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ARTICLE

From Isolated 1*H*-Pyrazole Cryptand Anion Receptors to Hybrid Inorganic-Organic 1D Helical Polymeric Anion Receptors.

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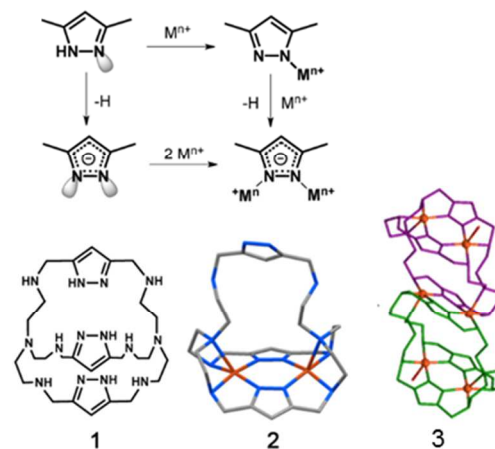
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We report on a novel 1-D helical coordination polymer formed by protonated polyamine 1*H*-pyrazole cryptands interconnected by Cu²⁺ metal ions able to encapsulate anionic species behaving as a multianion receptor. Switching from the monomeric to the polymeric receptor is activated by metal ions and pH.

1D-Coordination polymers (1D-CPs) have been widely explored in the last years.¹ However, although several examples of coordination polymers based on macrocycles have been reported,^{1,2} as far as we know 1D-CPs built up connecting cryptands have not yet been described. On the other hand, as it is known that cryptand receptors when protonated can tightly confine in its interior anionic guest by means of electrostatic attraction and hydrogen bonding interactions,³ the idea of constructing CPs that can serve as multi-anion receptors is very appealing. Here we report on an 1D-CP that fulfils these characteristics.

To achieve this goal we have made use of cryptand **1** consisting of two *tren* polyamine subunits connected to three 1*H*-pyrazole macrocycles through methylene spacers. We had previously proved that this receptor forms above pH 5 binuclear or hexanuclear dimer Cu²⁺ complexes depending on whether the metal: cryptand ratio is 2 or 3 (see structures **2** and **3** in Scheme 1).⁴ In such complexes pyrazole was deprotonated behaving as a bis(monodentate) or exobidentate ligand (Scheme 1). However to interconnect cryptands we need to move from this endo coordination, in which the metal ions are located inside the cavity, to an exo coordination with the metal ions placed outside the cavity acting as connectors between different macrocycles.^{1,2} This change would in principle require of an appropriate acidic pH range so that the amine groups are protonated while the pyrazole groups are in the neutral form and therefore bind the Cu²⁺ ions in a monodentate mode (Scheme 1).⁵ In this way a polymeric strand of charged

cryptands ready to include anions in a multivalent fashion might be fabricated.



Scheme 1. Most usual 1*H*-pyrazole binding modes (left), cryptand **1** (middle) and binuclear Cu²⁺ complex **2** and hexanuclear complex **3** (right).

Previously to these studies we analysed the ability of the individual cryptands to bind chloride anions. Crystals with a chloride anion included in the protonated macrocycle, [H₆(**1**)Cl(H₂O)₂]Cl₅·6H₂O (**4**) (Tables S1-S2 in the ESI), were obtained by slow evaporation of aqueous solutions of **1** acidified to pH = 3 with HCl. The crystal structure of **4** consists of [H₆(**1**)Cl(H₂O)₂]⁵⁺ cations in which a chloride anion (Cl1) and two water molecules (OW1 and OW2) are fully included in the macrocyclic cavity. The Cl1, OW1 and OW2 atoms are hydrogen bonded to each other forming a cascade complex (Figure 1).⁶ Apart from the encapsulated chloride, there are other four chlorides and lattice water molecules at the faces of the cage (see Figure S1 in ESI), chloride counter-anions and bulk water molecules. The chloride anions and water form an intricate hydrogen bonded network. While all six secondary

amino groups of the macrocycle are protonated, the tertiary amino groups and the pyrazole moieties are not protonated at the acidic pH values which the crystals evolved. The included chloride sits off-centre towards one side of the cage cavity; the distance from Cl1 to the bridgehead nitrogen atoms being 3.650(4) and 5.630(4) Å.

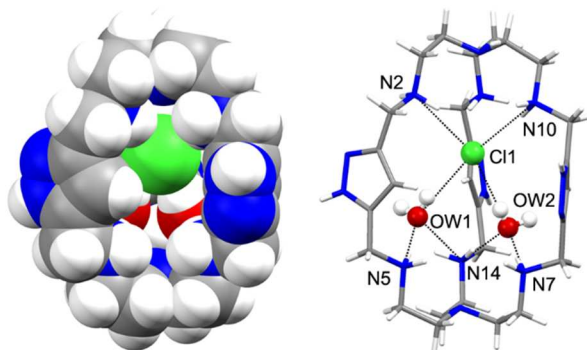


Figure 1. Space fill (left) and stick representation (right) of the $((\text{H}_6(1)\text{Cl})(\text{H}_2\text{O})_2)^{5+}$ cation in **4** showing relevant intramolecular hydrogen bonds.

In addition to OW1 and OW2, the Cl1 is hydrogen bonded to two of the ammonium groups of its macrocyclic side (N2 and N10, Figure 1 right). Moreover, the distance to the third ammonium group of this side (3.349(3) Å) suggests also an additional weak hydrogen bond contact. On the other hand, the water molecules OW1 and OW2 accept hydrogen bonds from the ammonium groups N5, N14 and N7, respectively, all these at the macrocyclic side not occupied by the chloride anion (Figure 1 right). The OW1 and OW2 complete their tetrahedral hydrogen bond arrangement with one exo chloride anion and a water molecule, respectively, both of them placed outside the cage. A list of relevant hydrogen bond contacts is reported in Table S2. Interestingly, the nitrogen atoms at the edges of the 1*H*-pyrazole moieties point outwards from the macrocyclic cavity establishing two hydrogen bonds to an exo chloride anion and a water molecule while the third one hydrogen bonds to a water molecule and a pyrazole sp^2 nitrogen of an adjacent cryptand.

To evaluate the stability of the included chloride we have first performed potentiometric titrations of the aqueous solutions of the cryptand using sodium trifluoromethanesulfonate (NaTFMS) as background electrolyte since the large size of the TFMS anion prevents its inclusion in the cage cavity.⁷ From these measurements the protonation constants of **1** were derived. Then, from titrations of the macrocycle in the presence of chloride we obtained the stability constants of the anion complexes formed (Table S3 and Figure S3). At pH 2 the effective binding constant⁸ is in the order of 10^5 and such high values prevented their derivation from ^1H NMR titrations (Figure S5). The JOB plots obtained from the ^1H NMR measurements supported the 1:1 stoichiometry of the complexes formed inferred from the potentiometric titrations

(Figure S6). On the other hand, the stability of the chloride complex at pH 2 is higher than that of the fluoride complex as confirmed by ^{19}F NMR studies. The ^{19}F NMR spectrum of a solution containing fluoride and the macrocycle at pH=2 in 1:1 molar ratio displays peaks at -118 ppm, -140 ppm and -155 ppm that can be ascribed to F^- , HF and F-H-F interacting with the macrocycle (Figure S7-S8).⁹ Upon addition of sub-stoichiometric amounts of chloride, these signals start to disappear and new signals at -127 and -142 ppm attributable to free F^- and HF start to appear. When a stoichiometric amount of chloride is added only the signals of the free fluoride are observed (Figure S8).

As mentioned above, switching from an internal coordination of Cu^{2+} as that observed in **2**, to an exo coordination of Cu^{2+} through monodentate neutral pyrazole ligands requires of an appropriate pH range. The examination of the distribution diagrams of the Cu^{2+} -**1** system^{4c} indicates that pH values between 1 and 2 should be used, otherwise either protonation or Cu^{2+} -induced deprotonation of the pyrazole heterocycle would occur. Moreover, within these pH values the interior of the macrocyclic cavity is suitable for binding anionic species through the ammonium groups. Mixing aqueous solutions of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and of **1** in 3:2 molar ratio acidified to pH ca. 1.5 with aqueous HCl, followed by slow evaporation in an open vessel, led to crystals of $(5\text{H}_2\text{O}, 2\text{Cl}@[\text{Cu}_3(\text{H}_6(\mathbf{1}))_2\text{Cl}_9]\text{Cl}_7 \cdot 14.25\text{H}_2\text{O})$ (**5**) suitable for X-ray analysis (Table S1). The crystal structure can be defined as a racemic mixture of left- and right-handed helical 1D-coordination polymers (1D-CPs) in which every hexaprotonated macrocycle is connected to its two neighbours through monodentate pyrazole units by alternating sequence of one CuCl_3^- (Cu1) and two CuCl_3^- (Cu2, Cu3) triangular moieties (Figure 2a). In every macrocycle all the secondary amino groups are protonated as in the case of **4**.

The positive charge of the 1-D polymer is compensated by a chloride anion included in each one of the macrocycles and by chloride counter-anions. The coordination geometry around each connecting Cu^{2+} is trigonal bipyramidal with three chloride ligands occupying the equatorial plane and two pyrazole nitrogens at the shortened axial positions. Each helical turn is repeated every five macrocycles (Figure 3). MALDI-TOF spectra show a peak at m/z 1773.32 attributable to $[\text{K}(\text{Cu}_2(\text{H}_9\mathbf{1})_2)\text{Cl}_{13}]^+$ which corresponds to two macrocycles interconnected by two Cu^{2+} ions. A peak at m/z 1512.55 corresponds, on the other hand, to two macrocycles connected by a single Cu^{2+} ion (Figures S10-S14). These are the two basic building blocks of the 1D-chains. Interestingly enough the same crystal structure is obtained when the binuclear Cu^{2+} complex **2** is brought to pH 1.5 with HCl. Therefore, the acidification of the solutions leads to detachment of the metal from the amino groups and to re-organisation of the pyrazole units which change from a bis-monodentate (anionic pyrazolate) to a monodentate coordination mode (neutral pyrazole) (Scheme 1).

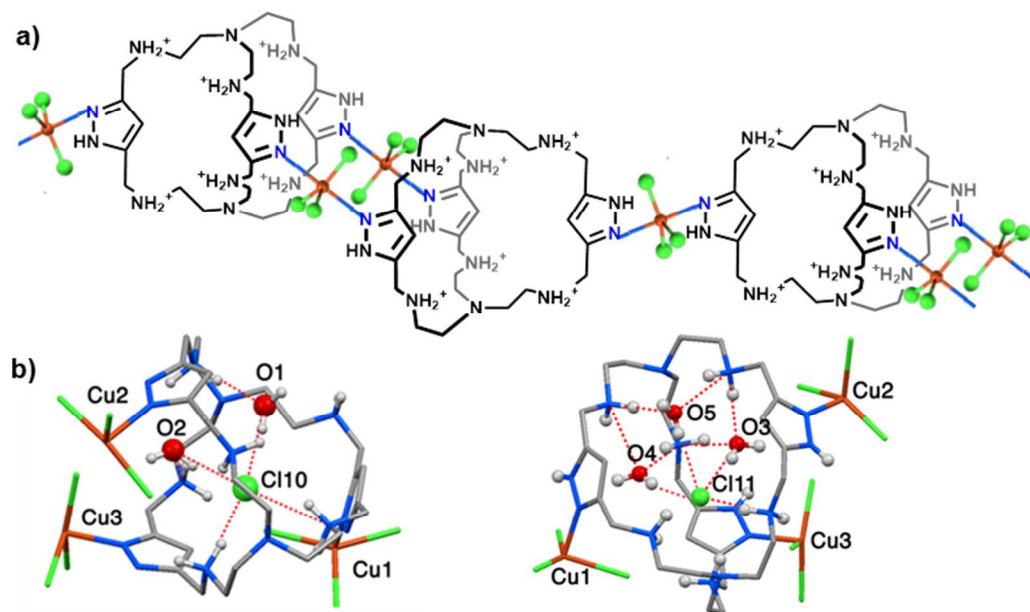


Figure 2. a) View of the two different monomers of Cu²⁺ cryptand complexes (hydrogen bonds are represented as red dotted lines). b) View of the two different cryptand subunits.

There are two different protonated macrocyclic subunits in the helix; one of them includes a chloride anion and two water molecules while the other one encapsulates one chloride anion and three water molecules (Figure 2b).

Each chloride anion is accepting hydrogen bonds from the neighbouring water molecules. In turn, each water molecule accepts hydrogen bonds from two secondary ammonium groups of the cryptand. A intricate hydrogen bonding network is

thus formed between the chloride anions and the water molecules inside of the macrocyclic cavity.

In summary, pH modulation permits to switch from an endo to an exo coordination of Cu²⁺ that, in this way, interconnects charged cryptand receptors forming a 1D-helical CP able to behave as a multi-anion receptor.

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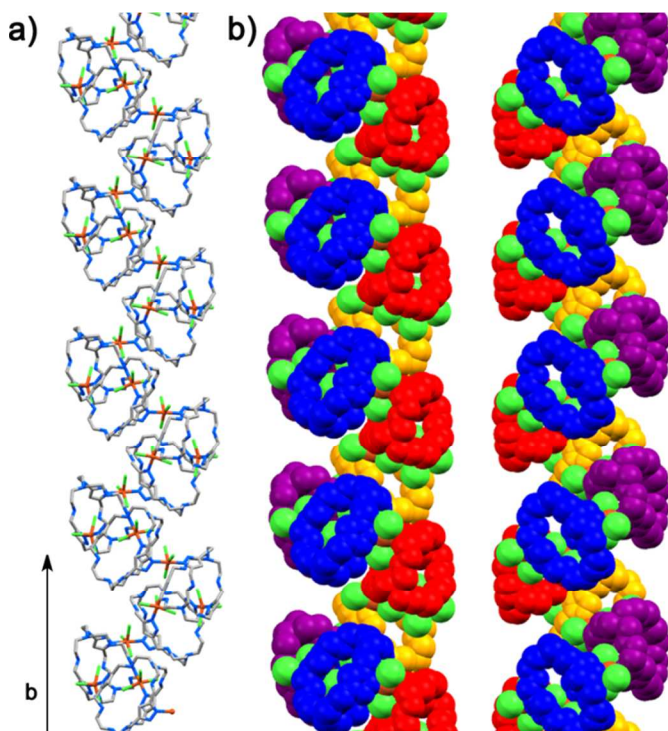


Figure 3. a) Stick view of cryptand Cu(II) helicate **5** along the b axis. b) Spacefill view. Green spheres stand for chloride anions.

Notes and references

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Electronic supplementary information (ESI) available: Full synthetic and crystallographic data (CCDC 1030676 (**4**) and 983275 (**5**)), MALDI TOF, potentiometric and NMR experiments. See DOI:10.1039/b000000x/

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From Isolated 1*H*-Pyrazole Cryptand Anion Receptors to Hybrid Inorganic-Organic 1D Helical Polymeric Anion Receptors.

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