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Nature of the Reactants and Influence of Water on the Supramolecular Assembly

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The influences of the nature of reactants and water on the self-assembly of cationic Cu(II) complex structures containing *N*-(2-pyridylmethyl)glycine (Hpgly) and *N*-(2-pyridylmethyl)-L-alanine (Hpala) ligands have been investigated. A metallamacrocycle $[Cu_6(pgly)_3(spgly)_3]\ (ClO_4)_6{\cdot}9H_2O$ has been formed by the reaction of $[Cu(pgly)_2]{\cdot}2H_2O$ with $Cu(ClO_4)_2{\cdot}6H_2O$. The hexameric cation has Schiff base and reduced Schiff base ligands alternatively bonded to Cu(II) to provide cyclohexane-like conformation with a cavity diameter of 9.4 Å. The reaction of $Cu(ClO_4)_2{\cdot}6H_2O$ with Hpgly·HCl yielded $[Cu(pgly)(H_2O)](ClO_4)$, which is presumed to have 1D coordination polymeric structure. A $\{K\subset[12\text{-MC-}3]\}$ metallacrown, $[K(ClO_4)_3\{Cu_3(pala)_3\}](ClO_4)$ has been isolated by reacting $Cu(ClO_4)_2$ with Kpala in MeCN/MeOH. This $\{K\subset[12\text{-MC-}3]\}$ metallacrown further reacts with water to form an infinite 1D coordination polymer $[Cu(pala)(H_2O)(ClO_4)]_n$, which can also be obtained by conducting the reaction in aqueous MeOH.

Introduction

Self-assembly is an important process in the formation of metal-based supramolecular architectures.[1,2] However, the formation of such structures depends on the nature of external stimuli, such as pH of the medium, presence of certain metal ions, the size of the counterions used, solvent, and concentration. For example, the existence of two different metallamacrocycles has been found to depend on the nature of the solvent used. The tetranuclear metallocyclophane was favored in nitromethane solvent while it converts into a hexanuclear metallocyclophanes as the major product in acetonitrile.[3] On the other hand, a triple helicate has been converted to the entropically disfavored tetrahedral cluster in the presence of Me_4N^+ cation.[4] Sequential formation of linear and circular helicate as kinetic and thermodynamic products, respectively, has been studied by Lehn and co-workers.[5] The pH dependence of formation of polymeric structures in solution has been exemplified by the work of Matsumoto and co-workers[6] and others.[7] pH-driven self-assembly/disassembly of transition metal helicates has been the subject of intense interest from the point of information storage in solution.[8] A mononuclear Co(II) has been found to form an infinite ladder structure by heating to 150 °C in the solid state.[9] A few multidimensional network structures

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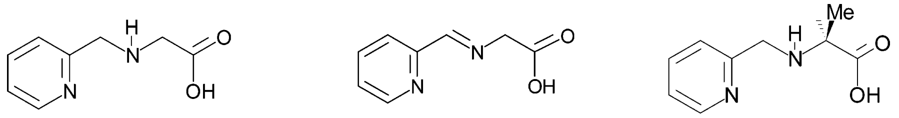
Chart 1



Hpgly **Hspgly** **Hpala**

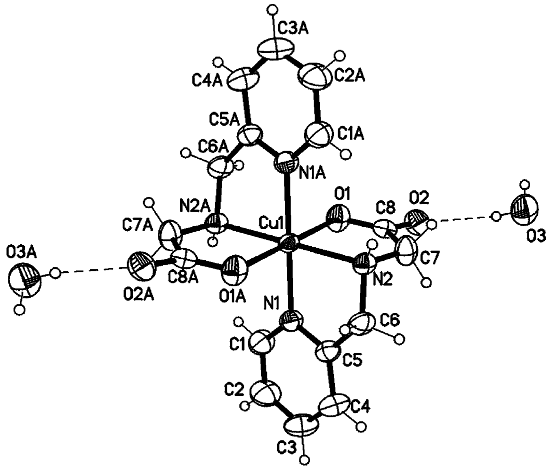


Figure 1. ORTEP diagram of **1** with 50% probability of thermal ellipsoids.

Table 1. Selected Bond Distances (Å) and Angles (°) for **1**

Cu(1)−N(2)	2.032(2)	N(2)−C(7)	1.469(3)
Cu(1)−N(1)	2.065(2)	C(7)−C(8)	1.524(3)
Cu(1)−O(1)	2.251(1)	C(8)−O(2)	1.244(2)
C(6)−N(2)	1.479(2)	C(8)−O(1)	1.247(2)
N(2)−Cu(1)−N(1)[a]	98.69(6)	N(2)−C(6)−C(5)	110.5(2)
N(2)#1−Cu(1)−N(1)[a]	81.31(6)	C(7)−N(2)−C(6)	113.8(2)
N(2)−Cu(1)−O(1)	81.05(6)	C(7)−N(2)−Cu(1)	112.1(1)
N(1)−Cu(1)−O(1)	91.17(6)	C(6)−N(2)−Cu(1)	105.9(1)
N(2)−Cu(1)−O(1)[a]	98.95(6)	N(2)−C(7)−C(8)	115.9(2)
N(1)−Cu(1)−O(1)[a]	88.83(6)	O(2)−C(8)−O(1)	124.7(2)
O(1)−Cu(1)−O(1)[a]	180.00(5)	O(2)−C(8)−C(7)	116.1(2)
C(5)−N(1)−C(1)	118.9(2)	O(1)−C(8)−C(7)	119.2(2)
C(5)−N(1)−Cu(1)	112.2(1)	C(8)−O(1)−Cu(1)	111.4(1)
C(1)−N(1)−Cu(1)	128.8(1)		

[a] Symmetry transformations used to generate equivalent atoms: *a*, $-x + 1, -y + 1, -z + 1$.

have been converted to new dimensional structures by reacting with different reagents in solution.[10]

In this paper, we report the synthesis of a novel molecular hexamer, namely, $[Cu_6(pgly)_3(spgly)_3](ClO_4)_6{\cdot}9H_2O$ from an equimolar ratio of $[Cu(pgly)_2]{\cdot}2H_2O$ and $Cu(ClO_4)_2{\cdot}6H_2O$ (Hpgly = *N*-(2-pyridylmethyl)glycine and Hspgly = *N*-(2-pyridylidene)glycine, as shown in Chart 1) in aqueous MeOH, while $[Cu(pgly)(H_2O)]_n{\cdot}n(ClO_4)$, presumably a one-dimensional coordination polymer, resulted when Hpgly·HCl was reacted with $Cu(ClO_4)_2{\cdot}6H_2O$ directly. On the other hand, a MC cation, $[K(ClO_4)_3\{Cu_3(pala)_3\}]^+$ was obtained from $Cu(ClO_4)_2$ with Kpala (Hpala = *N*-(2-pyridylmethyl)-L-alanine) in MeCN/MeOH. This {K⊂[12-MC-3]} metallacrown cation further reacts with water to form an infinite 1D coordination polymer $[Cu(pala)(H_2O)](ClO_4)$.

Results and Discussion

Complexes with Ligand *N*-(2-Pyridylmethyl)glycine. The reaction between Hpgly·HCl and $Cu(ClO_4)_2{\cdot}6H_2O$ or $Cu(CH_3COO)_2{\cdot}H_2O$ in the molar ratio of 2:1 furnished dark blue crystals of $[Cu(pgly)_2]{\cdot}2H_2O$ **1**. Complex **1** has two tridentate pgly ligands, each bonded to Cu(II) in a *facial* manner, as illustrated in Figure 1. Selected bond distances and angles are given in Table 1. The molecule has a crystallographic inversion center at Cu(II) in which the Cu(II) has distorted octahedral geometry with a *trans*-N_4O_2 donor set. Of the two five-membered rings formed by each pgly ligand, the ring containing Cu(1)−N(2)−C(7)−C(8)−O(1) is planar (with rms deviation, 0.0246 Å), and the ring containing pyridine has envelope conformation with N(2) deviated from Cu(1)−N(1)−C(5)−C(6) plane by 0.640 Å. The Cu−N−C angles at N(1) atom are markedly unsymmetrical (112.2(1) and 128.8(1)° as a result of chelation. Furthermore, the substituents at the N(2)−C(7) bond form an *eclipsed* conformation, as noted from the H(2)−N(2)−C(7)−H(7b) torsion angle, 2.7°. A tetranuclear cobalt(III) complex of pgly, $[(\mu_3\text{-}O)_4Co_4(sgly)_4]$ has been found to have similar geometry.[11]

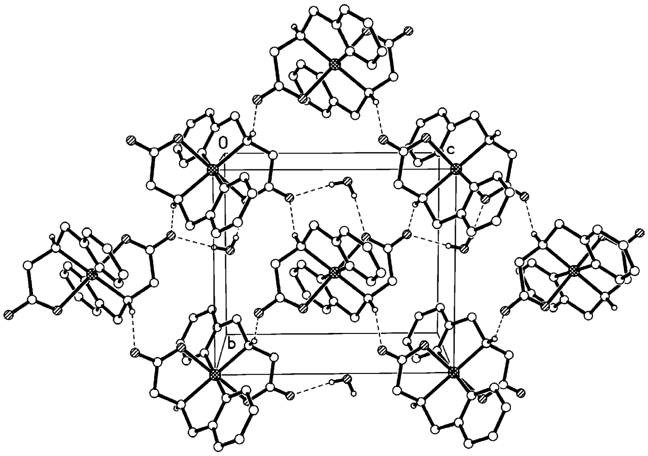


Figure 2. Packing diagram of **1** showing hydrogen bonding interactions. The hydrogen atoms attached to carbon atoms have been omitted for clarity.

The N−H donor and C═O acceptor groups in the pgly ligand and water in the lattice participate in the hydrogen bonding and form an interesting 2D sheet structure in *bc* plane (shown in Figure 2) in which the hydrogen atoms from water molecules bond to two different oxygen atoms and fill the empty space in the lattice. The hydrogen bonds are considered to be medium because the D···A distances vary from 2.810(2) to 2.994(2) Å, tabulated in Table 2.

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Table 2. Hydrogen Bond Parameters for **1**

D−H	*d*(D−H)	*d*(H···A)	∠DHA	*d*(D···A)	symm operator
N2−H2	0.79(2)	2.24(2)	159(2)	2.994(2)	O2 [$-x + 1, y + 1/2, -z + 1/2$]
O3−H3A	0.76(2)	2.06(2)	171(3)	2.810(2)	O2
O3−H3B	0.76(2)	2.09(2)	171(3)	2.839(2)	O1 [$x, -y + 1/2, z - 1/2$]

Table 3. Selected Bond Lengths (Å) and Angles (°) for **2**

Cu(1)−O(4)[a]	1.933(7)	C(7)−C(8)	1.489(13)
Cu(1)−N(2)	1.956(8)	C(8)−O(2)	1.266(12)
Cu(1)−O(1)	1.961(7)	C(8)−O(1)	1.267(12)
Cu(1)−N(1)	1.979(8)	C(14)−N(4)	1.310(15)
Cu(2)−O(2)	1.940(7)	N(4)−C(15)	1.433(14)
Cu(2)−N(4)	1.959(10)	C(15)−C(16)	1.498(14)
Cu(2)−O(3)	1.968(7)	C(16)−O(3)	1.253(12)
Cu(2)−N(3)	1.974(8)	C(16)−O(4)	1.263(12)
C(6)−N(2)	1.441(13)	O(4)−Cu(1)[b]	1.933(7)
N(2)−C(7)	1.486(12)		
O(4)[a]−Cu(1)−N(2)	172.2(3)	N(2)−C(7)−C(8)	108.7(8)
O(4)[a]−Cu(1)−O(1)	90.3(3)	O(2)−C(8)−O(1)	121.8(9)
N(2)−Cu(1)−O(1)	84.8(3)	O(2)−C(8)−C(7)	117.4(10)
O(4)[a]−Cu(1)−N(1)	103.4(4)	O(1)−C(8)−C(7)	120.7(9)
N(2)−Cu(1)−N(1)	82.1(4)	C(8)−O(1)−Cu(1)	112.9(6)
O(1)−Cu(1)−N(1)	165.5(3)	C(8)−O(2)−Cu(2)	126.8(7)
O(2)−Cu(2)−N(4)	173.5(4)	N(4)−C(14)−C(13)	114.3(11)
O(2)−Cu(2)−O(3)	89.8(3)	C(14)−N(4)−C(15)	130.3(11)
N(4)−Cu(2)−O(3)	84.2(4)	C(14)−N(4)−Cu(2)	115.1(9)
O(2)−Cu(2)−N(3)	103.4(3)	C(15)−N(4)−Cu(2)	111.0(7)
N(4)−Cu(2)−N(3)	82.5(4)	N(4)−C(15)−C(16)	110.5(9)
O(3)−Cu(2)−N(3)	166.4(3)	O(3)−C(16)−O(4)	123.2(10)
N(2)−C(6)−C(5)	109.3(9)	O(3)−C(16)−C(15)	119.4(9)
C(6)−N(2)−C(7)	119.1(8)	O(4)−C(16)−C(15)	117.4(10)
C(6)−N(2)−Cu(1)	108.3(6)	C(16)−O(3)−Cu(2)	113.3(6)
C(7)−N(2)−Cu(1)	110.3(6)	C(16)−O(4)−Cu(1)[b]	125.6(7)

[a] Symmetry transformations used to generate equivalent atoms: $-y + 1, x - y, z$. [b] Symmetry transformations used to generate equivalent atoms: $-x + y + 1, -x + 1, z$.

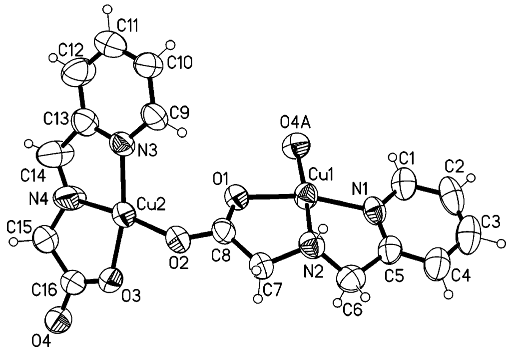

Figure 3. View of the selected asymmetric unit in **2** showing the atom labeling.

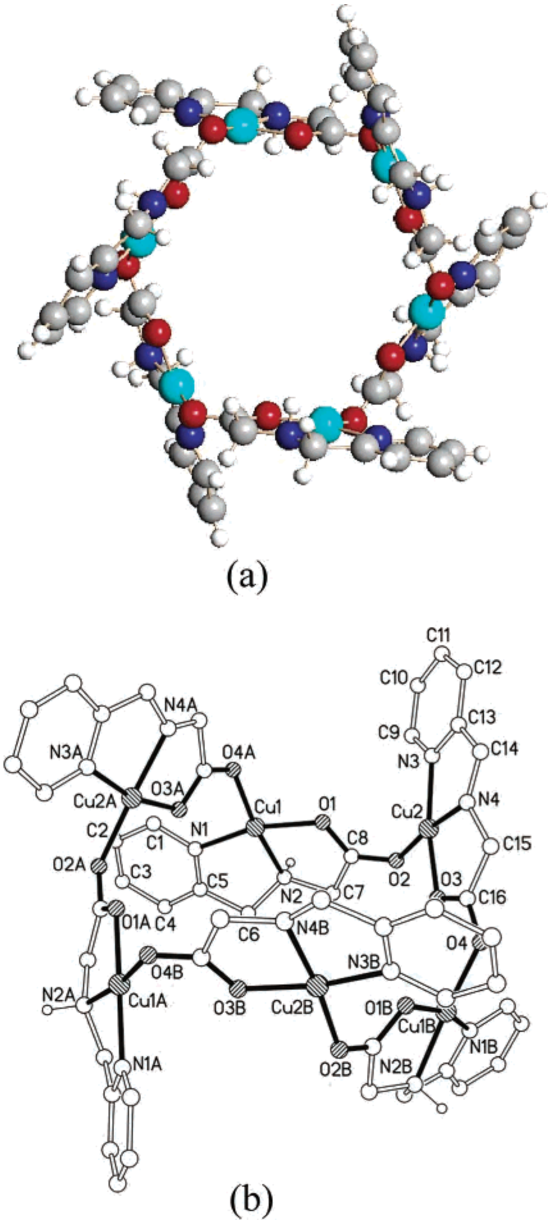

Figure 4. (a) Ball and stick model of the cation in **2**. (b) Side view of the cation showing the cyclohexane-like Cu_6 conformation.

When **1** was reacted with an equivalent amount of $Cu(ClO_4)_2{\cdot}6H_2O$ in aqueous MeOH, dark blue hexagonal crystals of $[Cu_6(pgly)_3(spgly)_3](ClO_4)_6{\cdot}9H_2O$ **2** were isolated. X-ray crystallographic analysis shows that the hexameric cation consists of two crystallographically independent Cu(II) atoms, a reduced Schiff base ligand (pgly) and, surprisingly, a Schiff base ligand (spgly) in the asymmetric unit and as depicted in Figure 3. Table 3 displays selected bond parameters of the cation in **2**. Each tridentate ligand is bonded to Cu(II) in *meridonal* geometry, forming two five-membered rings, and the fourth position of the square planar geometry at Cu(II) is completed by the oxygen atom of the carboxylate group from the neighboring repeating unit in the ring. The Schiff base and the reduced Schiff base ligands are arranged alternatively in the hexanuclear cation, which has a crystallographic 3-fold rotational symmetry, as shown in Figure 4a. Although the presence of pgly and spgly ligands has not changed geometric parameters at the two Cu(II) centers very much, there are differences in the conformation of the backbone of these two complex fragments to unequivocally prove their identity. The nitrogen atom N(4) of the spgly is perfectly planar, as expected with rms deviation, 0.046 Å versus 0.189 Å at N(2) of pgly. The five-membered ring containing Cu(2), N(3), C(13), C(14), and N(4) in spgly is planar (rms deviation, 0.024 Å, while the corresponding ring at Cu(1) is not (rms deviation, 0.159 Å)) due to pyramidal N(2). The shorter C(14)−N(4) distance, 1.31(2) Å is observed for the conjucated C═N double bond, as compared to the C(6)−N(2) distance, 1.44(1) Å, for a C−N single bond (Table 3).

The molecular hexamer is highly puckered in which the Cu(II) centers form a "cyclohexane-like" ring (as shown Figure 4b) where all the Schiff base ligands are distributed on one face of the metallacyclic ring, and the pgly ligands are on the other face. The adjacent Cu⋯Cu distances are 5.093 and 5.100 Å, and the ∠Cu−Cu−Cu are 98.7 and 105.7°. The diagonal Cu⋯Cu distance in the ring is 9.424 Å. Most of the hexanuclear metallamacrocycles have cavity-filled with another metal.[12] Such rings with no metal in the cavities are rare and have been reported by Matsumoto,[6a] Saalfrank,[13a] and Lah;[13b,c] however, the cation in **2** appears to be the first molecular hexamer containing mixed ligands.

The reaction between Hpgly·HCl and $Cu(ClO_4)_2·6H_2O$ yielded $[Cu(pgly)(H_2O)](ClO_4)$ **3** instead of the expected cyclic oligomer, although the stoichiometric ratio of the ligand to metal is the same as used in the synthesis of **2**. Unfortunately, no crystal structure is available for **3**; however, the difference between $\nu_{as}(CO_2^-)$ and $\nu_s(CO_2^-)$ in the IR spectrum has been successfully used to derive information regarding bonding modes of carboxylate anions.[14] The $\Delta\nu$ of 178 cm^{-1} indicated the bridging mode of the carboxylate group in **3**. On the basis of this information, the structure of **3** may be presumed to be a polymer rather than a monomer. Further, the electrospray ionization mass spectrometry (ESI-MS) has been used to distingush **2** from **3**. Whereas the ESI-MS of **3** in aqueous MeOH gave two major peaks due to $[Cu(pgly)_2Na]^+$ (*m/z* 416, 100%) and $[Cu(pgly)_2 - H^+]$ (394, 50%), the corresponding ESI-MS of **2** shows the presence of various oligomeric species from monomer to hexamer in MeOH−H_2O solution. The major species (*m/z*, % peak height) are $[Cu_3(pgly)_3(ClO_4)_2]^+$ (883.7, 100), $[Cu(pgly)(ClO_4)(MeOH)_2(H_2O)-H^+]$ (411, 85), $[Cu_2(pgly)_2(ClO_4)]^+$ (556.7, 72), $[Cu_4(pgly)_4(ClO_4)_3]^+$ (1212.6, 55), $[Cu_5(pgly)_5(ClO_4)_4]^+$ (1534.9, 7), and $[Cu_6(pgly)_5(spgly)(ClO_4)_5]^+$ (1868.2, 5). Unlike the other metallacrown cation containing a similar reduced Schiff base ligand derived from L-alanine (see below), it appears that the species present in the solution are in equilibrium, and the concentration of the solution yielded crystals of **2** exclusively, which is probably attributed to the relative solubilities of these species. It may be noted that the molecular ion peaks due to the parent cation containing three spgly ligands were not observed. It is likely that the cation in **2** dissociates under the experimental conditions used to obtain ESI-MS and may be responsible for the observed behavior.

The oxidation of CH_2−NH to CH═NH in the synthesis of **2** is very similar to that of amino acid and related ligands in the coordination sphere of transition metals.[15] Although the origin of this oxidation is yet to be further explored, it appears that the nature of the starting materials is clearly responsible for the observed difference in the product formation.

Complexes with Ligand *N*-(2-Pyridylmethyl)-L-alanine. A variety of MCs are known;[16] however, only a few structural examples have been reported for [12-MC-3].[17−19] Recent work by Severin et al. has shown that an organometallic analogue [12-MC-3] has been found to be a highly potent ionophore with remarkable affinity for Li^+ and Na^+.[17] Although these MCs are very robust in solution, other MCs are not.[12b,4a,18,20]

The ligand Hpala (shown in Chart 1) is a flexible tridentate ligand with a chiral center. The reaction of $Cu(ClO_4)_2$ with Hpala and KOH in the equimolar ratio in MeOH-MeCN gives a potassium ion-incorporated tricopper metallamacrocyclic compound, $[K(ClO_4)_3\{Cu_3(pala)_3\}](ClO_4)$ **4**. The structure of **4** has been characterized by X-ray crystallography. Selected bond parameters are given in Table 4. The basic unit of the cation consists of a trimer formed by cyclization of Cu(pala) moieties in which the pala ligand is coordinated to Cu(II) in *mer* geometry. The exogenous oxygen of the carboxylate group in the pala ligand is intramolecularly bonded to the fourth position of the square base to provide a N_2O_2 donor set to the metal atom, as shown in Figure 5a. The $Cu_3(pala)_3$ trimer has an approximate noncrystallographic C_3 symmetry, and the geometrical parameters indicates that all the N−H protons should be on one side of the Cu_3 plane. A K^+ ion is found above the Cu_3 plane by 1.897 Å and bonded to three oxygen atoms of the $[Cu_3(pala)_3]^{3+}$ anion, as depicted in Figure 5b. The highly distorted pentagonal bipyramidal coordination geometry at K(1) is completed by the oxygen atoms of three ClO_4^- ions.

The three perchlorate ions further interact with the MC through $Cu⋯OClO_3$ bonds and medium N−H⋯O hydrogen bonds (Figure 5b). The Cu⋯O distances are from 2.430(5) to 2.580(5) Å. The N−H⋯O interactions are in the range 3.008(9)−3.156(9) Å. In the solid-state structure, these $[K(ClO_4)_3\{Cu_3(pala)_3\}]^+$ units pack along the *c* axis through weak Cu−O_{axial} bonding from the perchlorate oxygen atoms to form an infinite 1D polymeric structure, as illustrated in Figure 6. In other words, $[K(ClO_4)_3]^{2-}$ units are sandwiched

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Table 4. Selected Bond Parameters for **4**

K(1)−O(1)	2.415(6)	Cu(3)−N(5)	1.980(6)
K(1)−O(3)	2.377(6)	Cu(3)−N(6)	1.982(6)
K(1)−O(5)	2.412(6)	Cu(3)−O(18)	2.430(10)
K(1)−O(10)	2.545(7)	C(6)−N(2)	1.473(9)
K(1)−O(12)	2.627(10)	N(2)−C(7)	1.513(9)
K(1)−O(16)	2.370(14)	C(8)−O(2)	1.227(8)
Cu(1)−O(1)	1.960(5)	C(8)−O(1)	1.267(8)
Cu(1)−O(4)	1.966(5)	C(16)−N(4)	1.484(10)
Cu(1)−N(1)	1.968(6)	N(4)−C(17)	1.481(10)
Cu(1)−N(2)	1.994(6)	C(18)−O(4)	1.257(9)
Cu(2)−O(6)	1.962(5)	C(18)−O(3)	1.260(8)
Cu(2)−O(3)	1.976(5)	C(26)−N(6)	1.488(10)
Cu(2)−N(3)	1.986(6)	N(6)−C(27)	1.492(9)
Cu(2)−N(4)	2.010(6)	C(28)−O(6)	1.260(8)
Cu(3)−O(5)	1.965(5)	C(28)−O(5)	1.267(9)
Cu(3)−O(2)	1.970(5)		
O(1)−Cu(1)−O(4)	102.8(2)	O(2)−Cu(3)−O(18)	94.8(4)
O(1)−Cu(1)−N(1)	163.9(2)	N(5)−Cu(3)−O(18)	98.6(4)
O(4)−Cu(1)−N(1)	93.1(2)	N(6)−Cu(3)−O(18)	90.8(4)
O(1)−Cu(1)−N(2)	82.1(2)	C(6)−N(2)−C(7)	117.5(6)
O(4)−Cu(1)−N(2)	173.9(2)	C(6)−N(2)−Cu(1)	109.9(5)
N(1)−Cu(1)−N(2)	82.2(2)	C(7)−N(2)−Cu(1)	108.5(4)
O(6)−Cu(2)−O(3)	102.9(2)	C(8)−O(1)−Cu(1)	116.1(4)
O(6)−Cu(2)−N(3)	93.5(2)	C(8)−O(2)−Cu(3)	129.7(4)
O(3)−Cu(2)−N(3)	163.6(2)	C(17)−N(4)−C(16)	115.9(6)
O(6)−Cu(2)−N(4)	176.2(2)	C(17)−N(4)−Cu(2)	108.9(4)
O(3)−Cu(2)−N(4)	80.8(2)	C(16)−N(4)−Cu(2)	109.9(5)
N(3)−Cu(2)−N(4)	82.9(2)	C(18)−O(3)−Cu(2)	115.7(4)
O(5)−Cu(3)−O(2)	102.6(2)	C(18)−O(4)−Cu(1)	129.0(4)
O(5)−Cu(3)−N(5)	166.2(2)	C(26)−N(6)−C(27)	115.8(6)
O(2)−Cu(3)−N(5)	91.0(2)	C(26)−N(6)−Cu(3)	108.4(4)
O(5)−Cu(3)−N(6)	83.1(2)	C(27)−N(6)−Cu(3)	110.1(4)
O(2)−Cu(3)−N(6)	172.5(2)	C(28)−O(5)−Cu(3)	114.6(4)
N(5)−Cu(3)−N(6)	83.2(2)	C(28)−O(6)−Cu(2)	128.7(5)
O(5)−Cu(3)−O(18)	82.8(4)		

between $[Cu_3(pala)_3]^{3+}$ alternatively. The Cu−O$_{axial}$ distances are in the range 2.43(1)−2.58(1) Å. One noncoordinating ClO_4^- ion has been found to fill the empty space in the lattice.

Saalfrank and co-workers have shown[21] that the inclusion of small cations should lead to a metallocoronate with 1:1 stoichiometry, and for larger ions, such as K^+, sandwich-type structures resulted with alkali metal/MC = 1:2. In the case of $\{K(ClO_4)_3[12\text{-}MC\text{-}3]\}^+$, a 1D polymeric structure has been observed where the MCs appear to encapsulate the potassium ion and three perchlorate ions in each deck. Construction of such multidimensional architectures using MCs as building blocks has attracted attention recently.[1a,22] The solubility of the complex, steric consideration of the backbone of the pala ligand, the ability of the pala ligand to form *mer* geometry, and the nature of Cu(II) to form square planar geometry are probably responsible for the uptake of K^+ ions by $[Cu_3(pala)_3]^{3+}$ cation.

When the same reaction was repeated in the absence of the K^+ ion in water, a one-dimensional coordination polymeric compound, $[Cu(pala)(H_2O)]_n \cdot n(ClO_4)$ **5**, resulted as the only isolable product in moderate yield. In **5**, the pala ligand has the *mer* conformation similar to that observed in **4**. As a result, the two hydrogen atoms bonded to N(2) and C(7) have staggered conformation, as in **4**. However, an aqua ligand is strongly bonded at the apex with Cu(1)−O(3) distance 2.366(7) Å to form a distorted square pyramidal

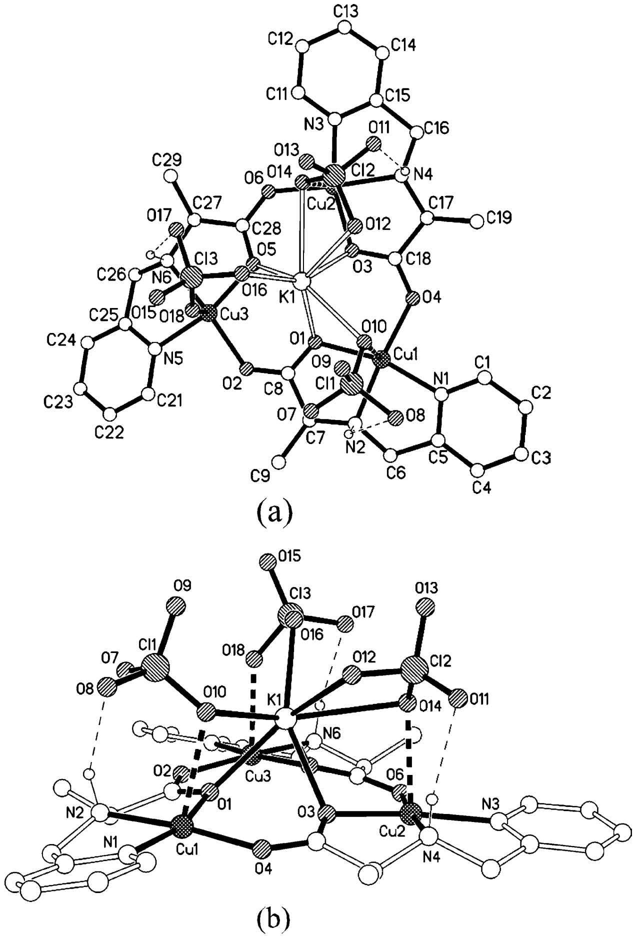

Figure 5. Top (a) and side (b) views of $[K(ClO_4)_3\{Cu_3(pala)_3\}]^+$ cation.

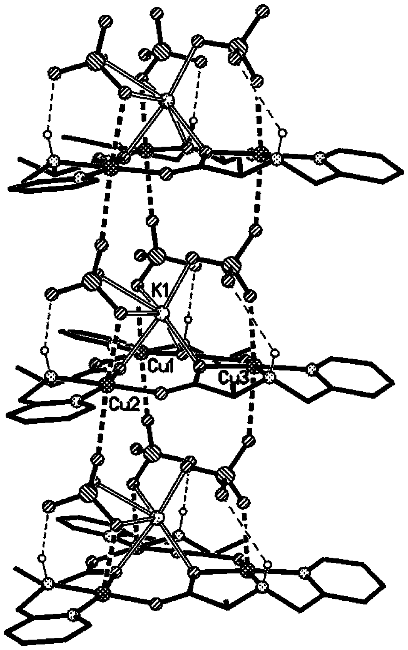

Figure 6. Stacking of the cation in **4** along the *c* axis.

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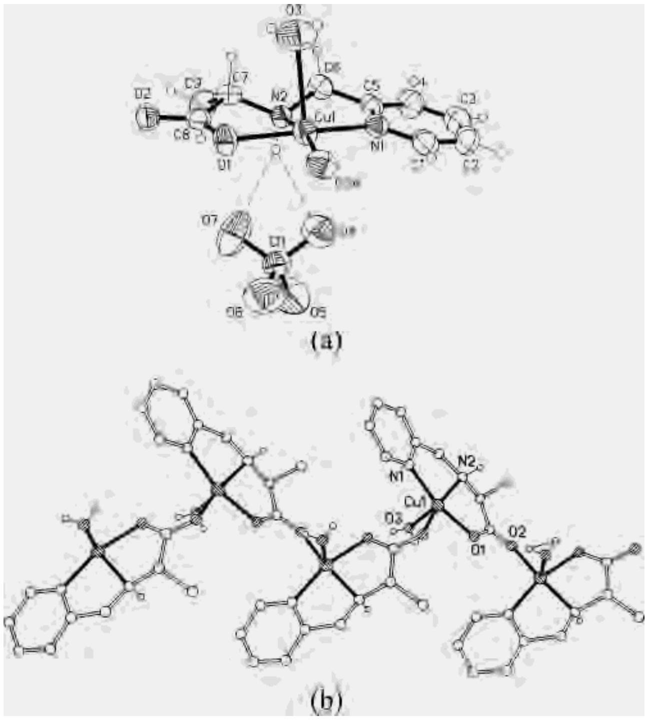


Figure 7. (a) Perspective view of the asymmetric unit in **5**. (b) Coordination polymeric structure of **5**.

Table 5. Bond Lengths (Å) and Angles (°) for **5**

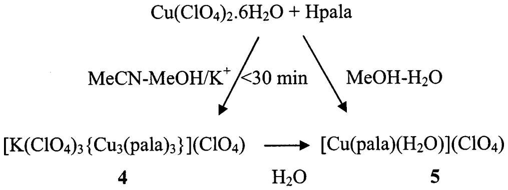
Cu(1)−O(2)[a]	1.934(4)	C(6)−N(2)	1.476(6)
Cu(1)−O(1)	1.968(4)	N(2)−C(7)	1.478(7)
Cu(1)−N(2)	1.984(4)	C(7)−C(9)	1.528(8)
Cu(1)−N(1)	1.993(5)	C(7)−C(8)	1.542(8)
Cu(1)−O(3)	2.366(7)	C(8)−O(1)	1.252(6)
O(2)[a]−Cu(1)−O(1)	89.8(2)	C(8)−O(2)	1.253(6)
O(2)[a]−Cu(1)−N(2)	167.2(2)	C(6)−N(2)−Cu(1)	108.1(3)
O(1)−Cu(1)−N(2)	82.6(2)	C(7)−N(2)−Cu(1)	108.5(3)
O(2)[a]−Cu(1)−N(1)	103.6(2)	N(2)−C(7)−C(9)	112.4(5)
O(1)−Cu(1)−N(1)	165.0(2)	N(2)−C(7)−C(8)	106.7(4)
N(2)−Cu(1)−N(1)	83.0(2)	C(9)−C(7)−C(8)	112.8(5)
O(2)[a]−Cu(1)−O(3)	100.5(2)	O(1)−C(8)−O(2)	125.5(6)
O(1)−Cu(1)−O(3)	88.5(3)	O(1)−C(8)−C(7)	118.1(5)
N(2)−Cu(1)−O(3)	89.6(2)	O(2)−C(8)−C(7)	116.4(5)
N(1)−Cu(1)−O(3)	95.7(3)	C(8)−O(1)−Cu(1)	114.4(4)
C(6)−N(2)−C(7)	117.7(5)	C(8)−O(2)−Cu(1)[b]	126.2(4)

[a] Symmetry transformations used to generate equivalent atoms: $x + 1/2$, $-y + 1/2$, $-z$. [b] Symmetry transformations used to generate equivalent atoms: $x - 1/2$, $-y + 1/2$, $-z$.

geometry at the metal center, as illustrated in Figure 7. Selected bond parameters are given in Table 5. The distance between O(4) and Cu(1), 2.933(8) Å, is more than the sum of the van der Waals radii, 2.9 Å. Further, two oxygen atoms of the ClO_4^- anion are involved in weak N−H···O hydrogen bonding to the N−H proton ($d_{O\cdots H}$, 2.48(2) and 2.54(2) Å) which accounts for the highly ordered behavior in this anion crystal lattice.

Dark blue **4** crystallized as a major product from MeCN−MeOH−H_2O solution after only 10 min of stirring. Prolonged stirring of the reaction mixture resulted in the formation of **5**, as depicted in Chart 2. It has been found that **5** is exclusively formed in the aqueous solution, and the potassium ion has no influence on the formation of final product, **5**. Such a solvent-dependent formation of sumpramolecular species has been discussed by Lehn and co-workers.[3,5]

Chart 2. Solvent-Dependent Formation of **4** and **5**



When NaOH was used instead of KOH, a mixture of $[Na(ClO_4)_3\{12\text{-MC-}3\}]ClO_4$ and 1D polymeric compound **5** was isolated. The addition of LiOH or CsOH in the place of KOH also yielded only **5** quantitatively. The ESI mass spectrum of the freshly prepared solution of **4** containing a MeCN−MeOH solvent mixture indicated the presences of various oligomeric species, including $[Cu_4(pala)_4(ClO_4)_3]^+$ (*m*/*z* 1268.6, 100%), $[Cu_3(pala)_3(ClO_4)_2]^+$ (*m*/*z* 925.7, 80%), $[Hpala-H_2O-H]^+$ (*m*/*z* 198, 56%), $[Cu_2(pala)_2(ClO_4)]^+$ (*m*/*z* 584.9, 55%), $[Cu(pala)_2(H_2O) - H^+]$ (*m*/*z* 439, 40%), $[Cu(pala)(MeCN)]^+$ (*m*/*z* 282.8, 17%), $[Cu_5(pala)_5(ClO_4)_4]^+$ (*m*/*z* 1609.4, 15%), and $[Cu_6(pala)_6(ClO_4)_5]^+$ (*m*/*z* 1952.2, 10%). All the bands due to the oligomeric species completely disappeared by the addition of water, and at the end of 3 min, only the band due to the mononuclear species $[Cu(pala)(MeCN)]^+$ remained as the major species in the ESI-MS spectrum, which resembled that of **5**. The metallacrown cation is, therefore, very unstable and completely converted into **5** by reacting with water.

Reaction of Hpgly with $Cu(ClO_4)_2$ did not yield compounds similar to **4** or **5** in the presence or absence of K^+ or Na^+ ions. It is also surprising to find that Cu(II) compounds similar to **1** and **2** could not be obtained with pala ligand. Recently,[23] a similar reduced Shiff base ligand, *N*-(2-pyridylmethyl)-L-histidine (Hphis) has been found to form tricopper(II) complex incorporating Li^+. The versatility of pgly anion to have both facial and meridonal conformations has been demonstrated in **1** and **2**, respectively. It appears that pala anion forms only mer conformation. Further, there is no simple neutral ML_2 monomer that has been reported in the literature for the related ligand, *N*-(2-hydroxybenzyl)-L-alanine, sala and in all the other known complexes, sala has only *mer* conformation.[24] The difference in the reactivity may be attributed to the chiral center or the methyl substituent present in Hpala ligand. It is likely that the 1D polymer cation $[Cu(pala)]_n^{n+}$, which might be present in the neutral "$[Cu(pala)_2]$" solution, has been isolated as a kinetic product as a result of its poor solubility, and this may be responsible for the difficulty in the isolation of neutral $[Cu(pala)_2]$. The presence of molecular ion peak due to $[CuL_2(H_2O)-H^+]$ in the solution of **4** among various oligomeric species further supports this assumption.

Summary

It is well-known in crystal engineering that the isolation of coordination polymeric compounds having different

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connectivity depends on various factors, including the ratio of the reactants used, concentration, temperature, pH of the medium, counterions, etc.[2] Such a dependency is relatively uncommon in the chemistry of MCs.[1,16,22] We have found that a novel molecular hexamer containing two different but closely related ligands, namely, $[Cu_6(pgly)_3(spgly)_3](ClO_4)_6$ has been obtained from the reaction between $[Cu(pgly)_2]\cdot 2H_2O$ and $Cu(ClO_4)_2\cdot 6H_2O$ in 1:1 ratio in aqueous MeOH solution and $[Cu(pgly)(H_2O)](ClO_4)$ has resulted when Hpgly·HCl was reacted with $Cu(ClO_4)_2\cdot 6H_2O$ directly. The hexameric cation has "cyclohexane-like" conformation. The reactivity of Hpala ligand has been found to be completely different. When Kpala was reacted with $Cu(ClO_4)_2\cdot 6H_2O$, a $\{K\subset[12\text{-MC-}3]\}$, namely, $[K(ClO_4)_3\{Cu_3(pala)_3\}]^+$, cation has been found to assemble to form 1D supramolecular sandwich cations in the solid-state. The solution behavior is more complicated, showing the presence of several oligomeric ring compounds, unlike the other [12-MC-3] compounds reported in the literature.[17−19] The conversion of the metallacrown cation into a one-dimensional coordination polymeric chain is influenced by the presence of water. Such a reaction appears to be rare in metallacrown chemistry.[1] This $\{K\subset[12\text{-MC-}3]\}$ cation seems to be the kinetic product of the reaction between $Cu(ClO_4)_2$ and the K salt of pala. The difference in the reactivity of the structurally closely related reduced Schiff base ligands toward $Cu(ClO_4)_2$ in the formation of different products under various experimental conditions has been exemplified in this study.

Experimental Section

The ^1H NMR spectra were recorded on a Bruker ACF 300FT-NMR spectrometer at 25 °C, and the infrared spectra (KBr pellet) were recorded using an FTS165 Bio-Rad FTIR spectrophotometer in the range 4000−450 cm^{-1}. The electronic transmittance spectra were recorded on a Shimadzu UV-2501/PC UV−vis spectrophotometer in Nujol mull. The elemental analyses were performed in the microanalytical laboratory, Department of Chemistry, National University of Singapore. Water present in the compounds was determined using a SDT 2980 TGA thermal analyzer with a heating rate of 10 °C min^{-1} in a N_2 atmosphere using a sample size of 5−10 mg per run. *Caution! Perchlorate salts are potentially dangerous as explosives and should be handled only in small quantities, although we worked with these* ClO_4^- *salts without any incident.*

***N*-(2-Pyridylmethyl) glycine.** To an aqueous solution (10 mL) of glycine (1.38 g, 20.0 mmol) and KOH (1.12 g, 20.0 mmol), 2-pyridine aldehyde (2.14 g, 20.0 mmol) in EtOH (10 mL) was added slowly. The solution was stirred for 30 min and cooled in an ice bath. $NaBH_4$ (0.74 g, 20.0 mmol) in 10 mL of water was added. The mixture was stirred for 1 h, and HCl was used to adjust the pH to 3−5. The solution was then evaporated to dryness. The solid was extracted in hot and dry MeOH (150 mL × 3), and the filtrate was evaporated to get white powder, Hpgly·HCl. Yield: 0.8 g, 20%. mp191−193 °C. Anal. Calcd for $C_8H_{10}N_2O_2\cdot HCl$: C, 47.4; H, 5.5; N, 13.8. Found: C, 47.7; H, 5.8; N, 13.9. ^1H NMR [D_2O] (ppm), 3.8 (s, 2H), 4.5 (s, 2H), 7.6 (m, 2H), 8.0 (t, 1H), 8.7 (d, 1H); ^{13}C NMR [D_2O] (ppm), ^{13}C NMR δ 52.0 (C_7), 53.9 (C_6), 126.9 (C_2), 127.22 (C_4), 141.3 (C_3), 152.2 (C_1), 153.6 (C_5), 175.2 (C_8). IR (KBr, cm^{-1}): ν_{OH}, 3421; $\nu_{as}(CO_2^-)$, 1595; $\nu_s(CO_2^-)$, 1410.

***N*-(2-Pyridylmethyl)-L-alanine.** To a solution of L-alanine (1.78 g, 20.0 mmol) and KOH (1.12 g, 20.0 mmol) in 10 mL of H_2O, 2-pyridaldehyde (2.14 g, 20.0 mmol) in 10 mL of EtOH was added slowly. $NaBH_4$ (0.74 g, 20.0 mmol) in 10 mL of water was added after the solution was stirred for 30 min and cooled in an ice bath. The mixture was stirred for 1 h, and CH_3CO_2H was used to adjust the pH to 3−5. The solution was then evaporated to dryness. The solid was extracted into hot MeOH (150 mL × 3), and the filtrate was concentrated to 3 mL, which was layered with Et_2O to get tiny white crystals. Yield, 2.9 g (72%). Anal. Calcd. for $C_9H_{12}N_2O_2\cdot 1.25H_2O$: C, 53.3; H, 7.2; N, 13.8. Found: C, 53.3; H, 6.7; N, 13.8. The solid was recrystallized in MeOH below 0 °C to obtain big platy white crystals. mp 202−204 °C. ^1H NMR in D_2O (ppm), 1.7 (3H, d), 4.0(1H, q), 4.5 (2H, s), 7.7 (1H, t), 7.8 (1H, d), 8.2 (1H, t), 8.7 (1H, d). ^{13}C NMR in D_2O, 17.8 (C_8), 52.6 (C_7), 60.5 (C_6), 126.9 (C_2), 127.2 (C_4), 141.2 (C_3), 152.2 (C_1), 153.1 (C_5), 177.4 (C_9). IR (KBr, cm^{-1}): ν_{OH}, 3446; ν_{N-H}, 2977; $\nu_{as}(CO_2^-)$, 1717; ν_{C-N}, 1610; and $\nu_s(CO_2^-)$, 1389.

$[Cu(pgly)_2]\cdot 2H_2O$ (1). To a methanolic solution (10 mL) of Hpgly·HCl (4.1 g, 20.0 mmol), $Cu(ClO_4)_2\cdot 6H_2O$ (3.74 g, 10.0 mmol) or $Cu(CH_3COO)_2\cdot H_2O$ (2.00, 10.0 mmol) in an aqeous solution (5 mL) was added, and the clear solution was left undisturbed to get blue crystals. Yield: 3.5 g, 80%. Anal. Calcd for $C_{16}H_{18}CuN_4O_4\cdot 2H_2O$: C, 44.7; H, 5.2; N, 13.0. Found: C, 44.3; H, 5.2; N, 12.7. Selected IR data (KBr, cm^{-1}): ν_{OH}, 3401; ν_{NH}, 3213; $\nu_{C=O}$, 1691; $\nu_{as}(CO_2^-)$, 1591; $\nu_s(CO_2^-)$, 1393. UV−vis (Nujol, nm): 256 (CT) and 686 (d−d transition).

$[Cu_6(pgly)_3(spgly)_3](ClO_4)_6\cdot 9H_2O$ (2). $[Cu(pgly)_2]\cdot 2H_2O$ (0.429 g, 1.00 mmol) and $Cu(ClO_4)_2\cdot 6H_2O$ (0.374 g, 1.00 mmol) were added as solids in a mixture of MeOH (10 mL) and water (3 mL). The mixture was stirred and filtered to get a dark blue solution, from which the dark blue hexagonal crystals were obtained. Yield: 0.22 g, 63%. Anal. Calcd for $C_{48}H_{48}Cl_6Cu_6N_{12}O_{36}\cdot 9H_2O$: C, 27.1; H, 3.1; N, 7.9. Found: C, 27.1; H, 3.0; N, 7.7. Selected IR data (KBr, cm^{-1}): ν_{OH}, 3425; $\nu_{as}(CO_2^-)$, 1610; $\nu_s(CO_2^-)$, 1439; $\nu(ClO_4)$, 1141, 1120, 1090. UV−vis (Nujol, nm): 273 (CT) and 590(d−d transition).

$[Cu(pgly)(H_2O)](ClO_4)$ (3). To a solution of Hpgly·HCl (0.203 g, 1.00 mmol) in EtOH (10 cm^3), $Cu(ClO_4)_2\cdot 6H_2O$ (0.371 g, 1.00 mmol) in H_2O (5 cm^3) was added. The mixture was stirred for 30 min and filtered. The filtrate was evaporated to get a blue precipitate, which was separated, washed with EtOH (3 × 5 mL), and dried. Yield: 0.10 g, 30%. Anal. Calcd for $C_8H_{11}ClCuN_2O_7$: C, 27.8; H, 3.2; N, 8.1. Found: C, 28.2; H, 3.2; N, 7.7. Selected IR data (KBr, cm^{-1}): ν_{OH}, 3448; $\nu_{C=O}$, 1691; $\nu_{as}(CO_2^-)$, 1610; $\nu_s(CO_2^-)$, 1432; $\nu(ClO_4)$, 1141, 1120, 1090. UV−vis (Nujol, nm): 253 (CT) and 687(d−d transition).

$[K(ClO_4)_3\{Cu_3(pala)_3\}](ClO_4)$ (4). Hpala (0.180 g, 1.00 mmol) in EtOH (5 mL) was mixed with $Cu(ClO_4)_2\cdot 6H_2O$

Table 6. Crystal Data and Structure Refinement

	1	2	4	5
formula	$C_{16}H_{22}CuN_4O_6$	$C_{48}H_{66}Cl_6Cu_6N_{12}O_{45}$	$C_{27}H_{33}Cl_4Cu_3KN_6O_{22}$	$C_9H_{13}ClCuN_2O_7$
fw	429.92	2125.07	1165.11	360.20
temp, °C	20	−50	20	20
λ, Å	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	trigonal	orthorhombic	orthorhombic
space group	$P2_1/c$	R3	$P2_12_12_1$	$P2_12_12_1$
a, Å	8.9058(3)	13.7507(7)	20.9192(3)	8.8500(7)
b, Å	9.3868(4)	13.7507(7)	27.4692(2)	11.2033(8)
c, Å	10.9447(4)	74.763(6)	7.2465(1)	13.754(11)
β, °	91.731(1)	90	90	90
V, Å^3	914.53(6)	12242.5(13)	4164.08(9)	1363.7(2)
Z	2	6	4	4
D_{calc}, g/cm^3	1.561	1.729	1.858	1.754
μ, mm^{-1}	1.236	1.835	1.966	1.829
reflns collcd	4573	18477	21348	7036
unique reflns	1606	3575	7307	2391
	R(int) = 0.0177	R(int) = 0.0570	R_{int} = 0.0378	R_{int} = 0.0747
GOF on F^2	1.041	1.076	1.119	0.916
R1^a, wR2 [I > 2σ(I)]^b	0.0233, 0.0685	0.0873, 0.2548	0.0542, 0.1375	0.0475, 0.0958
R1^a, wR2 (all data)^b	0.0262, 0.0699	0.1149, 0.2719	0.0637, 0.1453	0.0694, 0.1012

[a] $R1 = (||Fo| - |Fc||)/(|Fo|)$; $wR2 = [(w(Fo^2 - Fc^2)/(wFo^4]^{1/2}$.

(0.371 g, 1.00 mmol) in CH_3CN (10 mL), followed by the addition of KOH (0.078 mL, 50% (wt %), 1.00 mmol). The contents was stirred for 10 min, and a dark blue precipitate was filtered and dried in air. The crystals suitable for X-ray analyses were obtained from the undisturbed filtrate. Yield: 0.23 g (60%). Anal. Calcd for $C_{27}H_{33}Cl_4Cu_3KN_6O_{22}$ (M = 1165.11): C, 27.8; H, 2.9; N, 7.2, Cl, 12.2. Found: C, 27.4; H, 2.8; N, 7.1, Cl, 12.3. IR (KBr, cm^{-1}): ν_{N-H}, 3220; $\nu(ClO_4)$, 1138, 1117, 1090, and 940; $\nu_{as}(CO_2^-)$ 1610; $\nu_s(CO_2^-)$ 1438. UV−vis (Nujol, nm): 250, 330 (CT) and 590 (d−d transition).

[Cu(pala)(H_2O)]$_n$·n(ClO_4) (5). To a methanolic solution (10 mL) of Hpala (0.180 g, 1.00 mmol), $Cu(ClO_4)_2 \cdot 6H_2O$ (0.370 g, 1.00 mmol) in water (3 mL) was added. The resultant dark blue solution was stirred for 1 h and filtered to obtain a blue powder, which was washed with Et_2O and dried in a vacuum. Yield: 0.24 g (68%). Single crystals suitable for X-ray analysis were obtained from the filtrate. Anal. Calcd for $C_9H_{13}ClN_2O_7Cu$: C, 30.0; H, 3.6; N, 7.8; Cl, 9.9. Found: C, 30.0; H, 3.5; N, 7.7; Cl, 9.7. IR (KBr, cm^{-1}): ν_{OH}, 3418; ν_{N-H}, 3241; $\nu_{as}(CO_2^-)$ 1593; $\nu_s(CO_2^-)$ 1409; $\nu(ClO_4)$, 1138, 1117, 1090, and 940. UV−vis (Nujol, nm): 250, 330 (CT) and 685 (d−d transition).

X-ray Crystallography. The diffraction experiments were carried out on a Bruker SMART CCD diffractometer with a Mo Kα radiation from a sealed tube. The program SMART[25] was used for collecting frames of data, indexing reflections and determination of lattice parameters; SAINT,[25] for integration of the intensity of reflections and scaling. SADABS[26] was used for absorption correction, and SHELXTL,[27] for space group and structure determination and least-squares refinements on F^2. For **2**, a Cl−O bond in each of the three ClO_4^- anions is sitting in the 3 axis. Cl(5) and O(15) were also on the crystallographic 3 axis but the occupancy for the anion was fixed at 0.5. The perchlorate anion containing Cl(4) has been found to be crystallographically disordered near the −3 axis. Only the common isotropic thermal parameter was refined for the oxygen atoms. For the ClO_4^- anion with Cl(6), a common isotropic thermal parameter was refined for all the atoms with fixed site occupancy at 0.3333. The perchlorate ion containing a Cl(5)−O(15) bond in the crystallographic 3 axis is also crystallographically disordered near the inversion center. A common isotropic thermal parameter was refined for the two oxygen atoms. Nine lattice water molecules were found disordered near the crystallographic inversion center. Despite the crystallographic disorder present in **2** that hampered high quality results, the structure and connectivity of the hexameric cations were proved beyond any doubt. In **4**, two perchlorate anions were disordered. In one anion, three oxygen atoms were triply disordered related by rotation along the Cl(3)−O(15) bond. Common thermal parameters were refined for all the disordered O atoms. Two tetrahedral dispositions of oxygen atoms were resolved for the fourth ClO_4^- anion containing Cl(4). The relevant crystallographic data and refinement details are shown in Table 6.

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Supporting Information Available: Table of X-ray data, CIF format; also .tif and .jpg files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(27) SHELXTL Reference Manual, Version 5.03, Siemens Energy & Automation, Inc., Analytical Instrumentation, Madison, WI, 1996.