Sandwich-shaped silver(I) metallomacrocycles encapsulating a $\text{XF}_6^{2-}$ (X = Si, Ge and Sn) anion

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A series of sandwich-shaped complexes based on two square tetranuclear Ag(I) metallomacrocycles, $\{\text{Ag}_4\text{pprd} \text{[CF}_3\text{SO}_3\text{]}}_2 (\text{BF}_3\text{H})_2 \text{MeNO}_2$ (pprd = 4-(2-pyridyl)pyrimidine; X = Si, Ge and Sn), in which a $\text{XF}_6^{2-}$ 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. 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. However, in contrast to the well studied templating properties of cationic and neutral species, 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 $\text{NO}_3^{-}, \text{BF}_4^{-}, \text{PF}_6^{-}, \text{Cl}^{-}\text{and} \text{L}^{2-\text{to}}$ 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 $\text{XF}_6^{2-}$ (X = Si, Ge and Sn) anion into metallomacrocycles, in which the $\text{XF}_6^{2-}$ 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 $\{\text{Ag}_4\text{pprd} \text{[CF}_3\text{SO}_3\text{]}}_2 (\text{BF}_3\text{H})_2$ (1)$^a$ to a rectangular tetranuclear $\{\text{Ag}_4\text{pprd} \text{[CF}_3\text{SO}_3\text{]}}_2 $ complex and a 1D helical infinite polymer $\{\{\text{Ag}_4\text{pprd}[\text{NO}_3]\}_n\}^9$. When we reacted AgBF$_4$ with pprd in MeNO$_2$ under C$_2$H$_4$, a new Ag pprd complex $\{\text{Ag}_4\text{pprd} \text{[SiF}_6\text{]}}_2 (\text{BF}_3\text{H})_2$ (2a) was preferentially produced.† The X-ray crystallographic analysis showed that there are two $\{\text{Ag}_4\text{pprd}\}^{4+}$ 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 $\{\text{Ag}_4\text{pprd}\}^{4+}$ metallomacrocyclic, 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](image-url) (a) Top view and (b) side view of $\{\text{Ag}_4\text{pprd} \text{[SiF}_6\text{]}}_2 (\text{BF}_3\text{H})_2$·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.
in the central vacant space between the two \([Ag_4(pprd)_4]^{4+}\) metallocmacrocycles, 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 metallocmacrocycles 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 metallocmacrocycles, in contrast to only one example of an organic \(\text{C}_2\text{H}_4\) shape with relatively broad \(\text{H}^1\) NMR signals at 0.03 and 0.13 ppm for the pyridyl ring 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\(_2\))\(_2\)XF\(_6\) salts (X = Si, Ge and Sn) in MeNO\(_2\) have been carried out using PFA-mixed 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\(_4\))\(_6\) \((X = \text{Si (2b), Ge (3) and Sn (4)})\) complexes were synthesized and structurally characterized.† The structure of the 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 tetraneunar \([Ag_4(pprd)_4]^{4+}\) metallocmacrocycles. These facts indicate that the XF\(_6^{2-}\) anion plays an important role in the anion-directed self-assembly of \([Ag_4(pprd)_4]^{4+}\) metallocmacrocycles 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 \(\text{H}^1\) and \(\text{C}^{13}\)\(^{1}\text{H}\) NMR methods, with resonances being assigned by \(\text{H}^1–\text{H}^1\) COSY and HMHC NMR techniques.† As shown in Fig. 2, complex 2b redissolved in MeNO\(_2\)-d\(_3\) showed relatively broad \(\text{H}^1\) NMR signals at \(\delta 10.61\) (H\(_2\)), 9.33 (H\(_5\)) and 8.43 (H\(_6\)) for the pyrimidine ring, and \(\delta 8.37\) (H\(_3\)), 8.11 (H\(_4\)) and 7.80 (H\(_5\)) and 9.04 (H\(_6\)) for the pyrydil ring at 23 °C. In contrast, complex 1 gave well-resolved \(\text{H}^1\) NMR signals at \(\delta 9.76\) (s, H\(_2\)), 9.27 (d, H\(_3\)) and 8.63 (s, H\(_4\)) for the pyrimidine ring, and \(\delta 8.62\) (d, H\(_5\)), 8.33 (t, H\(_6\)) and 9.02 (d, H\(_7\)) for the pyrydil ring in MeNO\(_2\)-d\(_3\) at 23 °C, whose signals are obviously different from those for complex 2b. The coordination shift values (\(\Delta \delta = \delta_{\text{complex}} - \delta_{\text{metal-free}}\)) of complex 2b are \(\delta 1.40\) (H\(_2\)), 0.46 (H\(_3\)) and 0.05 (H\(_4\)) for the pyrimidine ring, and \(\delta 0.13\) (H\(_5\)), 0.13 (H\(_6\)) and 0.17 (H\(_7\)) for the pyridyl ring. Complex 2c showed similar results.

Notes and references

† Synthesis of \([Ag_4(pprd)_4]^{2+}\)\(/\text{BF}_4^-\) (1): In a modification of the literature method,7 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 dried in vacuo. Anal. calc. for C\(_{36}\)H\(_{28}\)Ag\(_4\)B\(_4\)F\(_{16}\)N\(_{12}\): C, 30.72; H, 2.01; N, 11.56%. Found: C, 30.80; H, 2.03; N, 11.56%. \(\text{C}^{13}\)\(^{1}\text{H}\) NMR (\(\delta \text{MeNO}_2\)-d\(_3\), 23 °C): \(\delta 7.96\) (H\(_2\)), 9.27 (H\(_5\)) and 8.63 (H\(_6\)) for the pyrimidine ring and \(\delta 8.62\) (H\(_3\)), 8.33 (H\(_4\)), 7.91 (H\(_5\)) and 9.02 (H\(_6\)) for the pyridyl ring. \(\text{C}^{13}\)\(^{1}\text{N}\) NMR (\(\delta \text{MeNO}_2\)-d\(_3\), 23 °C): \(\delta 119.5\) (C\(_3\)), 159.0 (C\(_9\)), 160.1 (C\(_5\)) and 119.0 (C\(_8\)) for the pyrimidine ring and \(\delta 147.7\) (C\(_2\)), 124.0 (C\(_1\)), 139.4 (C\(_6\)), 127.6 (C\(_4\)) and 151.6 (C\(_7\)) for the pyridine ring.

Synthesis of \([Ag_4(pprd)_4]^{2+}\)\(/SiF_6^{2-}\)\(/\text{BF}_4^-\)\(/8\text{MeNO}_2\) (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\(_3\)H\(_6\). 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\(_3\)H\(_6\). 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 C₈₀H₈₀Ag₈B₆F₃₀N₃₂O₁₆Si: C, 28.47; H, 2.34; N, 12.98%. 1HN M R(2.059 cm⁻¹, 2.049 cm⁻¹) for the pyridine ring. 13CN M R(2.040 cm⁻¹, 2.032 cm⁻¹) for the pyrimidine ring. 128.1 (C₅), 128.2 (C₅) and 128.3 (C₅) for the pyrimidine ring and 145.8 (C₅), 145.7 (C₅) and 145.5 (C₅) for the pyridine ring.

Complex 2b: Anal. calc. for C₈₀H₈₀Ag₈B₆F₃₀N₃₂O₁₆Si: C, 28.47; H, 2.32; N, 12.97%. F o r m u l a C₈₀H₈₀Ag₈B₆F₃₀N₃₂O₁₆Si, d = 1.053 M e N O₂⁻.

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