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Ammonium, Alkylammonium, and Amino Acid Complexes of a Hexacopper Fluoro-Metallacrown Cavitand

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Abstract: Reaction of CuF_2 with one equivalent of 3{5}-(pyrid-2-yl)-5{3}-(*tert*butyl)pyrazole (HL) and excess NH_4OH in MeOH affords crystalline $[NH_4\{Cu(\mu\text{-}F)(\mu\text{-}L)\}_6(CH_2Cl_2)_2]HF_2$ in moderate yield. This compound contains the 12-MC-6 metallacrown $[\{Cu(\mu\text{-}F)(\mu\text{-}L)\}_6]$ (**1**) with a NH_4^+ ion at its center, and CH_2Cl_2 molecules complexed in bowl-shaped cavities above and below the Cu_6F_6 ring. Similar reactions using the bases $MeNH_2$, glycine, L-alanine or β-alanine afforded solvated crystals of $[\mathbf{1}(H_3NMe)_2]Cl_2$, $[\mathbf{1}(gly)_2]$, $[\mathbf{1}(\text{L-ala})_2]$, and $[\mathbf{1}(\beta\text{-ala})_2]$, respectively. The metallacrown **1** in these products contains methylammonium and zwitterionic amino-acid guests in its two bowl-shaped cavities; each of the amino acids hydrogen-bonds to three F atoms. A related reaction using 1,6-diaminohexane resulted in fixation of CO_2 from the air to give solvated $[\mathbf{1}(H_3NC_6H_{12}NHCO_2)_2]$, again with a zwitterionic guest. NMR, ESI-MS and UV/vis measurements suggest that the metallacrown **1** retains its integrity in several organic solvents, although it is unclear to what extent guest binding takes place in solution.

Keywords: complexation · copper · host–guest systems · metallacrowns · supramolecular chemistry

Introduction

Metallacrowns and molecular wheels are cyclic metal/organic compounds, that usually bear donor atoms projecting into a cavity at the center of their ring structure.[1–3] These donors are often hydroxamate,[1] alkoxy[4,5] or pyridonate[2,6] functions that are derived from polydentate ligands surrounding the metal ions in the wheel; alternatively, they can be smaller bridging ligands like hydroxide,[7,8] methoxide or other alkoxides,[9,10] and/or fluoride.[11–13] Metallacrowns are often considered as crown ether analogues in their ability to bind a guest species in their central cavity,[1] and many metallacrown structures are in fact templated about such a guest. These are often metal ions,[1,6,10,14] although examples templated by inorganic anions[8] or organic guests[12] are also known. Metallacrowns that can be controllably isolated in the presence or absence of a guest species are rare, with only two such systems having been well studied. The first, is a series of trinuclear platinum metal metallacrowns linked by pyridonates, which can facially complex alkali metal ions through their O-donors, in solution and the solid state.[2] Second, is a series of hexanuclear metallacrowns with di- and tri-ethanolamine ligands, that can be controllably obtained in the presence or absence of a central metal ion.[4,5]

As part of our continuing studies of the supramolecular chemistry of metal-organic complexes of NH pyrazoles,[15–17] we have recently described that reactions of CuF_2 and 3{5}-(pyrid-2-yl)-5{3}-(*tert*butyl)pyrazole (HL) in the presence of base, yield the 12-MC-6 metallacrown[1] $[\{Cu(\mu\text{-}F)(\mu\text{-}L)\}_6]$ (**1**, Scheme 1).[13] Depending on the base used, **1** can either be prepared with Na^+ or K^+ ions complexed to its six F donors, or as an uncomplexed metallacrown with no guest in its central cavity. Moreover, the L^- ligands in **1** project out of the plane of the $[Cu_6F_6]^{6+}$ ring, to form two bowl-shaped cavities of approximate dimensions 2.1 × 5.6 × 6.5 Å (base × rim × height). These cavities are chiral, owing to the head-to-tail disposition of the L^- ligands at their periphery, but the two cavities in each molecule are of opposite handedness. In the above compounds, the cavities are occupied by water or dichloromethane molecules, which donate hydrogen bonds to one or more of the three F atoms at the base of each cavity. Thus, **1** can bind guests in two different ways, acting as both a crown ether analogue and a cavitand. The formation of metallacrown structures from copper(II) and HL is dependent on the copper salt used; the [{Cu(μ_3-

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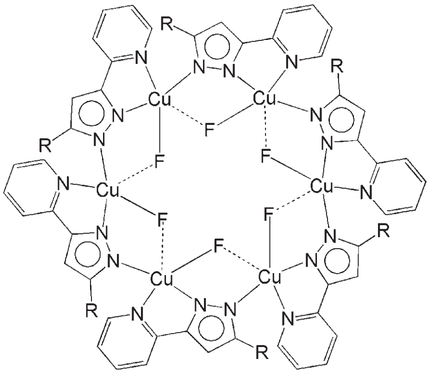

Scheme 1. Structure of the metallacrown **1** (R = *tert*butyl). The dashed lines show the longer apical Cu−F bonds at the square pyramidal copper(II) centers.

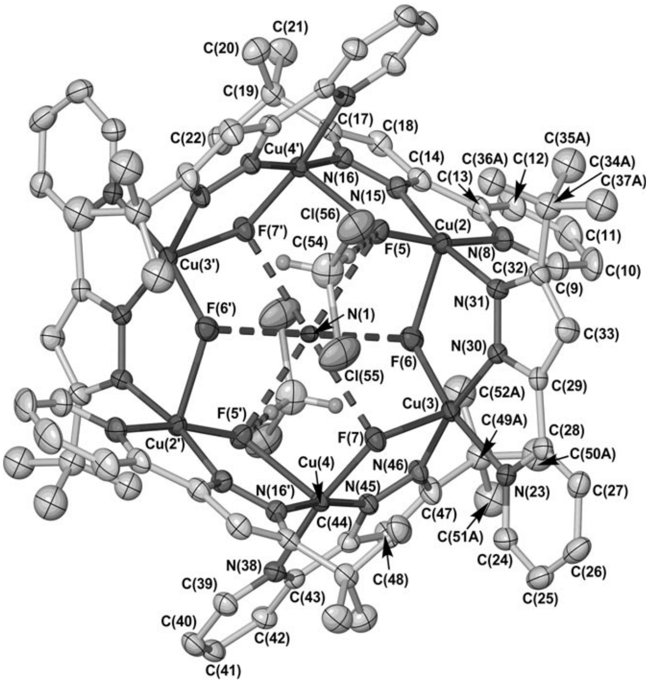

Figure 1. View of the $[(NH_4)\subset\mathbf{1}(CH_2Cl_2)_2]^+$ cation in $[(NH_4)\subset\mathbf{1}(CH_2Cl_2)_2]HF_2\cdot5.6\,CH_2Cl_2\cdot0.4\,(C_2H_5)_2O$, and the atom numbering scheme employed. All atoms have 50 % probability radii. Only one orientation of the disordered *tert*butyl groups is shown, while all H atoms in the **1** metallacrown have been omitted.

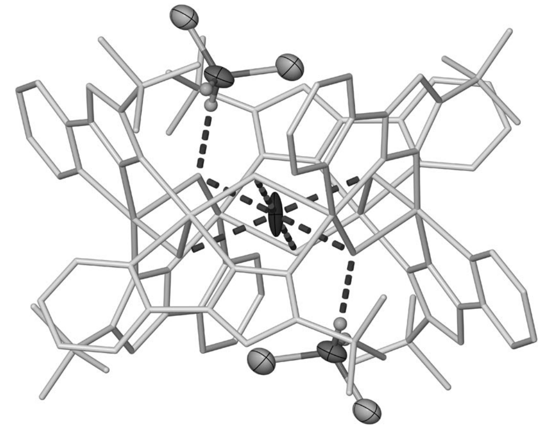

Figure 2. Alternative view of the $[(NH_4)\subset\mathbf{1}(CH_2Cl_2)_2]^+$ ion in $[(NH_4)\subset\mathbf{1}(CH_2Cl_2)_2]HF_2\cdot5.6\,CH_2Cl_2\cdot0.4\,(C_2H_5)_2O$, that shows the hydrogen bonding interactions in the structure. For clarity all atoms from the metallacrown have been de-emphasized; other atoms have 50 % probability radii. Only one orientation of the disordered *tert*butyl groups is shown, while all H atoms not donating hydrogen bonds have been omitted.

$OH)(HL)\}_4]^{4+}$ cubane complexes, for example, are obtained in the presence of less-coordinating anions.[18]

We describe here a wider investigation of the affinity of **1** for complexed guest molecules. Crystal structures and other physical characterization are reported for new solid complexes of **1** with NH_4^+, $MeNH_3^+$ and four different amino acids. Solution-phase measurements to establish the integrity of **1** in organic solvents are also discussed.

Results and Discussion

Reaction of CuF_2 with one molar equivalent of HL[19] in MeOH in the presence of aqueous NH_4OH afforded a blue solution, which was then slowly evaporated to dryness under ambient conditions. Recrystallization of the residue from CH_2Cl_2/Et_2O afforded a 30 % yield of blue crystals, whose composition was established as $[(NH_4)\subset\mathbf{1}(CH_2Cl_2)_2]HF_2\cdot5.6\,CH_2Cl_2\cdot0.4\,(C_2H_5)_2O$ by an X-ray diffraction analysis. The compound is isostructural with the corresponding solvate of $[Na\subset\mathbf{1}(CH_2Cl_2)_2]HF_2$,[13] and contains a centrosymmetric metallacrown **1**, with approximate S_6 symmetry if the positions of the *tert*butyl groups are ignored (Figure 1 and Figure 2). Neighboring copper ions in the crown are linked by a chelating L^- ligand, bridging through its pyrazolido group, and by a μ-F^- ligand that coordinates to a basal coordination site of one copper ion and the apical site of the other (Scheme 1). The copper ions all have near-identical square-pyramidal stereochemistries, with τ very close to the ideal value of 0 for this geometry (Table 1).[20] The NH_4^+ ion N(1) occupies the crystallographic inversion center at the center of the molecule, but with an elongated displacement ellipsoid that suggests its true position might be slightly proud of the Cu_6 plane rather than at its centroid (Figure 2). The H atoms of the NH_4^+ ion are disordered about the inversion center and so could not be located. As in the sodium complex,[13] the bowl-shaped cavities of the metallacrown are occupied by CH_2Cl_2 molecules, which form one C−H···F hydrogen bond an F donor in the crown (Figure 2). The distance N(1)···Cl(55) = 3.6888(14) Å suggests there may also be a weak N−H···Cl hydrogen bond between the ammonium and solvent guests (not shown in Figure 2).

Crystals of this compound decompose to a turquoise powder on drying, which analysis confirms to be $[(NH_4)\subset\mathbf{1}(CH_2Cl_2)_2]HF_2$. Analysis of the IR spectra confirmed the presence of NH_4^+ in this solid as a nujol mull. The spectra contains a broad absorption of medium intensity at $\tilde{\nu} =$

Table 1. Selected metric parameters for the crystalline compounds in this work. Corresponding data for $[\mathbf{1}(H_2O)_2]$, $[Na\subset\mathbf{1}(CH_2Cl_2)_2]HF_2$ and $[K\subset\mathbf{1}(CH_2Cl_2)_2]F_{0.6}[HF_2]_{0.4}$ are given in ref. [13]. See ref. [20] for the definition of τ.

	$[(NH_4)\subset\mathbf{1}(CH_2Cl_2)_2]HF_2$	$[\mathbf{1}(H_3NCH_3)_2]Cl_2$	$[\mathbf{1}(gly)_2]$	$[\mathbf{1}(\text{L-ala})_2]$	$[\mathbf{1}(\beta\text{-ala})_2]$	$[\mathbf{1}(H_3NC_6H_{12}NHCO_2)_2]$
Cu–N [Å]	1.945(3)–2.071(3)	1.935(3)–2.057(3)	1.952(2)–2.069(2)	1.952(3)–2.086(3)	1.928(4)–2.048(4)	1.923(4)–2.069(5)
Cu–F[a] [Å]	1.907(2)–1.9252(19)	1.920(3)	1.9313(17)	1.932(2)–1.951(2)	1.914(3)–1.925(3)	1.914(3)–1.930(3)
Cu–F[b] [Å]	2.2541(19)–2.315(2)	2.240(2)	2.2509(17)	2.249(2)–2.282(2)	2.241(3)–2.251(3)	2.233(3)–2.268(3)
Cu-F-Cu [°]	114.49(11)–115.87(9)	114.16(11)	114.43(8)	112.96(10)–114.43(10)	114.03(12)–115.20(13)	114.05(14)–114.96(14)
Cu···Cu [Å]	3.5311(6)–3.5802(7)	3.4965(5)	3.5203(3)	3.5148(7)–3.5464(7)	3.5012(8)–3.5127(8)	3.5005(9)–3.5272(9)
τ	0.012(3)–0.068(3)	0.010(3)	0.073(2)	0.004(3)–0.036(3)	0.042(4)–0.071(4)	0.020(4)–0.075(4)
N[c]···F [Å]	2.706(2)–2.739(2)	2.590(12)–2.632(7)	2.663(13)	2.686(4)–2.708(4)	2.643(5)–2.677(5)	2.646(6)–2.680(5)
Cavity						
base [Å]	2.2(1)	2.2(1)	2.2(1)	2.2(1)	2.1(1)	2.2(1)
rim [Å]	5.4(3)	5.6(2)	5.8(2)	5.6(2)	5.3(4)	5.5(4)
height [Å]	6.4(2)	6.3(1)	6.8(1)	6.4(1)	6.6(2)	6.5(2)

[a] Basal. [c] Apical. [c] Guest.

1791 cm^{-1} that is not shown by other complexes of **1** (Figure 3A). This is of appropriate energy to be assigned as the $\nu_4(\delta\{H-N-H\})+\nu_6$ (lattice torsion) combination vibration of NH_4^+,[21] which is usually observed in solids in which the ammonium ion is strongly hydrogen bonded.[22,23] Other vibrations expected from the NH_4^+ guest are contained in a broad envelope centered at $\tilde{\nu}=3384$ cm^{-1} (ν_3; $\nu_{as}\{N-H\}$, plus combination bands),[22,23] and at 1486 cm^{-1} (ν_4). A medium-intensity peak at $\tilde{\nu}=1248$ cm^{-1} is also shown by $[Na\subset\mathbf{1}(CH_2Cl_2)_2]HF_2{\cdot}CH_2Cl_2$ but not the other compounds in this work, and may correspond to the $\delta\{F-H-F\}$ vibration of the bifluoride anion.[24]

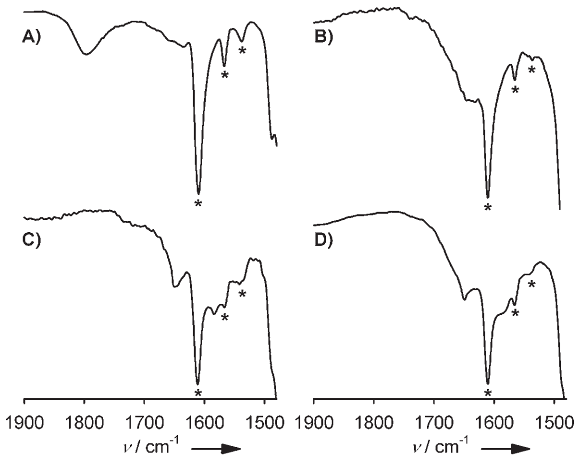

Figure 3. Partial nujol mull IR spectra of A) $[(NH_4)\subset\mathbf{1}(CH_2Cl_2)_2]HF_2$, B) $[\mathbf{1}(H_3NCH_3)_2]Cl_2{\cdot}\frac{2}{3}H_2O{\cdot}2CH_2Cl_2$, C) $[\mathbf{1}(\beta\text{-ala})_2]{\cdot}2H_2O{\cdot}CHCl_3$ and D) $[\mathbf{1}(H_3NC_6H_{12}NHCO_2)_2]{\cdot}1.6H_2O{\cdot}3.5CHCl_3$. The starred peaks originate from metallacrown **1**, while the other peaks are from the ammonium or amino acid guest species, and/or lattice water. See the text for further details.

An analogous reaction was carried out using $MeNH_2$ as base, rather than NH_4OH. The resultant blue-green CH_2Cl_2 solution slowly deposited a small number of blue crystals over several days. These proved to have the crystallographic composition $[\mathbf{1}(H_3NCH_3)_2]Cl_2{\cdot}\frac{2}{3}H_2O{\cdot}3CH_2Cl_2$. The chloride counterions in the compound presumably originate from trace HCl in the undistilled recrystallisation solvent, which accounts for the low 7% yield of this material. The metallacrown **1** in this compound has crystallographic $\bar{6}$ symmetry, with a single unique copper ion. The center of the metallacrown is empty; instead, there are two methylammonium guests occupying the bowl-shaped cavities, forming strong N–H···F hydrogen bonds to the three F donors at the base of each cavity (Figure 4, Table 1). The poor fit of the small $MeNH_3^+$ ion in the large host cavities is reflected in its disorder over four sites, generated by two unique orientations near (major site) or directly on (minor site) the crystallographic C_3 axis bisecting the cavity. The microanalysis of the dried compound is consistent with the formula $[\mathbf{1}(H_3NCH_3)_2]Cl_2{\cdot}\frac{2}{3}H_2O{\cdot}2CH_2Cl_2$, close to that derived from the crystal structure. A broad peak in the IR spectrum of this solid at $\tilde{\nu}=3401$ cm^{-1} is indicative of the $\nu\{N-H\}$ vibrations of the $CH_3NH_3^+$ ion, while a broad absorption at $\tilde{\nu}=1635$ cm^{-1} might be the $\delta_{as}\{NH_3\}$ vibration from $CH_3NH_3^+$,[26] a $\delta\{H-O-H\}$ peak from lattice water,[25] or a mixture of both (Figure 3B). Other strong IR absorptions expected in the spectra from the $CH_3NH_3^+$ guest species near $\tilde{\nu}=1450$ and 950 cm^{-1} could not be distinguished from other peaks in the spectrum.[26]

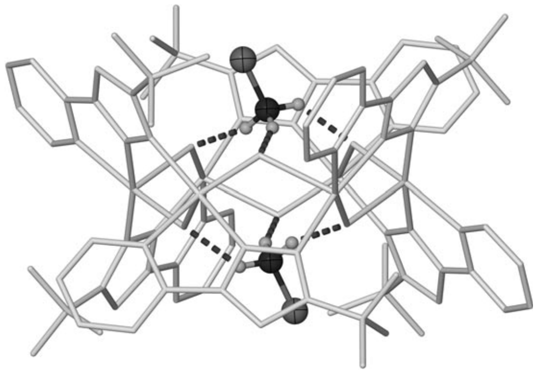

Figure 4. View of the $[\mathbf{1}(H_3NCH_3)_2]^{2+}$ dication in $[\mathbf{1}(H_3NCH_3)_2]Cl_2{\cdot}\frac{2}{3}H_2O{\cdot}3CH_2Cl_2$,and the hydrogen bonding interactions in the structure. For clarity all atoms from the metallacrown have been de-emphasized; other atoms have 50% probability radii. Only one of the four orientations of the disordered methylammonium guest is shown, whereas all H atoms not donating hydrogen bonds have been omitted.

In the light of this result, the synthesis of complexes of **1** with amino acid guests was pursued. Reactions similar to those above gave ca. 10 % yield of blue crystalline products, with the formulae [**1**(gly)$_2$]·2 H_2O·6 CH_2Cl_2, [**1**(L-ala)$_2$]·5 H_2O·3 CH_2Cl_2 and [**1**(β-ala)$_2$]·2 H_2O·8 $CHCl_3$ (gly = glycine, L-ala = L-α-alanine and β-ala = β-alanine). The lower yields of these complexations may reflect the limited solubilites and/or the low basicities of the amino acid reagents used. As before, each crystal contained a molecule of **1** with either $\bar{1}$ or $\bar{6}$ crystallographic symmetry, with a molecule of the amino acid guest in each bowl-shaped cavity (Figure 5 and Figure 6). The neutrality of the guest molecules, which adopt their zwitterionic tautomers $^{+}H_3N\{CH(R)\}_nCO_2^{-}$, was confirmed by the absence of any anions in the lattices and by the IR study described below. The carboxy groups in all these compounds protrude from the bowl-shaped cavities, and accept a hydrogen bond from one molecule of water and, in some cases, from the organic solvent in the lattice (Figure 5, Figure 6, and the Supporting Information). Unusually, the crystal structure of [**1**(L-ala)$_2$]·5 H_2O·3 CH_2Cl_2 could only be refined successfully in the centric space group $P2_1/c$, despite the chirality of the amino acid employed (confirmed from its optical rotation). This pseudo-centering is an artefact that probably arises because molecules of **1** pack in a centrosymmetric manner (as in all the other compounds in this work), which is not influenced by the chirality of the guests buried inside them.

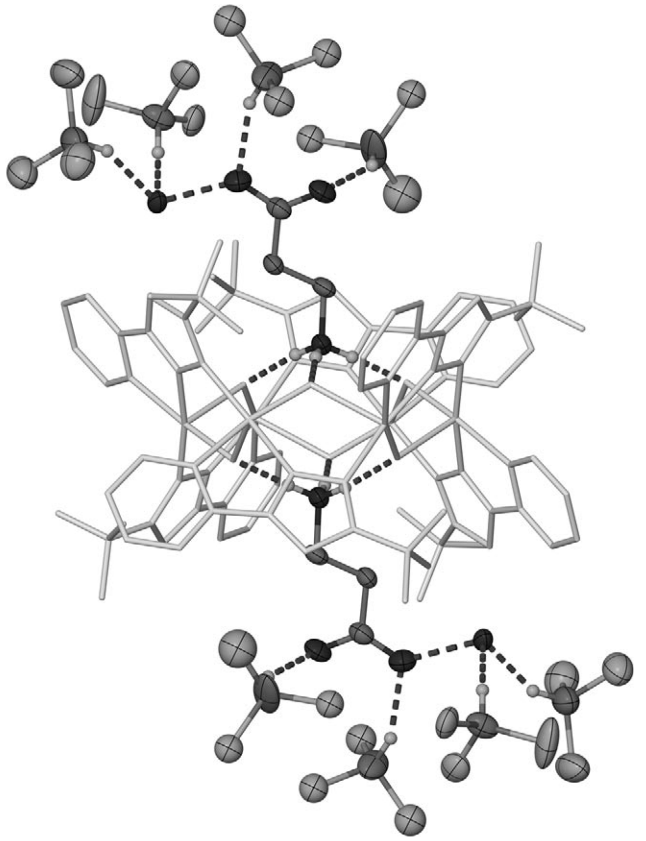

Figure 5. View of the formula unit in [**1**(β-ala)$_2$]·2 H_2O·8 $CHCl_3$, and the hydrogen bonding interactions in the structure. For clarity all atoms from the metallacrown have been de-emphasized; other atoms have 50 % probability radii. Only one orientation of the disordered *tert*butyl groups and chloroform molecules is shown, whereas all H atoms not donating hydrogen bonds have been omitted. The H atoms on the water molecule were not located in the crystal structure.

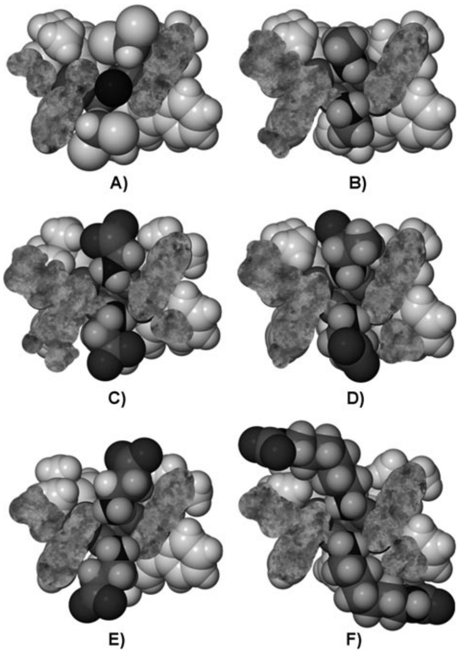

Figure 6. Cutaway space-filling views of A) [$(NH_4)\subset$**1**$(CH_2Cl_2)_2$]$^+$, B) [**1**-$(H_3NCH_3)_2$]$^{2+}$, C) [**1**(gly)$_2$], D) [**1**(L-ala)$_2$], E) [**1**(β-ala)$_2$], and F) [**1**$(H_3NC_6H_{12}NHCO_2)_2$], and the guest species in the bowl-shaped cavities of **1**. The C, H and N atoms of the metallacrown have pale shading for clarity, and only one orientation is shown of the disordered residues in the structures.

Drying these three compounds in vacuo afforded turquoise powders, that each retain their complement of lattice water plus one equivalent of the relevant chlorinated solvent by microanalysis. The zwitterionic nature of the amino acid guests was also confirmed by IR spectroscopy. These spectra showed a peak of medium intensity at $\tilde{\nu} = 1580–1586\ cm^{-1}$, that does not originate from the metallacrown and can be assigned as a $\nu_{as}\{O-C-O\}$ vibration from a zwitterionic amino acid (Figure 3C).[27] The expected $\nu_s\{O-C-O\}$ stretch, predicted to lie between $\tilde{\nu} = 1360–1420\ cm^{-1}$, was not detected and was presumably obscured by the nujol absorption at $1377\ cm^{-1}$. Importantly no $\nu\{C=O\}$ peak above $\tilde{\nu} = 1700\ cm^{-1}$, which would be expected from an amino acid in its alternative neutral tautomer,[27] was observed for either compound. As before, the $\nu\{N-H\}$ vibrations of all three products lie within a broad IR peak of medium intensity centred near $\tilde{\nu} = 3400\ cm^{-1}$, while a broad absorption around $\tilde{\nu} = 1635–1645\ cm^{-1}$ could contain contributions from the $\delta_{as}\{NH_3\}$ vibration from the amino acid[27] and/or the $\delta\{H-O-H\}$ peak from lattice water (Figure 3 C).[25]

Finally, in an attempt to link molecules of **1** together using a bifunctional guest, the synthesis of **1** in the presence of 1,6-diaminohexane was investigated. Molecular models suggested this straight chain α,ω-diamine was of an appropriate length to bridge between two molecules of **1** overlying each other in van der Waals contact. The crystals obtained from this reaction showed that the guests did not bridge between host molecules in the desired fashion. Rather the product, $[\mathbf{1}(H_3NC_6H_{12}NHCO_2)_2]\cdot 1.6\,H_2O\cdot 3.8\,CHCl_3$, contains two *N*-(6-aminohexyl)carbamic acid guest molecules[28] in the bowl-shaped cavities (see the Supporting Information). The guest molecules protrude over the edges of the cavities, and the pendant amino group has been converted to a carbamate function by fixation of atmospheric CO_2 (Figure 6). Aerobic conversion of aliphatic amines to carbamates is a well-known transformation in chemistry and biology.[29] Electroneutrality considerations again imply that the guests adopt their zwitterionic tautomer, $^+H_3NC_6H_{12}NHCO_2^-$, to maximize the hydrogen bond from its amino group to the host F acceptors. This was supported by the IR spectrum of the dried solid, whose microanalysis could be fit as $[\mathbf{1}(H_3NC_6H_{12}NHCO_2)_2]\cdot 1.6\,H_2O\cdot 3.5\,CHCl_3$ (Figure 3D). The amide I and amide II ν-$\{NHCO_2\}$ peaks expected from an anionic carbamato function, may be present in the IR spectrum of this compound at $\tilde{\nu}=1646$ (superimposed on the broad $\delta_{as}\{NH_3\}$/lattice water peak) and $1590\ cm^{-1}$ (a shoulder on a stronger peak from **1** at $1610\ cm^{-1}$).[30] Although these assignments are tentative, there was clearly no peak in the spectrum that correlated to an amide I peak, which would be expected from the alternative neutral carbamic acid tautomer, $H_2NC_6H_{12}NHCO_2H$ ($\approx 1725\ cm^{-1}$).[31]

Comparison of the six crystal structures of complexes of **1** in this work (Table 1, Figure 6), and the three in our earlier report,[13] reveals that the dimensions of the metallacrown are barely affected by the different guest species present. The only metric parameters about the Cu ions to differ significantly in these compounds are the apical Cu–F bond lengths (Scheme 1), which span a range of 2.193(2)–2.315(2) Å between the nine structures. That is consistent with the well-known plasticity of apical and axial Cu–L bonds in tetragonal copper(II) complexes.[32] Differences in the dimensions of the bowl-shaped cavities in the compounds (notably the rim diameter, Table 1) mostly reflect the differing positions and disorder of the *tert*butyl groups in the molecules. The N···F distances between the guest and the host F atoms in this study are consistently 2.6–2.7 Å, which are in the typical range observed for hydrogen bonds between an ammonium cation and a fluorometallate acceptor.[33]

The X-band EPR spectra at 110 K of all the solid compounds in this work are essentially identical to each other, and to those of $[\mathbf{1}(H_2O)_2]$ and $[M\subset\mathbf{1}(CH_2Cl_2)_2]^+$ ($M^+=Na$ or K^+).[13] All the products show a broad, unsymmetric isotropic peak at $g=2.13$, together with a weak half-field signal near 1600 G. This is a typical EPR pattern for an integer spin system with a small zero-field splitting,[35] as expected for an exchange-coupled hexanuclear copper(II) spin system (see the Supporting Information). The invariability of the spectrum between the compounds is consistent with our previous conclusion, that the presence or absence of guest species has no significant effect on the magnetic structure of **1**.[13] In frozen $MeNO_2$ glasses at the same temperature, the compounds all showed a slightly unsymmetric EPR peak at $g=2.13$ as before, although the poor solubility of the compounds meant that a half-field resonance was no longer unambiguously detectable against the background. The solution spectra of the amino acid complexes all contained weak features ascribable to the $g_{\parallel}$ peak from a mononuclear copper(II) impurity. No such impurity was apparent in solutions of $[M\subset\mathbf{1}(CH_2Cl_2)_2]^+$ ($M^+=Na^+$, K^+ or NH_4^+).

Electrospray (ESI) mass spectra of the complexes of **1** from MeCN feed solutions were somewhat variable, which may reflect their limited solubilities and/or partial hydrolysis of **1** under the conditions of the technique. However, the spectra consistently showed a mass peak at $m/z=847$, assignable to the dication, $[Cu_6F_6L_6]^{2+}$ ($\mathbf{1}^{2+}$), and one or more doubly charged peaks corresponding either to loss of F^- or L^- from $\mathbf{1}^{2+}$, or their substitution by MeCN. Only two unambiguous molecular ions from adducts of intact **1** with guest species were detected from any of the compounds. First, was a weak peak at $m/z=857$ present in several of the spectra, which corresponds to $[\mathbf{1}(H_2O)]^{2+}$, and/or to $[(NH_4)\mathbf{1}]^{2+}$ in the case of the ammonium complex. Second, were two ions shown only by $[\mathbf{1}(H_3NCH_3)_2]Cl_2\cdot{}^{2}\!/_{3}\,H_2O\cdot 2\,CH_2Cl_2$, at $m/z=890$ and 880, that could be assigned to $[\mathbf{1}(H_3NCH_3)_2Y_m]^{2+}$ ($Y=H_2O$ or F; $m=1$ and 0). In addition to lower nuclearity fragmentation and hydrolysis products, several of the spectra also contained weak peaks assigned to $[Cu_7F_6L_6]^{2+}$ species on the basis of their isotope patterns. These data confirm that **1** is present in solution, although it fragments significantly under ESI conditions. In contrast, field desorption mass spectra of $[\mathbf{1}(H_2O)_2]$ and salts of $[M\subset\mathbf{1}(CH_2Cl_2)_2]^+$ ($M^+=Na^+$ or K^+) gave no peak assignable to $\mathbf{1}^{n+}$.[13] It may be that the uncharged metallacrown **1** was not ionized successfully by that technique.

The ^1H NMR spectra of the compounds in CD_3NO_2 at 293 K are weak, owing to the poor solubility of the samples. However, they all cleanly show the signals expected for a single L^- environment, as six strongly broadened peaks whose contact shifts differ little between the compounds. Peaks from the lattice chlorinated solvent, with integrals similar to those predicted by microanalysis, were also present in the spectra at either 5.5 (CH_2Cl_2) or 7.6 ppm ($CHCl_3$). The alkyl ^1H resonances from the gly, L-ala, β-ala and $^+H_3NC_6H_{12}NHCO_2^-$ guest molecules were clearly distinguishable in the spectra of those four complexes, as additional broadened peaks in the diamagnetic region. No individual peak assignable to $CH_3NH_3^+$ was present in the spectrum of $[\mathbf{1}(H_3NCH_3)_2]Cl_2\cdot{}^{2}\!/_{3}\,H_2O\cdot 2\,CH_2Cl_2$. However, two very broad peaks at 2.5 and 1.4 ppm, whose integrals sum to 6H against the rest of the spectrum, may arise from this group. No ^1H peaks assignable to NH_4^+, or to any of the RNH_3^+ groups in the compounds, were observed. No contact-shifted peaks were detected in the ^{19}F or ^{23}Na NMR spectra of $[Na\subset\mathbf{1}(CH_2Cl_2)_2]HF_2$ in CD_3NO_2.[6,36] Rather, the ^{19}F spectrum only showed peaks assignable to one or more of the following inorganic anions: SiF_6^{2-} ($\delta = -130$ ppm, s[37]); BF_3OH^- ($\delta = -146$ ppm, $J\{^{11}B–^{19}F\} = 15$ Hz[38]); and, a peak at $\delta = -154$ ppm ($J\{^{1}H–^{19}F\} = 35$ Hz) which we assign to a mixture of F^- ($\delta = -150$ ppm in CD_3NO_2[39]) and HF_2^- ($\delta = -154$, $J\{^{1}H–^{19}F\} = 120.5$ Hz in the same solvent[40]) in rapid chemical exchange. The putative SiF_6^{2-} and BF_3OH^- content of the samples would arise by leaching from the borosilicate glass NMR tubes by free fluoride in the solutions.[41,42]

The solution properties of $[Na\subset\mathbf{1}(CH_2Cl_2)_2]HF_2{\cdot}CH_2Cl_2$, $[(NH_4)\subset\mathbf{1}(CH_2Cl_2)_2]HF_2$ and $[\mathbf{1}(\beta\text{-ala})_2]{\cdot}2H_2O{\cdot}CHCl_3$ were investigated further by UV/vis measurements. These compounds show only small variations in their *d–d* maximum between each other and, for each compound, in the four solvents examined (listed in the Supporting Information). The observed values of λ_{max} (673–695 nm) and ε_{max} (264–320 $M^{-1}cm^{-1}$, or 44–53 $M^{-1}cm^{-1}$ per metal ion) are typical for square-pyramidal copper(II) complexes.[43] The lack of significant solvatochromism in these spectra shows that the solution structures of these compounds are not solvent dependent. This would again imply that the metallacrown structure of **1** is retained in these solvents. A full solvatochromism study of $[\mathbf{1}(H_3NCH_3)_2]Cl_2{\cdot}\frac{2}{3}H_2O{\cdot}2CH_2Cl_2$ was not attempted, owing to the limited quantity of material available, but this compound gave a similar visible spectrum to the others in $MeNO_2$ ($\lambda_{max} = 684$ nm, $\varepsilon_{max} = 280\,M^{-1}cm^{-1}$).

Conclusion

Metallacrown **1** $[\{Cu(\mu\text{-}F)(\mu\text{-}L)\}_6]$ (HL = 3{5}-(pyrid-2-yl)-5{3}-(*tert*butyl)pyrazole) has an unusually robust structure for this type of compound, which can form in the absence of a template and has two modes of guest binding. Alkali metal ions of an appropriate size, and NH_4^+, are accommodated endogenously at the centre of the Cu_6F_6 ring. The host properties of **1** resemble a typical metallacrown in that regard.[1] Conversely, larger guests can bind exogenously to the two bowl-shaped cavities above and below the Cu_6F_6 core, forming up to three hydrogen bonds to the three fluoride ions at the base of each cavity. These fluoro acceptors are particularly geometrically pre-organized to form three strong N−H···F hydrogen bonds to alkylammonium or zwitterionic amino acid guests. The molecular structure of **1** varies very little in the presence of either type of guest species, and its magnetic structure is also barely affected by guest binding. ESI-MS data demonstrate that intact **1** is present in solutions of these compounds, while EPR, ^{1}H NMR and UV/vis spectra suggest that **1** is the major copper-containing species in those solutions (although EPR showed the presence of a weak mononuclear impurity in solutions of the amino acid complexes).

This work, combined with our earlier study,[13] shows that the presence of guest species has no detectable effect on the EPR spectrum or magnetic moment of **1**, while the UV/vis spectrum of its copper chromophores should be almost unaffected by guest binding. The paramagnetism of **1** also limits the information that can be extracted from its NMR spectra. Therefore, it is difficult to determine the extent to which the guest binding to **1**, observed in the solid state, is retained in solution. The strongest circumstantial evidence in that regard comes from $[\mathbf{1}(H_3NCH_3)_2]Cl_2{\cdot}\frac{2}{3}H_2O{\cdot}2CH_2Cl_2$. First, the ESI-MS spectrum of that compound is the only one to show unambiguous peaks that arise from guest-containing molecular ions, derived from $[\mathbf{1}(H_3NCH_3)_2]^{2+}$. Second, its ^{1}H NMR spectrum is unique in showing two distinct resonances that might arise from bound and unbound $CH_3NH_3^+$, although the poor solubility of the compound means that this assignment should be treated with caution. Notably, $CH_3NH_3^+$ is the smallest exogenous guest we have studied, and is only the only one giving rise to a doubly charged complex with **1** (which should result in stronger N−H···F hydrogen bonding). Both those factors would be consistent with $CH_3NH_3^+$ forming a stronger complex to **1** than the amino acid guests. Additional experiments to address those questions, and studies of new metallacrowns formed from L^- with other metal ions, are in progress.

Experimental Section

Instrumentation: Elemental microanalyses were performed by the University of Leeds School of Chemistry microanalytical service. Infra-red spectra were obtained as nujol mulls pressed between NaCl windows, between 600–4000 cm^{-1}, by using a Nicolet Avatar 360 spectrophotometer. X-band EPR spectra were obtained by using a Bruker EMX spectrometer fitted with an ER4119HS resonator and ER4131VT cryostat. ^{1}H NMR spectra employed a Bruker DPX300 spectrometer operating at 300.2 MHz, whereas ^{19}F and ^{23}Na NMR spectra used a Bruker DRX500 instrument, operating at 470.6 (^{19}F) and 132.3 MHz (^{23}Na). UV/Vis measurements were performed by using a Perkin–Elmer Lambda900 spectrophotometer, and 1 cm quartz solution cells.

ESI-MS spectra were obtained by means of a Waters ZQ4000 spectrometer, from MeCN feed solutions. All mass peaks have the correct isotopic distributions for the proposed assignments. Additional molecular ions of $\leq 3\%$ intensity compared to the main peak, which arise from hydrolysis products, are present in the spectra, but not listed. See the Supporting Information for representative Figures.

Materials and methods: All reactions were carried out in air, using non-predried AR-grade solvents. 3{5}-(Pyrid-2-yl)-5{3}-(*tert*butyl)pyrazole (HL) was prepared by the literature method,[19] whereas all other reagents were used as commercially supplied. Given the ambiguity about the space group of $[\mathbf{1}(\text{L-ala})_2]{\cdot}5H_2O{\cdot}3CH_2Cl_2$ (see below), the chirality of the L-alanine employed (Aldrich) was confirmed from its specific optical rotation $\alpha_D = +12.9°$ in 5 M HCl ($\alpha_{D(lit)} = +14.5°$[44]). The syntheses and analytical data for $[\mathbf{1}(H_2O)_2]{\cdot}3CH_2Cl_2$, $[Na\subset\mathbf{1}(CH_2Cl_2)_2]HF_2{\cdot}CH_2Cl_2$ and $[K\subset\mathbf{1}(CH_2Cl_2)_2]F_{0.6}[HF_2]_{0.4}$ are given in ref. [13].

Synthesis of $[(NH_4)\subset\mathbf{1}(CH_2Cl_2)_2]HF_2$: Solid CuF_2 (0.25 g, 2.45 mmol) and HL (0.50 g, 2.45 mmol) were dissolved in MeOH (30 cm^3) at room temperature to give a dark green solution. Excess NH_4OH (9.8 M aqueous solution; 1.0 cm^3, 9.8 mmol) was added dropwise to this mixture, and the resultant blue solution was then stirred for a further 16 h. The solution was then evaporated to dryness under ambient conditions, yielding a solid residue composed of mixed green and blue solids. The residue was washed quickly with CH_2Cl_2 (10 cm^3, to remove a soluble green impurity), then extracted again into a second 15 cm^3 aliquot of the same solvent. Slow diffusion of Et_2O vapor into the resultant filtered, blue-green solution yielded blue block-like crystals, which decomposed to a turquoise powder on drying in vacuo. Yield 0.24 g, 30%. ^{1}H NMR (CD_3NO_2, 298 K): $\delta = 5.5$ (s, 4H; CH_2Cl_2), 6.1 (s, 54H; $C(CH_3)_3$), 11.9 (s,6H; Py

H^4), 41.1, 43.8 (both 6H; Py H^3 and H^5), 69.2 (s, 6H; Pz H^4), 101.4 ppm (s, 6H; Py H^6); IR (nujol): $\tilde{\nu}=3384$(br m), 3153(w), 2725(w), 2664(w), 1791(br m), 1609(s), 1563(m), 1533(w), 1486(m), 1401(w), 1336(m), 1261(m), 1248(m), 1205(m), 1167(m), 1149(m), 1086(w), 1045(m), 1019(w), 989(w), 888(w), 774(s), 749(w), 685(w), 644 cm^{-1}(m); ESI-MS: m/z (%): 857 (2, $[(NH_4)Cu_6F_6L_6]^{2+}$ or $[Cu_6F_6L_6(H_2O)]^{2+}$), 847 (13, $[Cu_6F_6L_6]^{2+}$), 838 (2, $[Cu_6F_5L_6]^{2+}$), 747 (5, $[Cu_6F_6L_5]^{2+}$), 716 (4, $[Cu_5F_6L_5]^{2+}$), 666 (8, $[Cu_3(OH)_2L_2(NCMe)]^{+}$), 526 (25, $[Cu_2L_2]^{+}$), 465 (100, $[Cu(LH)_2]^{+}$); elemental analysis calcd (%) for $[C_{74}H_{92}Cl_4Cu_6F_6N_{19}]$-$[HF_2]$: C 46.2, H 4.9, N 13.8; found: C 46.1, H 5.0, N 14.0.

Synthesis of $[\mathbf{1}(H_3NCH_3)_2]Cl_2\cdot{}^2/_3\,H_2O\cdot 2\,CH_2Cl_2$: To a green solution of CuF_2 (0.25 g, 2.45 mmol) and HL (0.50 g, 2.45 mmol) in MeOH (30 cm^3) was added dropwise a 2 M solution of $MeNH_2$ in MeOH (2.5 cm^3, 5.0 mmol). The resultant dark blue solution was stirred for a further 16 H; then evaporated to dryness under ambient conditions. The mixed green and blue solid residue was quickly washed with CH_2Cl_2 as before, then reextracted into CH_2Cl_2 (15 cm^3), and the blue-green solution was filtered. Blue crystals of the product formed over a period of several days upon slow diffusion of Et_2O into this solution. Yield 0.06 g, 7%. ^{1}H NMR (CD_3NO_2, 298 K): $\delta=1.4$ and 2.5 (total integral, 6H; H_3NCH_3), 5.5 (s, 4H; CH_2Cl_2), 6.2 (s, 54H; $C\{CH_3\}_3$), 12.5 (s, 6H; Py H^4), 42.9, 45.5 (2×s, both 6H; Py H^3 and H^5), 68.4 (s, 6H; Pz H^4), 106.0 ppm (s,6H; Py H^6); IR (nujol): $\tilde{\nu}=$ 3401(br m), 3181(w), 2730(w), 2659(w), 1635 (br m), 1610(s), 1561(m), 1533(w), 1403(w), 1303(m), 1264(m), 1201(m), 1167(m), 1147(m), 1122(w), 1091(w), 1042(m), 1017(w), 990(w), 963(w), 888(w), 779(s), 749(w), 683(w), 644 cm^{-1}(w); ESI-MS: m/z (%): 918 (3, $[Cu_7F_6L_6(NCCH_3)(H_2O)_2]^{2+}$), 909 (1, $[Cu_7F_6L_6(NCCH_3)(H_2O)]^{2+}$), 897 (1, $[Cu_7F_6L_6(H_2O)_2]^{2+}$), 890 (12, $[Cu_6F_6L_6(H_3NCH_3)_2F]^{2+}$ or $[Cu_6F_6L_6(H_3NCH_3)_2(H_2O)]^{2+}$), 880 (1, $[Cu_6F_6L_6(H_3NCH_3)_2]^{2+}$), 868 (2, $[Cu_6F_6L_6(NCCH_3)]^{2+}$), 859 (30, $[Cu_6F_5L_6(NCCH_3)]^{2+}$), 847 (5, $[Cu_6F_6L_6]^{2+}$), 838 (1, $[Cu_6F_5L_6]^{2+}$), 829 (6, $[Cu_6F_4L_6]^{2+}$), 759 (5, $[Cu_6F_5L_5(NCMe)]^{2+}$), 465 (100, $[Cu(LH)_2]^{+}$); elemental analysis calcd (%) for $[C_{74}H_{96}Cu_6F_6N_{20}]Cl_2\cdot{}^2/_3\,H_2O\cdot 2\,CH_2Cl_2$: C 45.3, H 5.0, N 13.9; found: C 45.4, H 5.1, N 14.1.

Synthesis of $[\mathbf{1}(gly)_2]\cdot 2\,H_2O\cdot CH_2Cl_2$: A mixture of $CuF_2\cdot x\,H_2O$ (0.25 g, 2.45 mmol), HL (0.50 g, 2.45 mmol) and glycine (0.18 g, 2.45 mmol) in MeOH (30 cm^3) was stirred for 16 H; resulting in a gradual color change from dark green to dark blue. The solution was then evaporated to dryness under ambient conditions. The mixed blue and green residue was washed quickly with CH_2Cl_2, as before, then redissolved in a second aliquot of CH_2Cl_2 (15 cm^3). Blue crystals were obtained upon slow diffusion of Et_2O vapor into the filtered solution. Yield 0.09 g, 11%. ^{1}H NMR (CD_3NO_2, 298 K): $\delta=1.7$ (s, 4H; $H_3NCH_2CO_2$), 5.5 (s, 2H; CH_2Cl_2), 6.3 (s, 54H; $C\{CH_3\}_3$), 12.5 (s, 6H; Py H^4), 43.4, 45.6 (2×s, both 6H; Py H^3 and H^5), 68.8 (s, 6H; Pz H^4), 106.5 ppm (s, 6H; Py H^6); IR (Nujol): $\tilde{\nu}=$ 3408(br m), 3179(w), 2726(w), 2666(w), 1635(br m), 1611(s), 1582(m), 1565(m), 1535(w), 1404(w), 1333(m), 1262(m), 1248(m), 1205(m), 1165(m), 1154(m), 1115(w), 1088(w), 1042(m), 1017(w), 990(m), 965(w), 888(w), 823(m), 779(s), 750(w), 683(w), 644 cm^{-1}(m); ESI-MS: m/z (%): 918 (8, $[Cu_7F_6L_6(NCCH_3)(H_2O)_2]^{2+}$), 909 (4, $[Cu_7F_6L_6(NCCH_3)(H_2O)]^{2+}$), 897 (7, $[Cu_7F_6L_6(H_2O)_2]^{2+}$), 857 (5, $[Cu_6F_6L_6(H_2O)]^{2+}$), 847 (3, $[Cu_6F_6L_6]^{2+}$), 792 (2, $[Cu_3L_3+H]^{+}$), 726 (5, $[Cu_2L_3]^{+}$), 465 (100, $[Cu(LH)_2]^{+}$); elemental analysis calcd (%) for $[C_{76}H_{94}Cu_6F_6N_{20}O_4]\cdot 2\,H_2O\cdot CH_2Cl_2$: C 47.0, H 5.1, N 14.2; found: C 47.2, H 5.3, N 14.4.

Synthesis of $[\mathbf{1}(\text{L-ala})_2]\cdot 5\,H_2O\cdot CH_2Cl_2$: Method as for $[\mathbf{1}(gly)_2]$, by using L-alanine (0.22 g, 2.45 mmol). The product formed blue crystals from CH_2Cl_2/Et_2O. Yield 0.08 g, 9%. ^{1}H NMR (CD_3NO_2, 298 K): $\delta=2.1$ (s, 6H; $H_3NCH(CH_3)CO_2$), 3.4 (s, 2H; $H_3NCH(CH_3)CO_2$), 5.5 (s, 2H; CH_2Cl_2), 6.4 (s, 54H; $C\{CH_3\}_3$), 12.8 (s, 6H; Py H^4), 43.8, 45.1 (2×s, both 6H; Py H^3 and H^5), 69.4 (s, 6H; Pz H^4), 106.9 ppm (s, 6H; Py H^6); IR (Nujol): $\tilde{\nu}=3412$(br m), 3181(w), 2725(w), 2670(w), 1635(br m), 1611(s), 1586(sh), 1563(m), 1539(w), 1404(w), 1333(m), 1262(m), 1250(m), 1205(m), 1167(m), 1152(m), 1113(w), 1092(w), 1044(m), 1017(w), 989(m), 965(w), 904(w), 888(w), 823(m), 781(s), 749(w), 683(w), 645 cm^{-1}(m); ESI-MS: m/z (%): 918 (2, $[Cu_7F_6L_6(NCCH_3)(H_2O)_2]^{2+}$), 909 (1, $[Cu_7F_6L_6(NCCH_3)(H_2O)]^{2+}$), 897 (2, $[Cu_7F_6L_6(H_2O)_2]^{2+}$), 857 (5, $[Cu_6F_6L_6(H_2O)]^{2+}$), 847 (1, $[Cu_6F_6L_6]^{2+}$), 728 (4, $[Cu_2L_3]^{+}$), 465 (100, $[Cu(LH)_2]^{+}$); elemental analysis calcd (%) for $[C_{78}H_{98}Cu_6F_6N_{20}O_4]\cdot 5\,H_2O\cdot CH_2Cl_2$: C 46.3, H 5.4, N 13.7; found: C 46.1, H 5.2, N 13.7.

Synthesis of $[\mathbf{1}(\beta\text{-ala})_2]\cdot 2\,H_2O\cdot CHCl_3$: Method as for $[\mathbf{1}(gly)_2]$, by using β-alanine (0.22 g, 2.45 mmol). The product formed blue crystals from $CHCl_3/Et_2O$. Yield 0.11 g, 13%. ^{1}H NMR (CD_3NO_2, 298 K): $\delta=2.1$, 3.3 (2×s, both 4H; $H_3NC_2H_4CO_2$), 6.3 (s, 54H; $C\{CH_3\}_3$), 7.6 (s, 1H; $CHCl_3$), 12.5 (s, 6H; Py H^4), 43.3, 45.6 (2×s, both 6H; Py H^3 and H^5), 68.8 (s, 6H; Pz H^4), 106.8 ppm (s, 6H; Py H^6); IR (Nujol): $\tilde{\nu}=3401$(br m), 3175(w), 2725(w), 2664(w), 1646(br m), 1611(s), 1580(m), 1566(m), 1539(w), 1404(w), 1333(m), 1262(m), 1245(m), 1201(m), 1165(s), 1116(w), 1086(w), 1042(m), 1020(w), 990(m), 888(w), 779(s), 749(w), 683(w), 644 cm^{-1}(m); ESI-MS: m/z (%): 857 (2, $[Cu_6F_6L_6(H_2O)]^{2+}$), 847 (5, $[Cu_6F_6L_6]^{2+}$), 838 (1, $[Cu_6F_5L_6]^{2+}$), 792 (2, $[Cu_2L_2+H]^{+}$), 747 (2, $[Cu_6F_6L_5]^{2+}$), 716 (1, $[Cu_5F_6L_5]^{2+}$), 666 (3, $[Cu_3(OH)_2L_2(NCMe)]^{+}$), 527 (14, $[Cu_2L_2+H]^{+}$), 465 (100, $[Cu(LH)_2]^{+}$); elemental analysis calcd (%) for $[C_{78}H_{98}Cu_6F_6N_{20}O_4]\cdot 2\,H_2O\cdot CHCl_3$: C 46.7, H 5.1, N 13.8; found: C 46.5, H 5.1, N 13.9.

Synthesis of $[\mathbf{1}(H_3NC_6H_{12}NHCO_2)_2]\cdot 1.6\,H_2O\cdot 3.5\,CHCl_3$: Method as for $[\mathbf{1}(gly)_2]$, by using 1,6-diaminohexane (0.14 g, 1.23 mmol). The product formed blue crystals from $CHCl_3/Et_2O$. Yield 0.18 g, 18%. ^{1}H NMR (CD_3NO_2, 298 K): $\delta=-0.7$–3.4 (br m, 24H; $H_3NC_6H_{12}NHCO_2$), 6.2 (s, 54H; $C\{CH_3\}_3$), 7.6 (s, 3H; $CHCl_3$), 12.5 (s, 6H; Py H^4), 43.3, 45.9 (2×s, both 6H; Py H^3 and H^5), 68.9 (s, 6H; Pz H^4), 106.8 ppm (s, 6H; Py H^6); IR (Nujol): $\tilde{\nu}=3405$(br m), 3181(w), 2725(w), 2670(w), 1646(br m), 1610(s), 1590(sh), 1566(m), 1535(w), 1333(w), 1300(m), 1259(m), 1243(m), 1204(m), 1156(m), 1084(w), 1042(w), 990(w), 935(w), 888(w), 795(w), 781(m), 746(s), 683(w), 644 cm^{-1}(w); ESI-MS: m/z (%): 918 (8, $[Cu_7F_6L_6(NCCH_3)(H_2O)_2]^{2+}$), 909 (4, $[Cu_7F_6L_6(NCCH_3)(H_2O)]^{2+}$), 897 (7, $[Cu_7F_6L_6(H_2O)_2]^{2+}$), 886 (2, $[Cu_6F_6L_6(gly)]^{2+}$), 847 (2, $[Cu_6F_6L_6]^{2+}$), 726 (5, $[Cu_2L_3]^{+}$), 527 (2, $[Cu_2L_2+H]^{+}$), 465 (100, $[Cu(LH)_2]^{+}$); elemental analysis calcd (%) for $[C_{86}H_{116}Cu_6F_6N_{22}O_4]\cdot 1.6\,H_2O\cdot 3.5\,CHCl_3$: C 43.6, H 5.0, N 12.5; found: C 43.8, H 5.1, N 12.8.

X-ray data collection and structural determinations: Diffraction data for $[(NH_4)\subset\mathbf{1}(CH_2Cl_2)_2]HF_2\cdot 5.6\,CH_2Cl_2\cdot 0.4\,(C_2H_5)_2O$, $[\mathbf{1}(gly)_2]\cdot 2\,H_2O\cdot 6\,CH_2Cl_2$ and $[\mathbf{1}(\text{L-ala})_2]\cdot 5\,H_2O\cdot 3\,CH_2Cl_2$ were measured using a Bruker X8 Apex diffractometer, with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ Å) generated by a rotating anode. The other structure determinations were carried out on a Nonius KappaCCD area detector diffractometer, by using graphite-monochromated $Mo_{K\alpha}$ radiation from a sealed tube source. Both diffractometers were fitted with an Oxford Cryostream low temperature device. Crystallographic data for each structure are summarized in Table 2. The unit cell of each structure was refined using all data. All the structures were solved by direct methods[45,46] and developed by least-squares refinement on F^2.[47] The refinement of each structure is described in more detail below. All crystallographic figures were prepared using *XSEED*,[48] which incorporates *POVRAY*.[49]

CCDC 657403 ($[\mathbf{1}(H_3NCH_3)_2]Cl_2\cdot{}^2/_3\,H_2O\cdot 3\,CH_2Cl_2$), 657404 ($[(NH_4)\subset\mathbf{1}(CH_2Cl_2)_2]HF_2\cdot 5.6\,CH_2Cl_2\cdot 0.4\,(C_2H_5)_2O$), 657405 ($[\mathbf{1}(\beta\text{-ala})_2]\cdot 2\,H_2O\cdot 8\,CHCl_3$), 657406 ($[\mathbf{1}(H_3NC_6H_{12}NHCO_2)_2]\cdot 1.6\,H_2O\cdot 3.8\,CHCl_3$), 657407 ($[\mathbf{1}(gly)_2]\cdot 2\,H_2O\cdot 6\,CH_2Cl_2$) and 657408 ($[\mathbf{1}(\text{L-ala})_2]\cdot 5\,H_2O\cdot 3\,CH_2Cl_2$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

The asymmetric unit of $[(NH_4)\subset\mathbf{1}(CH_2Cl_2)_2]HF_2\cdot 5.6\,CH_2Cl_2\cdot 0.4\,(C_2H_5)_2O$ contains half a complex molecule with the ammonium ion N(1) lying on the inversion center $[{}^1/_2,0,0]$; half a bifluoride anion, whose H atom lies on the inversion center $[0,{}^1/_2,0]$; two molecules of dichloromethane; and, a badly disordered region of solvent that was modeled by using a mixture of dichloromethane and diethyl ether. Two of the three unique *tert*butyl groups are disordered, and were modeled using two orientations labeled A and B. The occupancy ratios of the A and B sites of both disordered groups refined to 0.65:0.35, and were fixed at those values in the final least squares cycles. The refined restraints $C{-}C=1.54(2)$ and $1,3\text{-}C\cdots C=2.51(2)$ Å were applied to these disordered groups. One of the two unique dichloromethane molecules is disordered over two half-occupied sites, while two partial dichloromethane molecules with occupancies of 0.6 and 0.2 were also included in the badly disordered solvent region. The refined restraints $C{-}Cl=1.79(2)$ and $Cl\cdots Cl=2.92(2)$ Å were applied

Table 2. Experimental details for the new single crystal structure determinations in this study.

	$[(NH_4)\subset\mathbf{1}(CH_2Cl_2)_2]HF_2\cdot5.6\,CH_2Cl_2\cdot0.4\,(C_2H_5)_2O$	$[\mathbf{1}(H_3NCH_3)_2]Cl_2\cdot{}^2/_3\,H_2O\cdot3\,CH_2Cl_2$	$[\mathbf{1}(gly)_2]\cdot2\,H_2O\cdot6\,CH_2Cl_2$
formula	$C_{79.2}H_{104.2}Cl_{11.2}Cu_6F_8N_{19}O_0.4$	$C_{77}H_{103.32}Cl_8Cu_6F_6N_{20}O_{0.66}$	$C_{82}H_{110}Cl_{12}Cu_6F_6N_{20}O_6$
M_r	2259.10	2098.60	2392.54
space group	*P*21/*c*	*P*63/*m*	$R\bar{3}$
crystal class	monoclinic	trigonal	trigonal
a [Å]	15.3822(11)	14.9232(4)	18.4140(5)
b [Å]	14.9401(12)	–	–
c [Å]	21.7254(15)	25.1994(5)	27.3615(18)
β [°]	92.977(4)	–	–
V [Å^3]	4986.0(6)	4860.1(2)	8034.6(6)
Z	2	2	3
T [K]	150(2)	150(2)	150(2)
μ [mm^{-1}]	1.622	1.571	1.535
ρ [Mgm^{-3}]	1.505	1.434	1.483
measured reflns	52814	46932	49172
independent reflns	12161	3812	4328
independent reflns [$I>2\sigma(I)$]	8305	2585	3711
R_{int}	0.127	0.130	0.027
R_1,[a] wR_2[b]	0.051, 0.157	0.058, 0.212	0.045, 0.144
peak/hole [$e\,Å^{-3}$]	1.02/−1.66	1.22/−0.58	0.87/−0.94
	$[\mathbf{1}(\text{L-ala})_2]\cdot5\,H_2O\cdot3\,CH_2Cl_2$	$[\mathbf{1}(\beta\text{-ala})_2]\cdot2\,H_2O\cdot8\,CHCl_3$	$[\mathbf{1}(H_3NC_6H_{12}NHCO_2)_2]\cdot1.6\,H_2O\cdot3.8\,CHCl_3$
formula	$C_{81}H_{114}Cl_6Cu_6F_6N_{20}O_9$	$C_{86}H_{110}Cl_{24}Cu_6F_6N_{20}O_6$	$C_{89.8}H_{123}Cl_{11}.4Cu_6F_6N_{22}O_{5.6}$
M_r	2219.86	2865.98	2499.67
space group	*P*21/*c*[c]	*P*21/*n*	*P*21/*n*
crystal class	monoclinic	monoclinic	monoclinic
a [Å]	15.1767(13)	14.0160(1)	15.1695(2)
b [Å]	14.7977(12)	19.2653(2)	18.9415(4)
c [Å]	22.7977(19)	22.5387(3)	20.5027(3)
β [°]	102.887(4)	96.7992(6)	104.5720(11)
V [Å^3]	4991.0(7)	6043.15(11)	5701.60(16)
Z	2	2	2
T [K]	150(2)	150(2)	150(2)
μ [mm^{-1}]	1.488	1.632	1.433
ρ [Mgm^{-3}]	1.477	1.575	1.456
measured reflns	51430	75360	106057
independent reflns	12011	13814	13100
independent reflns [$I>2\sigma(I)$]	10311	8667	7983
R_{int}	0.026	0.150	0.180
R_1,[a] wR_2[b]	0.057, 0.129	0.075, 0.246	0.077, 0.262
peak/hole [$e\,Å^{-3}$]	1.02/−0.68	1.05/−2.18	1.32/−0.78

[a] $R_1=\Sigma[|F_o|-|F_c|]/\Sigma|F_o|$. [b] $wR_2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^4]^{1/2}$. [c] The apparent crystallization of this chiral compound in a centric space group is an artefact, reflecting pseudo-centering caused by the packing of the molecules of **1** in the lattice. See text for more details.

to these residues. Finally, the badly disordered solvent region also contains one partial diethyl ether site, which was modeled as 0.2-occupied. The fixed restraints C−C = 1.54(2), C−O = 1.43(2), 1,3-C···C = 2.34(2), and 1,3-C···O = 2.43(2) Å were applied to this residue. All wholly occupied non-H atoms were refined anisotropically. All H atoms were placed in calculated positions and refined using a riding model except for the bifluoride H atom, which was located in a Fourier map on its special position and fixed there, with a thermal parameter equal to 1.2× that of its neighboring F atom. The four H atoms of the ammonium ion N(1), which are disordered about the inversion center on which it lies, could not be located and were not included in the final refinement, but were incorporated into the density calculation. The highest residual Fourier peak (+1.0 $e\,Å^{-3}$) and hole (−1.6 $e\,Å^{-3}$) both lie within the same disordered solvent molecule.

The complex molecule in $[\mathbf{1}(H_3NCH_3)_2]Cl_2\cdot{}^2/_3\,H_2O\cdot3\,CH_2Cl_2$ spans the crystallographic $\bar{6}$ site [0,0,$^1/_2$], so that the asymmetric unit contains a single unique copper site and one-third of a methylammonium cation, disordered over two sites about the C_3 axis [0,0,*z*]. The asymmetric unit also contains one-third of a chloride anion and one-ninth of a water molecule, both lying on the mirror plane (*x*,*y*,$^1/_4$); and, half a dichloromethane molecule also spanning the mirror plane (*x*,*y*,$^1/_4$). The disordered methylammonium cation was modeled over two orientations, each have the N atom lying on [0,0,*z*]. The major site has its methyl group on a general position close to the C_3 axis (and disordered about it), while the methyl group of the minor site lies directly on that special position. The C−N bonds in these two residues were restrained to 1.48(1) Å. The chloride ions and partial water molecule occupy a three-fold cavity about [$^2/_3$,$^1/_3$,$^1/_4$], and each cavity contains two Cl^- ions and one partial water site distributed evenly about their three possible orientations. The assignment of the anions as Cl^-, rather than F^-, is supported by the two unique intermolecular C−H···Cl contacts to the anion: C(7)−H(7)···Cl(20) = 2.9 Å and C(13) −H(13)···Cl(20) = 2.8 Å. These are close to the sum of the van der Waals radii of a H and a Cl atom (3.0 Å), but are 0.3–0.4 Å longer than the sum of the radii of H and F atoms (2.55 Å).[50] All crystallographically ordered non-H atoms were refined anisotropically. All H atoms were placed in calculated positions and refined using a riding model. H atoms bound to the partial water molecule were not included in the final refinement, but were used in the density calculation. The highest residual Fourier peak of 1.18 $e\,Å^{-3}$ lies on a general position near the disordered methylammonium residue.

The hexanuclear metallacrown in $[\mathbf{1}(\mathrm{gly})_2]{\cdot}2\,H_2O{\cdot}6\,CH_2Cl_2$ lies on the crystallographic $\bar{6}$ site $[^{1}/_{3},^{2}/_{3},^{1}/_{6}]$, so that the model only contains one unique copper ion and L^- ligand. The unique one-third glycine and water molecules lie near the C_3 axis $[^{1}/_{3},^{2}/_{3},z]$; the glycine molecule is further disordered over two different unique positions, as described below. The one unique dichloromethane site lies on a general position in the lattice. The disordered glycine molecule was modeled over two equally occupied orientations, labeled A and B. These two sites share a common ammonium N atom N(18) and carboxy C atom C(20), both of which lie on the C_3 axis $[^{1}/_{3},^{2}/_{3},z]$. The following restraints were applied to this group: C–N = 1.48(2), C–C = 1.52(2), C–O = 1.25(2) and 1,3-C···O = 2.38(2) Å. The unique *tert*-butyl group is also disordered over two sites, refined with a 0.75:0.235 occupancy ratio. The refined restraints C–C = 1.53(2) and 1,3-C···C = 2.50(2) Å were applied to this group. The solvent molecule was refined over four equally occupied sites, with the refined restraints C–Cl = 1.79(2) and Cl···Cl = 2.92(2) Å. All non-H atoms with occupancy >0.5, plus the ordered glycine and water atoms N18, C20 and O23, were refined anisotropically. All H atoms were placed in calculated positions and refined using a riding model. Two different sets of H atoms were placed on ammonium group N(18), positioned to be staggered against disordered C(19 A) and C(19B) respectively. H atoms bound to the water molecule were not included in the final refinement, but were used in the density calculation.

The structure of $[\mathbf{1}(\textsc{l}\text{-ala})_2]{\cdot}5\,H_2O{\cdot}3\,CH_2Cl_2$ was originally solved and refined in the acentric space group $P2_1$, to reflect the presence of optically pure L-alanine in the crystal (confirmed from its optical rotation, see above). A full solution was obtained in that space group, and contained a whole formula unit per asymmetric unit, with two ordered alanine molecules that were clearly of the L optical isomer. However, subsequent refinement led to a highly correlated model with fifteen non-positive-definite C and N atoms. The *ADSYMM* routine in *PLATON*[51] suggested transformation to $P2_1/c$, which was then carried out. Re-solution and refinement of the structure in that space group led to a significantly superior refinement, with an asymmetric unit containing half a formula unit in which the alanine molecule is disordered over equally occupied L- and (apparently) D-isomer sites. All of the crystal structures of **1** with different guest species, in this work and in ref. [13], adopt centric space groups with the metallacrown itself having crystallographic inversion symmetry. Since the chiral center of the alanine guest is buried within the metallacrown host, it should have no influence on the packing of the crystal. Therefore, we propose that the apparently centric symmetry of this chiral crystal is pseudo rather than real, determined by the packing of the metallacrown. The 50 % D-alanine present in the final model rather reflects a 50 % molecule of L-alanine reflected through the pseudo inversion center.

The asymmetric unit of the compound contains: half a complex molecule, lying on the crystallographic inversion center $[^{1}/_{2},^{1}/_{2},^{1}/_{2}]$; one alanine molecule on a general position; three peaks near the alanine carboxy group, 2.3–2.5 Å apart, that were refined as three molecules of water (two fully occupied, and half-occupied); one dichloromethane molecule on a general position, that is disordered over four equally occupied sites, and half a dichloromethane molecule near the C_2 axis $[0,1,^{1}/_{2}]$ that was modeled over three sites. The refined restraints C–Cl = 1.77(2) and Cl···Cl = 2.89(2) Å were applied to the disordered solvent molecules. Two of the three *tert*-butyl groups in the model are also disordered, over two sites with occupancy ratios close to 0.70:0.3. The refined restraints C–C = 1.54(2) and 1,3-C···C = 2.51(2) Å were applied to these groups. Finally, the asymmetric C atom and methyl group of the alanine molecule are also disordered over two equally occupied orientations (see above). Attempts to refine two different disorder sites for the carboxyl group (as in the $[\mathbf{1}(\mathrm{gly})_2]$ structure) were unsatisfactory, however, so this residue was left as ordered in the final analysis. This group was modeled by using the fixed restraints C–N = 1.48(1), C–C = 1.52(1) and 1,3-C···C = 2.48(2) Å. An antibumping restraint was also applied between alanine methyl group C(54 A) and the minor *tert*-butyl disorder site C(49B). All non-H atoms with occupancies >0.5, plus the disordered alanine atoms, were refined anisotropically, and all H atoms were placed in calculated positions and refined using a riding model. Two different sets of H atoms were placed on ammonium group N(52), positioned to be staggered against disordered C(53A) and C(53B). H atoms from the water molecules could not be reliably located in the Fourier map, and so were not included in the final refinement but are accounted for in the density calculation. The highest residual Fourier peak of $+1.02\,e\,\text{Å}^{-3}$ lies within one of the disordered *tert*butyl groups.

The complex molecule in $[\mathbf{1}(\beta\text{-ala})_2]{\cdot}2\,H_2O{\cdot}8\,CHCl_3$ lies across the inversion center $[^{1}/_{2},^{1}/_{2},^{1}/_{2}]$, so the asymmetric unit contains half a formula unit. The 3-aminopropionic acid, water, and four unique chloroform molecules all liie on general positions; three of the latter are disordered. Two of the three unique *tert*butyl groups in the model are also disordered, over two equally occupied sites. All disordered C–C bonds in these residues were restrained to 1.52(2) Å, and non-bonded C···C distances within each disordered group to 2.48(2) Å. All three disordered solvent molecules were refined over three sites, some of which shared a common C atom. The C–Cl bonds in these disordered residues were restrained to 1.77(2) Å, and Cl···Cl distances within each disordered group to 2.89(2) Å. All non-H atoms with occupancy = 0.5 were refined anisotropically, and all C- and N-bound H atoms were placed in calculated positions and refined by using a riding model. H atoms on the water molecule could not be located in the difference map and so were not incorporated into the final refinement, but were included in the density calculation. The highest residual Fourier peak of $+1.05\,e\,\text{Å}^{-3}$ lies within one of the disordered solvent molecules, while the Fourier hole at $-2.18\,e\,\text{Å}^{-3}$ is 0.9 Å from Cu(3).

The asymmetric unit of $[\mathbf{1}(H_3NC_6H_{12}NHCO_2)_2]{\cdot}1.6\,H_2O{\cdot}3.8\,CHCl_3$ contains half a complex molecule lying across the inversion center $[^{1}/_{2},^{1}/_{2},0]$; one molecule of 6-aminohexylcarbamic acid lies on a general position; two disordered chloroform sites and one more solvent site was modeled by using a mixture of partial chloroform and water molecules. One *tert*-butyl group in the model is disordered, and was modeled over two sites with occupancies of 0.7 and 0.3, sharing a common wholly occupied *ipso*-C atom. All disordered C–C bonds were restrained to 1.53(2) Å, and non-bonded C···C distances within each disordered group to 2.50(2) Å. The disordered chloroform molecules were refined using the restraints C–Cl = 1.76(2) and Cl···Cl = 2.87(2) Å. Large thermal ellipsoids on the 6-aminohexylcarbamic acid residue also suggested the presence of disorder, but this could not be modeled. In particular, no alternative disorder site for atoms C(56)-O(62) could be found in the Fourier map, even when the occupancy of those atoms was lowered. Therefore, the high U_{iso} values on these atoms may simply reflect a high degree of libration in this conformationally flexible residue. All wholly occupied non-H atoms, plus one partial chloroform molecule with occupancy >0.5, were refined anisotropically, and all H atoms were placed in calculated positions and refined by using a riding model. H atoms on the partial water molecules could not be located in the difference map and so were not incorporated into the final refinement, but were included in the density calculation. The highest residual Fourier peak of $+1.3\,e\,\text{Å}^{-3}$ occupies the inversion center at the center of the molecule.

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