An Infinite 2D Polyrotaxane Network in $Ag_2(bix)_3(NO_3)_2$ (bix = 1,4-Bis(imidazol-1-ylmethyl)benzene)

Bernard F. Hoskins, Richard Robson,* and Damian A. Slizys

School of Chemistry, University of Melbourne Parkville, Victoria 3052, Australia

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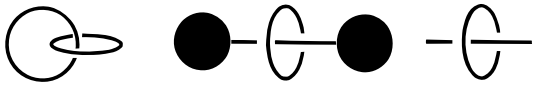
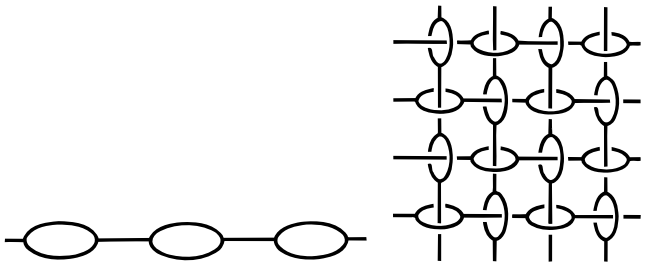
A quarter of a century after the appearance of Schill's famous book,[1] interest in catenanes, **I**, and rotaxanes, **II**, continues unabated.[2] In the true rotaxanes, **II**, the stops at the ends of the dumbell-like component condemn the two otherwise free and independent partners to everlasting intimacy: in the psuedorotaxanes, **III**, the stops are lacking.



I II III

It has been pointed out that interpenetrating networks, of which many new examples have been discovered in recent years, display ordered polycatenane associations on a grand scale.[3] Polypsuedorotaxanes in which macrocycles such as cyclic polyethers and cyclodextrins are threaded onto polymer chains of various sorts have been described.[4] Sauvage has recently reported yet another elegant application of coordination chemistry in the generation of polyrotaxane-like thin films on electrode surfaces.[5] A very recent report describes a true polyrotaxane in which every ring is restricted to a particular segment of the polymer by two flanking stoppers.[6] We report here a coordination polymer consisting of 1D polymeric chains of type **IV** which are knitted together, as in **V**, to generate a 2D polyrotaxane sheet.



IV V

The ligand affording this polyrotaxane coordination polymer is 1,4-bis(imidazol-1-yl-methyl)benzene, **VI**, hereafter bix, which has been previously reported[7] but which can be more conveniently obtained as follows: a solution containing imidazole (3.16 g, 46.4 mmol) and α,α′-dichloro-*p*-xylene (0.78 g, 4.46 mmol) in methanol (50 mL) was heated under reflux (18 h). Removal of methanol by evaporation gave a yellow syrup which was dissolved in aqueous K_2CO_3 (6.13 g, 100 mL). This solution, upon standing, yielded crystalline bix dihydrate which was further recrystallized from water. Yield of bix dihydrate: 0.65 g (53%). Anal. Calcd for $C_{14}H_{14}N_4 \cdot 2H_2O$: C, 61.3; H, 6.6; N, 20.4. Found: C, 61.3; H, 6.5; N, 20.3. The product was further characterized by single-crystal X-ray diffraction.[8] Unsolvated $Ag_2(bix)_3(NO_3)_2$ separated from reaction mixtures obtained by combining bix dihydrate (411 mg) in methanol (25 mL) with silver nitrate (170 mg) in aqueous methanol (3 mL of H_2O, 22 mL of CH_3OH). Anal. Calcd for $C_{42}H_{42}Ag_2N_{14}O_6$, i.e., $Ag_2(bix)_3(NO_3)_2$: C, 47.9; H, 3.7; Ag, 20.5; N, 18.6. Found: C, 47.8; H, 4.0; Ag, 20.5; N, 18.6. Crystals obtained directly from the reaction mixture in this way were suitable for single-crystal X-ray diffraction study.[9]

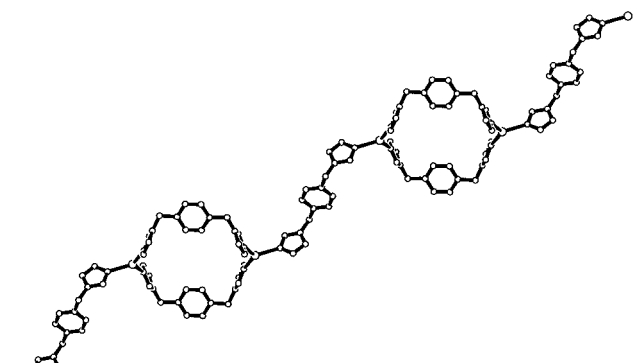


Figure 1. One of the $\{Ag_2(bix)_3\}_n$ linear polymeric chains. Larger circles represent Ag. Smaller circles represent C/N.

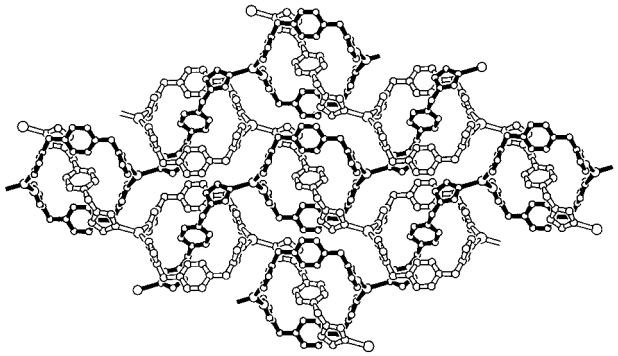
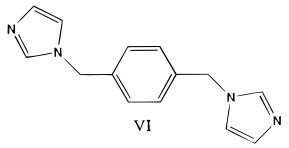


Figure 2. A 2D polyrotaxane network showing parts of six independent linear polymeric chains. Larger circles represent Ag.



VI

The C/N/Ag arrangement within an individual polymer chain of the basic type represented in **IV** is shown in Figure 1. The

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(9) Crystal data: $Ag_2(bix)_3(NO_3)_2$, MW = 1054.62, monoclinic, space group $P2_1/n$ (nonstandard setting of no. 14), a = 13.763(2) Å, b = 10.580-(2) Å, c = 14.812(2) Å, β = 95.94(1)°, Z = 2, ρ_c = 1.63 cm^{-3}, ρ_m = 1.64(1) g cm^{-3}, μ(Cu Kα) = 78.73 cm^{-1}, $F(000)$ = 1068. Intensity data were measured at 295(1) K with Cu Kα radiation (graphite monochromator) using an Enraf-Nonius CAD-4 MachS diffractometer and employing the $\omega/2\theta$ scan method; absorption and extinction corrections were applied. A full-matrix least-squares refinement based on F^2 (SHELXL-93) was then employed with anisotropic thermal parameters applied to all non-hydrogen atoms. At convergence R_1 = 0.0542 and wR_2 = 0.1444 for the 4144 reflections with $I \geq 2\sigma(I)$, where $R_1 = \sum|\Delta F|/\sum|F_o|$ and $wR^2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$.

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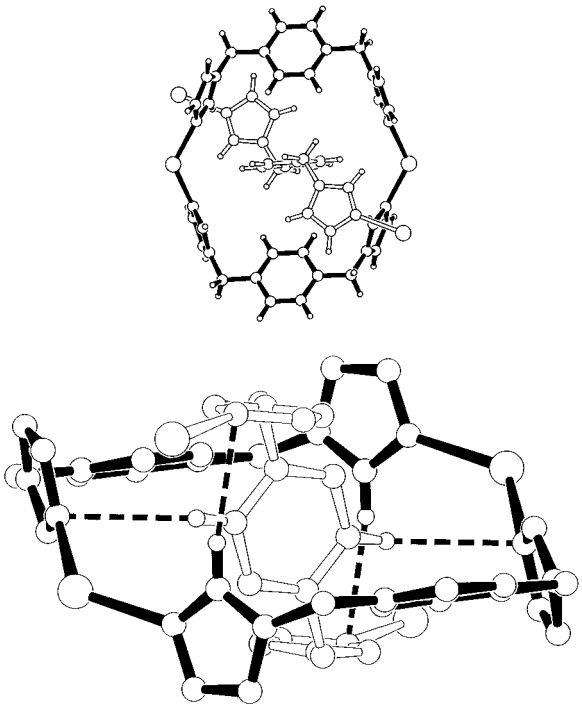

Figure 3. Two detailed views of one rotaxane association. Circles in order of decreasing radius represent Ag, C/N, and H, respectively. (a, top) A view almost perpendicular to the ring component. (b, bottom) A view showing, by broken lines, the two closest hydrogen-to-aromatic ring atom contacts (two symmetry-related pairs) (distance between the H of the central phenylene unit and the N indicated, 2.772(5) Å; distance between imidazole H and the N indicated, 2.684(4) Å).

3-connecting centers required for the topology shown in **IV** are provided by silver, all atoms of which are equivalent. The metal is located almost exactly within the plane of the N_3 donor set, the angle at silver internal to the ring being 127.3(1)°. Bix provides both the rodlike segments and two half-loops for each of the rings of composition $Ag_2(bix)_2$. Figure 2 represents the way the individual chains associate to produce the polyrotaxane sheets of type **V**. The nitrate ions, all of which are equivalent, are omitted from Figure 2 for the sake of clarity; they interact very weakly with two neighboring silver ions through a single one of their oxygen atoms (Ag···O = 2.926(5) and 3.166(6) Å).

All rings are equivalent, as are all rods. Ag···Ag distances are 14.626(2) Å along a rod and 10.503(1) Å across a ring. Two detailed views of the rod-to-ring rotaxane interaction are shown in Figure 3 in which no particular association of component funtional groups is immediately obvious. No face-to-face aromatic interactions are apparent. There are many contacts in the range 2.7−3.2 Å of the edge-to-face type recently surveyed by Dance et al.,[10] the two shortest of which are highlighted in Figure 3b.

$Ag_2(bix)_3(NO_3)_2$ is unquestionably a polyrotaxane and not a polycatenane, for no catenane associations are present. A related polycatenane coordination polymer utilizing a similar 1,4-xylene-based ligand was reported recently.[11] The structure reported here hints at the likelihood that bix and related ligands may provide other examples of unusual polyrotaxanes and polycatenanes. These are possibilities we are presently exploring.

Acknowledgment. We are very grateful to the Australian Research Council and the Petroleum Research Fund for support.

Supporting Information Available: Crystal data and data collection, structure determination and refinement, numbering scheme, and tables of crystal data, fractional atomic coordinates, isotropic thermal parameters, and interatomic distances and angles (13 pages). See any current masthead page for ordering and Internet access instructions.

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