[1] F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 5th ed., Wiley, New York, **1988**, Chap. 23.

[2] F. A. Cotton, R. A. Walton, *Multiple Bonds Between Metal Atoms*, 2nd ed., Clarendon Press, Oxford, **1993**.

[3] *Metal-Metal Bonds Clusters in Chemistry and Catalysis*, Plenum, New York, **1989**.

[4] E. C. Yang, M. C. Cheng, M. S. Tsai, S. M. Peng, *J. Chem. Soc. Chem. Commun.* **1994**, 2377.

[5] J. T. Sheu, C. C. Lin, I. Chao, C. C. Wang, S. M. Peng, *Chem. Commun.* **1996**, 315.

[6] L. P. Wu, P. Field, T. Morrissey, C. Murphy, P. Nagle, B. Hathway, *J. Chem. Soc. Dalton Trans.* **1990**, 3835.

[7] S. Aduldecha, B. Hathway, *J. Chem. Soc. Dalton Trans.* **1991**, 993.

[8] F. A. Cotton, R. Poli, *Inorg. Chem.* **1987**, *26*, 3653. Co-Co = 2.265(2) Å in $[Co^{II}_2(triaz)_4]$ (triaz = di-*p*-tolytriazenato).

[9] O. Jarchow, H. Schultz, R. Nast, *Angew. Chem.* **1970**, *84*, 43; *Angew. Chem. Int. Ed. Engl.* **1970**, *9*, 71. Ni-Ni = 2.32 Å in $[Ni^{I}_2(CN)_6]^{4-}$.

[10] L. Sacconi, C. Mealli, D. Gatteschi, *Inorg. Chem.* **1974**, *13*, 1985. Ni-Ni = 2.42 Å in $[Ni^{1.5}_2(napy)_4Br_2]^+$ (napy = 1,8-naphthyridine).

[11] M. Corbett, B. Hoskins, *Chem. Commun.* **1969**, 1602. Ni-Ni = 2.38 Å in $[Ni^{II}_2(PhN_3Ph)_4]$ (PhN_3Ph = diphenyltriazenato).

[12] C. Lin, C. Chou, S. Peng, unpublished. The *J* for $[Ni_3(\mu_3\text{-dpa})_4X_2]^{n+}$ (dpa = dipyridylamido ion) is −96, −122 and −550 cm^{-1} for X = Cl^- ($n = 0$), X = NCS^- ($n = 0$) and X = NCMe ($n = 2$), respectively.

An Interwoven Supramolecular Cage**

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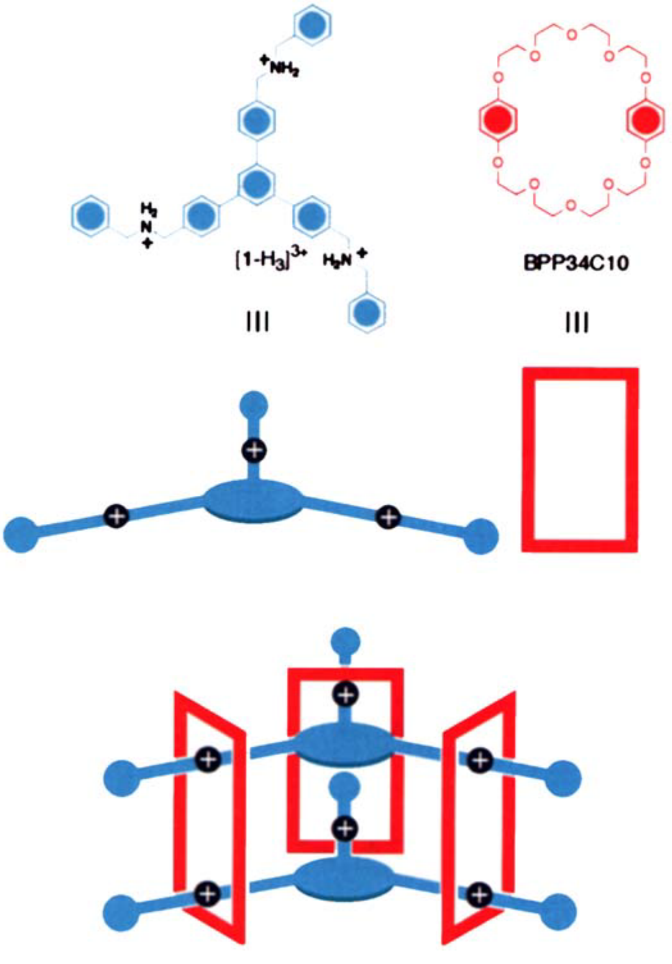
Matthew C. T. Fyfe, Peter T. Glink, Stephan Menzer,
J. Fraser Stoddart,* and David J. Williams

Dedicated to Professor Vincenzo Balzani
on the occasion of his 60th birthday

In recent times, supramolecular, noncovalent synthesis[1] has provided the chemist convenient access to some remarkable superstructures, many of which are produced with a high degree of architectural control and have the potential to perform specific functions. One of the most challenging domains within this field of endeavor involves self-assembling[2] discrete supramolecular cages that are held together by intermolecular interactions[3] and can act as synthetic receptors. However, none of the systems reported to date involve interlocked or interwoven structures.[4] We have designed such a system (Scheme 1), which relies upon the simultaneous threading of two secondary dialkylammonium ions through the cavity of a ditopic crown ether, namely bis-*p*-phenylene[34]crown-10 (BPP34C10).[5] The trifurcated trisammonium ion $[1\text{-}H_3]^{3+}$ has three secondary ammonium centers in branches radiating from a central polyaromatic core. Each branch can insert itself through the cavity of a BPP34C10 molecule, but then utilizes only half of the potential receptor sites. The vacant receptor sites remaining in each of the cavities of the three macrocyclic polyethers are then free to accept another branch from a second trication, which leads to a cagelike supermolecule. Here we report the synthesis of the trifurcated trisammonium salt $1\text{-}H_3\cdot3PF_6$ and the self-assembly of a five-component interwoven supramolecular cage in the solid state from the $[1\text{-}H_3]^{3+}$ ion and BPP34C10.



Scheme 1. Schematic representation of the anticipated [3 + 2] self-assembly between two $[1\text{-}H_3]^{3+}$ ions and three BPP34C10 macrocycles to form an interwoven supramolecular cage.

The trisammonium ion $[1\text{-}H_3]^{3+}$ was prepared as its hexafluorophosphate salt in good overall yield: condensation of 1,3,5-tris(4-formylphenyl)benzene[6] with benzylamine, followed by reduction of the resultant trisaldimine, gave the trifurcated trisamine 1,3,5-tris[(4-benzylaminomethyl)phenyl]benzene, which afforded $1\text{-}H_3\cdot3PF_6$ after treatment with hydrochloric acid and counterion exchange from chloride to hexafluorophosphate.

Single crystals suitable for X-ray analysis were obtained when a $MeNO_2$ solution containing BPP34C10 (3 equiv) and $1\text{-}H_3\cdot3PF_6$ (2 equiv) was layered with Et_2O. Gratifyingly, the crystallographic analysis of one of these crystals (Figure 1) reveals[7] the formation of a highly symmetrical cagelike superstructure in which two $[1\text{-}H_3]^{3+}$ ions are threaded through three BPP34C10 macrocycles.[8] The supermolecule has D_3 symmetry, and the principal axis passes through the centers of the two 1,3,5-triarylbenzene rings,[7] which have a mean interplanar separation of about 4.0 Å (Figure 2). The three *para*-phenylene rings of each trication are rotated by about 37° out of the plane

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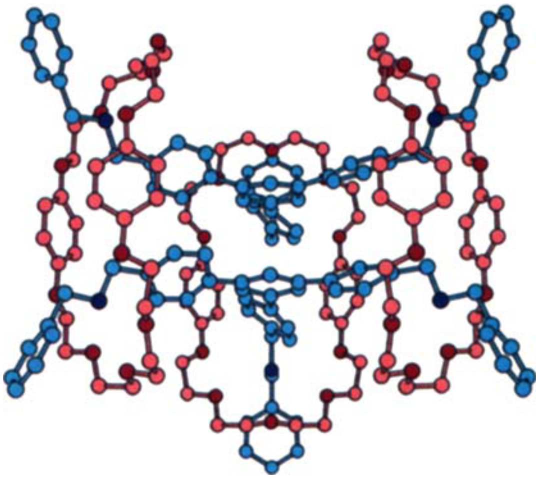

Figure 1. Ball-and-stick representation of the $[(BPP34C10)_3\cdot(\mathbf{1}\text{-}H_3)_2]^{6+}$ supermolecule in the solid state. Red: BPP34C10 components; blue: $[\mathbf{1}\text{-}H_3]^{3+}$ ions.

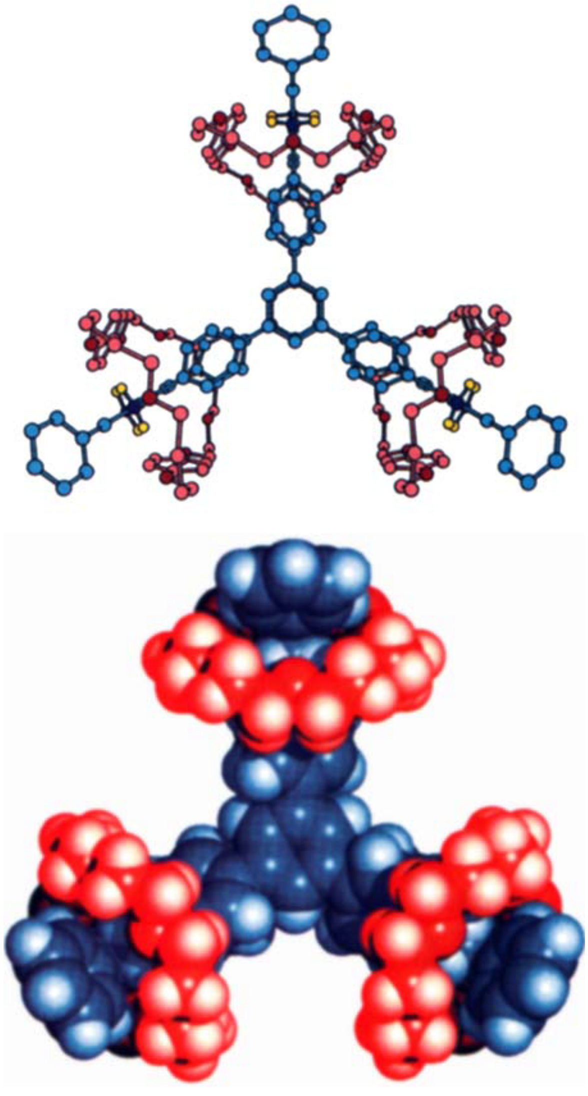

Figure 2. Top view of the five-component $[(BPP34C10)_3\cdot(\mathbf{1}\text{-}H_3)_2]^{6+}$ supermolecule. Top: Ball-and-stick representation. Bottom: Space-filling representation. Red: BPP34C10 molecules; blue: $[\mathbf{1}\text{-}H_3]^{3+}$ ions.

of the central benzenoid ring to produce a propellerlike geometry. In addition to this twisting, there is a slight "dishing" of these three rings away from the center of the supermolecule: the centroids of overlapping *para*-phenylene rings are separated by about 4.6 Å. The threading geometries of pairs of benzylammonium subunits through the BPP34C10 ring are highly reminiscent of those observed[5a–c] for the 2:2 complex formed between α,α'-bis(benzylammonium)-*p*-xylene bis(hexafluorophosphate) and BPP34C10. The nonbonded intraannular N···N distance is about 7.5 Å. The planes of the two hydroquinone rings are tilted inwards by about 20° from a parallel alignment; their centroid–centroid separation is 6.6 Å. The supermolecule is stabilized by nearly linear $[N^+\text{–}H\cdots O]$ hydrogen bonds between the NH_2^+ centers and the β-oxygen atoms of each polyether linkage ([N···O], [H···O] distances 3.02, 2.06 Å; [N–H···O] angle 176°). Adjacent supermolecules are rotated by 60° with respect to each other about their C_3 axes to form a partially interleaved assemblage (Figure 3), within which the separation between the nearest intercomplex 1,3,5-triarylbenzene rings is 12.9 Å.

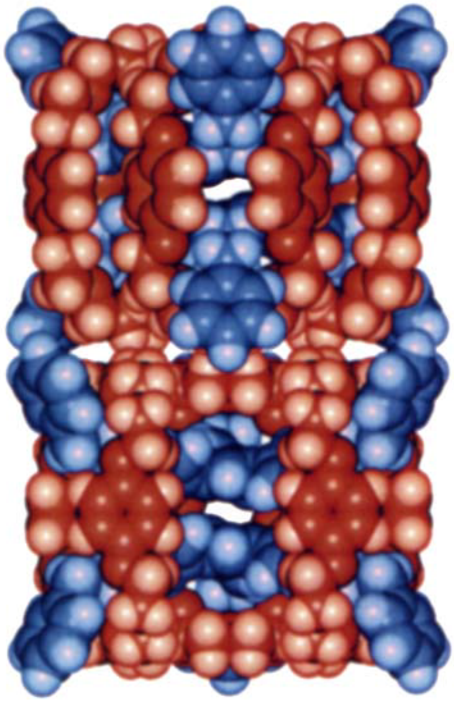

Figure 3. Space-filling representation of part of the interleaved array produced by the $[(BPP34C10)_3\cdot(\mathbf{1}\text{-}H_3)_2]^{6+}$ supermolecule. Red: BPP34C10 molecules; blue: $[\mathbf{1}\text{-}H_3]^{3+}$ ions.

We believe that this remarkable [3+2] self-assembly process is favored[9] for several reasons. Firstly, the principle of maximal site occupancy dictates[9] that the system progresses toward the species in which the maximum number of cationic centers within the $[\mathbf{1}\text{-}H_3]^{3+}$ trication, in addition to the receptor sites supplied by the macrocyclic polyether, are occupied. The $[(BPP34C10)_3\cdot(\mathbf{1}\text{-}H_3)_2]^{6+}$ supermolecule is a closed architecture: the binding sites of its constituents are completely occupied, with the result that the greatest number of hydrogen bonds are formed—thus, the supermolecule attains the thermodynamically most stable state. Secondly, entropic factors[9] dictate that the maximum number of supramolecular entities should be formed. The formation of a porous, three-dimensional, supramolecular array could also have been envisaged in the solid state: this would have occurred if the BPP34C10 "connectors" had linked each $[\mathbf{1}\text{-H}_3]^{3+}$ trication noncovalently to three different trications. The resulting superstructure—commensurate with a single "supermolecule"—would display a considerable entropy loss relative to a system comprising a large number of small, discrete supermolecules. Furthermore, the five-component cage supermolecule retains both translational and rotational entropy, whereas in the hypothetical polymeric supramolecular array, loss of these degrees of freedom amounts to a sizeable entropy deprivation. Finally, $\pi-\pi$ stacking interactions between the 1,3,5-triarylbenzene subunits—although probably quite weak at a distance of 4 Å—increase the stability of the [3+2] cage supermolecule. These energetically favorable interactions would not be present in the open supramolecular array.

The formation of the $[(\text{BPP34C10})_3\cdot(\mathbf{1}\text{-H}_3)_2]^{6+}$ supermolecule constitutes a notable example of molecular programming[10] in which the set of commands for the assembly of the supramolecular species is stored in the covalent framework of its molecular precursors. In this case, the information in the "program" is provided by the number and nature of each molecular component's binding sites: the $[\mathbf{1}\text{-H}_3]^{3+}$ ion possesses three ammonium centers located at the corners of a triangle and can therefore accommodate the binding of three complementary receptors, while the ditopic crown ether BPP34C10 possesses two recognition sites positioned within the same macrocyclic cavity, both of which can bind[5] a cationic ammonium center. The operation of the program through an algorithm based on hydrogen bonding and $\pi-\pi$ stacking leads to the desired cage-like supermolecule.

The constituents of this multicomponent self-assembly process should be able to be easily modified to yield cages of different shape and size. Although the cage presented here is too small to incorporate guests, one can envisage using even larger ditopic crown ethers[11] in order to increase the size of the cavity within the cage and so afford self-assembled hosts capable of binding small guests within their voids.

Experimental Section

$\mathbf{1}\text{-H}_3\cdot 3\,\text{PF}_6$: A mixture of 1,3,5-tris(4-formylphenyl)benzene (730 mg, 1.87 mmol) and PhCH_2NH_2 (603 mg, 5.62 mmol) in PhMe (125 mL) was heated under reflux for 14 h; the H_2O produced was collected in a Dean-Stark separator. The solution was filtered while hot, and the solvent evaporated off under reduced pressure to give 1,3,5-tris[(4-benzyliminomethyl)phenyl]benzene (1.19 g, 97%) as an off-white solid. ^{1}H NMR (300 MHz, CDCl_3, 20 °C): $\delta = 4.85$ (s, 6H), 7.24–7.36 (m, 15H), 7.74 (d, $J = 8$ Hz, 6H), 7.82 (s, 3H), 7.89 (d, $J = 8$ Hz, 6H), 8.45 (s, 3H). This solid (326 mg, 0.5 mmol) was dissolved in a 5/3 mixture of THF and MeOH (16 mL). NaBH_4 (197 mg, 5.2 mmol) was added and the solution was heated at reflux with stirring for 16 h. Upon cooling, the reaction mixture was treated with 12 N HCl to adjust the pH to 1. The solution was concentrated in vacuo, and the residue was partitioned between 1 N NaOH (60 mL) and CH_2Cl_2 (100 mL). The aqueous layer was extracted further with CH_2Cl_2 (3 × 100 mL). The combined organic extracts were washed with a 10% aqueous Na_2CO_3 solution (100 mL) and H_2O (100 mL), and then dried (K_2CO_3). Filtration and solvent evaporation gave 1,3,5-tris[(4-benzylaminomethyl)phenyl]benzene (329 mg, 100%) as a yellow oil. ^{1}H NMR (300 MHz, CDCl_3, 20 °C): $\delta = 3.84$ (s, 6H), 3.87 (s, 6H), 7.21–7.39 (m, 15H), 7.44 (d, $J = 8$ Hz, 6H), 7.65 (d, $J = 8$ Hz, 6H), 7.75 (s, 3H). This oil was dissolved in a THF/MeOH/EtOH solution (2/5/5, 60 mL). Then 4 N HCl was added with stirring to alter the pH to 1. After 2.5 h the solution was filtered and concentrated to give a white solid, which was washed with Et_2O (50 mL), before being dissolved in hot H_2O (210 mL). A white solid precipitated out of solution when a concentrated aqueous solution of NH_4PF_6 was added to the hot aqueous trisammonium salt solution. The resulting suspension was extracted with MeNO_2 (200 mL, followed by 3 × 100 mL). After the combined MeNO_2 extracts had been washed with H_2O (2 × 50 mL), the solvents were evaporated off under reduced pressure to give the trisammonium salt $\mathbf{1}\text{-H}_3\cdot 3\,\text{PF}_6$ as an off-white solid (525 mg, 96%, m.p. 139 °C with decomp.); ^{1}H NMR (300 MHz, CD_3CN, 20 °C): $\delta = 4.29$ (s, 6H), 4.32 (s, 6H), 7.05 (br s, 6H), 7.44–7.56 (m, 15H), 7.61 (d, $J = 8$ Hz, 6H), 7.92 (d, $J = 8$ Hz, 6H), 7.97 (s, 3H); ^{13}C NMR (75.5 MHz, CD_3CN, 20 °C): $\delta = 52.1$, 52.6, 126.3, 128.9, 130.1, 130.8, 130.9, 131.2, 131.3, 131.8, 142.4, 142.6. Analysis: found: C 52.17, H 4.42, N 3.81%; calcd for $\text{C}_{48}\text{H}_{48}\text{F}_{18}\text{N}_3\text{P}_3$: C 52.33, H 4.39, N 3.81%; MS (LSI): m/z: 810 $[(M - \text{PF}_6 - \text{HPF}_6)^+]$.

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[1] G. M. Whitesides, E. E. Simanek, J. P. Mathias, C. T. Seto, D. N. Chin, M. Mammen, D. M. Gordon, *Acc. Chem. Res.* **1995**, *28*, 37–44.

[2] a) D. S. Lawrence, T. Jiang, M. Levett, *Chem. Rev.* **1995**, *95*, 2229–2260; b) D. Philp, J. F. Stoddart, *Angew. Chem.* **1996**, *108*, 1242–1286; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1154–1196.

[3] For some recent examples, see a) P. Baxter, J.-M. Lehn, A. DeCian, J. Fischer, *Angew. Chem.* **1993**, *105*, 92–95; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 69–72; b) R. P. Bonar-Law, J. K. M. Sanders, *Tetrahedron Lett.* **1993**, *34*, 1677–1680; c) R. W. Saalfrank, R. Burak, A. Breit, D. Stalke, R. Herbst-Irmer, J. Daub, M. Porsch, E. Bill, M. Müther, A. X. Trautwein, *Angew. Chem.* **1994**, *106*, 1697–1699; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1621–1623; d) J. P. Mathias, C. T. Seto, E. E. Simanek, G. M. Whitesides, *J. Am. Chem. Soc.* **1994**, *116*, 1725–1736; e) M. Fujita, D. Oguro, M. Miyazawa, H. Oka, K. Yamaguchi, K. Ogura, *Nature (London)* **1995**, *378*, 469–471; f) R. G. Chapman, J. C. Sherman, *J. Am. Chem. Soc.* **1995**, *118*, 9081–9082; g) R. H. Vreekamp, J. P. M. van Duynhoven, M. Hubert, W. Verboom, D. N. Reinhoudt, *Angew. Chem.* **1996**, *108*, 1306–1309; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1215–1218; h) R. M. Grotzfeld, N. Branda, J. Rebek, Jr., *Science* **1996**, *271*, 487–489; i) J. Kang, J. Rebek, Jr., *Nature (London)* **1996**, *382*, 239–241; j) B. C. Hamann, K. D. Shimizu, J. Rebek, Jr., *Angew. Chem.* **1996**, *108*, 1425–1427; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1326–1329. k) For an example of a supramolecular cage produced by the "induced-fit" mechanism, see M. Fujita, S. Nagao, K. Ogura, *J. Am. Chem. Soc.* **1995**, *117*, 1649–1650.

[4] D. B. Amabilino, J. F. Stoddart, *Chem. Rev.* **1995**, *95*, 2725–2828.

[5] a) P. R. Ashton, E. J. T. Chrystal, P. T. Glink, S. Menzer, C. Schiavo, J. F. Stoddart, P. A. Tasker, D. J. Williams, *Angew. Chem.* **1995**, *107*, 2001–2004; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1869–1871; b) P. R. Ashton, E. J. T. Chrystal, P. T. Glink, S. Menzer, C. Schiavo, N. Spencer, J. F. Stoddart, P. A. Tasker, A. J. P. White, D. J. Williams, *Chem. Eur. J.* **1996**, *2*, 709–728; c) P. T. Glink, C. Schiavo, J. F. Stoddart, D. J. Williams, *Chem. Commun.* **1996**, 1483–1490; d) P. R. Ashton, P. T. Glink, M.-V. Martínez-Díaz, J. F. Stoddart, A. J. P. White, D. J. Williams, *Angew. Chem.* **1996**, *108*, 2058–2061; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1930–1933. e) Also, see R. Dagani, *Chem. Eng. News* **1996**, *74*(28), 26–30.

[6] E. Weber, M. Hecker, E. Koepp, W. Orlia, M. Czugler, I. Csöregh, *J. Chem. Soc. Perkin Trans. 2* **1988**, 1251–1257.

[7] Crystal data for $[(\text{BPP34C10})_3\cdot(\mathbf{1}\text{-H}_3)_2][\text{PF}_6]_6$: hexagonal, space group $P6_3/mcm$, $a = b = 19.212(1)$, $c = 33.876(7)$ Å, $V = 10829$ Å^3, $Z = 2$, $\rho_{\text{calcd}} = 1.164\ \text{g cm}^{-3}$, $\mu(\text{Cu}_{\text{K}\alpha}) = 12.5\ \text{cm}^{-1}$, $T = 293$ K. The 2643 independent reflections were measured on a Siemens P4 rotating anode diffractometer with graphite monochromated $\text{Cu}_{\text{K}\alpha}$ radiation and ω scans. Of these, only 1150 had $I_0 > 2\sigma(I_0)$ and were considered to be observed. The initial superstructural model was obtained by direct methods and the non-hydrogen atoms were refined anisotropically with F^2 data to give $R_1 = 0.1891$, $wR_2 = 0.4692$. The six PF_6^- anions are disordered and distributed over 24 partial occupancy positions and the *para*-phenylene rings have two alternative tilt orientations, each of 50% occupancy. These latter factors are the principal reasons for the high final value of R_1. The space group in which the superstructure was solved and refined requires the [3+2] supermolecule to have D_{3h} symmetry and the *para*-phenylene rings have two superimposed twist orientations (vide supra). This disorder can be explained readily in terms of an approximately even number of right-handed and left-handed propeller species of each trication in the crystal. However, the D_{3h} symmetry requirements necessitate pairs of adjacent trications within each supermolecule to be tilted toward each other, providing unacceptable $[\text{C-H}\cdots\text{H-C}]$ contacts between adjacent *para*-phenylene rings. The true molecular symmetry is thus incompatible with the symmetry requirement of the space group. Desymmetrization to space groups not requiring the horizontal and vertical mirror planes associated with D_{3h} symmetry resulted in highly unstable, nonconvergent refinements with substantially higher values for R_1. The SHELXTL package (version 5.03) was used for all computations. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-179-140. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: Int. code +(1223)336-033; e-mail: deposit@chemcrys.cam.ac.uk).

[8] Unfortunately our attempts to characterize a self-assembled [3+2] species in the solution and "gas" phases have not yet met with success. (Similar difficulties have been encountered in the characterization of the four-component

supermolecule formed between α,α'-bis(benzylammonium)-p-xylene bis(hexafluorophosphate) and BPP34C10 [5a, 5b].) The ^{1}H NMR spectrum (300 MHz) of a 3:2 molar ratio of BPP34C10 and $1\text{-}H_3\cdot 3PF_6$ in CD_2Cl_2/CD_3CN (4:1) at 20 °C showed several broad, featureless peaks, indicating that aggregation occurs in solution; however, no signals associated with the cage supermolecule could be identified. Liquid secondary ion mass spectrometry (LSIMS; VG Zabspec mass spectrometer equipped with a cesium ion source, *meta*-nitrobenzyl alcohol matrix) was employed for the characterization of the aggregate in the "gas phase"—no peaks corresponding to the [3 + 2] supermolecule were observed. Nevertheless, peaks at *m/z* 2595, 2449, and 2303 were detected, corresponding to the species $[BPP34C10\cdot(1\text{-}H_3)_2][PF_6]_6$, with the loss of one, two, and three PF_6^- counterions, respectively.

[9] Similar arguments have been used by Lehn and co-workers to explain self-recognition processes involving metal-ligand interactions in helicate self-assembly: R. Krämer, J.-M. Lehn, A. Marquis-Rigault, *Proc. Natl. Acad. Sci. USA* **1993**, *90*, 5394–5398. We note that in this seminal paper the authors remark that, "These considerations also apply to systems where binding involves interactions other than metal coordination such as hydrogen bonding or donor–acceptor forces."

[10] J.-M. Lehn, *Angew. Chem.* **1990**, *102*, 1347–1362; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1304–1319.

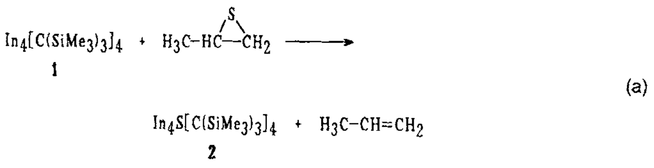
[11] A suitable crown ether could be 1,4,7,10,13,26,29,32,35,38-decaoxa[13.0.13.0]-paracyclophane where the hydroquinone rings of BPP34C10 are replaced by 4,4′-dioxybiphenyl units. See P. R. Ashton, D. Joachimi, N. Spencer, J. F. Stoddart, C. Tschierske, A. J. P. White, D. J. Williams, K. Zab, *Angew. Chem.* **1994**, *106*, 1563–1566; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1503–1506.

$In_4S[C(SiMe_3)_3]_4$: An Organoindium Compound with an In_4S Core Isovalence Electronic to Pentahydro-*closo*-pentaborate(2−)[**]

Werner Uhl,[*] Rene Graupner, Wolfgang Hiller, and Markus Neumayer

Novel and unprecedented organoelement cluster compounds of the heavier elements of the third main group aluminum, gallium, and indium were reported recently.[1–8] Some derivatives like $[Al(C_5Me_5)]_4$,[1] $K_2[Al_{12}iBu_{12}]$,[2] $[Ga-C(SiMe_3)_3]_4$,[3] and $[In-C(SiMe_3)_3]_4$[4, 5] were verified by crystal structure determinations, others like $[Al-Si(CMe_3)_3]_4$,[6] $[Al-CH_2CMe_3]_4$,[7] and $[Ga-CH_2CMe_3]_n$[8] by specific reactions, theoretical investigations, or further characterization. A few sterically highly shielded cyclopentadienides of the monovalent elements indium and thallium show a pseudodimeric or a pseudohexameric arrangement of the metal atoms; however, long distances between the atoms of the clusters confirm only a weak element–element bonding interaction,[9] the significance of which has been controversial.[10] Aluminum(I) and gallium(I) compounds were recently described in a concise survey by Schnöckel et al.[11] The cluster compounds cited above have already been employed in the syntheses of numerous further products with hitherto unknown molecular structures.[8, 11–13] At present we are interested in the chemical behavior of the tetrahedral cluster compound $In_4[C(SiMe_3)_3]_4$ **1**,[4, 12, 13] which is obtained in high yield by treatment of InBr with $LiC(SiMe_3)_3\cdot 2THF$.[4, 5] The reactions of **1** with an excess of elemental sulfur, selenium, or tellurium give $In_4X_4[C(SiMe_3)_3]_4$ derivatives that exhibit a In_4X_4 heterocubane framework.[4, 13] Because of the easy insertion of four sulfur atoms under mild conditions, we hoped to synthesize compounds with the composition $In_4S_{4-x}[C(SiMe_3)_3]_4$ ($x = 1$ to 3) by the reaction of elemental sulfur with an excess of **1**; unlike the heterocubane molecules such derivatives would still contain indium atoms in an unusual low formal oxidation state.

However, elemental sulfur proved to be unsuitable for the syntheses of these compounds, because regardless of the reaction conditions only mixtures of $In_4S_4[C(SiMe_3)_3]_4$ and the starting compound **1** were formed. As a very mild reagent for the transfer of sulfur atoms we finally used propylene sulfide, which, however, required extensive optimization of the reaction. A colorless solid precipitated from the reaction solution that could not be further characterized because of the small amounts formed; in addition, the In_4S_4 derivative is partially formed from the beginning of the reaction by the complete sulfurization of **1**. Nevertheless we found an easy and reproducible method for the syntheses of a further compound (**2**): A solution of **1** in hexane was treated with a small excess of propylene sulfide and heated to 60 °C for 90 minutes. ^{1}H NMR spectra recorded to monitor the reaction reveal the formation of a mixture of **1** ($\delta = 0.447$), $In_4S_4R_4$ ($\delta = 0.443$), and the new product **2** ($\delta = 0.455$). Subsequently, additional propylene sulfide was added in portions, and each time the mixture was heated to 60 °C for 90 minutes, until **1** was completely consumed; the color of the solution changed from violet to red. The addition of the propylene sulfide in small portions gave a better result than the addition of a large excess of the reagent at the beginning of the reaction. Compound **2** and $In_4S_4[C(SiMe_3)_3]_4$ are present in a molar ratio of about 0.6 to 0.4 (NMR spectroscopy), and **2** crystallizes almost quantitatively from a solution in pentane as the less soluble component. The reaction is summarized in Equation (a).



The deep red compound **2** is isolated in 44% yield (based on **1**). According to elemental analysis the In:S ratio is 4:1, and the molar mass determined cryoscopically in benzene shows that **2** exists in the undissociated form. Single crystals of **2** were obtained from solutions of the compound in diisopropyl ether; they exhibit the same cell dimensions and space group as the starting compound **1**; however, one face of the In_4 tetrahedron is capped by a sulfur atom leading to the formation of a trigonal In_4S bipyramid (Figure 1).

The addition of the four-electron donor atom sulfur to the molecular core of **1** makes compound **2** isovalence electronic to the hitherto unknown compounds pentahydro-*closo*-pentaborate(2−) $[B_5H_5]^{2-}$ and thia-*closo*-pentaborane(4) B_4H_4S[15] as well as to the isolated and completely characterized 1,5-dicarba-*closo*-pentaborane(5) $B_3C_2H_5$.[15] Almost identical structural parameters were observed or calculated for all three boron derivatives; the B–B distances to the axial atoms were appropriate for single bonds, the B–B distances in the equatorial plane

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