2.160(4), Zn1-N1 2.181 (3), Zn1-O2 2.332 (4), Zn1-O1 2.348 (5), N2-C7 1.423 (5), N2-C6 1.440 (6), N3-C17 1.404 (5), N3-C21 1.444 (5), N6-C33 1.374 (6), N6-C32 1.427 (6); N5-Zn1-O5 89.6 (1), N5-Zn1-N1 175.8 (1), O5-Zn1-N1 89.0 (1). Symmetry transformations used to generate equivalent atoms: #1 = −x + 3, −y + 2, −z + 2.
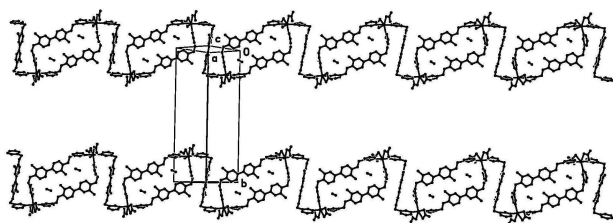
Figure 2. Packing diagram of polymer **1**.

generally known to be constructed on the basis of seven structural motifs: (a) a linear chain, (b) a zigzag chain, (c) a double chain, (d) a helix, (e) a fish-bone, (f) a ladder, and (g) a railroad. 1-D double-chain polymers of them, whose structure is closely related to that of polymer **1**, are typically observed for those containing flexible or angular linking ligands.[8] Some representative examples are $\{[Ni(L^a)_2(H_2O)_2]·(NO_3)_2·(L^a)·(H_2O)\}_\infty$,[40] $\{[Cd(NO_3)_2(L^b)_2(dmf)_2]·(dmf)_2\}_\infty$,[41] and $\{[Cd(L^c)(tert\text{-butylben-zene})]·(NO_3)_2\}_\infty$[42] ($L^a$-$L^c$ in Chart 2). In these polymers, the repeating units are metallacycles (loops); that is, two ligands bridge two closest metal atoms in the chains. The loops are linked by corner-sharing to form a 1-D double chain. In contrast, the loops in polymer **1** are linked by third ligands. Consequently, the structure of polymer **1** is a modified 1-D double chain. It is worth noting that the structure of the coordination polymer $[Zn(L1)(No_3)_2]_\infty$, in which **L1** is the parent species of ligand **L**, has a 1-D mono-chain.[28] Structures of polymers **1** and $[Zn(L1)(No_3)_2]_\infty$ indicate that the reduction of a diimine-based ligand may induce a large topological variation even though the linking donor groups remain unchanged.

Chart 2
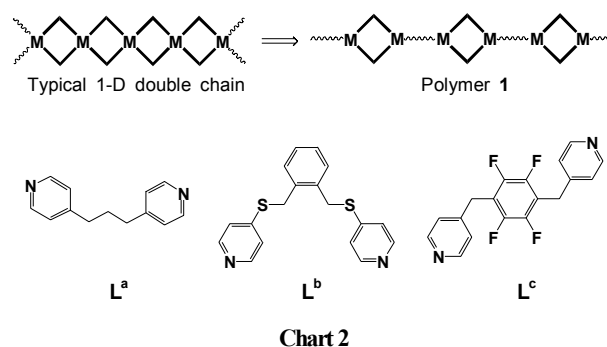
The local coordination environment of the 7-coordinate Cd^{2+} ion in polymer **2** is shown in Figure 3. Like polymer **1**, polymer **2** has an asymmetric unit consisting of one Cd^{2+} ion, one two nitrato ligands, and one and half ligands. The Cd metal is coordinated by three N atoms of three **L** ligands and four O atoms of two η^2-nitrato ligands. The only practical difference in structures between polymers **1** and **2** is the coordination mode of the nitrato ligands. Whereas polymer **1** has one η^1- and one η^2-nitrato ligands, polymer **2** has two η^2-nitrato ligands.

The projection of polymer **2** demonstrates a 1-D structure (Figure 4), in which a repeating unit is also a loop consisting of two Cd^{2+} ions and two ligands and contains two methanol guest molecules. The N1···N4 separation is 16.792(3) Å, and N5···N5A (−x + 2, −y, −z + 2) is 13.610(5) Å. There are two distinct Cd···Cd separations (19.297(1) and 15.061(1) Å). A wide variety of coordination networks have been prepared from metal nitrates and dipyridyl ligands, in which the dipyridyl ligands are grouped into three classes: bis (dipyridyl) (A), tris (dipyridyl) (B), and tetrakis (dipyridyl) (C).[5] The dipyridyl-
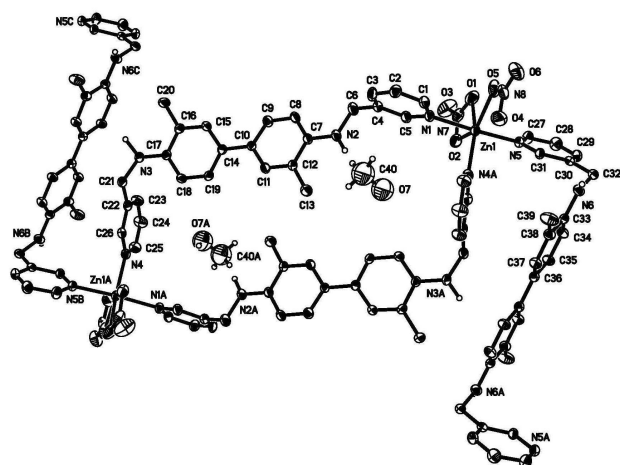
Figure 3. Local coordination environment around Cd in polymer **2**, with 30% probability thermal ellipsoids.. Selected bond lengths (Å) and angles (°): Cd1-N5 2.293(2), Cd1-N1 2.320(2), Cd1-N4#1 2.338 (2), Cd1-O2 2.364 (2), Cd1-O5 2.446 (2), Cd1-O4 2.488 (2), Cd1-O1 2.551 (2), N2-C7 1.376 (3), N2-C6 1.433 (4), N3-C17 1.390 (3), N3-C21 1.452 (4), N6-C33 1.369 (4), N6-C32 1.440 (4), N5-Cd1-N1 176.96 (8), N5-Cd1-N4#1 90.10 (8), N1-Cd1-N4#1 92.55 (8). Symmetry transformations used to generate equivalent atoms: #1 = –x, –y, –z + 1.

Figure 4. Packing diagram of a 1-D polymer **2**.

type ligands (**L**) in polymers **1** and **2** combine with the metal to form the so-called ''T-joint'' units of [M**L**$_3$(NO$_3$)$_2$] (M = Zn or Cd), and therefore their structural motif belongs to the class B.

In summary, a long, flexible dipyridyl-type linking ligand, {(3-py)-CH$_2$-NH-(CH$_3$)C$_6$H$_3$-C$_6$H$_3$(CH$_3$)-NH-CH$_2$-(3-py), **L**}, was prepared by reducing its parent diimine species. Treating ligand **L** with M(NO$_3$)$_2$·6H$_2$O produced a 1-D double-chain polymer [M**L**$_{1.5}$(NO$_3$)$_2$]$_\infty$ {M = Zn (**1**) or Cd (**2**)}. Both polymers have two distinct **L** ligands; one participates in the loop (M$_2$**L**$_2$) formation, and the other links the loops to complete a 1-D polymer. Reduction of other diimine ligands is under investigation.

References

1. Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629.
2. Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *319*, 34.
3. Janiak, C. *Dalton Trans.* **2003**, 2781.
4. Kesanli, B.; Lin, W. *Coord. Chem. Rev.* **2003**, *246*, 305.
5. Barnett, S. A.; Champness, N. R. *Coord. Chem. Rev.* **2003**, *246*, 145.
6. Rowsell, J. L. C.; Yaghi, O. M. *Micropor. Mesopor. Mater.* **2004**, *73*, 3.
7. Ockwig, N. W.; Friedrichs, O. D.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2005**, *38*, 176.
8. Robin, A. Y.; Fromm, K. M. *Coord. Chem. Rev.* **2006**, *250*, 2127.
9. Vittal, J. J. *Coord. Chem. Rev.* **2007**, *251*, 1781.
10. Kitagawa, S.; Matsuda, R. *Coord. Chem. Rev.* **2007**, *251*, 2490.
11. Li, K.; Olson, D. H.; Lee, J. Y.; Bi, W.; Wu, K.; Yuen, T.; Li, J. *Adv. Funct. Mater.* **2008**, *18*, 2205.
12. Fries, V. A.; Kurth, D. G. *Coord. Chem. Rev.* **2008**, *252*, 199.
13. Suh, M. P.; Cheon, Y. E.; Lee, E. Y. *Coord. Chem. Rev.* **2008**, *252*, 1007.
14. O'Keeffe, M.; Peskov, M. A.; Ramsden, S. J.; Yaghi, O. M. *Acc. Chem. Res.* **2008**, *41*, 1782.
15. Batten, S. R.; Neville, S. M.; Turner, D. R. *Coordination Polymers*: *Design, Analysis and Application*; The Royal Society of Chemistry: Cambridge, 2009.
16. Chen, C.-L.; Zhang, J.-Y.; Su, C.-Y. *Eur. J. Inorg. Chem.* **2007**, 2997.
17. Li, X.-J.; Cao, R.; Bi, W.-H.; Wang, Y.-Q.; Wang, Y.-L.; Li. X. *Polyheron* **2005**, *24*, 2955.
18. Zhu, H.-F.; Kong, L.-Y.; Okamura, T.-A.; Fan, J.; Sun, W.-Y.; Ueyama, N. *Eur. J. Inorg. Chem.* **2004**, 1465.
19. Quyang, X.-M.; Fei, B.-L.; Okamura, T.-A.; Bu, H.-W.; Sun, W.-Y.; Tang, W.-X.; Ueyama, N. *Eur. J. Inorg. Chem.* **2003**, 618.
20. Zaman, M. B.; Smith, M. D.; Curtin, D. M.; zur Loye, H.-C. *Inorg. Chem.* **2002**, *41*, 4895.
21. Bosch, E.; Barnes, C. L. *New J. Chem.* **2001**, *25*, 1376.
22. Dong, Y.-B.; Smith, M. D.; Layland, R. C.; zur Loye, H.-C. *Chem. Mater.* **2000**, *12*, 1156.
23. Dong, Y.-B.; Smith, M. D.; zur Loye, H.-C. *Inorg. Chem.* **2000**, *39*, 4927.
24. Dong, Y.-B.; Smith, M. D.; zur Loye, H.-C. *J. Solid State Chem.* **2000**, *155*, 143.
25. Withersby, M. A.; Blake, A. L.; Champness, N. R.; Cooke, P. A.; Hubbersty, P.; Li, W.-S.; Schröder, M. *Inorg. Chem.* **1999**, *38*, 2259.
26. Kim, H. N.; Lee, H. K.; Lee, S. W. *Bull. Korean Chem. Soc.* **2005**, *26*, 892.
27. Min, D.; Cho, Y.-B.; Lee, S. W. *Inorg. Chim. Acta* **2006**, *359*, 577.
28. Cho, Y.-B.; Min, D.; Lee, S. W. *Cryst. Growth Des.* **2006**, *6*, 342.
29. Kim, S. H.; Huh, H. S.; Lee, S. W. *J. Mol. Struct.* **2007**, *841*, 78.
30. Huh, H. S.; Lee, S. W. *Inorg. Chem. Commun.* **2007**, *10*, 1244.
31. Lee, H. K.; Lee, S. W. *Bull. Korean Chem. Soc.* **2007**, *28*, 421.
32. Kim, S. H.; Lee, S. W. *Inorg. Chim. Acta* **2008**, *361*, 137.
33. Huh, H. S.; Kim, S. H.; Yun, S. Y.; Lee, S. W. *Polyhedron* **2008**, *27*, 1229.
34. Huh, H. S.; Yun, S. Y.; Lee, S. W. *Bull. Korean Chem. Soc.* **2008**, *29*, 1065.
35. Huh, H. S.; Yun, H. J.; Lee, S. W. *Inorg. Chim. Acta* **2008**, *361*, 2101.
36. Min, D.; Huh, H. S.; Lee, S. W. *Polyhedron* **2008**, *27*, 2083.
37. Yun, H. J.; Lim, S. H.; Lee, S. W. *Polyhedron* **2009**, *28*, 614.
38. Sheldrick, G. M. *SADABS*; Program for Absorption Correction: University of Göttingen, 1996.
39. Bruker, *SHELXTL*; Structure Determination Software Programs; Bruker Analytical X-ray Instruments Inc.: Madison, Wisconsin, USA, 1997.
40. Sharma, C. V. K.; Diaz, R. J.; Hessheimer, A. J.; Clearfield, A. *Cryst. Eng.* **2000**, *3*, 201.
41. Wang, R.; Hong, M.; Weng, J.; Su, W.; Cao, R. *Inorg. Chem. Commun.* **2000**, *3*, 486.
42. Kasai, K.; Aoyagi, M.; Fujita, M. *J. Am. Chem. Soc.* **2000**, *122*, 2140.