A novel double-strand helical motif in a two-dimensional polymeric complex of silver(I) perchlorate with benzo[*e*]acephenanthrylene

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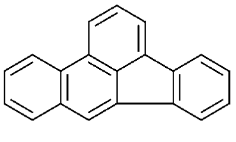
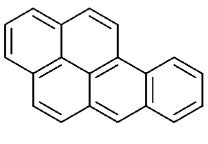
A 2-D double-strand helical complex with a strand of polycyclic aromatic hydrocarbons and a strand of silver(I) perchlorate has been isolated and crystallographically characterised.

Polymetallic helical complexes are of special interest because of their structural similarities to nucleic acids. They are also intrinsically interesting for their potential applications in the fields of supramolecular chemistry, asymmetric catalysis, and nonlinear optical materials.[1–3] Very often, these helicates are prepared by the coordination of metal ions to tailored polydentate organic strands, such as oligopyridines and some optically active organic ligands, in which nitrogen or oxygen atoms always serve as binding units along the strand.[1–6] In contrast, we report an unprecedented 2-D double-strand helical polymer synthesized from a polycyclic aromatic hydrocarbon (PAH), benzo[*e*]acephenanthrylene (bpa), and silver(I) perchlorate. It was proven in our earlier studies that metal complexes with planar PAH ligands have a tendency to form decker-like or multilayer architectures.[7–9] To our surprise, the planar bpa can lead to the formation of a helical structure with a sheet network. Here we present our results showing how the bpa molecules are self-assembled and wrapped about the flexible silver(I) ions to construct a unique double-strand helical architecture. Some physicochemical properties of the complex are also discussed.



benzo[*e*]acephenanthrylene (bpa)



benzo[*a*]pyrene (L)

The reaction of bpa with $AgClO_4$ in toluene leads to formation of the complex $[Ag_4(bpa)_3(ClO_4)_4]$ **1**.† The X-ray structural determination‡ reveals a two-dimensional framework constructed from cation–π interactions of Ag^I with bpa. While there are two crystallographically independent Ag^I cations, both of them have a similar pseudotetrahedral environment comprising two C=C π-bonds from two aromatic groups and two oxygen atoms from two perchlorate anions (taking the C=C group as one ligand) (Fig. 1). The Ag–O and Ag–C distances range from 2.402(6) to 2.69(1) Å, and 2.412(6) to 2.755(6) Å, respectively. The next closest contact between silver and carbon is 2.867(8) Å, well beyond the limits from 2.40 to 2.76 Å observed in the reported silver(I) aromatic complexes.[7] On the other hand, the aromatic ligand also involves two different coordination modes, one displaying μ-di-η^2 coordination with two metal ions above and below the aromatic plane, and the other exhibiting a μ-tri-η^2 motif with three metal centers on the same side of the aromatic plane. Furthermore, these aromatic ligands are coordinated to the silver(I) ions by wrapping about them to construct a double-helical chain with the silver(I) perchlorate groups in one strand and the μ-tri-η^2 aromatic ligands in the other (Fig. 2). The period of the helix is equal to the crystallographic *a* axis (14.11 Å). In addition, each μ-di-η^2 bpa moiety functions as a linkage bridging two adjacent helical chains *via* the Ag^I ions. This results in extended interactions of the double-strand helical chains to form the two-dimensional framework shown in Fig. 3.

The most significant structural feature presented here is the interesting arrangement of bpa molecules and unusual coordination of the silver ions forming a unique helical structure. As established in the literature,[2] for most helicates the governing factor of the structure is that the organic ligand is shaped into one strand and contains several binding units, such as N or O, along the strand allowing the recognition and coordination of the metal ions. By comparison, the organic strands in complex **1** are self-assembled *via* π–π interactions at the overlapped portion of two adjacent μ-tri-η^2 bpa molecules, with a shortest interplanar separation of 3.52 Å. On the other hand, the flexible silver(I) ions, linked by perchlorate anions, exhibit a special spiral structure, being bound both to these stacked aromatic strands forming the helical chains and to the μ-di-η^2 bpa molecules exhibiting a sheet framework. Such a structural feature, to the best of our knowledge, has not been described before. There is only one example in the literature describing a helical structure of a polycyclic aromatic hydrocarbon, $[Ag_4(L)_2(ClO_4)_4(toluene)_2]$ (L = benzo[*a*]pyrene), where no stacking interactions were observed along the organic strand, and the double-helical chains are formed by aromatic π–π interactions *via* interweaved strands of polycycles.[7]

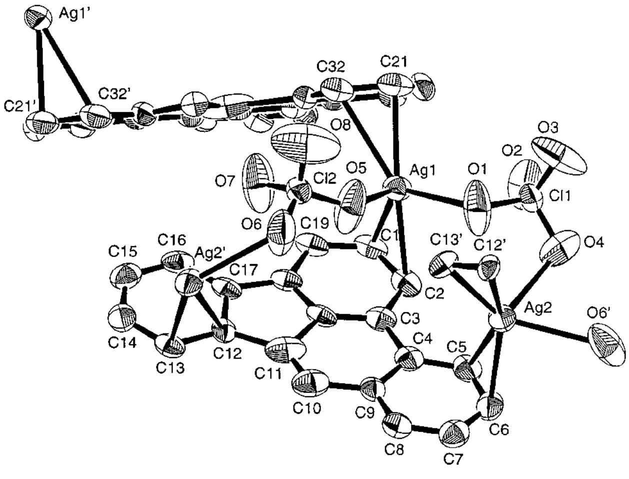


Fig. 1 Structure and partial labeling of $[Ag_4(bpa)_3(ClO_4)_4]$. Selected bond lengths (Å) and angles (°): Ag(1)–O(1) 2.452(7), Ag(1)–O(5) 2.402(6), Ag(1)–C(1) 2.502(6), Ag(1)–C(2) 2.555(6), Ag(1)–C(21) 2.446(7), Ag(1)–C(32) 2.720(7), Ag(2)–O(4) 2.69(1), Ag(2)–O(6) 2.532(8), Ag(2)–C(5) 2.622(7), Ag(2)–C(6) 2.454(6), Ag(2)–C(12) 2.755(6), Ag(2)–C(13) 2.412(6); O(1)–Ag(1)–O(5) 77.2(2), O(1)–Ag(1)–C(1) 125.0(3), O(1)–Ag(1)–C(21) 106.0(3), O(5)–Ag(1)–C(1) 118.9(3), O(5)–Ag(1)–C(21) 105.6(3), C(1)–Ag(1)–C(21) 116.8(2), O(4)–Ag(2)–O(6) 72.5(2), O(4)–Ag(2)–C(6) 104.7(3), O(4)–Ag(2)–C(13) 110.5(3), O(6)–Ag(2)–C(6) 86.3(3), O(6)–Ag(2)–C(13) 130.0(3), C(6)–Ag(2)–C(13) 135.2(3).

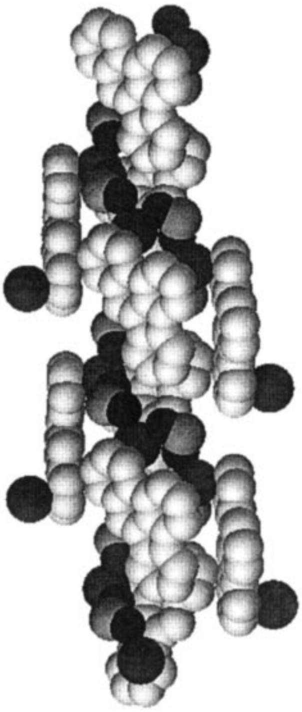


Fig. 2 Space-filling model of the double-strand helical structure of **1**.

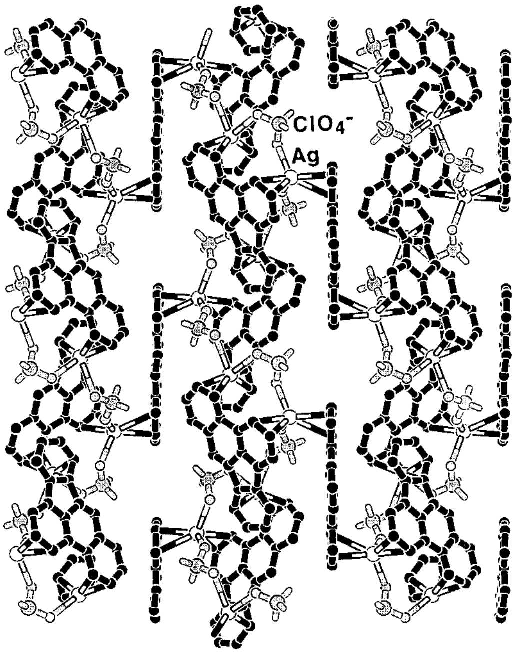


Fig. 3 Two-dimentional sheet framework of **1**.

The compound is soluble in most common organic solvents. It is reasonably stable in ambient daylight for 1 week, but shows slight moisture sensitivity under atmospheric conditions. The UV–VIS absorption spectrum of the free ligand bpa in toluene (2.5×10^{-4} M) displays an intense absorption around 350 nm, indicative of a $\pi \rightarrow \pi^*$ transition.[10] Upon complexation to Ag(I), the transition does not change significantly, probably due to the dissociation of the complex in solution. The electrical conductivity of the complex and its free ligand bpa was measured *via* the silver-coated two-probe technique with compacted pellets and showed that complex **1** displays semiconducting behavior with a σ value of 1.1×10^{-4} S cm^{-1}, whereas the bpa free ligand is non-conducting at room temperature.

It is obvious that helicates can sometimes be obtained from non-stranded polycyclic aromatic hydrocarbons through stacking interactions. Although structural control in this new system is rather difficult compared with the conventional polydentate strand-like organic ligands,[1,2] once structural control and molecular programming have been significantly explored and improved, the very interesting motifs isolated may broaden our insight into the helicate research field and introduce a novel perspective in the area of supramolecular chemistry. Further studies are directed toward the development of the structure-predicting process in this area with the aim of exploring the intrinsic nature and design of other novel helicate frameworks.

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Notes and references

† To a solution of benzo[*e*]acephenanthrylene (25.2 mg, 0.1 mmol) in 1 ml of toluene was added $AgClO_4$ (84 mg, 0.4 mmol). After about 20 min of stirring, the resultant colorless solution was introduced into a 7 mm diameter glass tube and layered with *n*-hexane as a diffusion solvent. The glass tube was sealed under Ar and wrapped with aluminium foil. After standing at room temperature for 3 days yellow brick-like crystals were obtained (calc. for $C_{60}H_{36}Cl_4Ag_4O_{16}$: C, 45.39; H 2.27. Found: C, 44.96; H, 2.31%). **CAUTION:** Perchlorate salts of metal complexes with organic ligands are potentially explosive. Suitable care should be taken during the synthesis.

‡ *Crystal data* for **1**: $C_{60}H_{36}Cl_4Ag_4O_{16}$, M = 1586.22, orthorhombic, space group *Pbcn* (#60), a = 14.114(1), b = 18.0670(7), c = 20.8589(4) Å, V = 5319.0(4) Å^3, Z = 4, D_c = 1.981 g cm^{-3}, μ(Mo-Kα) = 17.24 cm^{-1}, F(000) = 3120.00, T = 293(2) K, 6044 reflections collected (Quatum CCD diffactometer), 3628 unique reflections, R_1 = 0.060 (3628 reflections), wR = 0.158. The μ-di-η^2 bpa molecule was analyzed as disordered such that there is a mirror plane bisecting the longer molecular axis. CCDC 182/1308. See http://www.rsc.org/suppdata/cc/1999/1545/ for crystallographic data in .cif format.

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