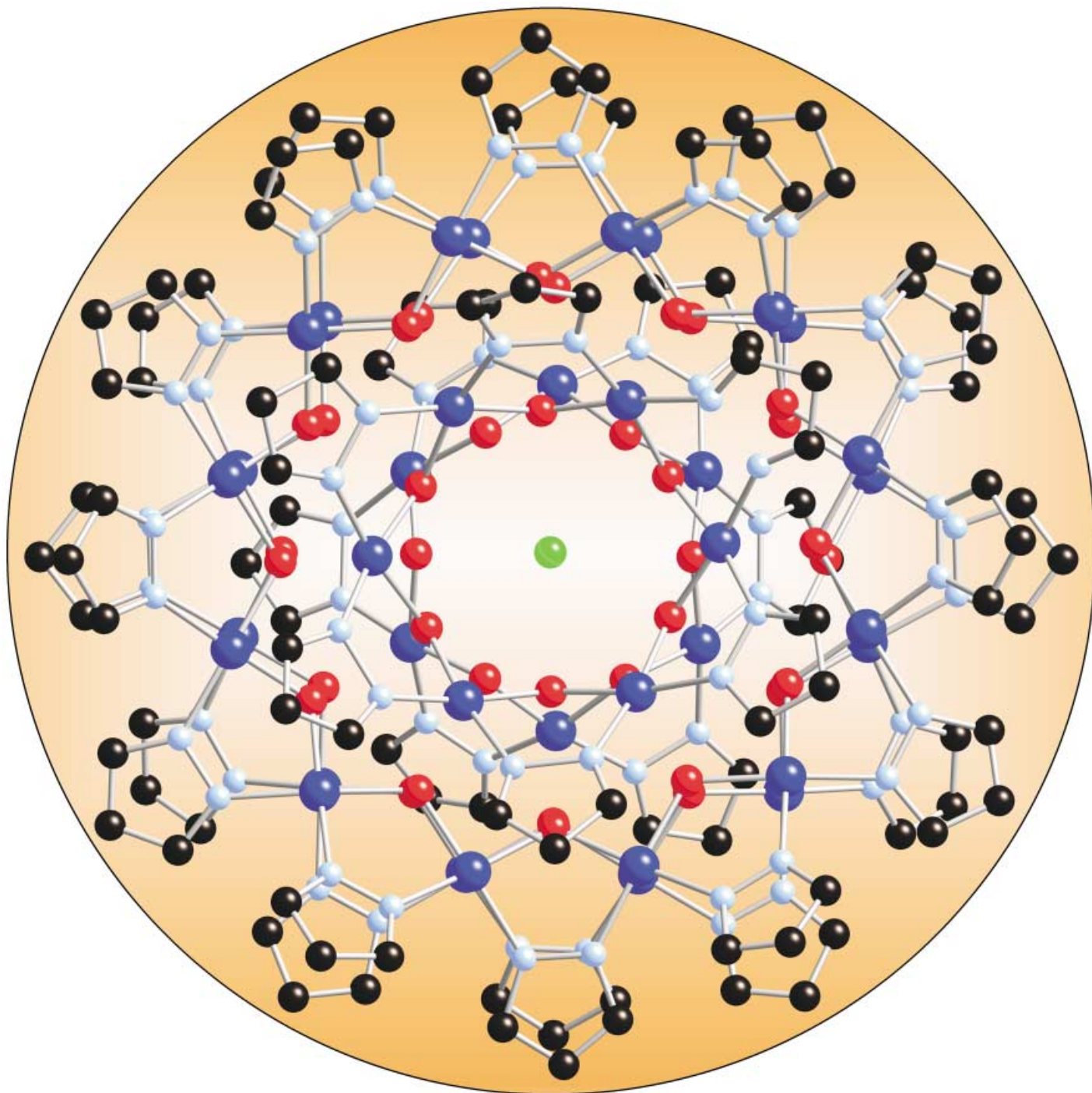


Zuschriften



Drei oder vier neutrale Metallacyclen vom Typ $\{[cis-Cu(\mu-OH)(\mu-pz)]_n\}$ ($n = 6, 8, 9, 12, 14$) bilden sich durch Selbstorganisation. Die lipophilen Pyrazol-Liganden (pz) richten sich nach außen, während die hydrophilen OH-Gruppen ein eingeschlossenes Anion stabilisieren. Mehr dazu entnehmen Sie der Zuschrift von R. G. Raptis et al. auf den folgenden Seiten.

Anion Encapsulation by Neutral Supramolecular Assemblies of Cyclic Cu^{II} Complexes: A Series of Five Polymerization Isomers, [*cis*-Cu^{II}(μ-OH)(μ-pz)]_n, n = 6, 8, 9, 12, and 14**

Gellert Mezei, Peter Baran, and Raphael G. Raptis*

In memory of Leigh Christopher Porter

We describe herein the characterization of three novel supramolecular anion-encapsulating assemblies, where neutral covalently-bound host units converge around the anionic guests, thus forming an elaborate set of host–guest and host–host H bonds. The organization of their architecture mimics the strategy of Nature in constructing ion carriers and channels.

The design and synthesis of biomimetic molecules has developed into a central theme of supramolecular chemistry.^[1] Anion recognition and encapsulation^[2] is an active research area of biomimetic chemistry that relates to the mechanism of hydrophilic anion transport across hydrophobic cell membranes by various translocases.^[3,4] Considerable effort has been devoted to the synthesis of artificial specific anion-recognition agents and several organic and inorganic systems, often cationic macrocyclic and polycyclic cages, are known.^[5–9] Several of the synthetic anion-binding hosts are polynuclear metal complexes, in which coordinatively unsaturated metal atoms are preorganized around the space designed to receive a guest anion.^[10] In contrast, only few of the biologically relevant, neutral anion-binding agents have been prepared to date.^[11–18]

We report preliminary studies of the synthesis of a five-membered series of metallacyclic [*cis*-Cu^{II}(μ-OH)(μ-pz)]_n polymerization isomers (pz = pyrazolato anion, C₃H₃N₂[−]), n = 6, 8, 9, 12 and 14. The X-ray crystal structures of anion-specific supramolecular assemblies of three or four [*cis*-Cu^{II}(μ-OH)(μ-pz)]_n rings—[PPN⁺][Cl[−]][Cu(μ-OH)(μ-pz)]₆₊₁₂ (1), [Bu₄N⁺][Cl[−]][Cu(μ-OH)(μ-pz)]₆₊₁₂ (2), [Bu₄N⁺]₂[CO₃^{2−}][Cu(μ-OH)(μ-pz)]₆₊₁₂₊₉ (3) and [PPN⁺]₂[SO₄^{2−}][Cu(μ-OH)(μ-pz)]₈₊₁₄₊₉ (4) (PPN⁺ = bis(triphenylphosphoranylidene)ammonium cation) are presented.^[19] The assemblies 1 and 4 were found cocrystallized in a single crystal structure.

The supramolecules 1 and 4 were originally prepared serendipitously in a reaction involving the removal of chlorides from the complex [PPN]₂[Cu₃(μ₃-O)(μ-pz)₃Cl₃],

followed evidently by ring-opening, oligomerization, and ring-closing of the Cu–pz backbone in a wet solvent.^[20] A similar procedure employing (Bu₄N)₂[Cu₃(μ₃-Cl)₂(μ-pz)₃Cl₃] yielded 3. Subsequently, 2 was prepared in a rational procedure from the reaction of Cu(OH)₂ and pzH, in the presence of Bu₄NCl (Supporting Information). The unusually high solubility of 1–4 in organic solvents has not allowed the development of a facile crystallization procedure to date and long periods of standing have been necessary for the growth of single crystals.

The [*cis*-Cu^{II}(μ-OH)(μ-pz)]_n rings (Figure 1) all consist of distorted square-planar Cu^{II}-centers connected by μ-pz ligands at the outer-and μ-OH ligands at the inner surface of a

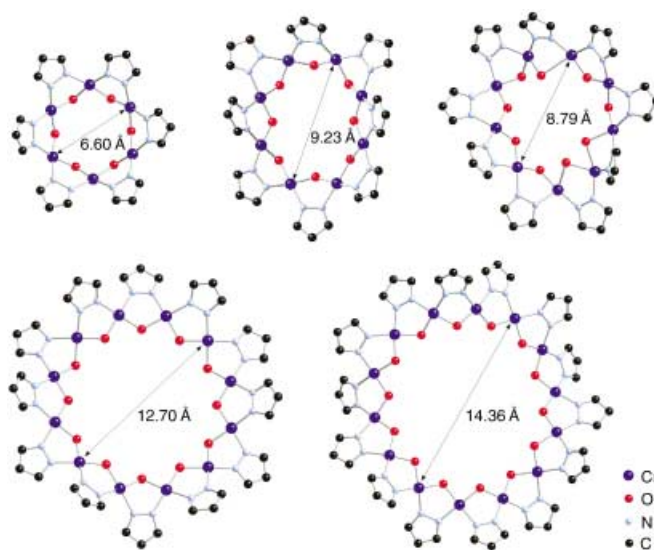


Figure 1. Ball-and-stick representations of the [*cis*-Cu(μ-OH)(μ-pz)]_n rings, n = 6, 8, 9, 12, 14; hydrogen atoms not shown. Bond length [Å] and angle [°] ranges: Cu...Cu = 3.130(2)–3.381(2), Cu–N = 1.91(1)–2.08(2), Cu–OH = 1.894(8)–2.013(14), N–Cu–N = 93.8(5)–101.4(5), O–Cu–O = 87.5(3)–95.3(2), and O–Cu–N = 82.4(4)–102.5(4).

toroid.^[21] In all four aggregates, 1–4, the larger rings act as hosts (O donors) for one or two smaller rings, binding them by multiple, weak O...Cu interactions. In this arrangement, the OH groups of both rings are directed to the center of the assembly and the pyrazoles to the periphery, thus defining hydrophilic and hydrophobic domains, respectively.

In the 12-membered [*cis*-Cu(μ-OH)(μ-pz)]₁₂ rings of 1 and 2, pyrazoles alternate in approximately in-plane and out-of-plane orientations (Figure 2). The out-of-plane pyrazoles direct their two *trans* OH groups (also out-of-plane) to the opposite side, while the in-plane pyrazoles point their respective *trans*-OH groups (also in-plane) to the center of the ring. In contrast, the six-membered rings adopt a crown shape with all atoms defining the conical surface. In the [*cis*-Cu(μ-OH)(μ-pz)]₆₊₁₂ assemblies, the six inward-pointing hydroxyl groups of the outer ring are appropriately oriented to interact with all six Cu-centers of the inner six-membered ring at the axial positions of what become square-pyramidal Cu-centers. The inter-ring Cu...O distances of 2.399(6) to 2.464(6) Å are significantly longer than the intraring Cu–(μ-

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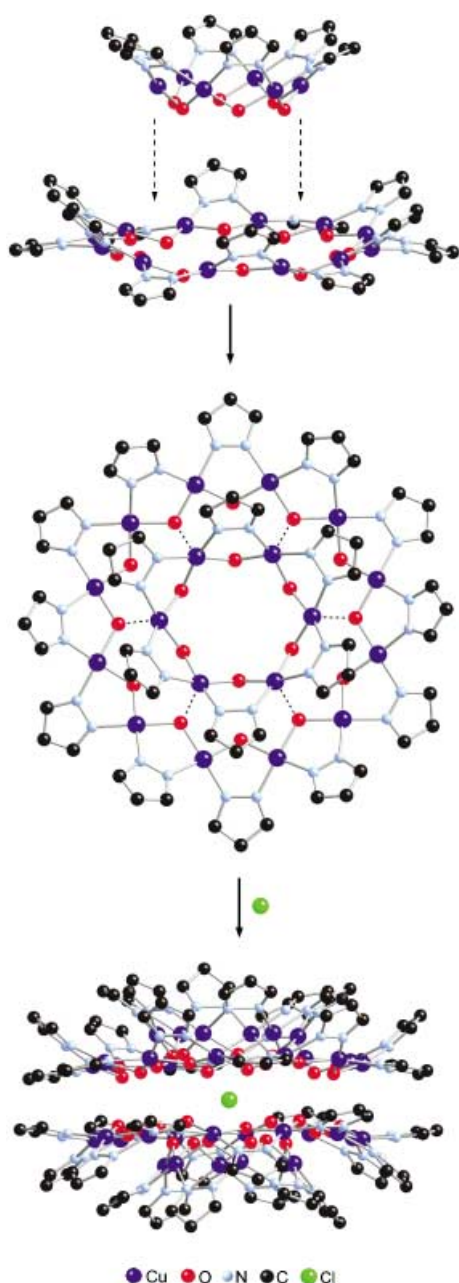


Figure 2. Scheme of ball-and-stick diagrams showing stepwise the assembly of $[\text{Cl}^- \subset \{[\text{Cu}(\mu\text{-OH})(\mu\text{-pz})]_{6+12}\}_2]$ in **1** and **2**; H-atoms not shown. Twelve H-bonded $\text{Cl}\cdots\text{O}$ distances of 3.306(7)–3.698(7) Å between all six OH-groups of the two $[\text{Cu}(\mu\text{-OH})(\mu\text{-pz})]_6$ rings and the encapsulated chloride. Twelve H-bonded $\text{O}\cdots\text{O}$ distances of 2.754(9)–2.995(9) Å between all twenty four OH-groups of the two $[\text{Cu}(\mu\text{-OH})(\mu\text{-pz})]_{12}$ rings—six in-plane HO's of one 12-membered ring and six out-of-plane OH's of the other, and vice versa.

OH) bonds of 1.894(8) to 1.982(8) Å within either the six- or twelve-membered rings. However, the cumulative effect of six such weak $\text{Cu}\cdots\text{O}$ interactions between the two rings may account for the formation of this “Russian doll” assembly. The neutral $[\text{Cu}(\mu\text{-OH})(\mu\text{-pz})]_{6+12}$ assembly has segregated hydrophilic (hydroxyl) and hydrophobic (pyrazole) groups in a structure resembling a metal-containing calixarene.

Two face-to-face $[\text{Cu}(\mu\text{-OH})(\mu\text{-pz})]_{6+12}$ units sandwich a chloride ion between their hydrophilic sides; the chloride ion is held by weak H bonds to twelve OH groups, six on each side, which belong to the six-membered rings forming the $\text{Cl}^- \subset \{[\text{Cu}(\mu\text{-OH})(\mu\text{-pz})]_{6+12}\}_2$ assembly (Figure 2). The assembly is further supported by a picket fence of twelve H bonds (not shown in Figure 2) formed between pairs of OH groups, one each from the two 12-membered rings. At the opposite side of the encapsulated chloride, either a phenyl (**1**) or a butyl group (**2**) of the PPN^+ and Bu_4N^+ counterions, respectively, dips into the hydrophobic bowl formed by the pyrazoles of the inner $[\text{Cu}(\mu\text{-OH})(\mu\text{-pz})]_6$ ring.

The $[\text{Cu}(\mu\text{-OH})(\mu\text{-pz})]_{6+12}$ unit is also present in the structure of **3**, in which a carbonate ion is encapsulated between this unit and a nine-membered ring (Figure 3). Each carbonate O atom is in H-bonding distance to all hydroxyl

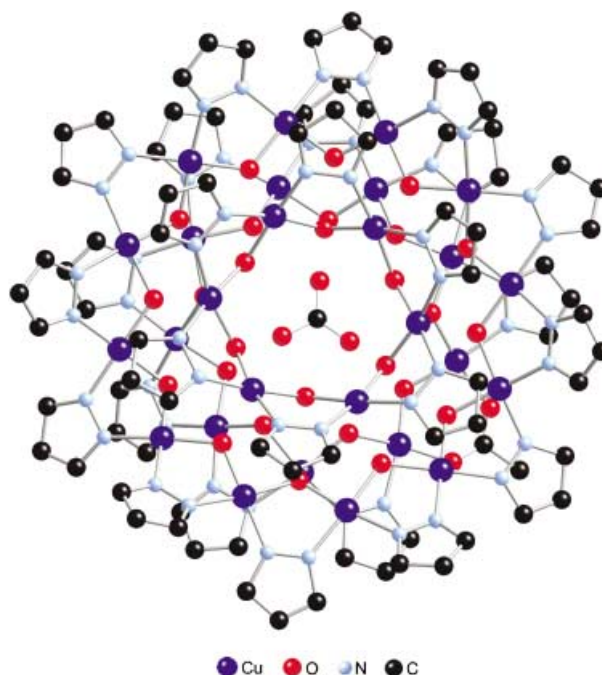


Figure 3. Ball-and-stick diagram of **3**. Each carbonate O-atom has four H-bonds— $\text{O}\cdots\text{O}$ distances of 2.73(1)–2.97(1) Å, and two longer interactions, 3.27(1)–3.52(1) Å, with OH-groups of the 6- and 9-membered rings. Six $\text{Cu}\cdots\text{O}$ inter-ring (6- and 12-membered rings) contacts of 2.390(8)–2.577(8) Å, and three more, 2.354(8)–2.428(8) Å, between Cu-atoms of the 9-membered ring and O-atoms of the 12-membered one. Six additional H-bonds between the 9- and the 12-membered rings: $\text{O}\cdots\text{O}$ distances, 2.75(1)–2.93(1) Å.

groups of the nine- and six-membered rings on either side, with $\text{O}\cdots\text{O}$ interatomic distances as short as 2.734(9) Å. Additional H bonds and $\text{O}\cdots\text{Cu}$ interactions between rings on either side of the carbonate plane are contributing to the assembly. A similar but more irregular H bonding and $\text{O}\cdots\text{Cu}$ interaction pattern is seen in the structure of **4** (Figure 4). The 14-membered ring acts as a host, binding to the Cu-atoms of the eight- and nine-membered rings, which, in turn, bind the encapsulated sulfate ion. While the H bonds holding the chloride, carbonate, and sulfate anions at the hydrophilic

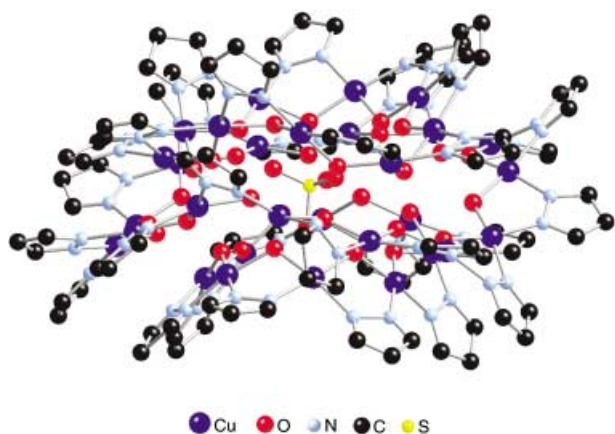


Figure 4. Ball-and-stick diagram of **4**. The sulfate O-atoms form eighteen O...O contacts of 2.83(1)–3.37(1) Å, with OH-groups of the 8- and 9-membered rings. Seven Cu...O contacts of 2.376(6)–2.736(6) Å between O-atoms of the 14-membered ring and Cu-atoms of the 8-membered one and six more, 2.392(6)–2.855(6) Å, with those of the 9-membered ring. Six additional H-bonds between the 14-membered ring and each of the 8- and 9-membered ones: O...O distances, 2.732(9)–3.018(9) Å.

pockets of **1–4** are weak, they are also numerous and their cumulative effect should amount to significant overall stability.

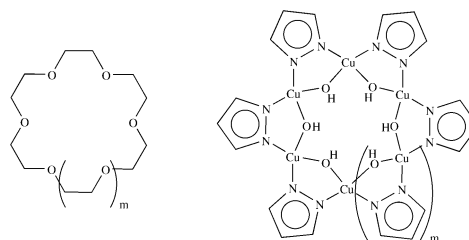
Several transition metals and bridging ligands have been employed in the synthesis of a variety of metallacyclic rings, including a $[\{trans-Cu(\mu-OH)(\mu-3,5-Me_2-pz)\}_8]$ ring and a $[\{Zn_2(\mu-5-Me-3-Ph-pz)_2(\mu-OCH_2CH_2S)\}_6]$ ring.^[24,25] Yet, there are only a few examples of polymerization isomers—complexes of the same empirical formula—in this group of compounds.^[10,26–31] The characterization in a single crystal structure (containing the assemblies **1** and **4**) of all five ring sizes reported here, implies that there are only small, entropy-controlled differences in the Gibbs free energy between rings of different sizes, thus allowing all five to coexist. As only a part of the reaction products has been isolated in crystalline form, while a major part remained in solution, it is possible that rings of different sizes other than the five described here are still present in the mother liquor, but lack the appropriate anions for their crystallization.

The metallacyclic ring sizes are not dependent on the nature of the encapsulated anion; six-membered rings are part of the structures of **1** (and **2**) and **3**, while nine-membered rings are encountered in **3** and **4**. In contrast, the aggregation of metallacycles is specific to the encapsulated anion; the smaller chloride finds a snug fit between two six-membered rings of **1** and **2**, the planar carbonate requires a six- and a nine-membered ring in **3**, while the tetrahedral sulfate is encapsulated among an eight-, a nine- and a fourteen-membered rings in **4**. Two different cations, PPN⁺ and Bu₄N⁺, have been found associated with the same host-guest anion in **1** and **2**, which suggests that the counterions do not play a determining role in this chemistry. Several metallacycles may be present in solution and the availability of anions determines which metallacycles aggregate to form the neutral supramolecular hosts. Different combinations of

metallacycles may also be required for the encapsulation of anions other than chloride, carbonate, or sulfate.

Four levels of self-organization are manifested in the structures of the three anion-encapsulating aggregates described here: First, the approximately square-planar coordination preference of the Cu^{II}-cations, coupled with the availability of only pyrazole and hydroxyl ligands, favor the formation of one-dimensional Cu(μ-OH)(μ-pz) chains, which eventually close into metallacyclic rings. Second, the residual positive charges of the Cu-centers and the partial negative charges associated with the μ-OH ligands make possible the formation of two-, or three-ring assemblies through Cu...OH interactions. Third, hydrogen bonds, between the encapsulated anions and the μ-OH ligands of the neutral host, orient the latter towards the center of the supramolecular ensemble and wrap the metallacycles around the guest anions. Fourth, a complement of peripheral H bonds between rings add to the stability of the assemblies. The interplay of covalent coordination algorithms, H bonding and weak dipolar interactions in orchestrating the formation of complex assemblies of highly specific function is imitating the strategies employed by Nature for similar purposes. None of the above chemical properties are unique to copper or pyrazole, thus raising the possibility that structures **1–4** are only the frontrunners of a new class of supramolecular anion-encapsulating agents.

The structures of the series of metallacycles $[\{cis-Cu(\mu-OH)(\mu-pz)\}_n]$, $n = 6, 8, 9, 12, 14$ (Figure 1), resemble those of crown ethers and natural ionophores and can be considered as fully protonated, copper-containing crowns; metallacrowns. However, while crown ethers and ionophores function as cation binders by virtue of their inward oriented oxygen electron lone pairs, the copper metallacrowns show an inverted function, namely anion binding through the cooperative H bonding to all μ-OH groups. Work is underway to



determine the effects of temperature, concentration, solvent, and the nature of the anion on the composition and structure of the supramolecular assemblies.

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- [19] X-ray crystal structure analysis of **1+4**: crystal dimensions $0.20 \times 0.10 \times 0.04$ mm; $T = 302$ K; triclinic, space group $P\bar{1}$; $a = 21.240(3)$ Å, $b = 30.420(4)$ Å, $c = 35.863(5)$ Å, $\alpha = 98.447(3)^\circ$, $\beta = 91.774(3)^\circ$, $\gamma = 99.056(3)^\circ$, $V = 22601(6)$ Å³, $Z = 2$; $\rho_{\text{calcd}} = 1.709$ g cm⁻³; $\mu = 3.181$ mm⁻¹; $3.1 < 2\theta < 46.6^\circ$; of 64863 unique reflections, 30064 were observed [$I > 2\sigma(I)$]; 4818 parameters; $R_1 = 0.0559$, $wR_2 = 0.1217$ for $I > 2\sigma(I)$; GOF = 0.936. X-ray crystal structure analysis of **2**: crystal dimensions $0.20 \times 0.18 \times 0.05$ mm; $T = 300$ K; monoclinic, space group $P2_1/n$; $a = 17.545(2)$ Å, $b = 34.275(4)$ Å, $c = 36.036(5)$ Å, $\beta = 90.541(3)^\circ$, $V = 21669(5)$ Å³, $Z = 4$; $\rho_{\text{calcd}} = 1.714$ g cm⁻³; $\mu = 3.531$ mm⁻¹; $2.3 < 2\theta < 46.6^\circ$; of 31296 unique reflections, 13276 were observed [$I > 2\sigma(I)$]; 2346 parameters; $R_1 = 0.0585$, $wR_2 = 0.1384$ for $I > 2\sigma(I)$; GOF = 0.915. X-ray crystal structure analysis of **3**: crystal dimensions $0.28 \times 0.18 \times 0.10$ mm; $T = 303$ K; monoclinic, space group $P2_1/n$; $a = 34.796(5)$ Å, $b = 26.036(4)$ Å, $c = 38.820(6)$ Å, $\beta = 95.337(3)^\circ$, $V = 35016(9)$ Å³, $Z = 4$; $\rho_{\text{calcd}} = 1.716$ g cm⁻³; $\mu = 3.276$ mm⁻¹; $3.3 < 2\theta < 46.6^\circ$; of 50472 unique reflections, 20614 were observed [$I > 2\sigma(I)$]; 3651 parameters; $R_1 = 0.0656$, $wR_2 = 0.1425$ for $I > 2\sigma(I)$; GOF = 0.979. Refinement details can be found as Supporting Information. CCDC-212810 (**1+4**), CCDC-212812 (**2**) and CCDC-212811 (**3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).
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