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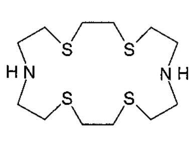
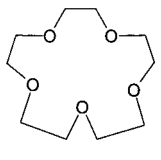
Template Assembly of Polyiodide Networks at Complexed Metal Cations: Synthesis and Structures of $[Pd_2Cl_2([18]aneN_2S_4)]_{1.5}I_5(I_3)_2$ and $[K([15]aneO_5)_2]I_9$**

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]aneN_2S_4



[15]aneO_5

Reaction of the binuclear complex $[Pd_2Cl_2([18]aneN_2S_4)](PF_6)_2$[13] with $n$$Bu_4NI$ 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) =

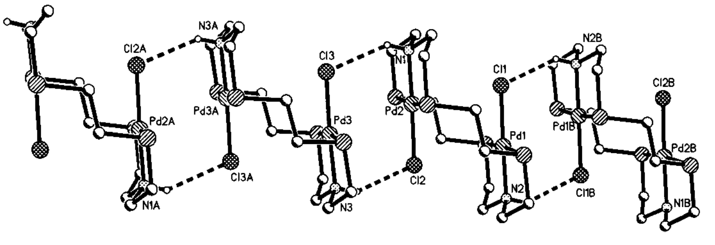


Figure 1. Structure of cation in $[Pd_2Cl_2([18]aneN_2S_4)]_{1.5}I_5(I_3)_2$.

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[**] This work was supported by the Engineering and Physical Sciences Research Council (UK). We thank the EPSRC National Mass Spectrometry Service, University of Swansea. ([18]aneN_2S_4 = 1,4,10,13-tetrathia-7,16-diazacyclooctadecane, [15]aneO_5 = 1,4,7,10,13-pentaoxacyclopentadecane).

176.47(6)°; I(7)–I(8) 2.948(2), I(8)–I(9) 2.929(2) Å; I(7)-I(8)-I(9) = 171.58(5)°]. The I_3^- ions, including those belonging to the I_5^- units, lie in parallel planes and form unprecedented continuous, planar two-dimensional layers. Each layer (Figure 2) may be visualized topologically as fused ribbons of 14-membered and 24-membered rings with cross-linking secondary interactions among the I_3^- ions ranging from 3.758(2) to 4.217(2) Å. Pairs of parallel and slightly interacting I_2 molecules [$I_2 \cdots I_2$ 4.257(2) Å, van der Waals diameter for I = 4.3 Å[11, 12]] from two symmetry-related I_5^- ions lie orthogonal to the parallel layers and connect two of these by passing through the centers of the 24-membered rings of a third layer located between them (Figure 3). The connection of two alternating layers takes place through a reasonably short $I_5^- \cdots I_3^-$ interaction of 3.573(2) Å giving rise to an overall I_8^{2-} unit observable as an $I_2 \cdot 2I_3^-$ adduct (Figure 3), which can be envisaged as the yarn interlocking the infinite two-dimensional poly-I_3^- sheets. The 24-membered rings of each layer measure about 25.31 × 13.31 Å: the dimensions of each half [ca. 12.65 × 13.31 Å] are similar to those of the 14-membered rings [ca. 12.18 × 14.73 Å], resulting in channels along the body diagonal of the unit cell. These channels are occupied by the chains of hydrogen-bonded binuclear complexes described above (Figure 4) and it appears that it is these chains rather than the individual dication that act as the template for the polyiodide architecture.

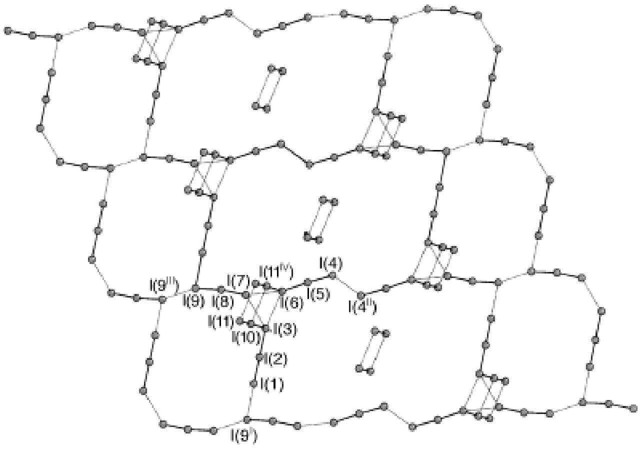

Figure 2. View of two-dimensional polyiodide layers in $[Pd_2Cl_2([18]aneN_2S_4)]_{1.5}I_5(I_3)_2$ comprising linked I_3^- ions and fused ribbons of 14-membered and 24-membered rings. Dications are omitted for clarity. Important distances [Å]: I(1)–I(2) 2.845(2), I(2)–I(3) 3.045(2), I(4)–I(5) 2.904(2), I(5)–I(6) 2.959(2), I(7)–I(8) 2.948(2), I(8)–I(9) 2.929(2), I(10)–I(11) 2.775(3), I(3)–I(10) 3.349(2), I(3)$\cdots$I(6) 4.217(2), I(3)$\cdots$I(7) 4.184(2), I(6)$\cdots$I(7) 4.006(2), I(1)$\cdots$I(9^I) 3.812(2), I(4)$\cdots$I(4^{II}) 4.017(2), I(9)$\cdots$I(9^{III}) 3.758(2), I(6)–I(11^{IV}) 3.579(2). Symmetry operation: I = $x-1$, $y-1$, $1+z$; II = $1-x$, $1-y$, $1-z$; III = $2-x$, $1-y$, $-z$, IV = $2-x$, $-y$, $1-z$.

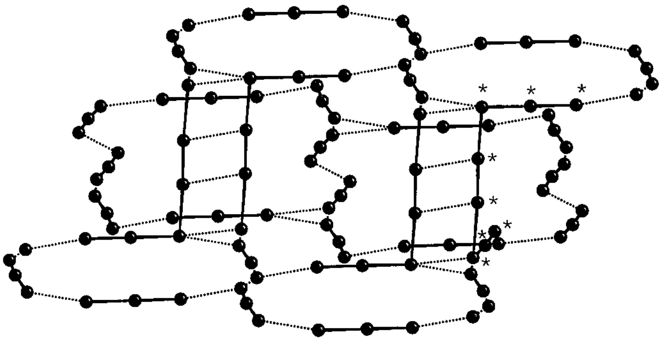

Figure 3. View of the poly-I_3^- layers linked by I_2 bridges, which connect two 14-membered rings through a 24-membered ring. Starred atoms identify one I_8^{2-} unit. Dications are omitted for clarity.

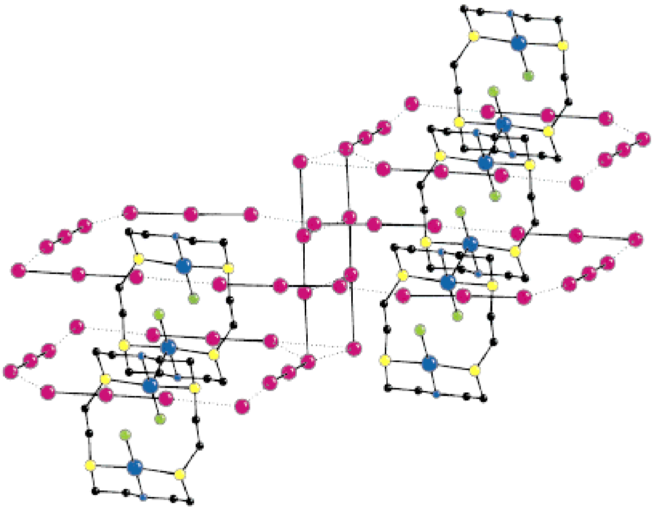

Figure 4. View of the structure of $[Pd_2Cl_2([18]aneN_2S_4)]_{1.5}I_5(I_3)_2$: chains of $[Pd_2Cl_2([18]aneN_2S_4)]^{2+}$ ions occupy channels in the three-dimensional polyiodide network.

In order to determine whether other macrocyclic complexes with different shape and charge can have the same templating effect on the self-assembly of extended polyiodide arrays, we treated $[K([15]aneO_5)_2]I$, prepared in situ by reaction of KI with two equivalents of $[15]aneO_5$, with an excess of I_2 in acetonitrile. After several days, dark red crystals were obtained by slow evaporation of the solvent. The crystal structure determination established the formulation $[K([15]aneO_5)_2]I_9$.[14] Within the cation, two crown ether ligands sandwich one K^+ ion within a ten-coordinate environment; the K–O bond lengths range between 2.62(2) and 3.21(2) Å.[20] Complex cations of this type are embedded in a three-dimensional polyiodide matrix made up of I_9^- units (Figure 5). Nonaiodides are very rare[21] and in this case each I_9^- ion can be described as an $[I_3^- \cdot (I_2)_3]$ charge-transfer complex; the three perturbed I_2 molecules have molecular distances ranging from 2.716(3) to 2.740(4) Å and interact with the slightly asymmetric I_3^- [I(7)–I(8) 2.874(3), I(8)–I(9) 2.978(3) Å; I(7)-I(8)-I(9) 178.2(2)°] through contacts of 3.396(4)–3.503(4) Å. Two of the three I_2 molecules [I(5)–I(6) and I(3)–I(4)] and the I_3^- ion [I(7)-I(8)-I(9)] lie approximately in the same plane, whereas the third I_2 molecule [I(1)–I(2)] is perpendicular to it [I(1)-I(9)-I(8) 92.4(5)°, I(1)-I(9)-I(3) 97.6(5)°]. This configuration for the I_9^- polyiodide units allows them to form a three-dimensional network of puckered cages through I$\cdots$I secondary interactions of 3.732(4)–4.074(4) Å (Figure 6). Each cage measures

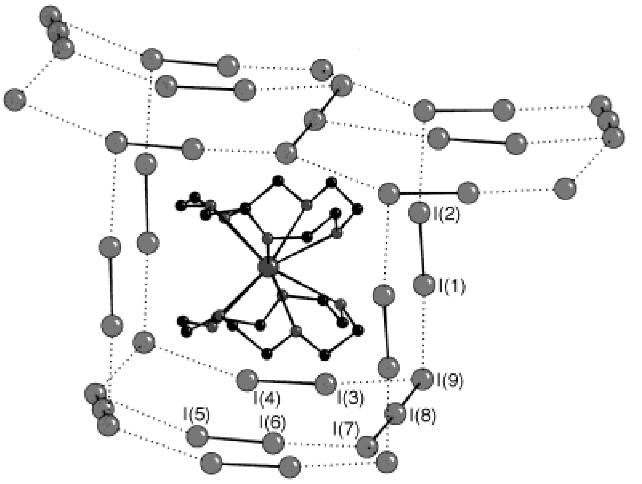

Figure 5. View of the puckered cage of I_9^- ions around the $[K([15]aneO_5)_2]^+$ cation template. Important distances [Å]: I(1)–I(2) 2.740(4), I(3)–I(4) 2.716(3), I(5)–I(6) 2.728(4), I(7)–I(8) 2.874(3), I(8)–I(9) 2.978(3), I(1)···I(9) 3.503(4), I(3)···I(9) 3.396(4), I(7)···I(6) 3.346(4).

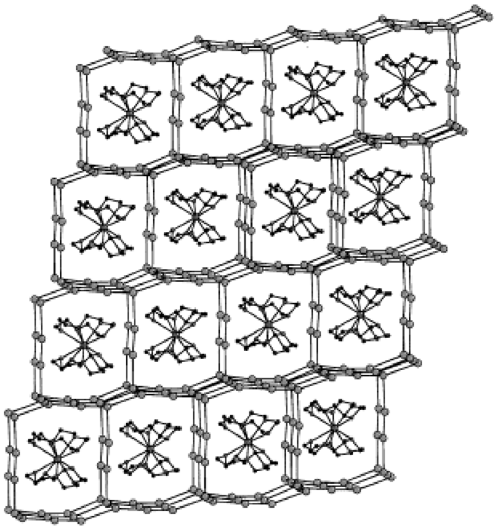

Figure 6. View of the structure of $[K([15]aneO_5)_2]I_9$ along the crystallographic *c* axis.

9.658 × 9.521 × 9.959 Å, with body diagonals of 17.371 and 17.393 Å, and the $[K([15]aneO_5)_2]^+$ ion lies nearly at the center of the cage. This polyiodide array is related to the ideal cube made up of I_7^- ions in $[Ag([18]aneS_6)]I_7$;[12] the main difference is an additional I_2 molecule in the I_9^- ion located in the middle of the lower face of each cage, which reflects the different topologies of the Ag^I and K^I complexes. There is therefore a clear link between the templating effect of I_7^-[12] and I_9^- ions. The puckered cages are arranged in a centered lattice and in projection along the crystallographic (100) axis each cage lies above the midpoint of four cages in the layer below.

Our results confirm the general principle of template condensation of three-dimensional polyiodide networks at metal cations complexed by macrocycles. The formation of polyiodide architectures may be regarded as a template reaction in the second coordination sphere of complex cations in which the unique topology of the resultant polyanionic networks depends upon the shape and charge of the template cations.

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[14] Elemental analysis: found (calc. for $[Pd_2Cl_2([18]aneN_2S_4)]_{1.5}I_5(I_3)_2$): C 9.25 (9.35), H 1.75 (1.70), N 1.85 (1.82); found (calc. for $[K([15]aneO_5)_2]I_9$): C 14.90 (14.80); H 2.65 (2.49). Crystal structure analysis: Stoe Stadi-4 four-circle diffractometer, graphite-monochromated $Mo_{K\alpha}$ radiation, $T = 220$ K, $\theta_{max} = 25°$. Both structures were solved by using direct methods[15, 16] and all non-H atoms were located by using subsequent difference Fourier methods.[17, 18] Hydrogen atoms were placed in calculated positions and were allowed to ride on their parent atoms during refinement. $[Pd_2Cl_2([18]aneN_2S_4)]_{1.5}I_5(I_3)_2$: $C_{18}H_{39}Cl_3I_{11}N_3Pd_3S_6$, $M = 2311.34$, triclinic, space group $P\bar{1}$ (no. 2), $a = 11.667(3)$, $b = 13.422(3)$, $c = 16.998(4)$ Å, $\alpha = 97.145(15)$, $\beta = 91.721(14)$, $\gamma = 106.589(16)°$, $V = 2527.2(10)$ Å^3, $Z = 2$, $F(000) = 2072$, $\rho_{calcd} = 3.037$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 8.201$ mm^{-1}, black facetted prism (0.27 × 0.19 × 0.16 mm^3). ψ scan absorption corrections ($T_{min} = 0.056$, $T_{max} = 0.141$), 8857 unique reflections [$R_{int} = 0.051$], of which 6470 had $I \geq 2\sigma(I)$. The weighting scheme $w^{-1} = [\sigma^2(F_o^2) + (0.052P)^2 + 48.0P]$, $P = [MAX(F_o^2, 0) + 2F_c^2]$, was applied. At final convergence R_1 [$I \geq 2\sigma(I)$] = 0.0571, wR_2 [all data] = 0.1608 for 393 refined parameters, $S = 1.11$, $(\Delta/\sigma)_{max} = 0.001$, $\Delta\rho_{max} = 1.73$ e Å^{-3} (near I^- atoms). $[K([15]aneO_5)_2]I_9$: $C_{20}H_{40}I_9KO_{10}$, $M = 1621.72$, monoclinic, Cc, $a = 24.348(5)$, $b = 9.521(2)$, $c = 19.244(7)$ Å, $\beta = 107.460(17)°$, $V = 4256$ Å^3 [from 2θ values for 41 reflections measured at $\pm\omega$ ($30 < 2\theta < 32°$),

$\lambda = 0.71073$ Å]. $Z = 4$, $\rho_{calcd} = 2.531$ g cm^{-3}, $F(000) = 2944$, $T = 220$ K, $\mu(\mathrm{Mo_{K\alpha}}) = 6.692$ mm^{-1}. Dark red block, $0.27 \times 0.27 \times 0.19$ mm^3. Absorption correction based on ψ-scans ($T_{min} = 0.051$, $T_{max} = 0.103$). Data collection and processing: The unit cell was obtained by using the program DIRAX[19] for 19 out of 25 reflections located during a random search. The two crystallographically unique macrocycles were restrained to be geometrically similar, while the displacement parameters of the C and O atoms were subject to rigid bond and body restraints. The refinement converged to a conventional R value of 0.069 with difference map extrema of $+2.61$ and -1.66 e Å^{-3} and a large number of poorly agreeing data with $l = 8n$. The matrix (-1 0 -0.75/0 -1 0/0 0 1) converts the cell into an equivalent cell. Reciprocal lattice points from these two cells will coincide only when l is a multiple of 4 and the sum of the transformed indices h and k is even (because of the lattice centering). Splitting the reflections in this way and proceeding with refinement with a scale factor relating the two twin components [0.147(4)] gave a final conventional R value of 0.0624 (based on F and 3839 data with $F > 4\sigma(F)$) and $wR2 = 0.1633$ (based on F^2 and all 4690 data used during refinement) for 362 parameters. The final difference map extrema were 1.44 and -1.46 e Å^{-3}; the Flack absolute structure parameter was 0.16(13). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100768. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code + (44)1223336-033; E-mail: deposit@ccdc.cam.ac.uk).

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Breaking the Mold of Discotic Liquid Crystals**

Joaquín Barberá, Oleg A. Rakitin, M. Blanca Ros,* and Tomás Torroba

Organic Chemistry is currently living its “supramolecular epoch”. Innovative and fascinating research has been focused on the synthesis and study of “living” molecules in an interdisciplinary field.[1] Development of the chemistry of complex molecules such as crown ethers, cryptands, phthalocyanines, dendrimers, catenanes, rotaxanes, and a variety of related compounds could seem, at first sight, interesting only from an exotic or theoretical point of view. However, possibilities have turned into reality for many of these systems.[1] Researchers in Chemistry, Biology, Materials Science, and even Physics are looking at these supramolecules as unique tools for achieving the ultimate aim of miniaturization. Alternatively, chemists are also becoming increasingly interested in investigating chemistry beyond the covalent bond; a concept expressed by J. M. Lehn as “the chemistry beyond the molecule”.[1b] In this case, the active supramolecular structures are obtained by simple interactions between suitable functional units.

Liquid crystals are well-known examples of supramolecular assemblies.[1, 2] Based on self-organization, they combine the properties of order and mobility, a combination which allows the broad range of applications already exploited for these systems. Calamitic liquid crystalline compounds have been known since the end of the last century. However, in 1977 a new type of liquid crystal emerged, the discotic liquid crystals (DLCs).[3] These compounds have enriched the research and the possibilities of the so-called fourth state of matter.

Discotic liquid crystals are characterized by their ability to self-organize into columns, giving rise to two-dimensional superlattices of different types.[1c, 2b, 4] Consequently, one of the main issues in relation to columnar liquid crystals is the possibility of generating one-dimensional molecular “pathways” for electron, photon, energy or ion migration.[5]

Many molecules, either of low molecular mass or polymeric, have been reported to arrange in columnar mesomorphic states.[2b, 4, 5b, 6] However, most of these systems follow common structural guidelines. In general, DLCs consist of a rigid central core (planar, conical, pyramidal, or other such geometry) surrounded by four or more flexible groups, which make up the “soft” region. In certain cases, individual molecules do not match these criteria, but they are capable of aggregating into units which do fulfill them.[6] Scarce variations to this general structure are the “carbonaceous” group of compounds,[7] which are large, disc-shaped, polycondensed aromatic molecules with high molecular mass or, in the field of the lyotropic mesophases, the chromonic liquid crystals. These latter compounds with no flexible hydrocarbon chains in their structure exhibit columnar phases in the presence of a solvent.[8] The role of the soft region is played by water or another suitable liquid.

This paper deals with a type of compound which constitutes the first exception to the above trends in the field of thermotropics. We report here the first examples of thermotropic DLCs which do not contain flexible groups, namely indenes **1**–**4** and pseudoazulene **5**.

Our interest in these organic compounds is twofold. Their synthesis has recently been reported[9] to proceed by a unified mechanism based on the initial abnormal Beckmann rearrangement of oximes to cyanides, followed by cyclization and/or exhaustive chlorination and dehydrochlorination. Furthermore, and surprisingly, when these small molecules were treated thermally and studied under polarized light, the

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