Sandwich-shaped silver(I) metallomacrocycles encapsulating a XF_6^{2-} (X = Si, Ge and Sn) anion

Masahiko Maekawa,*[a] Susumu Kitagawa,*[b] Takayoshi Kuroda-Sowa[c] and Megumu Munakata[c]

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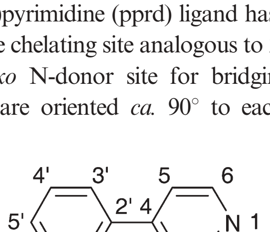
A series of sandwich-shaped complexes based on two square tetranuclear Ag(I) metallomacrocycles, $\{[Ag_4(pprd)_4]_2(XF_6)\}(BF_4)_6\cdot 8MeNO_2$ (pprd = 4-(2-pyridyl)pyrimidine; X = Si, Ge and Sn), in which a XF_6^{2-} anion is encapsulated, were prepared and their structures were characterized both in the solid state and solution.

In the last decade there has been a significant development in the preparation of inorganic and organometallic macrocycles and cages which have shown particular promise in the supramolecular chemistry of host–guest interaction.[1] One of the most successful approaches for metal-driven self-assembled supramolecules involves chemical templates. Templating agents usually make use of non-covalent interactions such as electrostatic forces, hydrogen bonding, π–π interactions and hydrophobic effects to pre-arrange the building blocks into a suitable geometry. Very recently, a new approach utilizing anion templation to construct macrocycles has been achieved in several instances.[2] However, in contrast to the well studied templating properties of cationic and neutral species,[3] anion templation is still in its infancy. In particular, less is known about the encapsulation of a divalent anion into macrocycles, although there have been several reports of the encapsulation of NO_3^-,[4] BF_4^-,[5] PF_6^-,[4a,4b,6] Cl^-[7] and I_2^{2-}[8] anions. It is of interest to understand the role of anions in self-assembly processes. Herein, we report the first examples of the encapsulation of a divalent XF_6^{2-} (X = Si, Ge and Sn) anion into metallomacrocycles, in which the XF_6^{2-} anion directed the self-assembly of two Ag metallomacrocycles in the sandwich-shaped structure.

The 4-(2-pyridyl)pyrimidine (pprd) ligand has two coordination sites; one is a simple chelating site analogous to 2,2′-bipyridine and the other is an *exo* N-donor site for bridging. Since the two coordination sites are oriented *ca.* 90° to each other, the pprd ligand is expected to produce both finite metallomacrocyclic compounds and infinite polymeric compounds. Indeed, several Ag(I) complexes of pprd have recently been synthesized, ranging from a square tetranuclear $[Ag_4(pprd)_4](BF_4)_4$ (**1**)† to a rectangular tetranuclear $[Ag_4(pprd)_4](CF_3SO_3)_4$ complex and a 1D helical infinite polymer $\{[Ag(pprd)(NO_3)]\}_n$.[9]



4-(2-pyridyl)pyrimidine
(pprd)

When we reacted $AgBF_4$ with pprd in $MeNO_2$ under C_2H_4, a new Ag pprd complex $\{[Ag_4(pprd)_4]_2(SiF_6)\}(BF_4)_6\cdot 8MeNO_2$ (**2a**) was preferentially produced.† The X-ray crystallographic analysis showed that there are two $[Ag_4(pprd)_4]^{4+}$ cation moieties, six BF_4^- anions, one SiF_6^{2-} anion and eight solvated $MeNO_2$ molecules in a unit cell.‡ As shown in Fig. 1, four Ag atoms are joined by the four pprd ligands in a head-to-tail fashion to afford a square $[Ag_4(pprd)_4]^{4+}$ metallomacrocycle, with dimensions of 6.24 and 6.22 Å for the Ag(1)···Ag(2) and Ag(1)···Ag(4) distances, respectively. It is to be noted that the SiF_6^{2-} anion is encapsulated

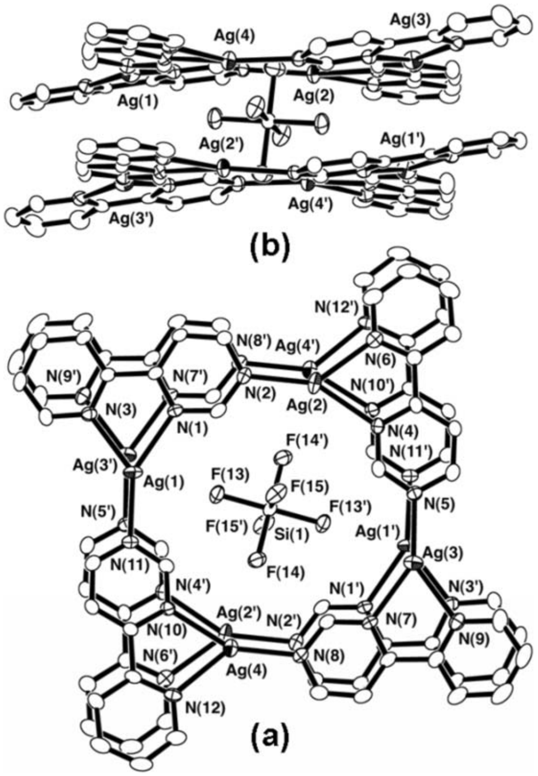


Fig. 1 (a) Top view and (b) side view of $\{[Ag_4(pprd)_4]_2(SiF_6)\}(BF_4)_6\cdot 8MeNO_2$ (**2a**). The six BF_4^- anions and the eight solvated $MeNO_2$ molecules are omitted for clarity. Displacement ellipsoids are shown at the 50% probability level.

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[a] *Research Institute for Science and Technology, Kinki University, Kowakae, Higashi-Osaka, Osaka 577-8502, Japan. E-mail: maekawa@rist.kindai.ac.jp*
[b] *Department of Synthetic Chemistry and Biological Chemistry, Kyoto University, Katsura Campus, Sakyo-ku, Kyoto 615-8510, Japan. E-mail: kitagawa@sbchem.kyoto-u.ac.jp*
[c] *Department of Chemistry, Kinki University, Kowakae, Higashi-Osaka, Osaka 577-8502, Japan*

in the central vacant space between the two $[Ag_4(pprd)_4]^{4+}$ metallomacrocycles, resulting in the formation of a sandwich-shaped structure. This feature is different from that of complex **1**. The parallel $[Ag_4(pprd)_4]^{4+}$ plates are located close to each other, with close separations of 3.42 and 3.33 Å for the Ag(1)···Ag(3′) and Ag(2)···Ag(4′) distances, respectively. In the encapsulated SiF_6^{2-} anion, the F atom is close to the H atom at the 2-position of the pyrimidine ring with a C(1)···F(15) distance of 3.12 Å, indicative of a H···F hydrogen bond interaction. This fact indicates that the sandwich-shaped structure is stabilized by two H···F hydrogen bond interactions in addition to the electrostatic interaction with the divalent anion, which stabilizes the dimerization of the cationic metallomacrocycles better than univalent anions. To the best of our knowledge, complex **2a** is the first example of the encapsulation of a divalent SiF_6^{2-} anion in metallomacrocycles, in contrast to only one example of an organic anion complex capturing a SiF_6^{2-} anion *via* N–H···F hydrogen bonding in a double helix structure.[10] It is interesting to know the source of SiF_6^{2-} anion in the preparative process, and presumably a SiF_6^{2-} anion could be introduced by the reaction of a BF_4^- anion and SiO_2 component from a glass-made reactor and tube.[10,11]

Attempts to prepare Ag–pprd–XF_6 complexes by the reaction of $AgBF_4$, pprd and $(NH_4)_2XF_6$ salts (X = Si, Ge and Sn) in $MeNO_2$ have been carried out using PFA-*made* beakers and test tubes to avoid the contamination of SiF_6^{2-} anions from glass-made vessels.† A series of $\{[Ag_4(pprd)_4]_2(XF_6)\}(BF_4)_6{\cdot}8MeNO_2$ (X = Si (**2b**), Ge (**3**) and Sn (**4**)) complexes were synthesized and structurally characterized.‡ The structure of complex **2b** is identical to that of complex **2a**. Complexes **3** and **4** are isomorphous to complex **2a**, where a GeF_6^{2-} or SnF_6^{2-} anion is encapsulated between the two square tetranuclear $[Ag_4(pprd)_4]^{4+}$ metallomacrocycles. These facts indicate that the XF_6^{2-} anion plays an important role in the anion-directed self-assembly of $[Ag_4(pprd)_4]^{4+}$ metallomacrocycles to produce the sandwich-shaped structure. In complexes **3** and **4**, the intramolecular Ag(1)···Ag(2) and Ag(1)···Ag(4) distances of *ca.* 6.2 Å are similar to those of complex **2a**, whereas the intermolecular Ag(1)···Ag(3′) and Ag(2)···Ag(4′) distances are 3.46 and 3.36 Å, and 3.55 and 3.45 Å for complexes **3** and **4**, respectively. The parallel separation between two $[Ag_4(pprd)_4]^{4+}$ cation moieties is slightly longer in the order **2a** (**2b**) < **3** < **4**. The encapsulated XF_6^{2-} (X = Ge and Sn) anions similarly form a H···F hydrogen bond interaction to the H atoms of the pyrimidine ring, with C(1)···F(15) distances of 3.12 and 3.10 Å for complexes **3** and **4**, respectively.

We investigated the structures of complexes **2b**, **3** and **4** in solution by ^1H and $^{13}C\{^1H\}$ NMR methods, with resonances being assigned by ^1H–^1H COSY and HMQC NMR techniques.† As shown in Fig. 2, complex **2b** redissolved in $MeNO_2$-d_3 showed relatively broad ^1H NMR signals at δ 10.61 (H^2), 9.33 (H^5) and 8.43 (H^6) for the pyrimidine ring, and δ 8.37 ($H^{3'}$), 8.11 ($H^{4'}$) 7.80 ($H^{5'}$) and 9.04 ($H^{6'}$) for the pyridyl ring at 23 °C. In contrast, complex **1** gave well-resolved ^1H NMR signals at δ 9.76 (s, H^2), 9.27 (d, H^5) and 8.63 (s, H^6) for the pyrimidine ring, and δ 8.62 (d, $H^{3'}$), 8.33 (t, $H^{4'}$) 7.92 (t, $H^{5'}$) and 9.02 (d, $H^{6'}$) for the pyridyl ring in $MeNO_2$-d_3 at 23 °C, whose signals are obviously different from those for complex **2b**. The coordination shift values ($\Delta\delta = \delta_{complex} - \delta_{metal\text{-}free}$) of complex **2b** are δ 1.40 (H^2), 0.46 (H^5) and 0.05 (H^6) for the pyrimidine ring, and δ −0.13 ($H^{3'}$), 0.13 ($H^{4'}$), 0.28 ($H^{5'}$) and 0.31 ($H^{6'}$) for the pyridyl ring. It is interesting that the ^1H NMR signal of the $H^{3'}$ position is shifted upfield compared to metal-free pprd, which is induced by the diamagnetic ring current effect of the neighbouring $[Ag_4(pprd)_4]^{4+}$ cation moiety. In contrast, the ^1H NMR signal of the H^2 position is largely shifted downfield with broadening, indicative of the H···F hydrogen bond interaction between the H^2 proton and the encapsulated SiF_6^{2-} anion. Complexes **3** and **4** redissolved in $MeNO_2$-d_3 afford similar ^1H NMR spectra to complex **2b** (Fig. 2). In the series of complexes **2b**, **3** and **4**, the ^1H NMR signal at the H^2 position is observed in downfield regions in the order **2b** (δ 10.61) > **3** (δ 10.48) > **4** (δ 10.21) depending on the electronegativity of the XF_6^{2-} anion. On the basis of these results, it is concluded that the sandwich-shaped structure encapsulating the XF_6^{2-} anion is maintained in solution.

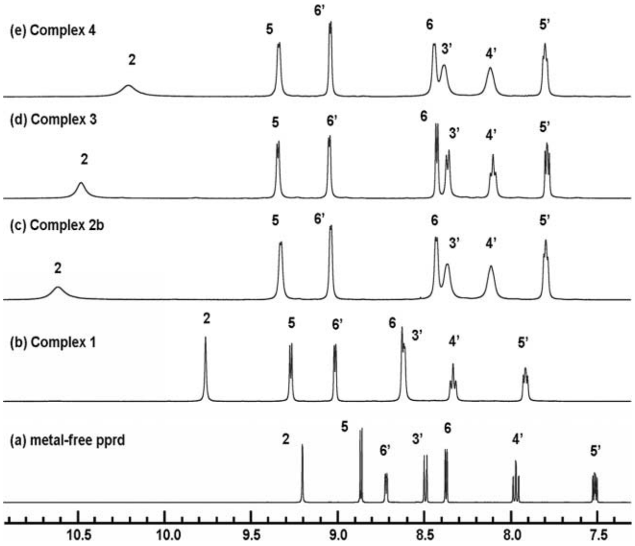

Fig. 2 ^1H NMR spectra of (a) metal-free pprd, (b) $[Ag_4(pprd)_4](BF_4)_4$ (**1**), (c) $\{[Ag_4(pprd)_4]_2(SiF_6)\}(BF_4)_6{\cdot}8MeNO_2$ (**2b**), (d) $\{[Ag_4(pprd)_4]_2(GeF_6)\}(BF_4)_6{\cdot}8MeNO_2$ (**3**) and (e) $\{[Ag_4(pprd)_4]_2(SnF_6)\}(BF_4)_6{\cdot}8MeNO_2$ (**4**) in $MeNO_2$-d_3 at 23 °C.

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Notes and references

† *Synthesis of* $[Ag_4(pprd)_4](BF_4)_4$ (**1**): In a modification of the literature method,[9] $AgBF_4$ (0.0973 g, 0.05 mmol) and pprd (0.0786 g, 0.05 mmol) were reacted in $MeNO_2$ (10 ml) under Ar. After stirring for 1 h, ether was added to the reaction solution. A brownish-white precipitate was filtered and then dried *in vacuo*. Anal. calc. for $C_{36}H_{28}Ag_4B_4F_{16}N_{12}$: C, 30.72; H, 2.01; N, 11.94. Found: C, 29.80; H, 2.03; N, 11.56%. ^1H NMR (δ, $MeNO_2$-d_3, 23 °C): {9.76 (H^2), 9.27 (H^5) and 8.63 (H^6)} for the pyrimidine ring and {8.62 ($H^{3'}$), 8.33 ($H^{4'}$), 7.91 ($H^{5'}$) and 9.02 ($H^{6'}$)} for the pyridine ring. ^{13}C NMR (δ, $MeNO_2$-d_3, 23 °C): {159.5 (C^2), 159.0 (C^4), 160.1 (C^5) and 119.0 (C^6)} for the pyrimidine ring and {147.7 ($C^{2'}$), 124.0 ($C^{3'}$), 139.4 ($C^{4'}$), 127.6 ($C^{5'}$) and 151.6 ($C^{6'}$)} for the pyridine ring.

Synthesis of $\{[Ag_4(pprd)_4]_2(SiF_6)\}(BF_4)_6{\cdot}8MeNO_2$ (**2a**): $AgBF_4$ (0.1947 g, 0.10 mmol) and pprd (0.1572 g, 0.10 mmol) were reacted in $MeNO_2$ (10 ml) under C_2H_4. After stirring for 1 h, the reaction solution was filtered. The dark-brown filtrate was sealed in several 7 mm diameter glass tubes under C_2H_4. The reaction solution was allowed to stand for

2 weeks at −20 °C. A small quantity of single crystals of **2a** were collected, together with a large amount of brownish-white precipitate. Anal. calc. for $C_{80}H_{80}Ag_8B_6F_{30}N_{32}O_{16}Si$: C, 29.37; H, 2.46; N, 13.70. Found: C, 29.06; H, 2.41; N, 13.02%.

Syntheses of $\{[Ag_4(pprd)_4]_2(XF_6)\}(BF_4)_6{\cdot}8MeNO_2$ (X = Si (**2b**), Ge (**3**) and Sn (**4**)): $AgBF_4$ (0.0973 g, 0.05 mmol) and pprd (0.0786 g, 0.05 mmol) were mixed in $MeNO_2$ (10 ml) in a PFA-*made* beaker for 1 h under Ar. $(NH_4)_2SiF_6$ (0.0891 mg, 0.05 mmol) was added to the pale brown solution. After stirring for 3 h, the reaction solution was sealed in several 17 mm diameter PFA-*made* test tubes together with ether. The reaction solution was allowed to stand for 1 week at room temperature. A small quantity of single crystals of **2b** were collected, together with a large amount of brownish-white precipitate. In the same manner as for **2b**, single crystals of **3** and **4** were also collected by the use of $(NH_4)_2XF_6$ salts (X = Ge and Sn) (0.05 mmol). *Complex* **2b**: Anal. calc. for $C_{80}H_{80}Ag_8B_6F_{30}N_{32}O_{16}Si$: C, 29.37; H, 2.46; N, 13.70. Found: C, 28.78; H, 2.33; N, 13.25% ^1H NMR (δ, $MeNO_2$-d_3, 23 °C): {10.61 (H^2), 9.33 (H^5) and 8.43 (H^6)} for the pyrimidine ring and {8.37 ($H^{3'}$), 8.11 ($H^{4'}$), 7.80 ($H^{5'}$) and 9.04 ($H^{6'}$)} for the pyridine ring. ^{13}C NMR (δ, $MeNO_2$-d_3, 23 °C): {162.1 (C^2), 157.6 (C^4), 161.3 (C^5) and 118.4 (C^6)} for the pyrimidine ring and {145.8 ($C^{2'}$), 123.9 ($C^{3'}$), 139.7 ($C^{4'}$), 128.2 ($C^{5'}$) and 152.0 ($C^{6'}$)} for the pyridine ring. *Complex* **3**: Anal. calc. for $C_{80}H_{80}Ag_8B_6F_{30}N_{32}O_{16}Ge$: C, 28.98; H, 2.43; N, 13.52. Found: C, 28.47; H, 2.32; N, 13.17%. ^1H NMR (δ, $MeNO_2$-d_3, 23 °C): {10.48 (H^2), 9.35 (H^5) and 8.43 (H^6)} for the pyrimidine ring and {8.36 ($H^{3'}$), 8.10 ($H^{4'}$), 7.79 ($H^{5'}$) and 9.05 ($H^{6'}$)} for the pyridine ring. ^{13}C NMR (δ, $MeNO_2$-d_3, 23 °C): {161.9 (C^2), 157.6 (C^4), 161.3 (C^5) and 118.4 (C^6)} for the pyrimidine ring and {145.8 ($C^{2'}$), 123.9 ($C^{3'}$), 139.7 ($C^{4'}$), 128.2 ($C^{5'}$) and 152.0 ($C^{6'}$)} for the pyridine ring. *Complex* **4**: Anal. calc. for $C_{80}H_{80}Ag_8B_6F_{30}N_{32}O_{16}Sn$: C, 28.58; H, 2.40; N, 13.33. Found: C, 28.13; H, 2.34; N, 12.98%. ^1H NMR (δ, $MeNO_2$-d_3, 23 °C): ^1H NMR (δ, $MeNO_2$-d_3, 23 °C): {10.21 (H^2), 9.34 (H^5) and 8.44 (H^6)} for the pyrimidine ring and {8.39 ($H^{3'}$), 8.12 ($H^{4'}$), 7.80 ($H^{5'}$) and 9.04 ($H^{6'}$)} for the pyridine ring. ^{13}C NMR (δ, $MeNO_2$-d_3, 23 °C): {166.4 (C^2), 157.8 (C^4), 161.1 (C^5) and 118.5 (C^6)} for the pyrimidine ring and {145.9 ($C^{2'}$), 123.9 ($C^{3'}$), 139.7 ($C^{4'}$), 128.1 ($C^{5'}$) and 152.1 ($C^{6'}$)} for the pyridine ring.

‡ *Crystal data for* **2a**: Formula $C_{80}H_{80}Ag_8B_6F_{30}N_{32}O_{16}Si$, M = 3721.56, triclinic, space group $P(\bar{1})$, a = 12.258(5), b = 14.979(6), c = 15.422(6) Å, α = 93.365(4), β = 103.919(5), γ = 100.868(5)°, V = 2683(1) Å^3, Z = 1, D_c = 2.024 cm^{-1}, μ(Mo-K$_\alpha$) = 15.65 cm^{-1}, T = 150 K. Measured reflections 20952 (total); observed reflections 11730 (all data); 8891 ($I > 2\sigma(I)$), R = 0.072, $R1$ = 0.044 ($I > 2\sigma(I)$), R_w = 0.100. CCDC 293736.

Crystal data for **2b**: Formula $C_{80}H_{80}Ag_8B_6F_{30}N_{32}O_{16}Si$, M = 3721.56, triclinic, space group $P(\bar{1})$, a = 12.269(5), b = 14.970(6), c = 15.408(6) Å, α = 93.424(4), β = 103.894(4), γ = 100.832(5)°, V = 2681(1) Å^3, Z = 1, D_c = 2.026 cm^{-1}, μ(Mo-K$_\alpha$) = 15.65 cm^{-1}, T = 150 K. Measured reflections 31397 (total), observed reflections 12197 (all data); 8494 ($I > 2\sigma(I)$), R = 0.070, $R1$ = 0.048 ($I > 2\sigma(I)$), R_w = 0.114. CCDC 293737.

Crystal data for **3**: Formula $C_{80}H_{80}Ag_8B_6F_{30}N_{32}O_{16}Ge$, M = 3316.06, triclinic, space group $P(\bar{1})$, a = 12.252(6), b = 14.989(7), c = 15.436(7) Å, α = 93.406(4), β = 103.691(5), γ = 100.946(6)°, V = 2687(2) Å^3, Z = 1, D_c = 2.049 cm^{-1}, μ(Mo-K$_\alpha$) = 18.25 cm^{-1}, T = 150 K. Measured reflections 20976 (total), observed reflections 11769 (all data); 9697 ($I > 2\sigma(I)$), R = 0.083, $R1$ = 0.051 ($I > 2\sigma(I)$), R_w = 0.117. CCDC 293738.

Crystal data for **4**: Formula $C_{80}H_{80}Ag_8B_6F_{30}N_{32}O_{16}Sn$, M = 3362.16, triclinic, space group $P(\bar{1})$, a = 12.246(6), b = 15.031(7), c = 15.517(7) Å, α = 93.390(5), β = 103.344(5), γ = 101.090(5)°, V = 2711(2) Å^3, Z = 1, D_c = 2.059 cm^{-1}, μ(Mo-K$_\alpha$) = 17.62 cm^{-1}, T = 150.0 K. Measured reflections 21017 (total), observed reflections 11835 (all data); 9107 ($I > 2\sigma(I)$), R = 0.077, $R1$ = 0.053 ($I > 2\sigma(I)$), R_w = 0.157. CCDC 293739. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b518411h

1 (*a*) J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, Wiley-VCH, Weinheim, 1995; (*b*) D. L. Caulder and K. N. Raymond, *Acc. Chem. Res.*, 1999, **32**, 975; (*c*) S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853; (*d*) P. J. Stang and B. Olenyuk, *Acc. Chem. Res.*, 1997, **30**, 502; (*e*) G. F. Swiegers and T. J. Malefetse, *Chem. Rev.*, 2000, **100**, 3483; (*f*) L. Cronin, *Annu. Rep. Prog. Chem., Sect. A: Inorg. Chem.*, 2003, **99**, 289; (*g*) M. Fujita, K. Umemoto, M. Yoshizawa, N. Fujita, T. Kusukawa and K. Biradha, *Chem. Commun.*, 2001, 509; (*h*) B. Olenyuk, A. Fechtenkötter and P. J. Stang, *J. Chem. Soc., Dalton Trans.*, 1998, 1707; (*i*) D. L. Caulder and K. N. Raymond, *J. Chem. Soc., Dalton Trans.*, 1999, 1185; (*j*) F. A. Cotton, C. Lin and C. A. Murillo, *Acc. Chem. Res.*, 2001, **34**, 759; (*k*) B. J. Holliday and C. A. Mirkin, *Angew. Chem., Int. Ed.*, 2001, **40**, 2022; (*l*) L. Raehm, L. Mimassi, C. Guyard-Duhayon and H. Amouri, *Inorg. Chem.*, 2003, **42**, 5654; (*m*) P. Thanasekaran, R.-T. Liao, Y.-H. Liu, T. Rajendran, S. Rajagopal and K.-L. Lu, *Coord. Chem. Rev.*, 2005, **249**, 1085; (*n*) F. Würthner, C.-C. You and C. R. Saha-Möller, *Chem. Soc. Rev.*, 2004, **33**, 133.

2 (*a*) A. Bianchi, K. Bowman-James and E. García-España, *Supramolecular Chemistry of Anions*, Wiley-VCH, Weinheim, 1997; (*b*) P. A. Gale, J. L. Sessler and V. Král, *Chem. Commun.*, 1998, 1; (*c*) J. L. Sessler and J. M. Davis, *Acc. Chem. Res.*, 2001, **34**, 989; (*d*) P. A. Gale, *Coord. Chem. Rev.*, 2000, **199**, 181; (*e*) P. D. Beer and P. A. Gale, *Angew. Chem., Int. Ed.*, 2001, **40**, 486; (*f*) P. A. Gale, *Coord. Chem. Rev.*, 2001, **213**, 79; (*g*) P. A. Gale, *Coord. Chem. Rev.*, 2003, **240**, 191; (*h*) R. Vilar, *Angew. Chem., Int. Ed.*, 2003, **42**, 1460; (*i*) C. S. Campos-Fernández, B. L. Schottel, H. T. Chifotides, J. K. Bera, J. Bacsa, J. M. Koomen, D. H. Russell and K. R. Dunbar, *J. Am. Chem. Soc.*, 2005, **127**, 12909.

3 (*a*) F. Diederich and P. J. Stange, *Templated Organic Synthesis*, Wiley-VCH, Weinheim, 2000; (*b*) R. Hoss and F. Vögtle, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 375.

4 (*a*) R.-D. Schnebeck, E. Freisinger and B. Lippert, *Angew. Chem., Int. Ed.*, 1999, **38**, 168; (*b*) R.-D. Schnebeck, E. Freisinger, F. Glahé and B. Lippert, *J. Am. Chem. Soc.*, 2000, **122**, 1381; (*c*) S.-H. Li, H.-P. Huang, S.-Y. Yu, Y.-Z. Li, H. Huang, Y. Sei and K. Yamaguchi, *Dalton Trans.*, 2005, 2346.

5 (*a*) J. S. Fleming, K. L. V. Mann, C.-A. Carraz, E. Psillakis, J. C. Jeffery, J. A. McCleverty and M. D. Ward, *Angew. Chem., Int. Ed.*, 1998, **37**, 1279; (*b*) S. Mann, G. Huttner, L. Zsolnai and K. Heinze, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2808; (*c*) H. Amouri, M. N. Rager, F. Cagnol and J. Vaissermann, *Angew. Chem., Int. Ed.*, 2001, **40**, 3636; (*d*) C. S. Campos-Fernández, R. Clérac and K. R. Dunbar, *Angew. Chem., Int. Ed.*, 1999, **38**, 3477.

6 D. A. McMorran and P. J. Steel, *Angew. Chem., Int. Ed.*, 1998, **37**, 3295.

7 (*a*) J. A. Wisner, P. D. Beer, M. G. B. Drew and M. R. Sambrook, *J. Am. Chem. Soc.*, 2002, **124**, 12469; (*b*) R. Vilar, D. M. P. Mingos, A. J. P. White and D. J. Williams, *Angew. Chem., Int. Ed.*, 1998, **37**, 1258; (*c*) S.-T. Cheng, E. Doxiadi, R. Vilar, A. J. P. White and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 2001, 2239.

8 (*a*) M. F. Hawthorne and Z. Zheng, *Acc. Chem. Res.*, 1997, **30**, 267; (*b*) Z. Zheng, C. B. Knobler, M. D. Mortimer, G. Kong and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1996, **35**, 1235.

9 D. A. Beauchamp and S. J. Loeb, *Chem. Commun.*, 2002, 2484.

10 (*a*) S. J. Coles, J. G. Frey, P. A. Gale, M. B. Hursthouse, M. E. Light, K. Navakhun and G. L. Thomas, *Chem. Commun.*, 2003, 568; (*b*) S. J. Coles, J. G. Frey, P. A. Gale, M. B. Hursthouse, M. E. Light, K. Navakhun and G. L. Thomas, *Chem. Commun.*, 2003, 1462 (addition and correction to ref. 10*a*) .

11 (*a*) J. Reedijk, *Comments Inorg. Chem.*, 1982, **1**, 379; (*b*) P. J. van Koningsbruggen, J. G. Haasnoot, R. A. G. de Graaff and J. Reedijk, *J. Chem. Soc., Dalton Trans.*, 1993, 483; (*c*) G. A. van Albada, O. Roubeau, I. Mutikainen, U. Turpeinen and J. Reedijk, *New J. Chem.*, 2003, 1693; (*d*) H. Casellas, A. Pevec, B. Kozlevčar, P. Gamez and J. Reedijk, *Polyhedron*, 2005, **24**, 1549.