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Hexa(2-pyridyl)[3]radialene: self-assembly of a hexanuclear silver array

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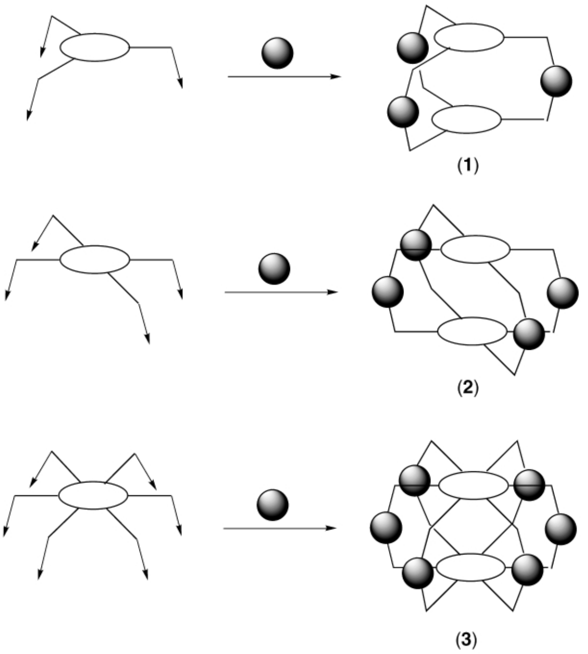
Reaction of the new ligand hexa(2-pyridyl)[3]radialene with silver tetrafluoroborate results in the formation of a M_6L_2 cage with an encapsulated μ_3-fluorido anion.

The programmed self-assembly of metallosupramolecular species derived from combinations of bridging organic ligands and transition metal precursors has been the subject of enormous study over the last decade.[1–3] Using combinations of linear and angular components, it is possible to effect the controlled assembly of various molecular architectures, such as two-dimensional polygons and three-dimensional polyhedra.[3] A family of polyhedra that has received scant attention is shown in Scheme 1 and consists of species of formula M_nL_2 that are comprised of two multipodal ligands bridging *n* metal centres. Fujita[4] first described the formation of a trigonal prismatic structure (**1**) with three palladium atoms bridged by two tripodal ligands. Other topologically related examples have since been reported and characterised.[5] The first tetragonal prismatic structure (**2**) employed symmetrical cavitands as bridges[6] and a novel organometallic example has recently been reported that used a cyclobutadienyl core.[7] Recently, an unsuccessful attempt was made to extend this methodology to a pentagonal prismatic structure.[8] To our knowledge, no hexagonal prisms (**3**) have yet been reported.

We are currently engaged in the synthesis and study of a completely new class of bridging ligands, which consist of a central radialene core with multiple heteroaryl substituents. We now report our first results in this area in the form of the synthesis of hexa(2-pyridyl)[3]radialene (**4**) and its use in the assembly of the first hexapodal prismatic structure (**3**).



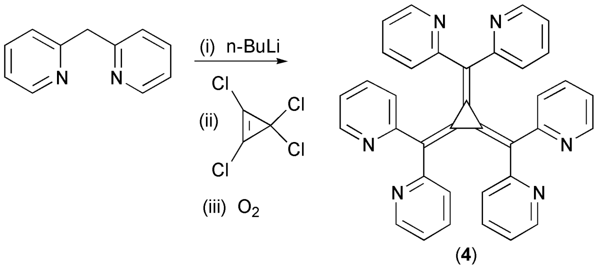
Scheme 1

Although hexamethyl[3]radialene was first synthesised in 1965,[9] the first hexaaryl derivative was reported relatively recently.[10] These can be prepared either by reaction of diarylmethyl anions with tetrachlorocyclopropene,[10] or, as described more recently,[11] by cyclisation of dibromo[3]dendralenes. We used the former approach to prepare hexa(2-pyridyl)[3]radialene (**4**), as shown in Scheme 2. Thus, reaction of di(2-pyridyl)methane with n-butyllithium, followed by addition of tetrachlorocyclopropene and oxidation of the resulting dianion with molecular oxygen, furnished the new hexadentate ligand (**4**) in 72% yield.† It forms bright red solutions (λ_{max} 463 nm, logε 4.4) and cyclic voltammetry reveals two reversible reduction waves consistent with reported properties for other hexaaryl[3]radialenes.[10]

One can envisage a variety of modes of coordination for this ligand, which is isomeric with hexa(2-pyridyl)benzene but has a quite different spatial arrangement of the pyridine rings. The ligand might act as a tritopic bridging ligand with three bidentate chelating binding domains. In fact, chelation is possible in two different modes: either six- or nine-membered chelate rings can be formed, depending upon whether the metal binds to pyridine donors attached to the same or adjacent arms of the radialene core. Alternatively, the ligand might act as a hexatopic ligand and bind to six different metals, or in a hypodentate manner with incomplete coordination by the six nitrogen donors.

This last mode of coordination was observed when we reacted (**4**) with either silver nitrate or silver hexafluorophosphate, which resulted in the formation of one-dimensional coordination polymers in which molecules of (**4**) acted as tetradentate or pentadentate bridges.[12] However, reaction with silver tetrafluoroborate resulted in the formation of a crystalline product that was shown to have the constitution $[Ag_6(\mathbf{4})_2F(BF_4)_5\cdot 11H_2O]$ by single crystal X-ray structure determination.‡ Fig. 1 shows two perspective views of the structure of the central M_6L_2F cage that results from the self-assembly of two molecules of (**4**), acting in a hexapodal hexadentate mode, and six silver atoms around a central μ_3-fluorido anion. External to the cage are five BF_4^- counterions and eleven water molecules that fill the nanoporous voids between the cage molecules.§

The structure has a number of novel features. We believe that this is the first report of the formation of a M_6L_2 complex involving a hexapodal N-ligand. This ligand seems to prefer to



Scheme 2

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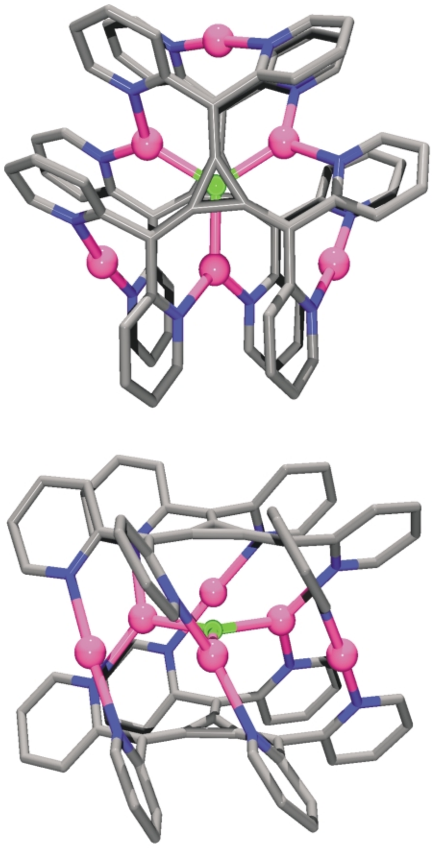

Fig. 1 Two perspective views of the Ag_6L_2F cage.

bridge metals through each N-donor rather than to chelate. The six silver atoms are coplanar (mean deviation from the plane = 0.012 Å). Although hexanuclear silver clusters are not uncommon,[13] they usually involve a three-dimensional arrangement of the atoms. In fact, the only planar Ag_6 array, that we are aware of, is that found in silver(I) imidazole perchlorate and this has a very different spatial arrangement of the six atoms.[14] Within each of the ligands in the complex, the six pyridine rings display a co-operative, propeller-like twisting about the central radialene core.¶ This imparts a helical character to the complex and therefore makes it chiral.

Within the structure, the 'silver platter' has a μ_3-fluorido anion at its centre. The fluorine atom is strongly bonded, in a trigonal arrangement, to three internal silver atoms [2.275–2.297 Å], about which the other three silvers are symmetrically disposed at distances in the range 3.296–3.641 Å, which indicate weak Ag–Ag interactions.[15] The fluoride ion undoubtedly originates from the BF_4^- counterion used in the synthesis, as has previously been observed with other metal complexes of nitrogen heterocycles.[16] This is the first example of a μ_3-fluorido silver complex, although, interestingly, a μ_3-F tricopper(I) complex has recently been structurally characterised.[17] We believe that the F^- anion may act as a template for the formation of the hexanuclear cage. Furthermore, the position and orientation of the fluorine atom in the structure raises the intriguing possibility that in this compound there might be a favourable interaction between the filled p-orbital of the electron rich sp^2-hybridized fluorine atom and an empty π^*-orbital of the highly electron deficient radialene ring system, *i.e.* a new type[18] of 'halogen bond'.‖

In summary, we have described the first example of a completely new class of multidentate ligand and its use in the formation of the first hexapodal prismatic metallosupramolecular assembly.

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Notes and references

† *Selected data for*: **4** mp 259–260 °C; ^1H NMR (CD_3OD): δ 7.84 (d, 6H, H6), 6.99 (t, 6H, H4), 6.95 (dd, 6H, H5), 6.69 (d, 6H, H3); ^{13}C NMR (CD_3OD): δ 158.6, 149.7, 137.5, 128.0, 127.4, 124.3, 123.7; HRMS $[M + H]^{+\cdot}$ calc. 541.2143, fd. 541.2141; Anal. calc. for $C_{36}H_{24}N_6{\cdot}H_2O$: C 77.40, H 4.69, N 15.04, fd. C, 77.14, H 4.69, N 14.74 %.

‡ *Crystal data*: $C_{72}H_{70}Ag_6B_5F_{21}N_{12}O_{11}$, *F.W.* 2379.67, monoclinic, $P2_1/n$, a 21.890(7), b 15.011(5), c 27.729(9) Å, β 112.604(4)°, V 8412 (5) Å^3, Z 4, ρ 1.879 Mg m^{-3}, μ 1.481 mm^{-1}, $F(000)$ 4680, red plate 0.30 × 0.25 × 0.04 mm, $2\theta_{max}$ 50°, Mo-Kα (λ 0.7107 Å), T 168 K, 96087 reflections, 14791 unique (99.9% completeness), 1144 parameters, GOF 1.047, $wR2$ 0.0887 for all data, R 0.0493 for 10121 data with $I > 2\sigma(I)$. CCDC 172692. See http://www.rsc.org/suppdata/cc/b1/b109214f/ for crystallographic files in .cif format.

§ All 11 water molecules were located in difference maps and are involved, along with the BF_4 anions, in a complex three-dimensional network of hydrogen bonds.

¶ These pyridine rings are inclined to the attached radialene units at angles ranging between 48.7 and 65.4°.

‖ The distance from the central F atom to the centroid of each of the cyclopropane rings is 2.70(1) Å.

1 For recent reviews, see: S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853; G. F. Swiegers and T. J. Malefetse, *Chem. Rev.*, 2000, **100**, 3483; B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629; M. Fujita, K. Umemoto, M. Yoshizawa, N. Fujita, T. Kusukawa and K. Biradha, *Chem. Commun.*, 2001, 509; B. J. Holliday and C. A. Mirkin, *Angew. Chem., Int. Ed.*, 2001, **40**, 2022.

2 C. M. Hartshorn and P. J. Steel, *Chem. Commun.*, 1997, 541; D. A. McMorran and P. J. Steel, *Angew. Chem., Int. Ed.*, 1998, **37**, 3295.

3 G. F. Swiegers and T. J. Malefetse, *Chem. Eur. J.*, 2001, **7**, 3637.

4 M. Fujita, S. Nagao and K. Ogura, *J. Am. Chem. Soc.*, 1995, **117**, 1649.

5 P. L. Jones, J. C. Jeffery, J. P. Maher, J. A. McCleverty, P. H. Rieger and M. D. Ward, *Inorg. Chem.*, 1997, **36**, 3088; C. Y. Su, B. S. Kang, C. X. Du, Q. C. Yang and T. C. W. Mak, *Inorg. Chem.*, 2000, **39**, 4843; H. K. Liu, W. Y. Sun, D. J. Ma, K. B. Yu and W. X. Tang, *Chem. Commun.*, 2000, 591; W. Y. Sun, J. Fan, T. Okamura, J. Xie, K. B. Yu and N. Ueyama, *Chem. Eur. J.*, 2001, **7**, 2557; W. Y. Sun, J. Xie and K. B. Yu, *Chem. Lett.*, 2001, 342; Z. Zhong, A. Ikeda, S. Shinkai, S. Sakamoto and K. Yamaguchi, *Org. Lett.*, 2001, **3**, 1085.

6 P. Jacopozzi and E. Dalcanale, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 613.

7 S. C. Johannessen, R. G. Brisbois, J. P. Fischer, P. A. Grieco, A. E. Counterman and D. E. Clemmer, *J. Am. Chem. Soc.*, 2001, **123**, 3818.

8 Z. Zhong, A. Ikeda, M. Ayabe, S. Shinkai, S. Sakamoto and K. Yamaguchi, *J. Org. Chem.*, 2001, **66**, 1002.

9 G. Koebrich and H. Heinemann, *Angew. Chem., Int. Ed. Engl.*, 1965, **4**, 594.

10 T. Enomoto, T. Kawase, H. Kurata and M. Oda, *Tetrahedron Lett.*, 1997, **38**, 2693; T. Enomoto, N. Nishigaki, H. Kurata, T. Kawase and M. Oda, *Bull. Chem. Soc. Jpn.*, 2000, **73**, 2109.

11 M. Iyoda, N. Nakamura, M. Todaka, S. Ohtsu, K. Hara, Y. Kuwatani, M. Yoshida, H. Matsuyama, M. Sugita, H. Tachibana and H. Inoue, *Tetrahedron Lett.*, 2000, **41**, 7059.

12 P. J. Steel and C. J. Sumby, unpublished results, 2001.

13 Recent examples: W. K. Wong, L. Zhang and W. T. Wong, *Chem. Commun.*, 1998, 673; Q. M. Wang and T. C. W. Mak, *Chem. Commun.*, 2000, 1435; K. Nomiya, S. Takahashi and R. Noguchi, *J. Chem. Soc. Dalton Trans.*, 2000, 2091.

14 G. W. Eastland, M. A. Mazid, D. R. Russel and M. C. R. Symons, *J. Chem. Soc., Dalton Trans.*, 1980, 1682.

15 P. Pyykko, *Chem. Rev.*, 1997, **97**, 597.

16 R. W. M. Ten Hoedt and J. Reedijk, *Inorg. Chim. Acta*, 1981, **51**, 23; J. S. Thompson, R. L. Harlow and J. F. Whitney, *J. Am. Chem. Soc.*, 1983, **105**, 3522; Y. Zang, H. G. Jang, Y. M. Chiu, M. P. Hendrich and L. Que, *Inorg. Chim. Acta*, 1993, **213**, 41; S. Herold and S. J. Lippard, *Inorg. Chem.*, 1997, **36**, 50.

17 B. F. Straub, F. Rominger and P. Hofmann, *Inorg. Chem.*, 2000, **39**, 2113.

18 P. Maetrangolo and G. Resnati, *Chem. Eur. J.*, 2001, **7**, 2511.