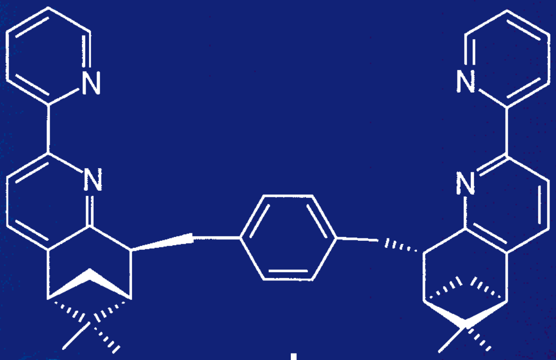
Chiral derivatives of pyridine and bipyridines with fused pinene groups are interesting for several applications. For example helicates with predetermined chirality can be obtained: $[Ag_6L_6]^{6+}$



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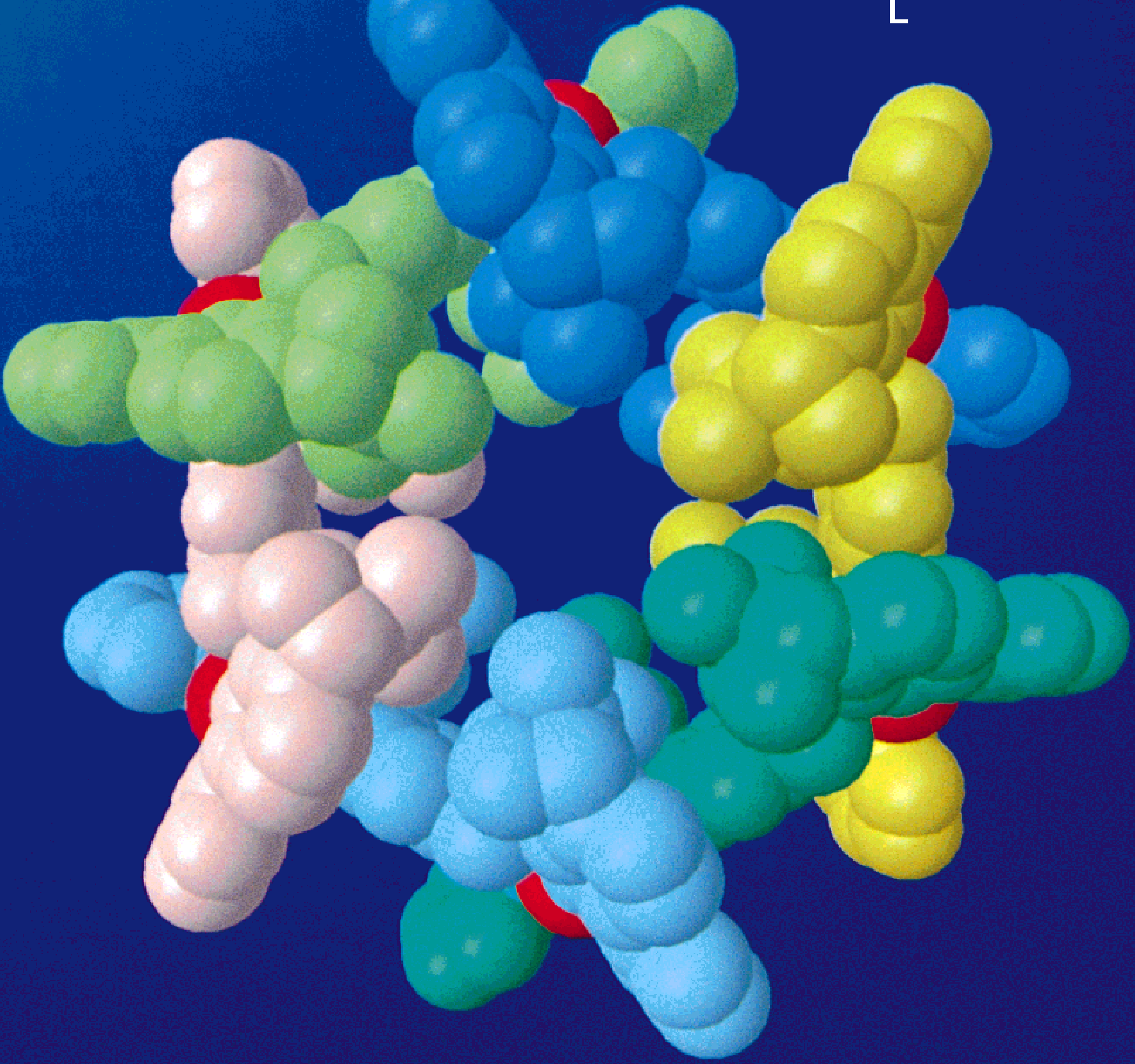

An esthetically highly pleasing structure, formed by a self-assembly process from Ag^+ ions and an enantiomerically pure bipyridine-type ligand, is described on the following pages.

Completely Stereospecific Self-Assembly of a Circular Helicate**

Olimpia Mamula, Alex von Zelewsky,* and
Gérald Bernardinelli

Self-assembly of helicates with labile metal centers has been recently a subject of great interest in the field of supramolecular chemistry.[1, 2] The inherently chiral helicates are formed as racemates if nonchiral ligands are used. Various procedures for resolution have been successfully applied in order to obtain the pure enantiomers.[3–6] The enantioselective synthesis of chiral structures in general and of supramolecular assemblies in particular is a challenge. Chiral helicating ligands can induce stereoselectivity; that is, the chiral centers of the ligands influence the chirality of the resulting helix.[7–15]

So far most studies in the coordination chemistry of helicates were carried out on structures that are noncyclic. In few cases circular helical assemblies have been reported.[5, 16–20] However, with the exception of a recently reported trinuclear species,[19] in all such cases racemates were obtained. Here we present an example of a completely stereospecific, self-assembled, circular helical structure.

We have recently shown that a family of ligands, which now comprises several molecules, is easily accessible from natural terpene type compounds.[21] These pyridine and bipyridine (bipy) ligands can be used to synthesize configurationally stable coordination compounds in which the stereochemistry at the metal center is completely predetermined by the configuration of the ligands.[22, 23] Here we describe the application of a related ligand, which was designed for stereoselective self-assembly processes.

An important feature of the molecules of the pinene-2,2′-bipyridine series is their reactivity at one center of the pinene group. Ligand **L1** (Figure 1) obtained from (−)-*α*-pinene is deprotonated regioselectively by lithium diisopropyl amide (LDA) at the methylene group in *α*-position to the pyridine ring. The carbanion obtained reacts stereoselectively (in the less hindered position opposite to the methyl groups) with almost any alkyl bromide to give various derivatives. One possibility is to connect two bipy-type moieties with *α*,*α*′-dibromo-*para*-xylene to obtain the ligand **L2**.

In contrast to other similar ligands,[23] for instance **L4** (Figure 1), **L2** cannot coordinate in a tetradentate manner to *one* coordination center because of steric constraints. We therefore tested the behavior of **L2** with labile coordination centers in view of the formation of polynuclear self-assembled structures.

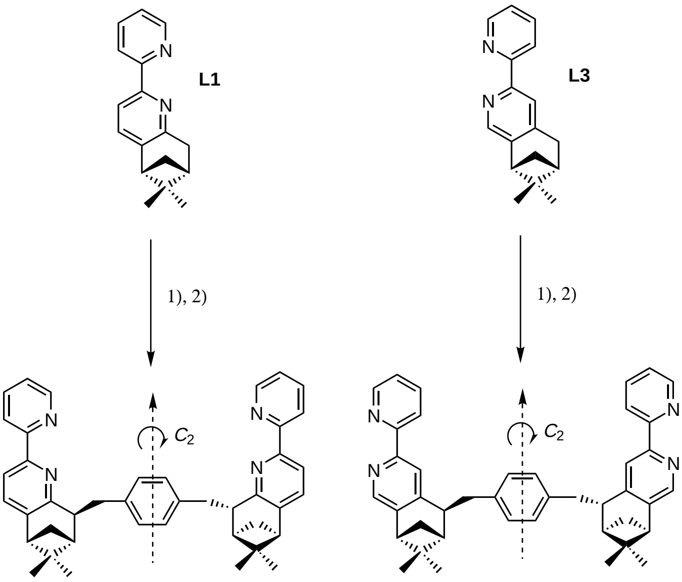

Figure 1. Synthetic pathways to chiral ligands **L2** and **L4**. 1) LDA; 2) *α*,*α*′-dibromo-*para*-xylene. The twofold axis is drawn in the structural formulas of **L2** and **L4**.

The ligand **L2** spontaneously forms a sixfold, circular single-stranded helicate with Ag^I ions (see Experimental Section), as indicated by X-ray diffraction in the solid state. NMR and circular dichroism (CD) spectroscopy in solution, as well as preliminary electrospray mass spectrometry (ES–MS) results, indicate that this species persists in the dissolved state, but detailed investigations have to be carried out to elucidate the exact behavior in solution. In addition, preliminary results with other metal ions like Cu^I show that helix formation with **L2** is a general phenomenon.

As indicated by the CD spectra of the solutions, complex formation leads to a chiral coordination unit with Ag^I. There is virtually no CD activity of **L2** in the $\pi-\pi^*$ region of the spectrum (230–320 nm). The CD activity ($\Delta\varepsilon_{314} = +16\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$ for one metal center) of the helicate in this spectral region can be attributed to an exciton coupling.[24]

The ^{1}H NMR spectrum of ligand **L2** shows a half-set of protons due to its C_2-symmetry axis. The complex obtained by mixing **L2** and $AgPF_6$ at room temperature in acetonitrile in a 1:1 stoichiometric ratio shows a ^{1}H NMR spectrum containing the same number of lines as the free ligand (Figure 2). Two features of the ^{1}H NMR signals of the complex are worth special mention: a) The signals of all the aromatic protons are shifted relative to those of the free ligand. Most notably is an upfield displacement (1.45 ppm) of C20 and C24 in the xylylene bridge. This signal is broadened significantly. Spectra taken at lower temperatures (down to −40°C in CD_3CN) show a distinct sharpening of this line leading eventually to a splitting into two lines. This behavior indicates the existence of at least two rapidly exchanging species in solution. b) The lines of the methyl groups from the pinene moieties (not shown) shift to a lesser degree (about 0.5 ppm) relative to the signals of protons from the xylylene bridge, and a broadening at room temperature is observed again.

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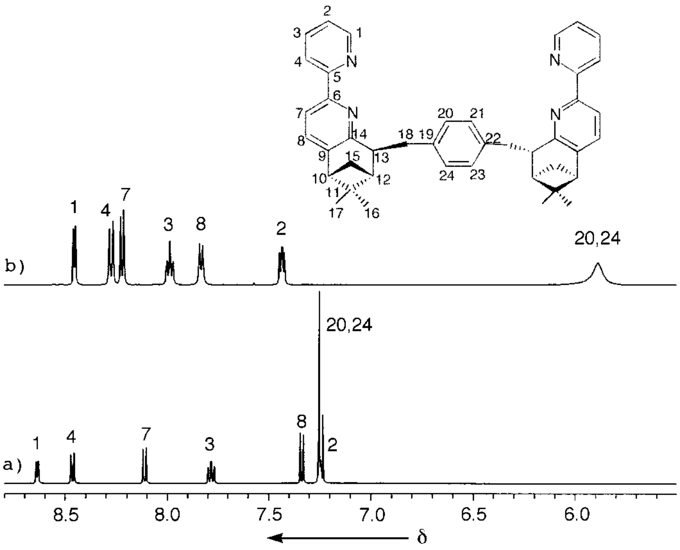

Figure 2. Partial ^1H NMR spectra (500 MHz, aromatic protons) of a) ligand **L2** (in $CDCl_3$ for solubility reasons; the displacements are the same in CD_3CN) and b) the Ag^I complex in CD_3CN. Assignment of the signals has been achieved with ^{13}C NMR, NOESY, COSY, HETCOR experimental data.

X-ray diffraction analysis of the salt of the silver complex shows the presence of a circular, hexameric, single-stranded helicate (Figure 3), which could be obtained by slow diffusion of diethyl ether into an acetonitrile solution containing **L2** and $AgPF_6$ in a 1:1 molar ratio. This structure represents a first example of a large self-assembled hexanuclear species, which is circular, helical, and predetermined in its absolute configuration. It can be considered a chiral macrocycle containing 78 atoms ($C_{60}N_{12}Ag_6$) in which one bisbidentate ligand forms a bridge between two adjacent Ag centers ($Ag\cdots Ag = 9.961(2)$ Å). The six Ag(**L2**) units making up the structure are related by a crystallographic C_6 axis (Figure 4). The silver ions are tetrahedrally coordinated by four almost equidistant (2.31 Å) nitrogen donor atoms located on two different ligands. The bite angles of the chelates are 72.0(4) and 72.7(5)°, and the dihedral angle between the two N-Ag-N chelate planes at one center is 66.8(2)°. Within each bipyridine unit of the ligand the two pyridine rings are twisted relative to each other (by 18.0(6) and 22.5(5)°). All chiral centers of the ligands, the pinene groups, are oriented towards the center of the circular structure making up two distinct layers, surrounding the chiral cavity.[25] The xylylene bridges are all nearly parallel (1.5°) to the C_6 axis and form the sides of the hexagonal skeleton (distance between two opposite xylene moieties $\approx$ 18.1 Å), whereas the terminal pyridines form the external shell of the circular complex. Both the absolute structure parameter (see Experimental Section) and the relation of the known chirality of the pinene group to that at the metal centers clearly indicate that the handedness of the helix is *P*. The same absolute configuration has been observed in helicates obtained with octahedral coordination centers with ligand **L4**,[26] as well as in mononuclear complexes[27] of Ru^{II}. The commercially available (+)-α-pinene yields **L1** in the other enantiomeric form, and the same sequence of reactions will afford the *M*-helical form of the circular helicate. Studies of chiral recognition when both isomers are present simultaneously in solution are in progress. The outside diameter of the hexagonal structure is about 3 nm and the cavity has a diameter of 0.84 nm. The thickness of a hexagonal disc is about 1.4 nm.

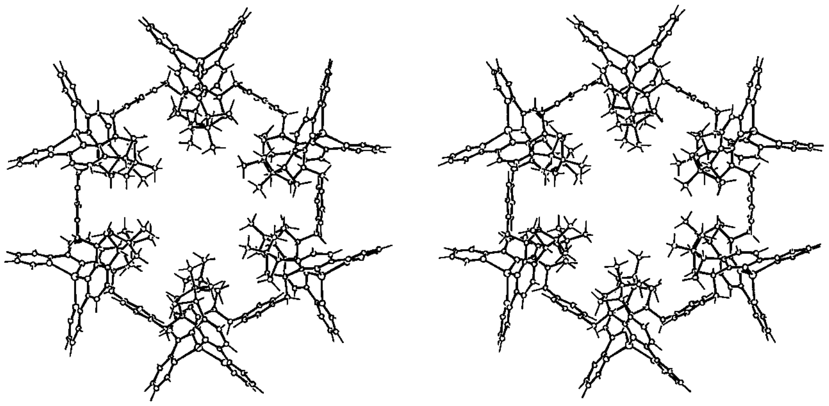

Figure 4. Stereoview of the $[Ag_6(L2)_6]^{6+}$ ion along its sixfold axis.

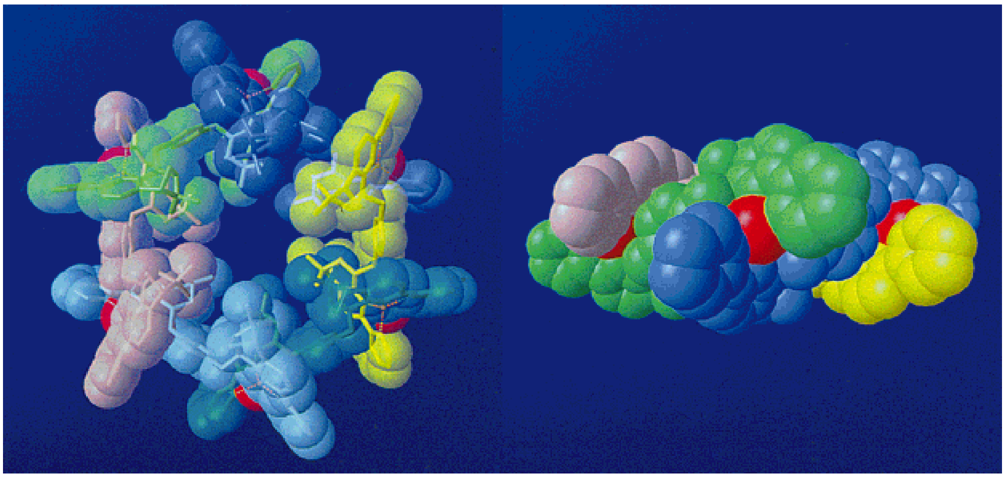

Figure 3. Crystal structure of **1** (hydrogen atoms are omitted for clarity). Left: Top view with superimposed stick model of the structure. Right: View from the side. The representation was generated by computer from X-ray diffraction data.

In contrast to other circular helical systems,[5, 17, 20] this structure self-assembles from the metal ion and the ligand alone. In this case there is no central element, for example an anion, which could act as a template for generating a circular structure. Thus it is demonstrated that careful design of the ligands can lead to large, highly organized systems, which is a prerequisite for the construction of molecular assemblies with well-defined functionalities. The facile ligand synthesis and the spontaneous formation of this new class of self-assembled structures makes them objects of great interest for investigations of hitherto not well understood phenomena in supramolecular chemistry. The chiral cavity of $[Ag_6(\mathbf{L2})_6]^{6+}$ looks promising for the study of stereospecific noncovalent interactions, chiral recognition, and possibly stereoselective catalytic processes.

Experimental Section

The ligand **L1** was synthesized according to published procedures.[21] Ligand **L2** was obtained from **L1** following the same procedure as for **L4**.[23]

$\mathbf{L2} \cdot H_2O$ (62.1 mg, 0.1 mmol) dissolved in 10 mL mixed solvent (acetonitrile/chloroform 5/1) was added rapidly under inert atmosphere (Ar) to a solution containing $AgPF_6$ (Fluka; 25.3 mg 0.1 mmol). The resulting colorless solution was stirred for few minutes, and after the removal of the solvents, the white powder was dried under high vacuum and analyzed. The complex can be obtained also by reaction between ligand and silver acetate in methanol followed by precipitation with NH_4PF_6.

L2: ^1H NMR (500 MHz, $CDCl_3$, 25°C): $\delta = 8.65$ (ddd, 2H, H(1), $^3J_{1,2} = 4.8$ Hz, $^4J_{1,3} = 1.8$ Hz, $^5J_{1,4} = 0.9$ Hz), 8.46 (ddd, 2H, H(4), $^3J_{4,3} = 8.0$ Hz, $^4J_{4,2} = 1.1$ Hz, $^5J_{4,1} = 0.9$ Hz), 8.12 (d, 2H, H(7), $^3J_{7,8} = 7.7$ Hz), 7.79 (ddd, 2H, H(3), $^3J_{3,4} = 8$ Hz, $^3J_{3,2} = 7.5$ Hz, $^4J_{3,1} = 1.8$ Hz), 7.34 (d, 2H, H(8), $^3J_{8,7} = 7.7$ Hz), 7.26 (s, 4H, H(20,24)), 7.25 (m, 2H, H(2)), 3.82 (dd, 2H, H(18b), $^2J_{18b,18a} = 13.7$ Hz, $^3J_{18b,13} = 3.8$ Hz), 3.42 (ddd, 2H, H(13), $^3J_{13,18b} = 3.8$ Hz, $^3J_{13,18a} = 11.0$ Hz, $^3J_{13,12} = 3$ Hz), 2.80 (dd, 2H, H(10), $^3J_{10,15b} = 5.5$ Hz, $^4J_{10,12} = 5.5$ Hz), 2.73 (dd, 2H, H(18a), $^2J_{18a,18b} = 13.7$ Hz, $^3J_{18a,13} = 11$ Hz), 2.58 (ddd, 2H, H(15b), $^3J_{15b,10} = 5.5$ Hz, $^3J_{15b,12} = 5.5$ Hz, $^2J_{15b,15a} = 9.8$ Hz), 2.16 (ddd, 2H, H(12), $^3J_{12,15b} = 5.5$ Hz, $^4J_{12,10} = 5.5$ Hz, $^3J_{12,13} = 3$ Hz), 1.43 (d, 2H, H(15a), $^2J_{15a,15b} = 9.8$ Hz), 1.36 (s, 6H, H(17)), 0.63 (s, 6H, H(16)). ^{13}C NMR (75.44 MHz, $CDCl_3$, 25°C): $\delta = 158.79$ (q), 156.89 (q), 153.29 (q), 149.05 (C(1)), 142.34 (q), 138.65 (q), 136.76 (C(13)), 133.73 (C(8)), 129.26 (C(20), C(21), C(23), C(24)), 123.10 (C(2)), 120.86 (C(4)), 118.00 (C(7)), 47.00 (C(10)), 46.26 (C(13)), 42.79 (C(12)), 41.25 (q, C(11)), 38.48 (C(18)), 28.40 (C(15)), 26.37 (C(17)), 20.97 (C(16)). $[\alpha]_D$ (25°C, 13.6 mg in 10 mL CH_2Cl_2) $= -132$. UV/Vis (CH_2Cl_2): λ_{max} (ε_{max}): 230 nm (2.4×10^4), 249 nm (2×10^4), 256 nm (2.1×10^4), 296 nm (3.9×10^4), 314 nm (2.9×10^4, sh). Elemental analysis calculated for $C_{42}H_{42}N_4 \cdot H_2O$: C 81.26, H 7.14, N 9.02 %; found: C 81.26, H 7.02, N 9.03 %. Thin-layer chromatography: Silica gel, hexane/ethyl acetate/triethylamine 2/1/0.1. $R_f = 0.39$.

$[Ag_6(L2)_6](PF_6)_6$: ^1H NMR (CD_3CN, 500 MHz, 25°C): $\delta = 8.44$ (d, 2H, H(1), $^3J_{1,2} = 5.1$ Hz), 8.27 (d, 2H, H(4), $^3J_{4,3} = 8.2$ Hz), 8.21 (d, 2H, H(7), $^3J_{7,8} = 8.0$ Hz), 7.98 (dd, 2H, H(3), $^3J_{3,4} = 8.2$ Hz, $^3J_{3,2} = 7.0$ Hz), 7.83 (d, 2H, H(8), $^3J_{8,7} = 8.0$ Hz), 7.43 (dd, 2H, H(2), $^3J_{2,1} = 5.1$ Hz, $^3J_{2,3} = 7.0$ Hz), 5.89 (s, 4H, H(20, 24)), 3.73 (d, 2H, H(18b), $^3J_{18b,18a} = 11.4$ Hz), 3.01 (dd, 2H, H(10), $^3J_{10,15b} = 5.6$ Hz, $^3J_{10,12} = 5.6$ Hz), 2.82 (d, 2H, H(13), $^3J_{13,18b} = 11.4$ Hz), 2.55 (ddd, 2H, H(15b), $^2J_{15b,15a} = 10.1$ Hz, $^3J_{15b,12} = 5.6$ Hz, $^3J_{15b,10} = 5.6$ Hz), 2.41 (dd, 2H, H(18a), $^2J_{18a,18b} = 11.4$ Hz, $^3J_{18a,13} = 11.4$ Hz), 1.57 (d, 2H, H(15a), $^2J_{15a,15b} = 10.1$ Hz), 1.39 (s, broad, 2H, H(12)), 1.17 (s, 6H, H(17)), 0.08 (s, 6H, H(16)). ^{13}C NMR (CD_3CN, 125.75 MHz, 25°C): $\delta = 159.95$ (q), 153.23 (q), 151.35 (C(1)), 151.14 (q), 146.19 (q), 140.23 (C(3)), 137.57 (q), 137.43 (C(8)), 129.29 (C(20), C(21), C(23), C(24)), 126.33 (C(2)), 123.50 (C(4)), 122.31 (C(7)), 50.36 (C(13)), 47.15 (C(10)), 42.99 (C(12)), 41.42 (q, C(11)), 38.20 (C(18)), 27.95 (C(15)), 26.44 (C(17)), 21.65 (C(16)). UV-Vis (CH_3CN, $c = 1.27 \times 10^{-5}$ M $[AgL]^+ L^{-1}$): λ_{max} (ε_{max}): 249 nm (1.7×10^4), 254 nm (2.16×10^4), 294 nm (3.73×10^4), 304 nm (2.82×10^4). Elemental analysis calculated for $Ag_6C_{252}H_{252}N_{24}P_6F_{36}$: C 58.96, H 4.95, N 6.55 %; found C 59.25, H 5.48, N 6.28 %. Crystal structure determination of $[Ag(C_{42}H_{42}N_4)]_6(PF_6)_6(CH_3CN)_6(C_4H_{10}O)_3(H_2O)_{1.5}$: $M_r = 5630$; $\mu = 4.052$ mm^{-1}, $F(000) = 2901$, $\rho_{calcd} = 1.25$ g cm^{-3}, hexagonal, $P6$, $Z = 1$, $a = 26.521(3)$, $c = 12.236(2)$ Å, $V = 7453(2)$ Å^3, colorless hexagonal prism $0.26 \times 0.26 \times 0.26 \times 0.75$ mm^3; $T = 200$ K; Stoe Stadi4 diffractometer; $Cu_{K\alpha}$ radiation ($\lambda = 1.5418$ Å), 2θ range $= 2-100°$; $0 < h < 22$; $0 < k < 22$; $0 < l < 12$ and all antireflections; 5424 measured reflections, 5109 unique of which 4688 observables ($|F_o| > 4\sigma(F_o)$); analytical absorption corrections[28] (A* min/max = 2.295/3.215). Structure solved by direct methods,[29] all other calculations used XTAL[30] system and ORTEP[31] programs. Full-matrix least-squares refinement (on F), absolute structure parameter[32] $x = 0.00(1)$, $S = 1.73(3)$, $R = 0.046$, $\omega R = 0.063$ ($\omega = 1/[\sigma^2(F_o) + 0.002(F_o^2]$), for 536 variables and 4688 reflections. Hydrogen atoms were placed in calculated positions. The diethyl ether and water molecules are disordered and refined with U_{iso} and population parameters of 0.5. The water molecules are located on sixfold axes with one of them at the center of the Ag_6L_6 complex. The molecular packing shows compact layers of cations with interstitial acetonitrile molecules separated by layers containing the anions, the diethyl ether molecule, and the remaining water molecules, explaining the easy cleavage of the crystals along the (110) planes. It should be noted that a large majority of crystals show important disorders or cleavages leading to a poor diffraction, very large overall displacement parameters, and enlarged or split diffraction profiles.[33]

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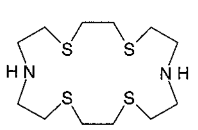
[33] Any disturbance of the equilibrium between the crystals and their mother liquor leads rapidly to the autocleavage of the crystals that become like pre-sliced salami.

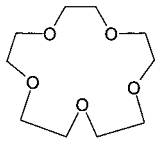
Template Assembly of Polyiodide Networks at Complexed Metal Cations: Synthesis and Structures of $[Pd_2Cl_2([18]aneN_2S_4)]_{1.5}I_5(I_3)_2$ and $[K([15]aneO_5)_2]I_9$**

Alexander J. Blake, Robert O. Gould, Wan-Sheung Li, Vito Lippolis, Simon Parsons, Christian Radek, and Martin Schröder*

Although crystal engineering has become an area of increasing activity over recent years,[1–4] most interest has centered upon the use of hydrogen-bonding between suitable organic molecules to generate three-dimensional arrays and networks.[1–3] The design of inorganic networks is much less well developed[4–8] but recent examples feature cationic three-dimensional networks based on linear bridging ligands bound to tetrahedral metal ions such as Cu^I and Ag^I.[5, 6, 9] Anionic, nonzeolitic inorganic supramolecular architectures are by contrast very rare, and the only examples known involve iodine-rich compounds.[10, 11] In this context we have been interested in ascertaining whether metal cations complexed by macrocycles can be used as templates in the synthesis of extended polyiodide arrays and to achieve control over the resulting three-dimensional architectures.[12] We report herein two unique inorganic matrices composed of polyiodide arrays assembled around a hydrogen-bonded $[Pd_2Cl_2([18]aneN_2S_4)]^{2+}$ cationic polymer and around the sandwich crown ether complex $[K([15]aneO_5)_2]^+$.



[18]aneN₂S₄



[15]aneO₅

Reaction of the binuclear complex $[Pd_2Cl_2([18]aneN_2S_4)](PF_6)_2$[13] with nBu$_4$NI and I_2 in a 1:2:4 molar ratio in acetonitrile, followed by several days of slow evaporation of the solvent, affords black prismatic crystals in 90% yield. X-ray diffraction studies were undertaken to determine their structure.[14] The asymmetric unit consists of one I_5^- and two I_3^- ions and one and a half binuclear $[Pd_2Cl_2([18]aneN_2S_4)]^{2+}$ dications. The Pd^{II} ions are each coordinated to one N- and two S-donor atoms, and a Cl^- ligand completes the square-planar coordination. The two coordination planes lie parallel to each other but the overall binuclear dication adopts a stepped conformation in order to minimize steric interactions. Significantly, unlike the structure of the corresponding PF_6^- salt,[13] the dications are linked pairwise by hydrogen bonds between the (N)H and Cl atoms to form infinite chains in the crystal lattice [Cl···N distances 3.254(14) – 3.356(12) Å; (N)H···Cl 2.57 Å] (Figure 1). The intracation Pd···Pd distances are 4.055(2) and 4.155(2) Å, while the Pd···Pd distances between adjacent cations are significantly shorter [3.449(2), 3.463(2) Å]. The infinite chains of binuclear dications are embedded in a unique matrix of polyiodides whose fundamental units are one "L"-shaped I_5^- ion consisting of an asymmetric I_3^- ion [I(1) – I(2) 2.845(2), I(2) – I(3) 3.045(2) Å; I(1)-I(2)-I(3) = 179.69(9)°] interacting with a I_2 molecule [I(10) – I(11) 2.775(3), I(3) – I(10) 3.349(2) Å; I(2)-I(3)-I(10) = 90.00(6)°], and two slightly asymmetric I_3^- ions [I(4) – I(5) 2.904(2), I(5) – I(6) 2.959(2) Å; I(4)-I(5)-I(6) =

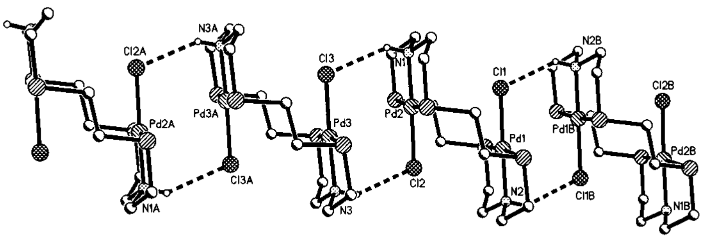


Figure 1. Structure of cation in $[Pd_2Cl_2([18]aneN_2S_4)]_{1.5}I_5(I_3)_2$.

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