Crystallization of 4,4′-Biphenyldicarbonitrile with Silver(I) Salts: a Change in Topology Concomitant with a Change in Counterion Leading to a Ninefold Diamondoid Network

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The preparation and X-ray crystal structures of two coordination networks $[Ag(BPCN)(CF_3SO_3)]\cdot C_6H_6$ **1** and $[Ag(BPCN)_2]PF_6$ **2** (BPCN = 4,4′-biphenyldicarbonitrile) are described; **1** consists of infinite chains; however, **2** exists as a ninefold interpenetrated diamondoid network.

The ability to control solid state organization at the molecular level towards the formation of supramolecular structures has been a major focus of research efforts in recent years.[1–4] Through the use of rigid organic building blocks, the formation of novel diamondoid frameworks and other networks has been realized *via* hydrogen bonds[5–9] and through the coordination of transition metal centres with polytopic donor ligands.[10–16] In hydrogen bonded systems, framework topology is controlled primarily by the inherent geometry of the pendant hydrogen bonding donors and acceptors. Paramount to the rational formation of transition metal coordination networks, however, is an understanding of the coordination geometry of the metal employed as influenced by the counterion and solvent. Towards this end, we have investigated the complexation of 4,4′-biphenyldicarbonitrile (BPCN) with both silver(I) triflate ($AgCF_3SO_3$) and silver(I) hexafluorophosphate ($AgPF_6$) by single crystal X-ray analysis. We report herein that crystallization of BPCN with $AgCF_3SO_3$ in benzene produces a one-dimensional polymeric structure. Changing the counterion to PF_6^- results in the formation of a ninefold interpenetrated diamondoid network for crystals grown from either ethanol or toluene. This represents the highest level of interpenetration observed for diamondoid networks.[17]

Crystallization of BPCN with $AgCF_3SO_3$ (1 : 1 molar ratio) from benzene by heating and slow cooling affords colourless needles of $[Ag(BPCN)(CF_3SO_3)]\cdot C_6H_6$ **1**.† Complex **1** exists as an infinite one-dimensional structure with chains running along [011] [see Fig. 1(*b*)]. The unit cell contains two crystallographically identical polymeric chains each comprised of one silver atom bonding to two BPCN moieties. Silver bonds to nitrogens of two nitrile groups at distances of 2.133(3) and 2.138(3) Å with a N–Ag–N bond angle of 174.4(1)°. Parallel chains exhibit π–π stacking at a plane-to-plane distance of 3.53 Å with aromatic rings offset 30.9° along the direction of propagation.[18] Two triflate counterions, each of which is disordered over three sites, and two benzene molecules are present in the unit cell as well. A weak interaction with a benzene molecule at a Ag–ring plane distance of 3.28 Å is observed. Also, a disordered triflate counterion bonds to silver at a weighted average Ag–O distance of 2.60 Å. It is this 'capping' of silver by triflate that is believed to prevent coordination to a third or even fourth ligand nitrogen which would allow the formation of a two- or three-dimensional network. The entry of triflate into the cation's coordination sphere is believed to be a result of poor solvation by benzene.

In contrast to the one-dimensional coordination polymer obtained using $AgCF_3SO_3$, crystallization of BPCN with $AgPF_6$ (1 : 1 molar ratio) by heating and slow cooling from ethanol or toluene produces yellow needles of $[Ag(BPCN)_2]PF_6$ **2**.† The structure of **2** is tetragonal and consists of a diamondoid network with ligand molecules bridging tetrahedrally coordinated silver atoms. This structure is noteworthy for several reasons. First, the framework is relatively undistorted as N–Ag–N bond angles range from 108.9(3)–110.6(6)° (this and all subsequent parameters were taken from the crystal structure of **2** from ethanol; similar observations were also made with the toluene example). Second, in order to efficiently fill space, the structure consists of nine interpenetrated diamondoid networks (see Fig. 2) projecting along the fourfold *c*-axis. This high degree of interpenetration is a result of the rather large ligand used (12.16 Å nitrogen-to-nitrogen distance). Indeed, a distance of 16.42 Å between tetrahedral centres (Ag–BPCN–Ag) is found in this structure which produces an adamantanoid cage that spans 43.60 Å in the *c*-direction (along the body diagonal) or 9*c* [*c* = 4.845(1) Å]. The large amount of void volume

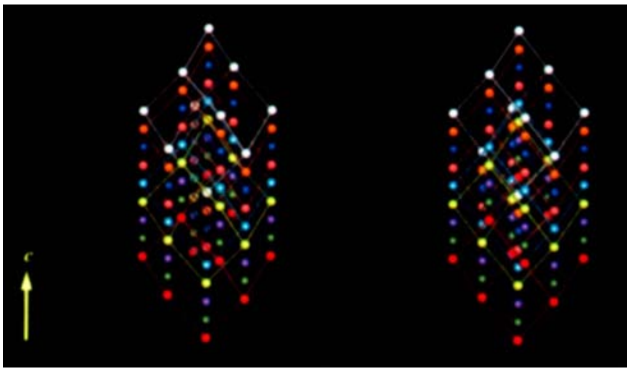

Fig. 2 Stereoview of the nine interpenetrated adamantanoid cages of **2**. BPCN molecules are represented by lines and silver atoms by balls. Counterions have been omitted for clarity.

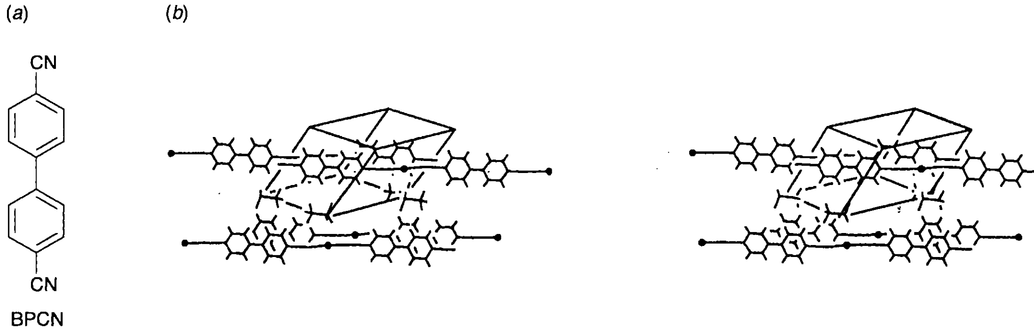

Fig. 1 (*a*) The chemical structure of BPCN. (*b*) Stereoview of the infinite chain structure **1**. Note that benzene molecules and minor site counterion positions have been removed for clarity.

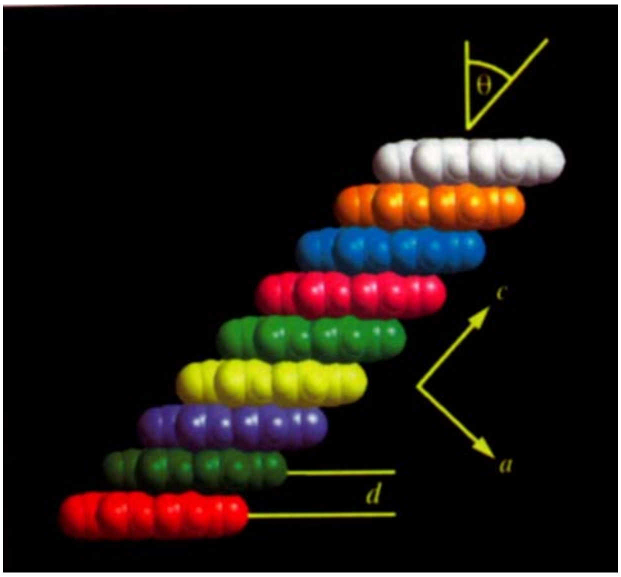

Fig. 3 The π–π stacking arrangement of BPCN in **2** created by the interpenetration of nine identical nets. The stacking distance, *d* (3.62 Å), and offset angle, θ (41.4°), are indicated.

created by a single network is filled by eight identical nets. These nets consist of parallel ligands offset along the long axis by 41.4° and display π–π stacking at a plane-to-plane distance of 3.62 Å (see Fig. 3). Columns of PF_6^- counterions, each of which is disordered over two sites, are revealed down the fourfold *c*-axis.

These results illustrate the influence that counterions can impart on topology in coordination networks. This is evidenced by the change in framework which results when $AgCF_3SO_3$ and $AgPF_6$ are used in solvents of similar polarity (benzene and toluene, respectively). Such a topological change is believed to be a consequence of the relatively low affinity of PF_6^- for silver(I) which allows increased ligand coordination. This rationale is further promoted by the observation that the diamondoid network is formed from two solvents of rather disparate polarities (ethanol and toluene). Therefore, the choice of a counterion that is weakly coordinating, irrespective of solvent polarity, is of great importance in the context of network design.

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Footnotes

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† *Crystal data* for **1**: triclinic, space group $P\bar{1}$ (no. 2), a = 9.978(3), b = 10.043(4), c = 12.124(3) Å, α = 84.97(3), β = 70.12(2), γ = 65.30(3)°, V = 1035.9(6) Å^3, D_c = 1.729 g cm^{-3}, Z = 2, M = 539.27, Mo-Kα, Lp corrected, 3200 reflections collected at 26 °C, 3037 unique reflections. The structure was solved using SHELXS-86 and refined using SHELXL-93. 3037 Reflections refined based on F_o^2 by full-matrix least squares; number of parameters = 427; $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ = 0.0332 (for $F > 4\sigma$) and 0.0504 (for all data); $wR2 = [\Sigma(w|F_o^2 - F_c^2|)/\Sigma w|F_o^2|^2]^{1/2}$ = 0.0834 (for $F > 4\sigma$) and 0.0929 (for all data); GOF = 1.068; residual electron density = +0.447 e Å^{-3} 0.85 Å from silver.

Crystal data for **2** (from ethanol): tetragonal, space group $I\bar{4}2d$ (no. 122), a = 24.552(3), c = 4.845(1) Å, V = 2920.6(8) Å^3, D_c = 1.504 g cm^{-3}, Z = 4, M = 661.29; Mo-Kα, Lp corrected, 3887 reflections collected at −75 °C, 971 unique reflections. The structure was solved using SHELXTL-PLUS and refined using SHELXL-93. 970 Reflections refined based on F_o^2 by full-matrix least squares, number of parameters = 96, $R1$ = 0.0788 (for $F > 4\sigma$) and 0.1104 (for all data); $wR2$ = 0.1987 (for $F > 4\sigma$) and 0.2255 (for all data); GOF = 1.209; residual electron density = +1.189 e Å^{-3} 0.98 Å from silver.

Crystal data for **2** (from toluene): tetragonal, space group $I\bar{4}2d$ (no. 122), a = 24.272(3), c = 4.937(1) Å, V = 2908.5(8) Å^3, D_c = 1.510 g cm^{-3}, Z = 4, M = 661.29, Mo-Kα, Lp corrected, 4497 reflections collected at −75 °C, 1023 unique reflections. The structure was solved using SHELXTL-PLUS, and refined using SHELXL-93. 1021 Reflections refined based on F_o^2 by full-matrix least squares; number of parameters = 91, $R1$ = 0.0654 (for $F > 4\sigma$) and 0.0931 (for all data), $wR2$ = 0.1949 (for $F > 4\sigma$) and 0.2339 (for all data); GOF = 1.218; residual electron density = +0.964 e Å^{-3} 1.05 Å from fluorine.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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