An octanuclear $[\mathrm{Co(II)}_2\text{–}\mathrm{Co(III)}_2]_2$ interlocked grid—example of an inorganic [2]catenane†

Tareque S. M. Abedin, Laurence K. Thompson* and David O. Miller

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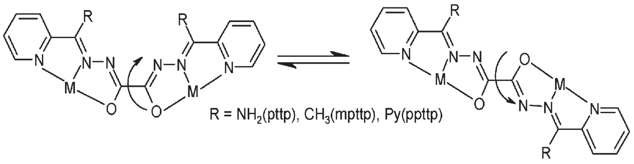
An oxalic dihydrazide based flexible polydentate amidrazone ligand undergoes spontaneous [2 × 2] grid assembly, followed by partial disassembly, and then reassembly in the presence of $\mathrm{Co(NO_3)_2{\cdot}6H_2O}$ and $\mathrm{NH_4(NCS)}$ to form a unique octanuclear $[\mathrm{Co(II)}_2\text{–}\mathrm{Co(III)}_2]_2$ interlocked, single braided 4 + 4 [2]catenane.

Singly or doubly intertwined macrocyclic catenanes have intrigued synthetic chemists since their first successful synthesis by Wasserman following a statistical method.[1] Catenanes are interesting not only because of their topological beauty but also because they form by an intricate molecular self-assembly, which had been a challenge for synthetic chemists for decades by classical synthetic routes.[2,3] Unlike other self-assembled molecules, the catenanes contain covalent bonds which are mechanically robust. The use of labile metal–ligand coordination bonds allows the synthesis and isolation of this type of macrocycle with high yield under thermodynamic control.

Sauvage *et al.* developed the first synthetic route to catenanes taking advantage of pre-organization by a metal template,[4] and metal atoms such as Li(I),[5] Ru(II),[6] Rh(III),[7] Zn(II),[8] Cu(I), Pd(II),[9] and Ni(I)[10] have been reported as metal templates in catenane synthesis. The dynamic nature of the metal–ligand bond is a classic feature of catenanes, with monomeric rings and interlinked rings in equilibrium in solution.[11] More organic like catenanes have been synthesized by Stoddart *et al.* exploiting the charge transfer interactions between electron deficient and electron rich species.[12]

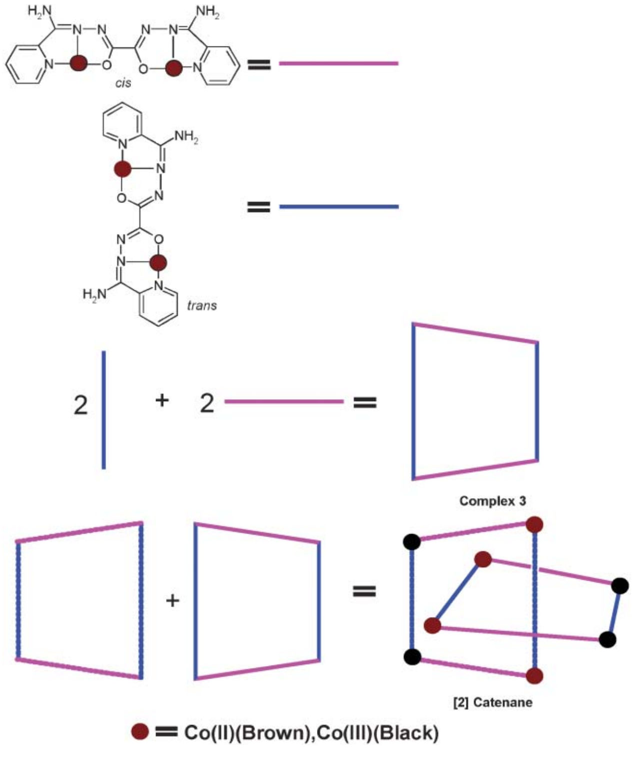
Organo-magnesium[13] and organo-gold[14] catenanes have also been reported. The stability of most of the organo-gold catenanes arises from the Au···Au aurophilic attraction between di-acetylide di-gold rings, leading to two intertwined rings clipped by di-phosphine ligands.[14] The degree of catenation, ring size and the ultimate outcome of the catenated product depend solely on the size of the oligomeric di-gold(I) di-acetylide and the spacer group in the alkynyl ligand.[15] A double braided [2]catenane involving two intertwined $\mathrm{Au_4}$ rings was reported.[15a]

Oxalic dihydrazide based polydentate ligands, *e.g.* pttp (Scheme 1), with flexible linker groups joining the terminal donor units, can exist in *cis* or *trans* conformations, and have the potential to bind metals in a variety of different ways. Depending on the relative orientation of the terminal donor sets, self-assembly can lead to di- or polymetallic clusters or square and rectangular [2 × 2] grid complexes.[16] In this article we report the synthesis and characterization of a new example of a single braided [2]catenane with a transition metal backbone from preformed tetranuclear $[\mathrm{Co(II)}_2\mathrm{Co(III)}_2(\mathrm{pttp})_4]$ rings (Scheme 2).‡



Scheme 1 Flexibility around the C–C bond leading to different coordination modes.

Reaction of pttp with $\mathrm{Co(II)Br_2{\cdot}6H_2O}$ and $\mathrm{Fe(II)(ClO_4)_2{\cdot}6H_2O}$ salts in air gave tetranuclear $\mathrm{L_4M_4}$ [2 × 2] square complexes $[\mathrm{Co_4(pttp)_4}]\mathrm{Br_6{\cdot}9H_2O}$ (**1**) and $[\mathrm{Fe_4(pttp)_4}](\mathrm{ClO_4})_6{\cdot}7.5\mathrm{H_2O}$ (**2**) respectively.[16] Partial oxidation occurred in both cases with the formation of $[\mathrm{M(II)_2M(III)_2}]$ (M = Co, Fe) derivatives. Reaction of pttp with $\mathrm{Co(NO_3)_2{\cdot}6H_2O}$ in $\mathrm{CH_3OH\text{–}CH_3CN}$ solvent mixture in air gave the dark red crystalline [2 × 2] grid complex $[\mathrm{Co(II)_2Co(III)_2(pttp)_4}](\mathrm{NO_3})_6{\cdot}4\mathrm{CH_3OH{\cdot}CH_3CN{\cdot}9H_2O}$ (**3**), confirmed by elemental analysis and magnetic measurements.§



Scheme 2 Self-assembly of the [2]catenane **4**.

Department of Chemistry, Memorial University, St. John's, NL, Canada A1B 3X7

† Electronic supplementary information (ESI) available: Fig. S1 Full structural representation of catenane **4**. See DOI: 10.1039/b510755e

Exposure of the reaction mixture to air leads to the oxidation of two of the Co(II) centres, similar to the situation found for **1**. This is evident from variable temperature magnetic measurements on a bulk sample of **3**, which show a room temperature moment of 7.47 μ_B, which then drops slightly to 6.13 μ_B at 2 K. This is consistent with two essentially isolated Co(II) centres and two diamagnetic Co(III) centres.

When a bulk sample of complex **3** was reacted with $NH_4(NCS)$ in methanolic solution in air, the catenane complex $\{[Co_4(pttp)_4]_2\}[Co(NCS)_4]_2(NCS)_4\cdot 8CH_3OH\cdot 11H_2O$ (**4**) was isolated as dark blue green crystals in good yield (>60%), and was characterized by structural analysis. ¶ The core structure of the catenane is depicted in Fig. 1 (a full structural representation is shown in Fig. S1†), with the aromatic rings abbreviated to just the donor atoms. Two tetracobalt [2 × 2] square grid subunits, derived from four metal centres and four ligands, intersect each other in a self-assembled manner to give the mono-braided catenane complex. The *mer*-N_2O donor groupings at the end of each ligand ensure that on coordination to a six-coordinate metal ion the appropriate 90° twist occurs to form the square grid. A close inspection of the Co–Co distances within each ring reveals that the 'squares' are slightly distorted with unequal Co–Co distances (Co(1)–Co(4) 6.723 Å, Co(6)–Co(7) 6.721 Å, Co(2)–Co(3) 7.164 Å, Co(5)–Co(8) 7.220 Å), consistent with the side by side arrangement of Co(II) and Co(III) pairs in each ring respectively. This grid structure is identical to that observed in **1**. Closer inspection of the metal–ligand bonds reveals that Co(1) (Av. 1.905 Å), Co(4) (Av. 1.893 Å), Co(6) (Av. 1.898 Å) and Co(7) (Av. 1.892 Å) have very short contacts typical of Co(III), while Co(2) (Av. 2.107 Å), Co(3) (Av. 2.104 Å), Co(5) (Av. 2.110 Å), and Co(8) (Av. 2.114 Å) have comparatively much longer contacts typical of Co(II). A space filling structural representation is shown in Fig. 2.

To confirm the oxidation state assignment Bond Valence Sum (BVS) calculations were carried out for each of the metal centres.[17] The results show that all four metal ions along the catenated intersection correspond to Co(II) (Av. BVS 2.35-2.39), while the other four Co centres on the periphery of the two intersecting rings have much higher values (Av. BVS 4.05–4.18) and clearly correspond to the Co(III) state. At this point it is not clear why the +III oxidation state for Co in this system has such a high BVS value, but there is no evidence to suggest Co(IV). **1** has average BVS values of 2.3 and 3.9 for Co(II) and Co(III) sites respectively, and a comparison with other $[Co(II)_4]$ and $[Co(II)_2Co(III)_2]$ systems with similar ligands reveals comparable values.[18,19]

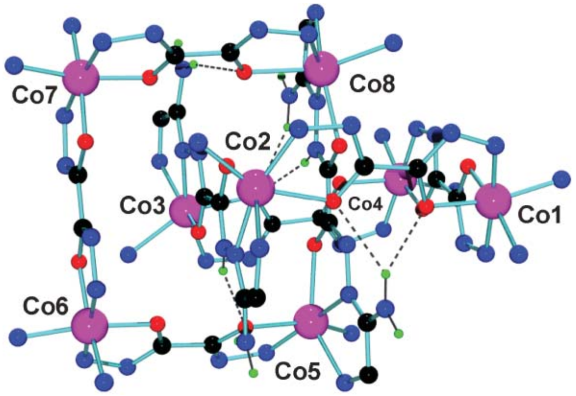


Fig. 1 Solid state core structure of the [2]catenane **4** (magenta = cobalt, blue = nitrogen, red = oxygen, green = hydrogen). Terminal pyridine rings are reduced to a single nitrogen donor atom for clarity.

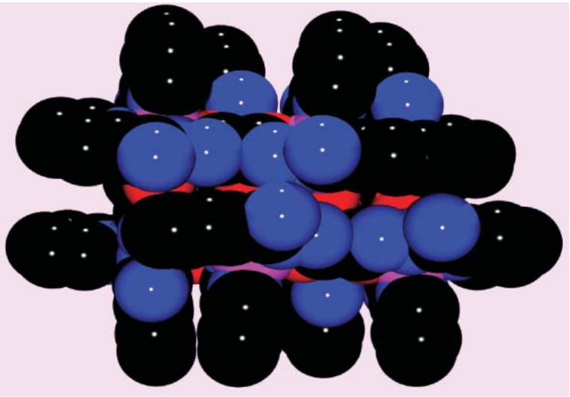


Fig. 2 Space filling structural representation of **4**.

Each ligand has two readily ionizable protons associated with the oxalic hydrazone fragment, and a charge balance in **4** would require a total charge of 12 negative charges spread out over the eight ligands. The external NH_2 groups are unlikely to deprotonate, and while locating other ligand protons is difficult, two hydrazone NH protons¶ do appear in difference maps in the central portion of the catenane structure in the region where the four Co(II) centres are located. A number of significant hydrogen bonds have been identified in this region also (Fig. 1, dotted lines), and highlight one important element in the stabilization of the catenane structure. The overall structure also reveals four NCS^- anions, and two $[Co(NCS)_4]^{2-}$ anions in the lattice in addition to solvent.

Since the catenane was formed from a [2 × 2] self-assembled square grid precursor, the mechanism for catenane formation must involve a dynamic ligand dissociation–association process and a grid-ring opening. Transition metal (*e.g.* Pt, Pd)–ligand bonds are fairly labile in nature, and do remain intact under ordinary conditions, but can become 'reversible' in highly polar media, and at elevated temperatures.[20] In the present case, where methanol was used as solvent, the presence of the moderately strong NCS^- ligand is likely to lead to some dissociation of the pttp coordination bonds in **3**, even at room temperature. Such dissociation is more likely to occur at the Co(II) sites, which are much more labile, and could lead to the opening of a [2 × 2] ring (unlocking). Insertion of an open ring (Scheme 2) through a complete ring could then occur, and lead to catenane formation by subsequent ring closure (locking). Implicit in this suggestion would be the fact that one ligand dissociates at one end only prior to ring insertion, and that ring closing is accompanied by re-coordination of the ligand. The polar nature of the solvent medium may have favoured ring opening, but it is much more likely that the NCS^- ion is responsible for pttp dissociation, and coordination to a Co(II) centre in some oligomeric intermediate. The presence of the $[Co(NCS)_4]^{2-}$ anion in the lattice is good evidence for such a mechanism taking place, and indicates that thiocyanate actually scavenges Co(II). However a 'Möbius strip' type mechanism, where intramolecular ligand exchange occurs between the intermediate structures, is not totally ruled out.[21] Another important factor, which may have influenced the catenane formation, is 'space filling'. The tetranuclear complexes **1** and **4** have large, roughly square central voids with separations of 6.7–7.0 Å between the oxygen atoms on the ligand.[16] Self-assembled 'aromatic' molecular boxes with similar dimensions have been shown to form catenanes by filling the molecular cavity in one box with a molecular self copy, allowing for suitable van der Waals separation between aromatic carbon atoms (~3.5 Å).[22] The catenane framework in **4** could therefore be stabilized in a similar way by filling its own cavity with another copy of itself (Fig. 2). However the significant hydrogen bonding interactions in the region where the rings interpenetrate (N–H···O contacts with N–O distances from 1.98 Å to 2.44 Å (Fig. 1)), suggest that a significant driving force for stabilization of the catenane structure must come from these hydrogen bonds.

Further studies with other ligands in this class and a variety of other metal ions are in progress, and the use of ligands with larger 'linker' groups between the separate donor pockets are being explored in the hope that further braiding can occur if the ring cavity size is increased.

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Notes and references

‡ Synthetic procedure for pttp was published earlier.[16]

§ Pttp (0.10 g, 0.31 mmol) was added to a warm solution of $Co(NO_3)_2·6H_2O$ (0.16 g, 0.55 mmol) in CH_3OH–CH_3CN. The resulting dark red-brown solution was stirred for several hours, filtered and kept for crystallization by slow evaporation. Deep red crystals were isolated after several weeks in good yield (overall 70%). Anal. found: C, 33.23; H, 3.13; N, 24.49. Calc. for $[(C_{14}H_{13}N_8O_2)_4Co_4](NO_3)_6(CH_3OH)_4\ CH_3CN·9H_2O$ (**3**): C, 33.25; H, 3.92; N, 24.41. Variable temperature magnetism shows a room temperature moment of 7.47 μ_B, consistent with two Co(II) centres and two diamagnetic Co(III) centres, which then drops to 6.13 μ_B at 2 K. **3** (0.035 g) was dissolved in CH_3OH forming a brown solution. A methanolic solution of $NH_4(NCS)$ (0.100 g, 1.31 mmol) was added and the mixture stirred for several hours with warming. The colour of the solution turned a dark greenish brown. The final solution was filtered and kept for crystallization. Dark blue green crystals suitable for X-ray diffraction were obtained (22.5 mg, overall 64%) by slow ether diffusion. IR (Nujol, ν/cm^{-1}): 2059 (NCS^-), 1680, 1658. Anal. found: C, 36.02; H, 2.58; N, 25.73. Calc. for $[(C_{14}H_{12}N_8O_2)_4(C_{14}H_{13}N_8O_2)_4Co_8][Co(NCS)_4]_2(NCS)_4·13H_2O$ (**4**) C, 36.15; H, 3.09; N, 25.86.

¶ Crystal data $C_{132}H_{149}O_{32}N_{76}S_{12}Co_{10}$, $M = 4286.21$, Dimensions 0.45 × 0.21 × 0.16 mm, primitive triclinic, $P\bar{1}$ (#2), $a = 17.359(2)$ Å, $b = 20.870(2)$ Å, $c = 27.545(2)$ Å, $\alpha = 81.671(1)°$, $\beta = 84.037(2)°$, $\gamma = 70.328(1)°$, $V = 9282(1)$ Å^3, $T = 193 \pm 1$ K, $Z = 2$, $F(000) = 4382.00$, μ(Mo-Kα) = 10.91 cm^{-1}, 67989 reflections 37713 unique ($R_{int} = 0.055$), $R1 = 0.087$, w$R2 = 0.302$. Hydrogen atoms bound to oxygen atoms of the lattice water and methanol molecules were not located. H97 and H98, bonded to hydrazone nitrogen atoms N60 and N12 respectively, were found in the difference map. Other hydrogen atoms were placed in calculated positions, but not refined. CCDC 279772. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b510755e

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