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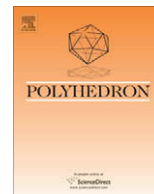


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Keen competition between electrostatic and argentophilic interactions in the formation and behavior of molecular rings

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ABSTRACT

The macrocyclic structures and behavior on the reaction of AgX ($\text{X} = \text{NO}_3$ and CF_3SO_3) with bis(nicotinoyl)-4,4'-(9-fluorenylidene)diphenolates (**L**) have been carried out. Discrete oblong rings and linked rings were constructed via the keen competition between the inter-ring argentophilic ($\text{Ag}\cdots\text{Ag}$) interaction and the electrostatic interaction between $\text{Ag}(\text{I})$ and its anion, and the interconversion of the two species was attempted by means of anion exchange.

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1. Introduction

Construction of metallo-organic macrocyclic architectures is based on a suitable balance of the electronic and geometric requirements of metal and organic tectonics [1–6]. Weak interactions such as van der Waals, MM bonds, electrostatic interaction, hydrogen-bonds, and π – π interaction play significant roles in the modulation of supramolecular construction [7–12]. The role of (counter)anions in the rational formation of molecular frameworks is a rapidly emerging field owing to recent interest from the perspectives of environmental pollution, industrial chemicals, biological processes, ionic liquids, catalysis, lithium batteries, and public health [13–16]. More recent developments include exciting advances in anion template assembly and ion-pair recognition as well as significant solvent effects, pH dependence, and the function of anions in architecture chemistry [13,14,17–19]. Direct competition between weak closed-shell MM interactions and electrostatic interaction is rare in the rational formation of molecular frameworks. Nonetheless, we here report a discrete ring and linked ring consisting of two $\text{Ag}(\text{I})$ ions with two bis(nicotinoyl)-4,4'-(9-fluorenylidene)diphenolates (**L**) as a hemi-ring tecton [20] via direct competition between electrophilic interaction between silver(I) cation and anion and closed-shell d^{10} argentophilic interactions [5,21–26].

2. Experimental

2.1. Materials and measurements

All commercial reagents including silver(I) nitrate and silver(I) trifluoromethanesulfonate were purchased from Aldrich and used without further purification. Bis(nicotinoyl)-4,4'-(9-fluorenylidene)diphenolates (**L**) was prepared according to the procedures outlined in the literature [20]. Infrared spectra were obtained on a Nicolet 380 FT-IR spectrophotometer, and samples were prepared as KBr pellets. Elemental analyses were performed on crystalline samples using a Vario-EL III at Pusan center, KBSI. Thermal analyses were carried out under a dinitrogen atmosphere at a scan rate of 10 °C/min using a Labsys TGA-DSC 1600.

2.2. Synthesis of $[\text{Ag}(\text{NO}_3)(\text{L})_2]$ (**1**)

A dichloromethane solution (10 mL) of **L** (0.1 mmol, 0.056 g) was slowly diffused into an ethanol solution (10 mL) of AgNO_3 (0.1 mmol, 0.017 g). After two weeks, colorless crystals were obtained in a 70% yield (0.057 g) based on $\text{Ag}(\text{I})$ salt. m.p. 215 °C (dec). *Anal.* Calc. for $\text{C}_{76}\text{H}_{52}\text{N}_6\text{O}_{14}\text{Cl}_4\text{Ag}_2$ (**1**·2 CH_2Cl_2): C, 55.97; H, 3.21; N, 5.15. Found: C, 56.10; H, 3.30; N, 5.09%. IR (cm^{-1}): 3461, 3064, 1740 (s, CO), 1597, 1502, 1385 (s, NO_3), 1279, 1200, 1169, 1093, 1016, 752, 735, 694.

2.3. Synthesis of $[\text{Ag}(\text{L})]_2(\text{CF}_3\text{SO}_3)_2$ (**2**)

A chloroform solution (10 mL) of **L** (0.1 mmol, 0.056 g) was slowly diffused into an ethanol solution (10 mL) of AgCF_3SO_3

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(0.1 mmol, 0.026 g). After one week, colorless crystals were obtained in a 78% yield (0.082 g) based on Ag(I) salt. m.p. 355 °C (dec). Anal. Calc. for $C_{80}H_{52}N_4O_{14}F_6S_2Cl_{12}Ag_2$ ($2 \cdot 4CHCl_3$): C, 45.48; H, 2.48; N, 2.65. Found: C, 45.20; H, 2.40; N, 2.45%. IR (cm^{-1}): 3487, 3022, 1741 (s, CO), 1601, 1502, 1279 (s, CF_3SO_3), 1248, 1201, 1169, 1095, 1026, 752, 735, 636 (m, CF_3SO_3).

2.4. Anion exchange of **1** with $NaCF_3SO_3$

An aqueous solution (3 mL) of $NaCF_3SO_3$ (0.3 mmol, 52 mg) was added to a suspension of microcrystalline **1** (0.06 mmol, 44 mg) in water (3 mL) at room temperature. The reaction mixture was stirred for 3 days, and was monitored with reference to the IR spectra. Anion exchanges of **2** with $NaNO_3$ and $NaPF_6$, respectively, were performed for 10 days by the same method as for the above reaction.

2.5. Crystal structure determination

X-ray data were collected on a Bruker SMART automatic diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) and a CCD detector at ambient temperature. Forty five frames of two dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. The data were corrected for the Lorentz and polarization effects. The absorption effects were corrected using the empirical ψ -scan method. The structures were solved using the direct method (SHELXS 97) and refined using the full-matrix least squares techniques (SHELXL 97) [27]. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed in calculated positions and refined only for the isotropic thermal factors. The crystal parameters and procedural information corresponding to the data collection and structure refinement are listed in Table 1.

3. Results and discussion

3.1. Synthesis and properties of silver(I) metallacyclic complexes

Self-assembly of AgX ($X = NO_3$ and CF_3SO_3) with **L** affords colorless crystals of $[Ag(NO_3)(L)]_2$ (**1**) and $[Ag(L)]_{2n}(CF_3SO_3)_{2n}$ (**2**), respectively, as shown in Scheme 1. The reactions were originally

Table 1
Crystal data and structure refinements for $[Ag(NO_3)(L)]_2 \cdot 2CH_2Cl_2$ (**1**) and $[Ag(L)]_{2n}(CF_3SO_3)_{2n} \cdot 4CHCl_3$ (**2**).

	1	2
Formula weight	1630.78	2112.52
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
<i>a</i> (Å)	10.492(4)	11.688(1)
<i>b</i> (Å)	11.635(4)	13.935(1)
<i>c</i> (Å)	28.403(1)	14.711(1)
α (°)	90	82.98(2)
β (°)	100.36(1)	69.00(2)
γ (°)	90	69.80(2)
Volume (Å ³)	3410.6(2)	2097.8(4)
<i>Z</i>	2	1
ρ_{calc} (g/cm ³)	1.588	1.672
μ (mm ⁻¹)	0.804	0.978
<i>F</i> (0 0 0)	1648	1056
θ Range for data collection (°)	1.90–28.33	1.97–28.32
Reflections collected	21 377	13 514
Independent reflections	8018 [$R_{int} = 0.0401$]	9419 [$R_{int} = 0.0660$]
Data/restraints/parameters	8018/3/469	9419/0/541
Goodness-of-fit (GOF) on F^2	1.021	1.040
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0563$ $wR_2 = 0.1220$	$R_1 = 0.0775$ $wR_2 = 0.1490$
<i>R</i> indices (all data)	$R_1 = 0.1025$ $wR_2 = 0.1456$	$R_1 = 0.1513$ $wR_2 = 0.1786$

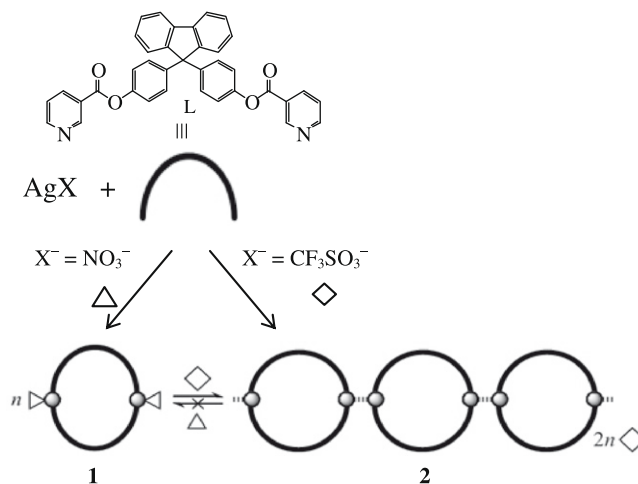
carried out at the 1:1 mole ratio, but the same products were obtained irrespective of the mole ratios. That is, the formation of the products is not significantly affected by the change of the reactant mole ratio or concentration, indicating that the products are thermodynamically favorable species. The crystals are air-stable and insoluble in common organic solvents. However, the crystalline solids are dissociated in acetonitrile and dimethyl sulfoxide (see Appendix: the ¹H NMR spectra in the solvents show the signals of the free ligand **L**), and are slowly turned to gray powder under light. Their elemental analyses and IR spectra are consistent with the expected structures.

3.2. Crystal structure description

The single crystal structures of **1** and **2** are depicted in Fig. 1, and relevant bond lengths and angles are listed in Table 2. Each **L** connects two Ag(I) ions ($AgN = 2.270(4)$, $2.276(4)$ Å for **1**; $2.166(5)$ Å for **2**) to yield a 40-membered metallacyclodimeric skeleton. The diameter of the dimeric ring is 14.187 Å ($Ag \cdots Ag \times 17.235$ Å ($C \cdots C$) for **1** and 15.471 Å ($Ag \cdots Ag \times 15.643$ Å ($C \cdots C$) for **2**). For **2**, the weak coordinating CF_3SO_3 anion [15,28] acts as a simple counteranion around the silver ion (shortest $Ag \cdots O = 2.614$ Å), thus instead, the inter-ring argentophilic $Ag \cdots Ag$ interaction ($3.061(1)$ Å) is seen. This argentophilic interaction occurs in an unusual phased style that is much stronger than that of the known $[Ag_3(NO_3)_3(Py_2S)_2] \cdot 2H_2O$ ($3.436(2)$ Å) [25]. By contrast, for **1**, the coordinating NO_3 anion [15,28] acts as a ligand ($Ag \cdots O = 2.402(5)$ Å) rather than a counteranion, affording a discrete molecular ring without the argentophilic interaction ($Ag(I) \cdots Ag(I) = 4.713$ Å). The $N-Ag-N$ angle ($122.24(1)^\circ$) of **1** supports the presence of the $Ag \cdots O_3N$ bond. The bent corresponding angle ($166.58(6)^\circ$) of **2** can be attributed to the presence of the argentophilic interaction. The most striking feature is that the final structure is determined by the competition between an $Ag \cdots Ag$ interaction and an $Ag \cdots X$ electrostatic interaction. These anion effects are consistent with the Hoffmeister series [29], and the metallophilic electrostatic interaction is comparable to the argentophilic interaction. Thus, the cyclodimer of the discrete **1** is an oblong ring, whereas that of the linked **2** is an elegant ring. The structural difference between **1** and **2** ascribes to different anions rather than different solvents ($CHCl_3$ and CH_2Cl_2).

3.3. Anion exchange

For the cationic ring system, an attempt was made to use the anion exchange [30] to reversibly tune interconversion of the



Scheme 1. Overall reaction procedure.

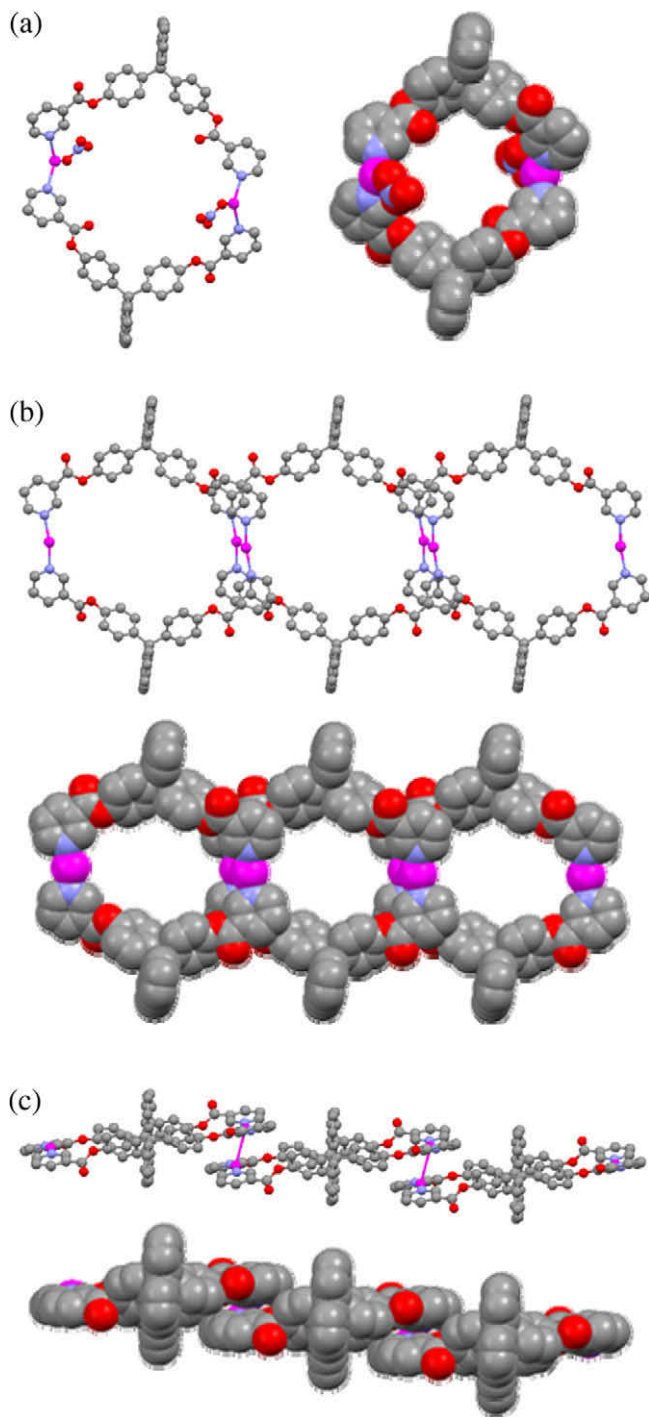


Fig. 1. Ball-and-stick and space-filling drawings of **1** (a) and **2** (b, top view; c, side view).

Table 2

Relevant bond lengths (Å) and bond angles (°) of $[\text{Ag}(\text{NO}_3)(\text{L})]_2$ (**1**) and $[\text{Ag}(\text{L})]_{2n}(\text{CF}_3\text{SO}_3)_{2n}$ (**2**).

	1	2
Ag–N	2.270(4)	2.166(5)
Ag...X	2.276(4)	
Ag...Ag	2.402(5)	3.061(1)
N–Ag–N	122.24(1)	166.58(2)
N–Ag...X	115.08(2)	
	122.49(2)	

discrete oblong ring with the linked ring. The initial evaluation revealed that the anion exchange of **1** with CF_3SO_3 smoothly occurs (Fig. 2). The reverse exchange was not easily achieved under the same conditions (see Appendix). Even though the CF_3SO_3 anion generally has been known to be a weak coordinating anion, the lack of anion exchange of **2** with NO_3 suggests that the $\text{Ag}\cdots\text{Ag}$ interaction is stronger than the $\text{Ag}\cdots\text{X}$ electrostatic interaction. Furthermore, another important factor in anion exchange is the water-solubility of the starting materials. That is, **2** is hardly soluble in water, but **1** is marginally soluble in water. The conductivity measurements in a saturated aqueous solution ($30.0\ \mu\text{S cm}^{-1}$ for $[\text{Ag}(\text{NO}_3)(\text{L})]_2$; $9.5\ \mu\text{S cm}^{-1}$ for $[\text{Ag}(\text{L})]_{2n}(\text{CF}_3\text{SO}_3)_{2n}$; $5.8\ \mu\text{S cm}^{-1}$ for distilled water) explain such a solubility difference. The smooth anion exchange of **1** with CF_3SO_3 seems to be partly attributable to the solubility of **1**. The anion exchange was monitored by the characteristic bending band of CF_3SO_3 ($636\ \text{cm}^{-1}$) because the CF_3SO_3 stretching band at $1279\ \text{cm}^{-1}$ was nearly overlapped with that of L. The infrared spectra showed the gradual disappearance of the intense band of NO_3 ($1385\ \text{cm}^{-1}$) and the appearance of a new CF_3SO_3 band ($636\ \text{cm}^{-1}$), implying that the NO_3 anions are completely exchanged with the CF_3SO_3 anions after 3 days (Fig. 2). The other peaks of the spectrum remained virtually unchanged, suggesting the preservation of the skeletal structure during the anion exchange. The elemental analysis and IR spectrum of the anion-exchanged species were proved to be consistent with those of the original product, indicating that the discrete cyclodimers are easily converted into the linked ring via anion exchange. However, there is not concrete evidence that the anion exchanges species has the exact linked ring structure. Furthermore, the anion exchange of **2** with PF_6 progresses up to 50% for 3 days (see Appendix). Of course, in this case, the linked ring seemed to be maintained along with the argentophilic interaction. Thus, the induction and modulation of such metal–metal interactions can be controlled by the metalphilicity of anions.

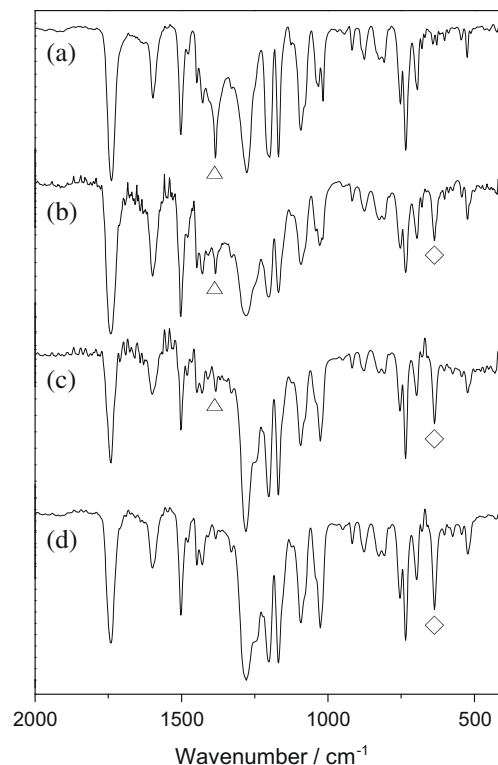


Fig. 2. IR spectra during the anion exchange of **1** with NaCF_3SO_3 after 0 h (a), 3 h (b), 1 day (c), and 3 days (d). The triangle and rhombus denote the NO_3 and CF_3SO_3 bands, respectively.

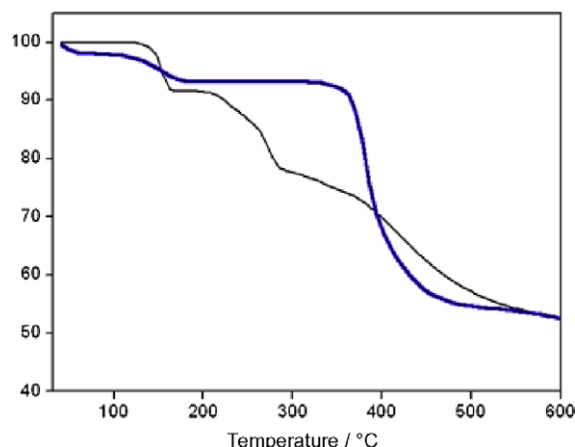


Fig. 3. TGA curves of **1** (thick) and **2** (thin).

3.4. Thermogravimetric studies

The thermogravimetric analysis (TGA) of **1** showed two drastic decompositions below 300 °C, in the ranges of 126–150 and 215–290 °C, as depicted in Fig. 3. The decomposition in the 126–150 °C range was consistent with the evaporation of solvate dichloromethane molecules (Calcd.: 10.42%, Found: 9.70%). The solvated molecules evaporate in high-temperature ranges, presumably owing to the weak interactions between Ag(I) and dichloromethane molecules (the shortest distance of Ag...Cl = 3.11 Å). The other decomposition can be attributed to the collapse of the cyclodimeric skeleton, including anions. The solvate chloroform molecules of **2** evaporated in two steps in the range of 30–170 °C (Calcd.: 22.63%). The first weight-loss is rare, owing to the easy evaporation of free solvate molecules during preparation of a sample. The two steps can be explained by the two kinds of solvate molecules, that is, the presence of both chloroform molecules around Ag(I) (the shortest distance of Ag...Cl = 3.36 Å) and free chloroform molecules in the crystal structure. The basic structure of **2** is stable up to 355 °C, indicating that **2** is thermally more stable than **1**. Of course, the decomposition temperature of the anion-exchanged product was consistent with that of the original product (see Appendix).

4. Conclusions

In conclusion, the formation of molecular rings is induced mainly by the ligand shape, and modulation of the dimensions is controlled by keen competition between the inter-ring argentophilic interaction and the electrostatic interaction between Ag(I) and its anion. The more metallophilic NO₃ anion prefers to form the discrete ring, whereas the less metallophilic CF₃SO₃ anion prefers to form the linked ring. The anion exchanges could be carried out in an aqueous solution without destruction of the skeleton. The ring framework could contribute to the development of new conceptual cyclic molecules or host–guest sensors for small organic molecules.

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Appendix A. Supplementary data

CCDC 738567 and 738568 contain the supplementary crystallographic data for **1** and **2**. 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. ¹H NMR spectra of **1**, **1**, and **2** in CD₃CN. Asymmetric structure units of **1** and **2**. IR spectral change during anion exchange of **2** with NaPF₆. TGA curve of product via anion exchange of **1** with NaCF₃SO₃. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2009.11.005.

References

- [1] P. Thanasekaran, R.T. Liao, Y.-H. Liu, T. Rajendran, S. Rajagopal, K.-L. Lu, *Coord. Chem. Rev.* 249 (2005) 1085.
- [2] B. Olenyuk, A. Fechtenkötter, P.J. Stang, *Dalton Trans.* (1998) 1707.
- [3] S.-S. Sun, C.L. Stern, S.T. Nguyen, J.T. Hupp, *J. Am. Chem. Soc.* 126 (2004) 6314.
- [4] O.-S. Jung, Y.-A. Lee, Y.J. Kim, J. Hong, *Cryst. Growth Des.* 2 (2002) 497.
- [5] O.-S. Jung, Y.J. Kim, Y.-A. Lee, S.W. Kang, S.N. Choi, *Cryst. Growth Des.* 4 (2004) 23.
- [6] H.J. Kang, T.H. Noh, J.S. Jin, O.-S. Jung, *Inorg. Chem.* 47 (2008) 5528.
- [7] C. Janiak, *Dalton Trans.* (2000) 3885.
- [8] S. Kitagawa, M. Kondo, *Bull. Chem. Soc. Jpn.* 71 (1998) 1739.
- [9] H. Gudbjartson, K. Biradha, K.M. Poirier, M.J. Zaworotko, *J. Am. Chem. Soc.* 121 (1999) 2599.
- [10] S.S.-Y. Chui, S.M.-F. Lo, J.P.H. Charmant, A.G. Orpen, I.D. Williams, *Science* 283 (1999) 1148.
- [11] L.P. Prins, D.N. Reinhoudt, P. Timmermann, *Angew. Chem. Int. Ed.* 40 (2001) 2382.
- [12] T. Steiner, *Angew. Chem. Int. Ed.* 41 (2002) 48.
- [13] P.A. Gale, *Coord. Chem. Rev.* 213 (2001) 79.
- [14] P.D. Beer, D.K. Smith, *Prog. Inorg. Chem.* 46 (1997) 1.
- [15] O.-S. Jung, Y.J. Kim, Y.-A. Lee, K.-M. Park, S.S. Lee, *Inorg. Chem.* 42 (2003) 844.
- [16] C.A. Reed, *Acc. Chem. Res.* 31 (1998) 133.
- [17] C.S. Campos-Fernandez, R. Clerac, K.R. Dunbar, *Angew. Chem. Int. Ed.* 38 (1999) 3477.
- [18] B. Turner, A. Shterenberg, M. Kapon, K. Suwinska, Y. Eichen, *Chem. Commun.* (2001) 13.
- [19] C.V.K. Sharma, S.T. Griffin, R.D. Rogers, *Chem. Commun.* (1998) 215.
- [20] A. Jouaiti, N. Kyritsakas, J.-M. Planeix, M.W. Hosseini, *CrystEngComm* 8 (2006) 883.
- [21] M. Jansen, *Angew. Chem., Int. Ed. Engl.* 26 (1987) 1098.
- [22] P. Pykkö, *Chem. Rev.* 97 (1997) 597.
- [23] K.S. Singh, J.R. Long, P. Stavropoulos, *J. Am. Chem. Soc.* 119 (1997) 2942.
- [24] M.-L. Tong, X.-M. Chen, B.-H. Ye, L.N. Ji, *Angew. Chem. Int. Ed.* 38 (1999) 2237.
- [25] O.-S. Jung, S.H. Park, C.H. Park, J.K. Park, *Chem. Lett.* (1999) 923.
- [26] Q.-M. Wang, T.C. Mak, *J. Am. Chem. Soc.* 123 (2001) 7594.
- [27] G.M. Sheldrick, *SHELXS-97: A Program for Structure Determination*, University of Göttingen, Germany, 1997; G.M. Sheldrick, *SHELXL-97: A Program for Structure Refinement*, University of Göttingen, Germany, 1997.
- [28] J.W. Lee, E.A. Kim, Y.J. Kim, Y.-A. Lee, Y. Pak, O.-S. Jung, *Inorg. Chem.* 44 (2005) 3151.
- [29] S. Mason, T. Clifford, L. Seib, K. Kuczera, K. Bowman-James, *J. Am. Chem. Soc.* 120 (1998) 8899.
- [30] O.-S. Jung, Y.J. Kim, Y.-A. Lee, J.K. Park, H.K. Chae, *J. Am. Chem. Soc.* 122 (2000) 9921.