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Cu^{2+}-Induced formation of cage-like compounds containing pyrazole macrocycles

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The crystal structure of the complex $[Cu_4(H_{-2}L)_2(H_2O)_2(ClO_4)_2](ClO_4)_2 \cdot 2H_2O$ where L is a new pyrazole ligand containing 1,5-diaminopentane spacers represents a new form of obtaining metal ion-induced inorganic–organic cages.

The build-up of compounds defining closed cavities plays a crucial role in supramolecular chemistry.[1] Classical approaches for the preparation of cage-type receptors very often involve long and multistep synthetic routes; the preparation of the first cryptands being a paradigm of this point. More recently several other approaches for the obtention of this kind of receptors have been put forward. Of particular relevance are those strategies in which the coordination of a specific substrate either of organic or inorganic nature induce the recognition site of a receptor in a determined shape. Within this approach, the work of Fujita's group on the Pd^{2+} induced-fit of pyridine based molecular host of different architectures and that of the groups of Mingos and Ramón-Vilar on the formation of nickel cages with thiourea type ligands under anion control are of particular relevance to this communication.[2,3]

Herewith we communicate on a novel way of organising a cage-like compound taking advantage of the particular characteristics of pyrazole as a ligand and the geometrical coordination preferences of Cu^{2+}.

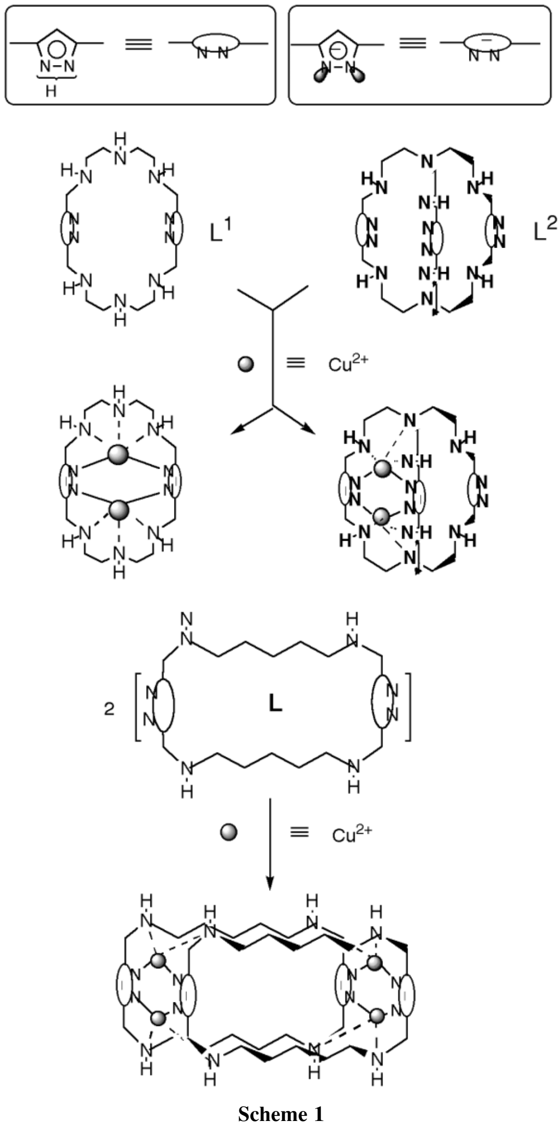
Recently we have reported on the Cu^{2+} complex formation of the 1*H*-pyrazole polyamine coronand L^1 and of the cage ligand L^2.[4–6] The first of these receptors L^1 takes up, both in solution and in the solid state, two Cu^{2+} metal ions. Its X-ray structure revealed a strongly distorted square pyramidal coordination geometry around each copper centre. The base of the pyramid is comprised of two nitrogen atoms of the two deprotonated pyrazolate moieties and by the two secondary nitrogen atoms closest to them in the chain (see Scheme 1). A central secondary nitrogen atom of the chain occupies the apical position. The binuclear Cu^{2+} complex of the cryptand type ligand L^2 displayed similar coordination features.[5]

Therefore, with the initial purpose of facilitating the coordinative interactions with axial ligands we proceeded to substitute the diethylenetriamine bridges in L^1 by 1,5-diaminopentane bridges to obtain receptor L.[7]

Interestingly, addition of Cu^{2+} to an aqueous solution of L in molar ratio Cu^{2+} : L of 2 : 1 originated a red coloured solution. Room-temperature evaporation of this solution yielded red crystals suitable for X-ray analysis. The crystal structure reveals the Cu^{2+}-induced formation of the centrosymmetric cage $[Cu_4(H_{-2}L)_2](H_2O)_2(ClO_4)_2](ClO_4)_2 \cdot 2H_2O$.

In contrast with L^1 which formed discrete binuclear $[Cu_2(H_{-2}L^1)]^{2+}$ species, the molecular features of L favour an arrangement in which two molecules of L are connected together by four Cu^{2+} metal ions. Each one of the four metal centres is bound by two secondary nitrogen and two pyrazole nitrogen atoms belonging to different macrocyclic subunits (Scheme 1) forming the base of a strongly distorted square pyramid. All the pyrazole fragments are deprotonated and behave as exobidentate ligands. The Cu–N distances involving the sp^2 pyrazolate nitrogen atoms are slightly shorter (Cu(1)–N(1) 1.91(1) Å, Cu(1)–N(2) 1.898(8) Å and Cu(2)–N(5) 1.925(9) Å, Cu(2)–N(8) 1.876(15) Å) than those involving the nitrogen atoms of the aliphatic bridge (Cu(1)–N(3) 2.07(2) Å, Cu(1)–N4) 2.064(8) Å and Cu(2)–N(6) 2.08(2) Å, Cu(2)–N(7) 2.07(1) Å). The severely distorted axial positions are occupied by an oxygen of a perchlorate anion (Cu(1)–O (4) 2.526(9) Å and by one water molecule (Cu(2)–O(10) 2.51(1) Å). (Fig. 1)

The other perchlorate anions in the structure that are acting as counter ions display strong disorder. The Cu(1)–Cu(2) distance of 3.967 Å falls within the range found for related complexes.† [4–6,8]



Scheme 1

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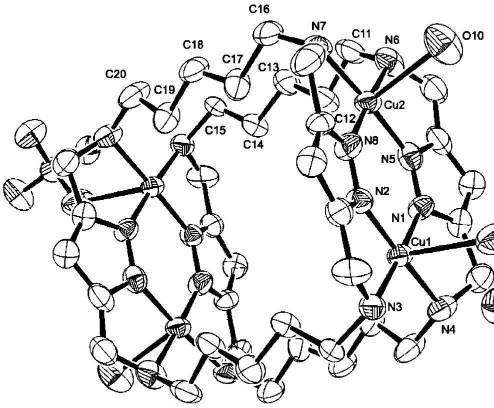

Fig. 1 ORTEP drawing of the complex $[Cu_4(H_{-2}L)_2(H_2O)_2(ClO_4)_2]^{2+}$. Selected distances (Å) and angles (°): Cu(1)–N(1) 1.91(1), Cu(1)–N(2) 1.898(8), Cu(1)–N(3) 2.07(2), Cu(1)–N(4) 2.064(8), Cu(1)–O(4) 2.526(9), Cu(2)–N(5) 1.925(9), Cu(2)–N(6) 2.08(2), Cu(2)–N(7) 2.07(1), Cu(2)–N(8) 1.88(2), Cu(2)–O(10) 2.51(1); N(1)–Cu(1)–N(2) 94.7(5), N(2)–Cu(1)–N(3) 82.1(5), N(4)–Cu(1)–N(3) 101.9(5), N(8)–Cu(2)–N(5) 93.5(5), N(8)–Cu(2)–N(7) 82.1(6), N(5)–Cu(2)–N(6) 82.5(5), N(7)–Cu(2)–N(6) 101.9(6).

The cage displays a rectangular prismatic shape with two opposite faces defined by the two metal ion binuclear coordination sites. These coordination faces would be interconnected by four edges constituted by the pentamethylene chains of the two receptors, which should afford a significant hydrophobic character to the cage interior. The torsion angles along the hydrocarbon chains are all close to 180°.

An idea of the cage dimensions can be extracted by constructing a polyhedron linking the secondary nitrogen atoms of L. This would lead to dimensions 7.555 × 6.583 × 3.214 Å. The shortest axes would be that connecting secondary nitrogens of different L receptors in the coordination faces and the largest one that of the pentamethylene chains. Its is interesting that the interior of the cage is completely empty (Fig. 2). None of the water molecules or chloride anions are placed within the cage. The different cages do not show interconnections through hydrogen bonds or other intermolecular forces. The hydrophobic edges of different cages present a separation of >4.5 Å.

Although there are not yet definitive proofs, this molecular arrangement seems to be also preserved in aqueous solution. Potentiometric studies suggest the formation of a very stable red $[Cu_4(H_{-2}L)_2]^{4+}$ species ($4Cu^{2+} + 2L = Cu_4(H_{-2}L)]^{4+} + 4H^+$, log $K = 29.96(3)$, $\lambda_{max} = 536$ nm, $\varepsilon = 183$ dm^3 cm^{-1} mol^{-1})) that would for a Cu^{2+}:L 2:1 molar ratios quantitatively be formed in solution above pH 5.5.[9] The formation of this compound implies the deprotonation of the pyrazole moieties in solution and this, as already observed for L^1 and L^2 implies a significant increase in the acidity of the pyrazole fragments induced by the coordination of the Cu^{2+} metal ions.

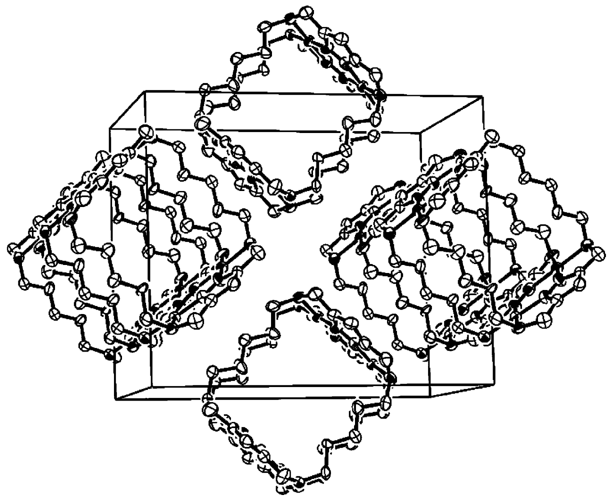

Fig. 2 Portion of the packing drawing of $[Cu_4(H_{-2}L)_2(H_2O)_2(ClO_4)_2]$-$(ClO_4)_2{\cdot}2H_2O$. Perchlorate anions and water molecules are omitted for clarity.

An explanation for this elaborate molecular organisation should rest on the combination of the coordination characteristics of pyrazole as a ligand,[10] and to the molecular topology of L. If similarly to L^1, a discrete binuclear $[Cu_2(H_{-2}L)]^{2+}$ complex had formed, the large pentamethylene would have originated two large unfavourable eight-membered chelate rings which would have substantially reduced the stability of the complex.

The results presented here prompt studies for deriving related cages with other metal ions and for searching their potential possibilities to encapsulate and recognise guest species.

Notes and references

† *Crystal data* for **1**: $C_{40}H_{76}N_{16}O_{20}Cl_4Cu_4$, $M = 1497.12$, monoclinic space group $P2_1/n$, $a = 11.152(5)$, $b = 18.361(5)$, $c = 15.437(5)$ Å, $\beta = 91.383(5)$. $V = 3160(2)$ Å^3, $Z = 4$, 5927 reflections collected of which 3015 were independent ($R_{int} = 0.0526$), $D_c = 1.573$ Mg m^{-3} R (R_w) = 0.0781 (0.2319). CCDC reference number 174510. See http://www.rsc.org/suppdata/cc/b1/b110409h/ for crystallographic data in CIF or other electronic format.

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7 L was obtained by reaction of 3,5-pyrazoledicarbaldehyde with 1,5-diaminopentane in MeOH under argon atmosphere at room temperature. $NaBH_4$ was added portionwise to a suspension of the resulting solid in MeOH at room temperature and was stirred overnight. The dry residue was extracted with toluene in a Soxhlet apparatus. Evaporation gave a solid, which was crystallised from the same solvent as white crystals (55%); mp. 181–183 °C. L gives satisfactory elemental analysis and spectroscopical data.

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9 Potentiometric measurements were carried out at 298.1 K in 0.15 mol dm^{-3} NaCl. The program HYPERQUAD (P. Gans, A. Sabatini, A. vacca, *Talanta*, 1996, **43**, 1739) was used to compute the stability constants. Protonation constants of L: $\log K_{HL/H.L} = 9.56(1)$, $\log K_{H_2L/HL.L} = 8.94(1)$, $\log K_{H_3L/H_2L.L} = 8.02(1)$, $\log K_{H_4L/H_3L.L} = 7.63(1)$. System Cu^{2+}–L: $Cu^{2+} + H^+ + L = [CuHL]^{3+}$, $\log K = 23.95(3)$, $Cu^{2+} + L = [CuL]^{2+}$, $\log K = 15.75(9)$, $4Cu^{2+} + 2L = [Cu_4(H_{-2}L)_2]^{4+} + 4H^+$, $\log K = 29.96(3)$.

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