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Influence of the Li^+ on the Structure of the $[Cu_3(phis)_3]^{3+}$ Cation

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When $[Cu_3(phis)_3](ClO_4)_3$, obtained from $Cu(ClO_4)_2{\cdot}6H_2O$ with the Na^+ or K^+ salt of the phis anion (Hphis = *N*-(2-pyridylmethyl)-L-histidine), is reacted with $LiClO_4$, the tricopper cationic structure rearranged to accommodate a Li^+ ion to form $[(ClO_4)Li\{Cu_3(phis)_3\}](ClO_4)_3$ which can also be prepared directly by reacting $Cu(ClO_4)_2{\cdot}6H_2O$ with the Li^+ salt of the phis anion.

Metallacrowns (MCs) with a variety of structural types are usually prepared in quantitative yields by a self-assembly process.[1] A majority of the metallacrowns are robust and retain their structures in solution, a property which can be used for exchange reactions with metal ions and anions.[2] However, the selectivity is determined by the cavity size of the metallacrown ethers and the radii of the ions used.[3−6] Although the ion exchange reactions are very similar to those known for the classical crown ether, the field of inorganic host−guest chemistry is still in its infancy. In the course of exploring the coordination chemistry of Cu(II) compounds containing reduced Schiff base ligands, we have assembled two metallacrown cations that are structurally different in the presence and absence of a Li^+ in the cavity. These metallacrown cations are very labile and dissociate into various oligomeric species in solution.

The ligand Hphis·HCl (Hphis = *N*-(2-pyridylmethyl)-L-histidine shown in Figure 1), prepared by a similar method as that described for Hpgly·HCl,[7] is very hygroscopic. Hence, it was prepared in situ as the potassium salt of phis and reacted with $Cu(ClO_4)_2{\cdot}6H_2O$ in 1:1 molar ratio to yield dark blue crystals of $[Cu_3(phis)_3](ClO_4)_3{\cdot}2H_2O$ (**1**·$2H_2O$)[8] which has been characterized by X-ray crystallography.[9] In the structure of the trinuclear cation, each Cu(II) is surrounded by a phis ligand in a meridonal fashion, and the donor atoms occupy the base of the square pyramid along with another carboxylate oxygen from the neighboring cation (Figure 1). The apical position of the distorted square pyramid is occupied by the oxygen atoms of the carboxylate group of

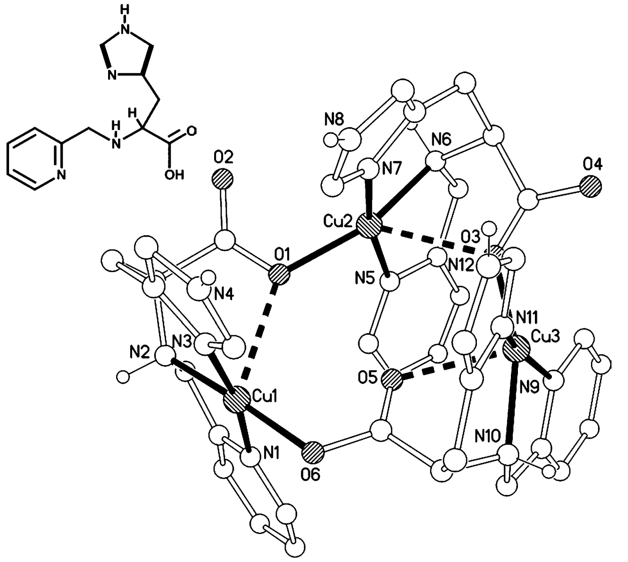

Figure 1. Ligand Hphis (top left-hand corner) and a perspective view of **1**. Selected distances (Å) and angles (deg): Cu(1)−N(3) 1.93(1), Cu(1)−O(6) 1.97(1), Cu(1)−N(2) 2.00(1), Cu(1)−N(1) 2.01(1), Cu(2)−N(7) 1.93(2), Cu(2)−O(1) 1.991(9), Cu(2)−N(5) 1.99(1), Cu(2)−N(6) 2.02(1), Cu(3)−O(3) 1.90(1), Cu(3)−N(11) 1.94(2), Cu(3)−N(9) 1.96(1), Cu(3)−N(10) 1.98(2), Cu(3)−O(5) 2.39(1), O(6)−Cu(1)−N(2) 175.0(6), N(3)−Cu(1)−N(1) 170.4(5), N(7)−Cu(2)−N(5) 168.2(6), O(1)−Cu(2)−N(6) 157.8(5), N(11)−Cu(3)−N(9) 163.6(6), O(3)−Cu(3)−N(10) 160.4(6).

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(8) To a solution of L-histidine (1.56 g, 10.0 mmol) in water (15 mL) and KOH (0.56 g, 10.0 mmol) was slowly added pyridine-2-aldehyde (1.07 g, 10.0 mmol) in EtOH (10 mL). The solution was stirred for 30 min, cooled in an ice bath, and then followed by the addition of $NaBH_4$ (0.37 g, 10.0 mmol) in water (10 mL). The mixture was stirred for 1 h more, before $Cu(ClO_4)_2{\cdot}6H_2O$ (3.71 mg, 10.0 mmol) in ethanol (10 mL) was added. $HClO_4$ (37%) was used to adjust the pH to 6. The dark blue precipitate was filtered, washed with ice-cold EtOH and ice water, and dried in air. The single crystals suitable for structure determination were obtained from the filtrate. Yield 40%. Calcd for $C_{36}H_{39}Cl_3Cu_3N_{12}O_{18}{\cdot}2H_2O$: C, 34.30; H, 3.44; N, 13.33. Found: C, 33.66; H, 3.57; N, 13.16. IR (KBr, cm^{-1}): ν(OH) 3446, ν_{sat}(C−H) 2918, 2850, ν_{as}(COO) 1656, ν_s(COO) 1350, ν(ClO_4) 1144, 1121, 1090. UV−vis (Nujol, nm): 267 (CT) and 543 (d−d transition). The same compound was also obtained when NaOH was used instead of KOH.

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the chelating phis ligand. The Cu−O$_{axial}$ distances 2.65(1) Å (Cu(1)−O(1)), 2.54(1) Å (Cu(2)−O(3)), and 2.39(1) Å (Cu(3)−O(5)) are weak. The oxygen atoms O(1) and O(3) are bridging Cu(II) atoms while O(2) and O(4) atoms are nonbonded. This makes the cavity in the ring very small, and the shortest distance, 3.033 Å, is between O(1) and O(5). This [8-MC-3] metallacrown is very unsymmetrical with Cu···Cu distances, 3.860, 4.310, and 5.273 Å. Such copper compounds have been used as a structural model for the trinuclear site in ascorbate oxidase from green zucchini.[10−12]

The compound [(ClO$_4$)Li{Cu$_3$(phis)$_3$}](ClO$_4$)$_3$·3H$_2$O (**2**·3H$_2$O) has been isolated when a molar equivalent of LiClO$_4$ was added to **1**. The same compound could also be obtained from the lithium salt of phis and Cu(ClO$_4$)$_2$·6H$_2$O in a 1:1 molar ratio.[13] The crystal structure[14] shows that the asymmetric unit consists of the [Li(ClO$_4$){Cu$_3$(phis)$_3$}]$^{3+}$ cation, three strongly hydrogen bonded lattice water molecules, and three perchlorate anions interacting with the cations and lattice waters. A perspective view of the cation is shown in Figure 2. In this trinuclear cation, phis anions are bonded to Cu(II) centers in *mer* fashion similar to **1**. The donor atoms occupy three corners of the square plane which is completed by the exogenous oxygens from the neighboring Cu(phis) moiety. The pyridyl and the imidazole rings are also roughly in plane with the CuN$_3$O plane. The trinuclear cation has the shape of a cone in which the phenyl rings are on the top as in **1**. The N−H protons of the imidazole groups at the bottom are hydrogen bonded to oxygen atoms of the three water molecules. The bottom of the cone does not appear to be completely closed as inferred from the O···O distances, 3.397−3.641 Å.

The three endogenous carbonyl oxygen atoms in the [Cu$_3$(phis)$_3$]$^{3+}$ cation are bonded to a Li(I) atom. The fourth distorted tetrahedral corner at Li(I) is completed by an oxygen atom of the disordered ClO$_4^-$ anion. The [Li{Cu$_3$(phis)$_3$}]$^{4+}$ cation has an idealized C_3 symmetry with three crystallographically independent Cu(II) centers. It is obvious that the [Cu$_3$(phis)$_3$]$^{3+}$ cation, [8-MC-3], has structurally reorganized to accommodate a lithium cation. Such dependency of the structure of the metallamacrocycles on the nature of guest molecules has been observed by Raymond, Fujita, Stang, and Lehn.[15−20] Unlike **2**, the [15-MC-3] metallacrowns characterized by Saalfrank and co-workers have been found to be planar and form both coronate and sandwich compounds.[4−6]

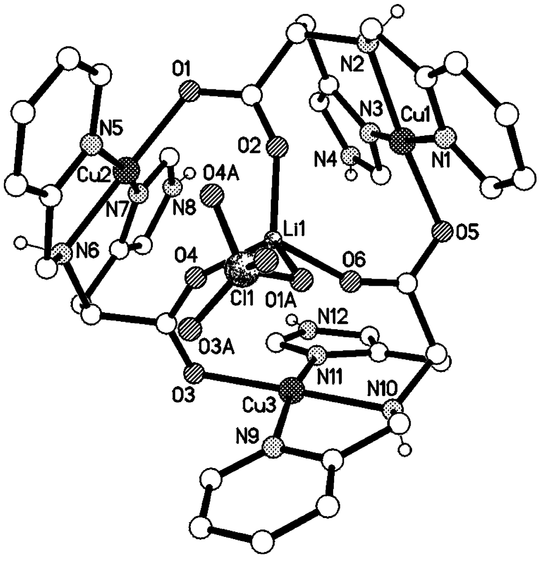

Figure 2. Top view of the cation in **2** showing the conelike conformation. Selected distances (Å) and angles (deg): Li−O 1.85(2)−1.87(2), Cu(1)−O(5) 1.968(5), Cu(1)−N(3) 1.968(7), Cu(1)−N(1) 1.995(6), Cu(1)−N(2) 2.042(7), Cu(2)−O(1) 1.983(6), Cu(2)−N(7) 1.971(7), Cu(2)−N(5) 1.980(8), Cu(2)−N(6) 2.038(7), Cu(3)−O(3) 1.984(5), Cu(3)−N(11) 1.969(7), Cu(3)−N(9) 1.984(7), Cu(3)−N(10) 2.042(6), O(5)−Cu(1)−N(3) 91.1(2), O(5)−Cu(1)−N(1) 93.3(3), N(3)−Cu(1)−N(1) 172.5(3), O(5)−Cu(1)−N(2) 175.3(3), N(7)−Cu(2)−N(5) 168.2(3), O(1)−Cu(2)−N(6) 177.2(3), N(11)−Cu(3)−N(9) 168.5(3), O(3)−Cu(3)−N(10) 175.7(3).

In the absence of a base, Hphis reacts with Cu(ClO$_4$)$_2$·6H$_2$O to form a 1D coordination polymeric compound [Cu(phisH)(H$_2$O)](ClO$_4$)$_2$, **3**, Figure 3.[21,22] In the cation, the Cu(II) center is five-coordinate, with the tridentate phis ligand bonded in a *mer* fashion at the square base and the fourth position completed by a carboxylate oxygen from the

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(9) Crystal data for **1**·2H$_2$O: orthorhombic space group, $P2_12_12_1$; a = 11.4697(1) Å, b = 16.2521(1) Å, c = 28.0955(1) Å; Z = 4; V = 5237.19(6) Å^3; D_c = 1.599 g·cm^{-3}. Data were collected on a Bruker AXS APEX CCD diffractometer at 25 °C. Of the 20663 reflections collected, 6795 were unique (R_{int} = 0.0749). The model refined to R1 = 0.1060, wR2 = 0.2755 for 5059 reflections with $I \geq 2\sigma(I)$, and the Flack parameter, χ = 0.04(4). Relatively high agreement factors and low quality of the structure of **1** may be attributed to the weakly diffracting nature of the single crystals.

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(13) The synthetic procedure is similar to that described for **1**, but LiOH was used in the place of KOH. Yield 66%. A suitable crystal for X-ray analyses was obtained from EtOH/H$_2$O (1:1). Calcd for $C_{36}H_{394}Cl_4$-$Cu_3LiN_{12}O_{22}$·3H$_2$O: C, 31.22; H, 3.27; N, 12.13; Cl, 10.23. Found: C, 31.49; H, 3.50; N, 12.01; Cl, 10.19. IR (KBr, cm^{-1}): ν(OH) 3420, ν_{sat}(C−H) 2918, 2850, ν_{as}(COO) 1617, ν_s(COO) 1318, ν(ClO$_4$) 1144, 1109, 1090. UV−vis (Nujol, nm): 267 (CT) and 693 (d−d transition).

(14) Crystal data for **2**·3H$_2$O at −50 °C: orthorhombic space group, $P2_12_12_1$; a = 12.0620(6) Å, b = 12.8198(7) Å, c = 34.313(2) Å; Z = 4; V = 5305.9(5) Å^3; D_c = 1.734 g·cm^{-3}. Of the 30952 reflections collected, 9340 were unique (R_{int} = 0.0574). The model converged at R1 = 0.0562 and wR2 = 0.1413 for 7271 reflections for $I \geq 2\sigma(I)$, and absolute structural parameter χ = 0.01(2).

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(21) A blue solution was obtained when Hphis·HCl (0.309 g, 1.00 mmol) in MeOH (5 cm^3) was mixed with an aqueous solution (3 cm^3) of Cu(ClO$_4$)$_2$·6H$_2$O (0.370 g, 1.00 mmol). When this solution was left to evaporate, blue crystals were obtained from which single crystals suitable for the X-ray diffraction analysis were selected. Yield 40%. Calcd for $C_{12}H_{16}Cl_2CuN_4O_{11}$: C, 27.36; H, 3.06; N, 10.64; Cl, 13.46. Found: C, 27.47; H, 3.05; N, 10.68; Cl, 13.78. IR (KBr, cm^{-1}): ν(OH) 3446, ν_{sat}(C−H) 2918, 2850, ν_{as}(COO) 1626, ν_s(COO) 1379, ν(ClO$_4$) 1142, 1119, 1090. UV−vis (Nujol, nm): 256 (CT) and 686 (d−d transition).

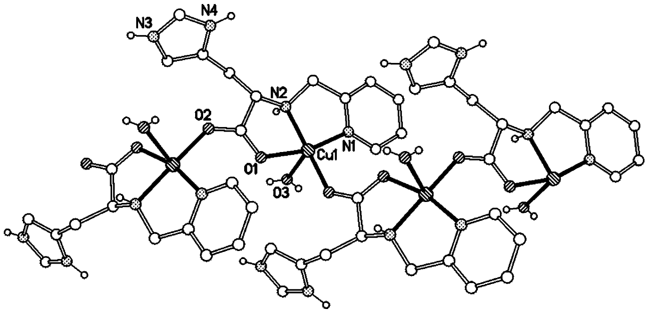

Figure 3. Segment of the 1D polymeric cation in **3**. Selected distance (Å) and angles (deg): Cu(1)−N(1) 1.989(5), Cu(1)−N(2) 1.992(5), Cu(1)−O(1) 1.987(4), Cu(1)−O(2)^a 1.938(4), Cu(1)−O(3) 2.341(7), N(1)−Cu(1)−O(1) 165.3(2), N(2)−Cu(1)−O(2)^a 173.4(2). Symmetry operator: a, $x + {}^1/_2$, $-y + {}^1/_2$, $-z + 1$.

neighboring repeating unit. A water molecule at the apex completes the distorted square pyramidal geometry at the Cu(II) center. The second carboxylate oxygen atom participates in intermolecular bonding to Cu(II) which generates a one-dimensional zigzag polymeric structure. Compound **3** also resulted when the pH of the solution containing **1** or **2** is adjusted to a pH of 3−4.

The ES mass spectrum of **3** exhibits a major band at *m*/*z* 408 originating from the $[Cu(phisH)(ClO_4)]^+$ ion while the ES mass spectrum of **2** in MeOH shows the presence of various dissociated species including $[Cu(phis)(MeOH)_3(H_2O)]^+$ (*m*/*z* 422.1, 100%), $[Cu_2phis)_2]^{2+}$ (*m*/*z* 309.2, 46%), $[Cu_3(phis)_3(ClO_4)]^{2+}$ (*m*/*z* 512.7, 30%), $[Hphis{\cdot}H_3O]^+$ (*m*/*z* 263.4, 25%), $[Cu_2(phis)_2(ClO_4)]^+$ (*m*/*z* 716.9, 17%), $[Cu_3(phis)_3(ClO_4)_2]^+$ (*m*/*z* 1123.9, 17%), and $[Cu(phis)(CH_3CN)(H_2O)]^+$ (*m*/*z* 368, 15%). The ES-MS of **1** also exhibits the presence of several dissociated species such as $[Cu(phis)(CH_3CN)(H_2O)]^+$ (*m*/*z* 368, 100%), $[Cu_2phis)_2]^{2+}$ (*m*/*z* 309.2, 60%), $[Cu(phis)(ClO_4)(MeOH)_2(H_3O)]^+$ (*m*/*z* 492.4, 42%), $[Cu_3(phis)_3(ClO_4)]^{2+}$ (*m*/*z* 512.4, 37%), $[Hphis{\cdot}H_3O]^+$ (*m*/*z* 263.4, 35%), $[Cu(phis)(ClO_4) - H]^+$ (*m*/*z* 408, 19%), $[Cu_2(phis)_2(ClO_4)]^+$ (*m*/*z* 716.8, 18%), and $[Cu_3(phis)_3(ClO_4)_2]^+$ (*m*/*z* 1123.8, 15%). On the other hand, the organometallic MCs reported by Severin[23−26] have been found to maintain their structure in solution while showing selectivity toward Li^+ and Na^+. To our surprise, **1** with similar structural features did not yield the $NaCu_3$ compound. It appears that the lability of these inorganic MCs in hydrophilic solvents is responsible for the observed behavior.[27]

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Supporting Information Available: Crystallographic files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) Crystal data for **3** at 25 °C: orthorhombic space group, $P2_12_12_1$; $a = 9.2741(3)$ Å, $b = 11.6970(3)$ Å, $c = 17.8322(4)$ Å; $Z = 4$; $V = 1934.42(9)$ Å^3; $D_c = 1.809$ g·cm^{-3}. Of the 9932 reflections collected, 3380 were unique ($R_{int} = 0.0470$). The model converged at R1 = 0.0477 and wR2 = 0.1023 for 2782 reflections with $I \geq 2\sigma(I)$, and $\chi = 0.0023(6)$.

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