FULL PAPER

Interactions between Copper(II) Complexes of Mono-, Bis-, and Tris(macrocyclic) Ligands and Inorganic or Organic Guests

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The copper(II)-assisted condensation of $[Cu(2,3,2\text{-tet})]^{2+}$ [2,3,2-tet = bis-N,N'-(2-aminoethyl)propane-1,3-diamine] with formaldehyde and melamine (melamine = 2,4,6-triamino-1,3,5-triazine) afforded melamine-based mono-, bis-, and tris(macrocyclic) ligand/copper(II) complexes in approx. 30% overall yield. Three different monocopper(II), one dicopper(II), and one tricopper(II) complex structures are reported, as well as two structures of host-guest assemblies of the tricopper(II) complex with benzene-1,3,5-tricarboxylate and one resulting from a reaction with hexacyanoferrate(II) to afford an octanuclear Cu_6Fe_2 complex. These structures are discussed together with those of five previously reported similar compounds, and it is concluded that the two conformations of the tricopper(II) complex are similar in energy and that they are easily interconverted. The range of the structural flexibility of the tricopper(II) host is analyzed on the basis of the experimental structural data. The formation of the Cu_6Fe_2 assembly is assumed to be a stepwise procedure, the formation of the structurally previously unknown $[Fe_2(CN)_{11}]^{7-}$ anion is assisted by the Cu_3 host cation, and the host-guest assembly is stable in solution.

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Introduction

Since the seminal work on the hexaamine cage ligands sepulchrate (sep)[1] and sarcophagine (sar) derivatives,[2,3] metal ion assisted Mannich-type condensations of primary amines with formaldehyde and amines or activated (acidic) alkanes have frequently been used to prepare open-chain, macrocyclic, and oligomacrocyclic ligands coordinated to various metal ions, primarily copper(II) and nickel(II).[4−14] Thanks to their rigidity, aromatic amines − and in particular the triamine melamine (melamine = 2,4,6-triamino-1,3,5-triazine) − are interesting candidates for "capping" groups in copper(II)-based template condensations. The poor acidity of the aniline-type amines in melamine is partially compensated by the presence of three azines, and we have established that the template reactions around copper(II) and nickel(II)[15] result in the desired products (see Scheme 1; similar results have also been published independently[16−18]).

Mono- and oligomacrocyclic ligands and their metal complexes have been used as hosts for organic and inorganic guest molecules.[19−24] Host-guest interactions range from π-stacking and van der Waals forces to hydrogen bonds and weak coordinative bonds. The last of these are interesting, specifically when labile sites such as the axial donors in Jahn−Teller active copper(II) complexes are involved, since the length and directionality of coordinative bonds allow the shape selectivity to be carefully tuned.[25] Examples of metal complex hosts include assemblies of tris[zinc(II)] compounds[26] and the stabilization of a reactive organic cation by a tetrahedral tetrakis[gallium(III)] complex host.[27] Here we present the syntheses of $[Cu(L^1)]^{2+}$, $[Cu_2(L^2)]^{4+}$, and $[Cu_3(L^3)]^{6+}$, together with structural studies of these complexes, as well as the structures of two host-guest complexes of $[Cu_3(L^3)]^{6+}$ with undecacyanodiferrate(II) and benzene-1,3,5-tricarboxylate.

Results and Discussion

Syntheses and Solution Properties of the Copper(II) Complexes

The reaction between $[Cu(2,3,2\text{-tet})]^{2+}$, formaldehyde, and melamine in the presence of base (triethylamine) resulted in the formation of a mixture of mono-, di-, and

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$[Cu(L^1)]^{2+}$

(1, 2, 3, 8, 9, 10, 11)

$[Cu_2(L^2)]^{4+}$

(4)

$[Cu_3(L^3)]^{6+}$

(5, 6, 7, 12)
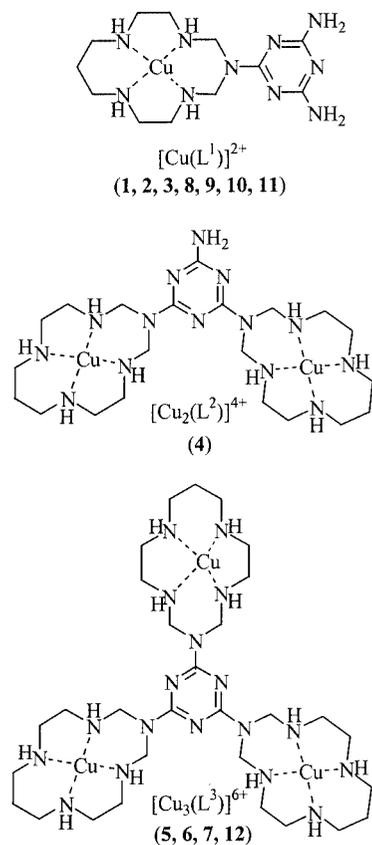
Scheme 1

trinuclear copper(II) compounds. Chromatographic separation yielded the pure copper(II) complexes of the mono-, bis- and tris(macrocyclic) melamine-based ligands: $[Cu(L^1)]^{2+}$, $[Cu_2(L^2)]^{4+}$ and $[Cu_3(L^3)]^{6+}$.

The infrared spectra of the three complexes were similar, and had features characteristic both of the melamine fragment and of the pentaazamacrocyclic ligand/copper(II) complexes. The number of bands corresponding to out-of-plane vibrations of the aromatic amino groups [$\delta(NH_2)$; 1660 cm^{-1} in crystalline melamine] were indicative of the nuclearity and the degree of protonation of the complexes: three bands (1690, 1640 and 1600 cm^{-1}) were observed in the protonated mono(macrocyclic) ligand complexes $[Cu(HL^1)](ClO_4)_3\cdot H_2O$ and $[Cu(HL^1)](Cl)(ClO_4)_2\cdot 0.5\ H_2O$, while two bands (1670 and 1600 cm^{-1}) were characteristic of the protonated bis(macrocyclic) ligand complex $[Cu_2(HL^2)](ClO_4)_5\cdot 3H_2O$. Only one band was present in the spectra of the nonprotonated complexes $[Cu(L^1)]$-$(ClO_4)_2\cdot H_2O$ (1600 cm^{-1}) and $[Cu_2(L^2)](ClO_4)_4\cdot 2.5H_2O$ (1610 cm^{-1}). As expected, tris(macrocyclic) ligand complexes showed no strong band in this spectral region.

The electronic absorption spectra of the three complexes were also similar, and consisted of three transitions. The band in the visible region at 515 nm was typical of the four unresolved d-d transitions of the tetragonal copper(II) chromophore in complexes with 14-membered tetraazamac-

rocyclic ligands with weakly coordinated axial donors.[25,28] This transition did not depend on the nuclearity of the complex, and the molar absorptivity was proportional to the number of macrocyclic subunits in the molecule (see Exp. Sect.). This also applied for the LMCT transition at 253 nm. These two observations indicated that there was no significant direct electronic interaction between the copper chromophores in the oligomacrocyclic species. However, the high-energy electronic transition at approx. 210 nm, assigned to an intramolecular transition of the triazine residue [λ_{max} = 204 nm (ε = 52000 L mol^{-1} cm^{-1}) in melamine] showed a moderate bathochromic shift and a hyperchromic effect in the series $[Cu(L^1)]^{2+}$, $[Cu_2(L^2)]^{4+}$, $[Cu_3(L^3)]^{6+}$. This indicates increasing perturbation of the electronic structure of the aromatic ring by the attached macrocyclic ligand copper(II) complexes. The EPR spectrum of the mononuclear complex $[Cu(L^1)]^{2+}$ was typical for a tetragonal copper(II) tetraamine, with $g_\parallel$ = 2.190, $g_\perp$ = 2.041, and A_{II} = 205 10^{-4} cm^{-1}. Dipole-dipole interactions between the isolated chromophores were observed in EPR spectra of the oligonuclear complexes.[29]

Electrochemical oxidation of $[Cu(L^1)]^{2+}$, $[Cu_2(L^2)]^{4+}$, and $[Cu_3(L^3)]^{6+}$, measured by cyclic voltammetry with a glassy carbon electrode in neutral aqueous solution, was an irreversible process in each case. In highly acidic media (9.0 mol L^{-1} HClO$_4$) the copper(III) oxidation state can be stabilized,[30] and it is possible to obtain single, ill-resolved redox transformations with E_f at approx. 1.15 V vs. Ag/AgCl for all species {under similar conditions we have obtained the value E_f = 0.910 V for the $[Cu(cyclam)]^{3+/2+}$ couple (cyclam = 1,4,8,11-tetraazacyclotetradecane)}. The difference of approx. 200 mV reflected the electron-withdrawing effect of the melamine fragment, destabilizing the copper(III) state. Apparently, the destabilizing electrostatic effect due to the protonation of the triazine nucleus in highly acidic media is less important; this was also observed for the analogous nickel complexes.[15] Similarly to the behavior in the anodic region, all three copper compounds showed poorly resolved quasi-reversible Cu$^{II/I}$ cathodic waves at approx. −0.9 V vs. a saturated calomel electrode {acetonitrile solution, 0.1 mol L^{-1} [(*n*Bu)$_4$N]ClO$_4$}.

Molecular and Crystal Structures of the Copper(II) Compounds

General Comments

Experimental solid-state structures of copper(II) complexes of mono-, di-, and trinucleating melamine-based ligands have been determined. They include the mono(macrocyclic) ligand complexes $[Cu(L^1)(OClO_3)_2]\cdot H_2O$ **(1)**, $[Cu(HL^1)(OClO_3)_2](ClO_4)\cdot H_2O$ **(2)**, and $\{[Cu(HL^1)$-$(OH_2)(Cl)][Cu(HL^1)(OClO_3)(Cl)]\}(ClO_4)_3$ **(3)**, the bis(macrocyclic) ligand complex $[Cu_2(L^2)(OClO_3)_4]\cdot H_2O\cdot CH_3OH$ **(4)**, and the tris(macrocyclic) ligand complex $[Cu_3(L^3)$-$(OH_2)_3](NO_3)_3(ClO_4)_3$ **(5)**. The structures of two host-guest complexes with $[Cu_3(L^3)]^{6+}$ − $\{[Cu_3(L^3)]_2[Fe_2$-$(CN)_{11}]\}(CN)(NO_3)_4\cdot 34H_2O$ **(6)** and $[Cu_3(L^3)(OH_2)_6]$-$(C_9H_3O_6)_2\cdot 40H_2O$ **(7)** ($C_9H_3O_6{}^{3-}$ = benzene-1,3,5-tri-

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carboxylate) − have also been determined. These structures are discussed together with those recently reported for [Cu(L¹)(OClO₃)₂]·H₂O **(8)**,[17] [Cu(L¹)(CA-H)-(OClO₃)]·H₂O **(9)** (CA-H = cyanurate),[17] [Cu(HL¹)-(OClO₃)](ClO₄)₂·2H₂O **(10)**,[16] [Cu(HL¹)(OClO₃)₂]-(BA-H)·3H₂O **(11)** (BA-H = barbiturate),[17] and [Cu₃(L³)(OH₂)₂(OClO₃)₄](ClO₄)₂·3H₂O **(12)**.[18]

The copper(II) ions in all structures reported here are coordinated to four nitrogen donors in the macrocycles, resulting in nearly planar CuN₄ chromophores (rms = 0.01−0.04 Å), with the copper(II) centers deviating from these planes only slightly (0.01−0.07 Å). The pentaaza macrocycles all have the expected *trans*-III (*RRSS*) configuration.[31] The metal−nitrogen distances (Table 1 and Supporting Information) fall in the range typical for copper(II) complexes with 14-membered tetraazamacrocyclic ligands.[32] Various coordination geometries are observed, including square-planar (4-coordinate, as in **10**), square-pyramidal (4 + 1, as in **6** and **9**), and square-bipyramidal [4 + 2, as in **4** and **7**; all interactions shorter than 3.0 Å are viewed as coordinative bonds, see Table 1].

The melamine rings in all complexes are nearly planar (rms = 0.00−0.02 Å). In view of the conjugation of the lone pairs of the melamine amino nitrogen atoms with the aromatic rings, the melamine residues were expected to be coplanar with the planes defined by the CNC fragments at the apexes of the substituted six-membered chelate rings

(angle α: see Figure 1 and Table 1). However, this was only observed for one macrocyclic unit in the tris(macrocyclic) ligand complex **5** (α = 0.3°); in all other cases there were various degrees of deviation from coplanarity (2° ≤ α ≤ 27°). Also, the melamine-substituted CNC fragment is generally slightly tilted and this results in nonorthogonality of the mean plane of the triazine rings and the planes bisecting the macrocycles along the long axes (angle β, see Figure 1 and Table 1). Because of the *chair* conformation of the substituted six-membered chelate rings and the close to sp² hybridization of the bridgehead nitrogen atoms, the melamine rings are bent relative to the mean CuN₄ planes (angle γ in Figure 1 and Table 1). Therefore, the oligomacrocyclic ligand complexes each exist in two major conformations, depending on the orientation of the macrocyclic rings relative to the aromatic spacer group: *syn* (two macrocyclic units on the same side) or *anti* (two macrocyclic units on opposite sides) isomers for the bis(macrocyclic) compounds, and *syn,syn* or *syn,anti* isomers for the tris(macrocyclic) ligand complexes.

The conformational freedom (*syn* and *anti*) and the variability of the structural parameters α, β, and γ result in a variety of shapes of the oligonuclear copper(II) complexes. The largest variation is due to the tilt angle γ, which ranges from 11 to 62° (see Table 1). This gives rise to appreciable variation in the intramolecular copper−copper distances

Table 1. Structural parameters of the copper(II) complexes of the melamine-based oligomacrocyclic ligands L¹, L², and L³

Complex	Intramolecular distances [Å]		Angles between the mean planes [°][a]				Orientation of the melamine rings	
	Cu−N (equatorial)	Cu−axial ligand(s)	Cu−Cu	α	β	γ	Angle [°]	Distance [Å]
1	2.015−2.025	2.458; 2.628 (OClO₃)	−	23.0	70.7	45.5	0	3.5
8[17]	2.009−2.026	2.511; 2.617 (OClO₃)	−	12.2	80.4	36.9	0	3.5
9[b] [17]	2.009−2.038	2.335[c]	−	16.4 18.7	80.0	51.3	−	−
	2.005−2.030	2.395;[c] 2.612 (OClO₃)			82.4	52.6		
2	2.013−2.029	2.585; 2.594 (OClO₃)	−	18.9	82.5	61.6	1.6	av.3.4
3[b]	2.011−2.028	2.718 (OH₂); 2.826 (Cl)	−	9.9	88.8	53.2	5.6	av. 3.6
	2.016−2.023	2.660 (Cl); 2.808 (OClO₃)		9.6	88.5	49.9		
10[b] [16]	2.008−2.019	2.521 (OH₂)	−	12.0	89.1	44.7	0	3.47
	2.006−2.052			12.4	86.4	46.7		
11[17]	1.999−2.041	2.457; 2.603 (OClO₃)	−	10.0	77.2	39.1	−	−
4	Cu(1) 2.009−2.035	2.461; 2.658 (OClO₃)	9.32	26.1	81.0	57.7	−	−
	Cu(2) 2.015−2.039	2.430; 2.614 (OClO₃)		19.3	79.1	43.5		
5	Cu(1) 1.996−2.017	2.405 (OH₂); 2.764 (OClO₃)	8.50 [Cu(1)−Cu(2)]	0.3	90.0	24.9	0	3.36
	Cu(2) 2.002−2.030	2.479 (OH₂)	7.99 [Cu(2)−Cu(2a)]	13.9	89.3	43.6		
6	Cu(1) 2.019−2.027	2.244 (NC)	7.72 [Cu(1)−Cu(2)]	4.0	86.9	25.4	5.0	av. 3.4
	Cu(2) 2.014−2.033	2.263 (NC)	8.22 [Cu(1)−Cu(3)]	16.8	80.8	53.2		
	Cu(3) 2.006−2.017	2.217 (NC)	7.66 [Cu(2)−Cu(3)]	12.0	90.0	49.7		
	Cu(4) 1.968−2.031	2.253 (NC)	7.99 [Cu(4)−Cu(5)]	6.8	87.5	27.7		
	Cu(5) 2.015−2.029	2.201 (NC)	7.51 [Cu(4)−Cu(6)]	10.4	84.8	50.6		
	Cu(6) 2.022−2.029	2.244 (NC)	7.77 [Cu(5)−Cu(6)]	11.6	88.9	52.5		
7	Cu(1) 2.005−2.024	2.454; 2.546 (OH₂)	10.05 [Cu(1)−Cu(2)]	15.4	84.6	10.7	2.5[d]	av. 3.4[d]
	Cu(2) 2.007−2.034	2.493; 2.512 (OH₂)	10.14 [Cu(1)−Cu(3)]	11.2	82.4	15.9	6.3[d]	av. 3.3[d]
	Cu(3) 2.007−2.032	2.416; 2.509 (OH₂)	9.66 [Cu(2)−Cu(3)]	4.2	81.5	21.3		
12[18]	1.982−2.023	2.654; 2.683 (OClO₃)	7.97; 9.36; 9.54	10.7	87.4	45.2	−	−
	2.002−2.034	2.425 (OH₂); 2.831 (OClO₃)		16.8	82.8	43.8		
	1.978−2.034	2.594 (OClO₃); 2.639 (OH₂)		2.3	88.9	34.0		

[a] For the definition of the angles see text and Figure 1. [b] Two independent molecules in the asymmetric unit. [c] Oxygen atom of cyanurate. [d] Melamine−carboxylate interactions.
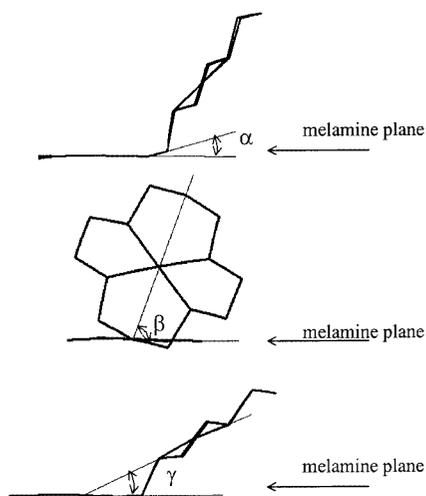
Figure 1. Definition of the geometric parameters of the melamine macrocycle fragments

and, for the trinuclear compounds, considerable plasticity of the cavities for anion binding.

Mono(macrocyclic) Ligand Complexes

Three new structures of copper(II) complexes of L^1 are reported here (for ORTEP plots[33] see Figure 2), while four have been published before;[16,17] structural parameters for these are also included in Table 1. In three of the structures (**1**, **8**, and **9**), copper(II) is coordinated to the parent ligand L^1, while in the other four (**2**, **3**, **10**, and **11**) the melamine fragment is protonated at the central nitrogen atom ([N(8) and N(18) in Figure 2b,c), and so copper(II) is coordinated to HL^1. In the published structures (**9** and **11**), specific supramolecular interactions of the melamine fragments with substrates (carboxylates) were discussed.[16,17]

The structural parameters of all complexes are very similar; the main variations are in the axial coordination and the angles α, β, and γ. The structures reported here are six-coordinate, with ClO_4^- (**1** and **2**) and H_2O, Cl^-, and ClO_4^- (**3**) as axial donors. The most pronounced variation of the angles describing the relative orientation of the macrocyclic and melamine planes is that of the angle γ (37–62°). There is no apparent correlation of these parameters with other features (e.g., the protonation of the ligand), as was also observed for the corresponding nickel(II) complexes.[15]

Crystal Packing of the Mono(macrocyclic) Ligand Complexes

A major structural motif observed in the crystal lattices of the mononuclear melamine-based macrocyclic ligand/copper(II) complexes is the presence of infinite ribbons of copper(II) macrocycles, connected by hydrogen bonds, involving water molecules (**1**, **2**, **8**, **10**) or perchlorate anions (**3**). With the nonprotonated melamine groups (**1**, **8**) double-stranded tapes are formed between the self-complementary melamine rings [acceptor-donor-acceptor (ADA) pattern]. Protonation of the aromatic nitrogen atom of the triazine fragment breaks the self-complementarity (AAA
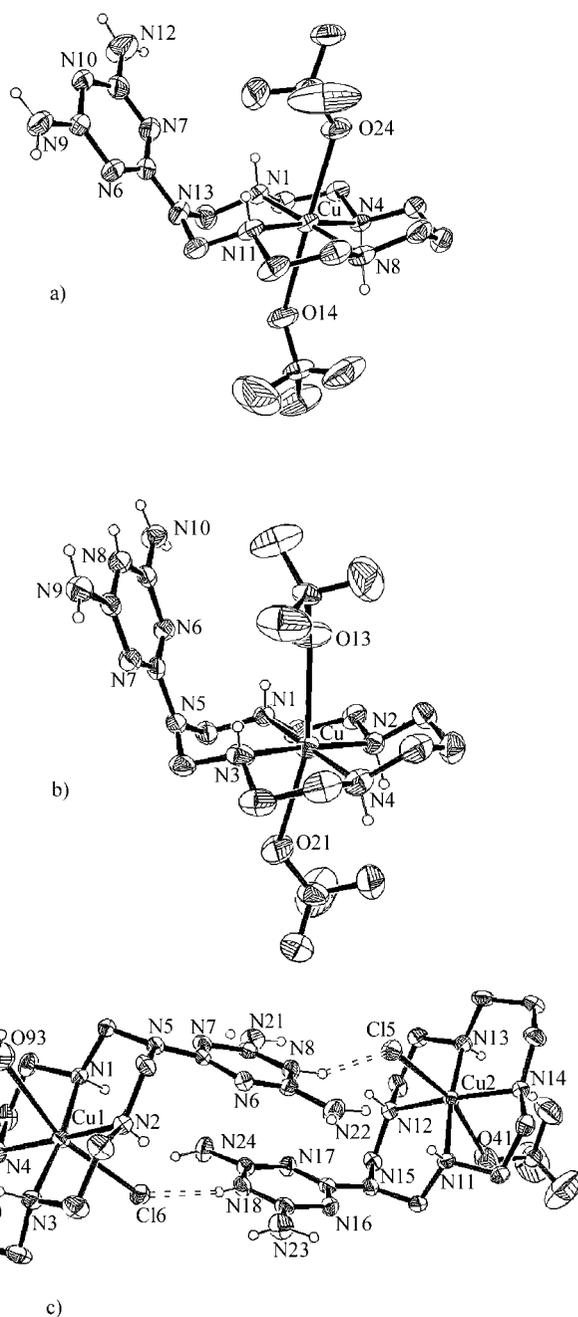
Figure 2. ORTEP[33] view (30% probability ellipsoids) of **1** (a), **2** (b), and **3** (c); C–H hydrogen atoms, lattice water molecules, and noncoordinated anions are omitted for clarity; selected distances and angles are shown in Table S1 (Supporting Information; see also footnote on the first page of this article)

pattern) and no double-stranded tapes are observed (**2**, **3**, **10**). Another common feature in the structures of the mono(macrocyclic) ligand complexes is an arrangement of the melamine rings that allows for π-stacking interactions; that is, the aromatic rings are nearly coplanar, with a distance of approx. 3.5.Å (Figure 3 and Table 1). An interesting variation in the structural motif of the π-stacked pairs within the hydrogen-bonded tapes is seen in **3** (see Figure 3, A- vs. B-type stacking for **1**, **2**, **8**, **10**, and **3**, respectively).
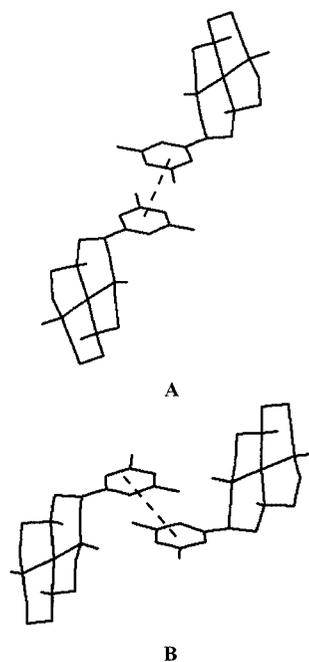
Figure 3. A- and B-type stacking in the lattices of the mono(macrocyclic) ligand complexes

Oligomacrocyclic Ligand Complexes

The bis(macrocyclic) ligand complex **4** crystallized as the *anti* isomer. Both copper(II) centers are six-coordinate (4 + 2, ClO_4^- donors, see Figure 4, Table 1 and Supporting Information) and the angle between the mean planes of the CuN_4 chromophores is 42.2°. Because of steric crowding there is no π-stacking of the melamine rings in the crystal lattice, but the aromatic rings of adjacent ligands are nearly coplanar.
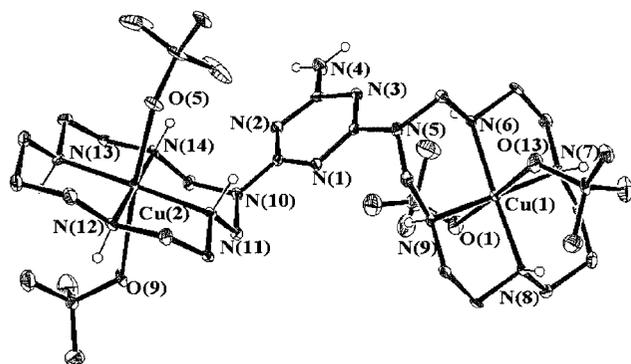
Figure 4. ORTEP[33] view (30% probability ellipsoids) of **4**; C–H hydrogen atoms and lattice solvent molecules are omitted for clarity; selected hydrogen bonds [Å]: Cl(5)···N(8) 3.072, Cl(6)···N(18) 3.099; selected distances and angles are shown in Table S2 (Supporting Information)

The three 14-membered rings of the tris(macrocyclic) ligand/copper(II) complex **5** are located on the same side of the melamine plane (*syn,syn* conformation), and the molecular cation looks like a flower with three petals (Figure 5a). This is a significant difference from the *syn,anti*

conformation of the previously reported $[Cu_3(L^3)]^{6+}$ structure **12**.[18] There is a symmetry plane in **5**, bisecting the molecular cation through C(2)Cu(1)N(3)C(11)N(4). The angles between CuN_4 mean planes in **5** are 58.8° for the Cu(1)−Cu(2) and 74.6° for the Cu(2)−Cu(2a) chromophores, respectively, significantly larger than in **4**, and this is primarily due to differences in γ (see Table 1).
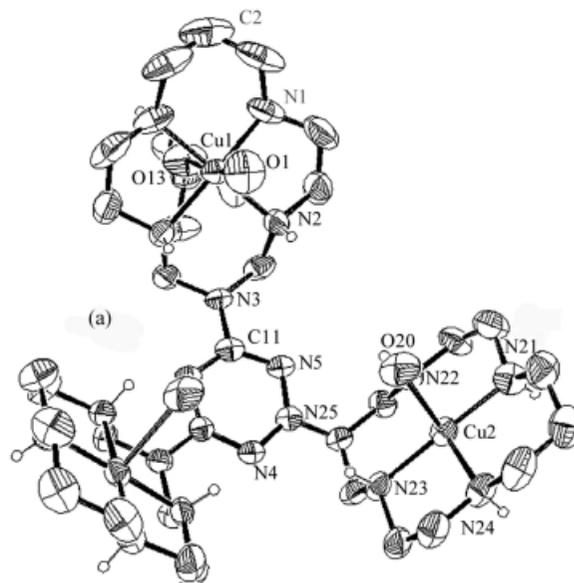
Figure 5. ORTEP[33] view (30% probability ellipsoids) of **5** (a) and its packing in the crystal lattice with the formation of the capsules (b); C–H hydrogen atoms, lattice water molecules, and anions are omitted for clarity; selected distances and angles are shown in Table S3 (Supporting Information)

In the crystal lattice, two concave "flowers" form an ellipsoidal "capsule", with the longest axis of approx. 15 Å (Figure 5b). The distance between parallel triazine rings in the capsule is 10.7 Å, and their centers are horizontally shifted by approx. 2.8 Å. Four disordered nitrate anions occupy the cavity of the capsule. Each of these forms hydro-

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gen bonds to coordinated water molecules and to secondary nitrogen atoms of the macrocyclic ligands. Apparently, this bonding of NO_3^- is to some extent responsible for the stabilization of the *syn,syn* conformation of $[Cu_3(L^3)]^{6+}$ in **5**. The remaining anions and water molecules are located outside the capsules and form a network of hydrogen bonds. Interestingly, there are no obvious attractive interactions between the two symmetrically related halves of the capsule. In the crystal lattice the capsules are packed in order to allow for π-stacking interactions between coplanar and co-axial melamine rings (Figure 5b and Table 1).

Host-Guest Complexes Based on the $[Cu_3(L^3)]^{6+}$ Cation

The tricopper(II) compound **5**, based on the tris(macrocyclic) ligand, is a rare example of a rigid, hemispherical, positively charged transition metal complex host molecule (see Introduction and corresponding refs.). The interactions with the NO_3^- guest anions are nonspecific, but the charge, size, and shape of **5**, and in particular the fact that six axial sites of copper(II) centers are available for interactions in the hexanuclear capsules (see Introduction) indicated that − in terms of size, shape, and charge − carefully chosen guest molecules should give rise to interesting host-guest interactions. Evaluation of the geometry of the cavity indicated that corner-shared bis(octahedral) complexes have an ideal size and structure for selective interactions with the host **5**. Also, the structural plasticity of **5** (see above and Table 1) allows for some variation of the size of the guest molecules. To evaluate these ideas, the host complex **5** was treated with hexacyanoferrate(II).

Treatment of **5** with $K_4Fe(CN)_6$ in warm water resulted in the formation, in high yield, of a precipitate with the composition $[Cu_3(L^3)][Fe(CN)_6](NO_3)_2 \cdot 17H_2O$. Structural analysis revealed the unique and unprecedented structure $\{[Cu_3(L^3)]_2[Fe_2(CN)_{11}]\}(CN)(NO_3)_4 \cdot 34H_2O$ (**6**). Figure 6a is a structural plot of the molecular cation, and Figure 6b shows the arrangement of the $[Cu_3(L^3)]_2^{12+}$ capsules with the coordinated decacyano(μ-cyano)diiron(II)(7−) anion in the crystal lattice. The cationic halves of the capsule in **6** are, as to be expected, kept together by six Fe−CN−Cu bridges. Each $[Cu_3(L^3)]^{6+}$ cation is bound by two CN bridges to one iron center and by one CN bridge to the other iron center. This results in a rather symmetrical octanuclear Cu_6Fe_2 cluster with Cu−Fe distances of 5.16 ± 0.04 Å (crystallographically all six macrocyclic fragments of the capsule are nonequivalent).

The copper centers in **6** are five-coordinate, with one apical cyanide each (Cu−NC distances of 2.20−2.26 Å; see Table 1 and Supporting Information). These axial copper(II)−donor distances are in the expected range,[34] although both shorter[35−38] and longer[39,40] bonds have been found in complexes with Fe^{II}−CN−Cu^{II} bridges. The relatively strong bonding of copper(II) to the axial ligands results in larger deviations of the atoms from the CuN_4 mean planes, as observed in the other copper(II) structures of L^1, L^2, and L^3 (rms = 0.08−0.09 Å), and in a significant shift of the copper centers towards the apical cyanide donors (0.15−0.21 Å). All CN bridges in **6** are bent
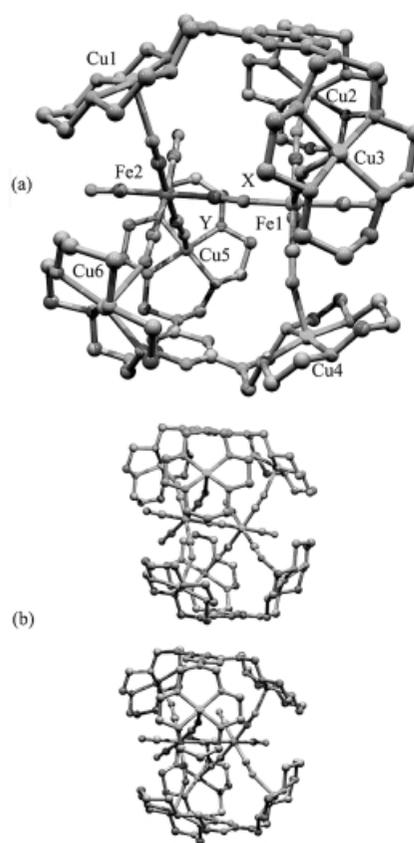
Figure 6. Structural plot of **6** (a) (X and Y = C or N) and its packing in the crystal lattice (b); hydrogen atoms, lattice water molecules, and anions are omitted for clarity; selected distances and angles are given as Supporting Information (Table S4)

(Cu−N−C in the range of 149−164°; see Supporting Information).

The coordination of the dinuclear anion inside the cavity does not give rise to large distortions of the host complex, and no changes in the conformation of the trinuclear cations are observed (see angles and intermetallic distances for **5** and **6** in Table 1). However, the distance of approx. 12.8 Å between the melamine rings in a capsule and a tilt of approx. 5.0° in **6** are significant changes in the shape of the cavity with respect to that in **5** (10.7 Å and 0°, respectively). Also, the relative orientation of the cationic halves is slightly different (rotation around the melamine−melamine axis). Therefore, as would be expected, there is considerable plasticity of the capsules, and this involves the angles α, β, and γ, as well as the relative orientation of the $[Cu_3(L^3)]^{6+}$ subunits and subtle changes in the copper(II) chromophores.

In the structural analysis, the decacyano(μ-cyano)diiron(II) core in **6** is unprecedented. The only other discrete polycyanodiiron anion that has been structurally characterized is pentacyanoiron(III)(μ-cyano)amminetetracyanoiron(III).[41,42] The main difference between the two structures is the degree of rotation of the iron chromophores around the NC−Fe−CN−Fe−CN axis. While the chromophores in the published diiron(III) structure are

practically eclipsed, there is a torsion of approx. 25° in the diiron(II) structure reported here. This is probably due more to the stereochemical demand of the cationic host than to the preferences of the decacyano(μ-cyano)diiron(II) anion. The coordination geometries of the iron(II) centers in undecacyanodiferrate(II) are nearly octahedral, with *cis*-C−Fe−C (or N) angles varying between 86 and 94° (see Supporting Information). The Fe−C distances (1.88−1.93 Å) are slightly shorter than those in other complexes (average of approx. 1.94 Å[34]). The relatively poor quality of the structure prevents a more detailed analysis. The remaining nitrate and cyanide anions in **6**, as well as the water molecules, are located outside the capsules and form an extended network of hydrogen bonds. As in **5** and the mononuclear complexes discussed above, there is a π-stacking interaction between the melamine rings of different capsules (Figure 6b and Table 1).

The inertness of hexacyanoferrate(II) suggests that $[Fe_2(CN)_{11}]^{7-}$ is assembled with assistance by the $[Cu_3(L^3)]^{6+}$ host, and the relatively strong (Fe−CN)−Cu bonds, together with the size and shape of the cavity of $[Cu_3(L^3)]_2^{12+}$, are assumed to be the driving force for the formation of the μ-cyano-bridged diiron(II) species. The previous observation of the *syn,anti* isomer of $[Cu_3(L^3)]^{6+}$ [18] and the species resulting from the reaction between **5** and benzene-1,3,5-tricarboxylate (see below) indicate that the *syn,syn* and *syn,anti* conformations of $[Cu_3(L^3)]^{6+}$ have similar energies and a low activation barrier for interconversion. Therefore, we do not assume that $[Fe_2(CN)_{11}]^{7-}$ is assembled inside the cavity of the host; the formation of **6**, rather, is assumed to be a stepwise process. Scheme 2 shows possible intermediates and reaction pathways for the formation of the Cu_6Fe_2 cluster (the plots are based on the observed structural parameters). The formation of oligonuclear cyanoferrate(II) species usually involves the reduction of the corresponding iron(III) compounds,[43,44] the reaction of aqua- or aminopentacyanoferrate(II) with hexacyanoferrate(II), or the photochemical labilization of cyanide ligands in $[Fe(CN)_6]^{4-}$.[45] Therefore, the host-guest complex **6** was assumed to be stable in solution.

The solution electronic and MS spectra supported this assumption. The electronic spectrum of **6** had the expected d-d transition at 547 nm (ε = 565 L mol⁻¹cm⁻¹, 94 L mol⁻¹cm⁻¹ per Cu^{II}), and the bathochromic shift of the absorption band relative to that in **5** is assumed to be due to the interactions with the axial CN donors. The absorption of $[Fe_2(CN)_{11}]^{7-}$ (λ = 385 nm[45]) was too weak to be observed, and was covered by the low-energy tail of intense charge-transfer transitions of the hexakis[copper(II)] capsule. Although the signal corresponding to the octanuclear unit was not detected in the ESI+ MS spectrum, there were several other sets of peaks that corresponded, on the basis of their isotopic pattern, to different polynuclear particles (see Figure 7 for examples). They can be assigned as follows: peaks of monocations with m/z = 1264.5 to {[Cu₃L³ Fe₂(CN)₁₁]¹⁻ − 2 H}⁺ (calcd. 1265.5), 1179.4 to {[Cu₃L³ Fe₂(CN)₇(H₂O)]³⁺ − 2 H⁺}⁺ (calcd. 1179.4), 1152.0 to {[Cu₃L Fe₂(CN)₆(H₂O)]⁴⁺ − 3 H⁺}⁺ (calcd. 1152.4),

{[Cu₃(L³)][Fe(CN)₆]}²⁺

{[Cu₃(L³)][Fe(CN)₆]₂}²⁻

{[Cu₃(L³)]₂[Fe(CN)₆]₂}⁴⁺

{[Cu₃(L³)][Fe₂(CN)₁₁]}⁻

{[Cu₃(L³)]₂[Fe₂(CN)₁₁]}⁵⁺
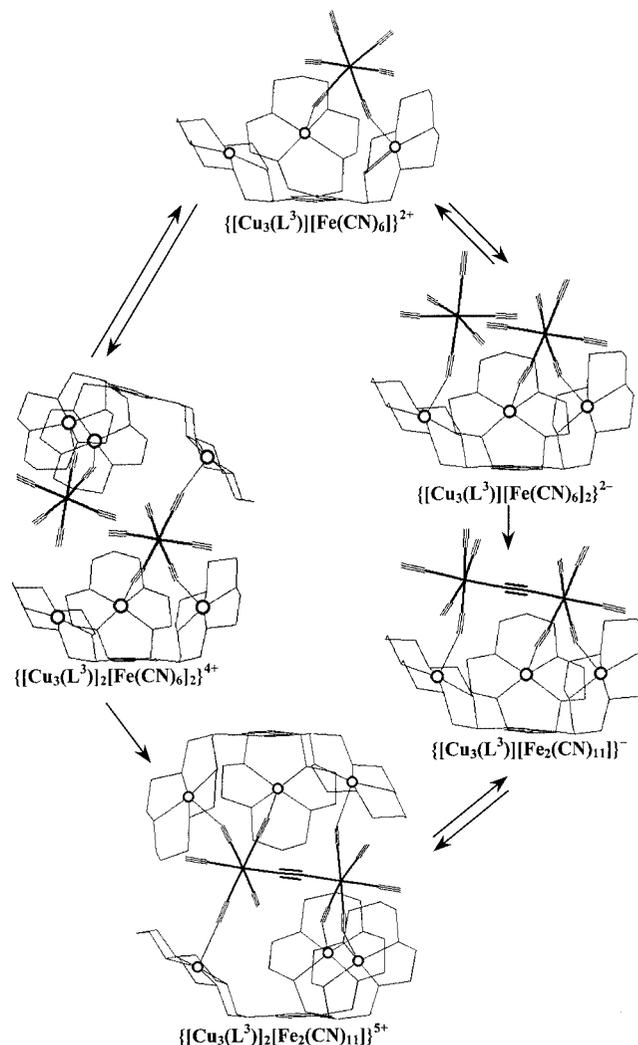
Scheme 2

1116.0 to {[Cu₃L Fe₂(CN)₄(H₂O)₂]⁶⁺ − 5 H⁺}⁺ (calcd. 1116.4); peak of a dication with m/z = 527.3 to {[Cu₃L³ Fe(CN)₅]³⁺ − H⁺}²⁺ (calcd. 1054.6). These data unequivocally confirmed the persistence in solution of the capsules observed in the solid state and indicated that the main pathway of fragmentation was the rupture of metal−cyanide bonds in **6**.

Benzene-1,3,5-tricarboxylate was chosen as an example for an organic host molecular anion. Molecular models indicated that the tricarboxylate $C_9H_3O_6^{3-}$ might be included in the capsule. However, the crystallographic data of $[Cu_3(L^3)(OH_2)_6](C_9H_3O_6)_2\cdot40H_2O$ (**7**) (see Figure 8) reveal that $[Cu_3(L^3)]^{6+}$ now exists in the *syn,anti* conformation, with two tricarboxylate substrates bound by hydrogen bonds to the axial water donors and π-stacked to the melamine ring (see Table 1). We assume that this assembly is just one of the various local minimum structures, and this example shows how difficult it is to predict structures of supramolecular assemblies. Preliminary selectivity studies with tricarboxylates and with *m*- and *p*-phthalate indicated that **5** is a highly regioselective host,[46] and thorough select-
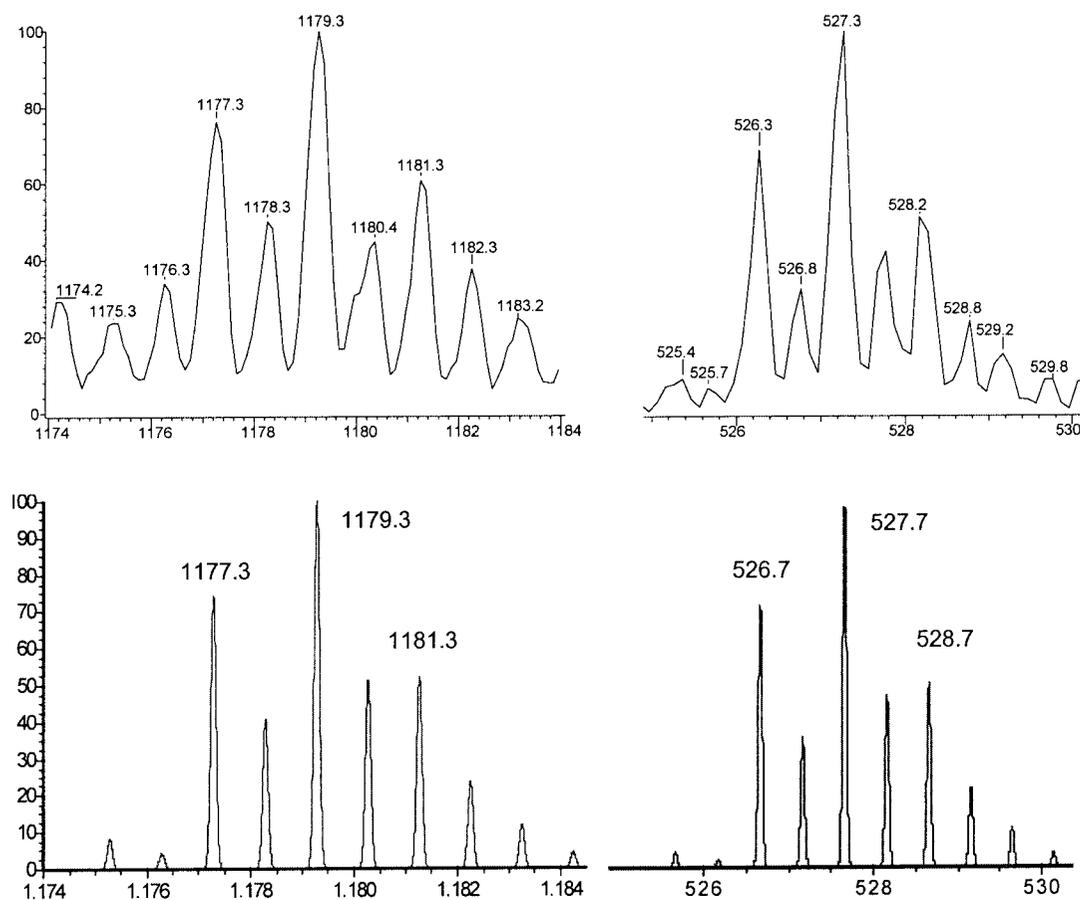
Figure 7. Fragments in the ESI MS of **6**: $\{[Cu_3L^3 Fe_2(CN)_7(H_2O)]^{3+} - 2 H^+\}^+$ (top left), $\{[Cu_3L^3 Fe(CN)_5]^{3+} - H^+\}^{2+}$ (top right); bottom: calculated spectra
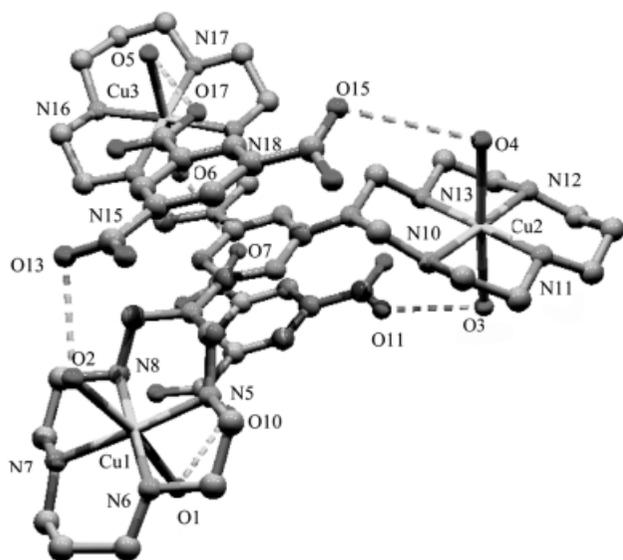
Figure 8. Structural plot of **7**; hydrogen atoms and lattice water molecules are omitted for clarity; selected H bonds [Å]: O(6)···O(7) 2.858(3), O(1)···O(10) 2.703(3), O(3)···O(11) 2.736(3), O(2)···O(13) 2.805(3), O(4)···O(15) 2.714(3), O(5)···O(17) 2.804(3); selected distances and angles are shown in Table S5 (Supporting Information)

ivity studies and their interpretation might help in understanding of the structural preferences.

The structure of **7** is also of importance to illustrate the conformational flexibility and plasticity of **5**, and it supports the assumption that **5** acts as a flexible host that allows guest molecules to assemble in multi-step procedures with the assistance of the host, which in favorable circumstances might finally encapsulate (i.e., protect and shield) the guest molecules, as in the case of **6**. An interesting structural feature in this context is a significant flattening of the tricopper(II) host in **7**, especially in comparison with the structure of **12** (see Table 1). This is particularly apparent from the Cu–Cu distances and the angles γ, which are much smaller in **7** than in any other structure (see Table 1). This indicates a rather tight binding of benzene-1,3,5-tricarboxylates to the $[Cu_3(L^3)]^{6+}$ cation and is further evidence for the plasticity of the host molecule.

Conclusion

The copper(II)-assisted synthesis of melamine-based macrocyclic ligands coordinated to copper(II) produced the expected three products in moderate yield (approx. 30%).

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The tris(macrocyclic) ligand complex (yield approx. 7%) exists in two major conformations, *syn,syn* and *syn,anti*, which are similar in stability. Structural studies indicated that the conformational equilibria may be influenced by host-guest interactions which may also influence the shape of each conformation of the tricopper(II) host through subtle structural changes. Preliminarily observed selectivities in host-guest complexation interactions, however, indicated that, although there is a certain structural plasticity of the melamine-based tricopper(II) host, deviation from the preferred geometry may result in a loss of steric energy. This also follows from the structural data of the entire set of copper(II) complexes.

The assembly of $[Fe_2(CN)_{11}]^{7-}$, assisted by the tricopper(II) host complex, and its full encapsulation is based on a combination of conformational flexibility of the host during the assembly procedure and a high degree of complementarity between the hexanuclear host and the dinuclear guest. The relatively strong and highly directional bonding of the guest to the axial copper(II) sites results an assembly that is stable in solution.

Experimental Section

Physical Methods: Infrared spectra (KBr pellets) were recorded with a Specord 75 IR (Carl Zeiss) spectrometer. Electronic absorption spectra were measured with a Specord M40 (Carl Zeiss) spectrophotometer. EPR spectra were recorded with a Bruker ESP300E spectrometer (9.4635 GHz) as approx. 1×10^{-3} mol dm^{-3} frozen (liquid nitrogen temperature) solutions in DMF/water (2:1). Triple-stage quadrupole mass spectra (ESI positive ion mode) were obtained with a Finnigan TSQ-700 mass spectrometer at 5.5 kV, 40 psi sheath gas and flow of liquid of 1.5 µL min^{-1}. Cyclic voltammograms were generated with a PI-50-1.1 potentiostat, equipped with a PR-8 function generator (Izmeritel, Gomel) and an N-307 X-Y recorder (ZIP, Krasnodar). A standard three-electrode scheme was used, consisting of a glassy carbon working electrode, a saturated calomel or Ag/AgCl reference electrode, and a Pt wire auxiliary electrode. All solutions for electrochemistry were purged with nitrogen before measurement. Analytical data were obtained from the microanalytical laboratory of the chemical institutes of the University of Heidelberg.

Structure Determinations: Reflections of representative crystals were measured with Siemens P4 (**1**, **2**, **3** and **5**) or Bruker AXS SMART 1000 (**4**, **6** and **7**) diffractometers with Mo-K_α radiation ($\lambda = 0.71073$ Å) and operating in the ω-scan mode. The absorption correction was applied in all cases. The structures were solved by direct methods (SHELXS86) and refined by full-matrix, least-squares methods based on F^2 (SHELXL97),[47] with use of anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms in **1**−**3** were placed in calculated positions; some disorder was observed for a water molecule and one of the perchlorate ions in **1**. Hydrogen atoms in **4** were also placed in calculated positions; only the hydrogen atoms at nitrogen atoms were located in a difference Fourier map and refined isotropically. Perchlorate anions are disordered. For **6**, one half of the capsule is disordered over two positions. Hydrogen atoms of the capsule were inserted in calculated positions. The anions and water molecules outside the capsule could not be located unambiguously and their hydrogen atoms were omitted. In **7**, only the hydrogen atoms of the molecular cat-

ion, the anions, and the coordinated water molecules were located and refined. The hydrogen atoms of the water clusters were located only partially, but not refined. Also, some water molecules in this part of the structure are probably disordered. The crystallographic data are given in Table 2. CCDC-171733 (**1**), -171702 (**2**), -171701 (**3**), -170075 (**4**), -134986 (**5**), -157762 (**6**), and -170076(**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Materials: AR grade chemicals and solvents were used as supplied for all reactions. [Cu(2,3,2-tet)](ClO$_4$)$_2$ [2,3,2-tet = bis-*N*,*N'*-(2-aminoethyl)propane-1,3-diamine] and [Cu(cyclam)](ClO$_4$)$_2$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) were prepared as described in the literature.[48]

Syntheses: *Caution!* Perchlorate salts of metal complexes are potentially explosive. Although we did not experience any problem, such complexes should be handled very carefully.

Template Synthesis: [Cu(2,3,2-tet)](ClO$_4$)$_2$ (2.0 g, 4.7 mmol), melamine (1.0 g, 7.9 mmol), and triethylamine (5 mL) were dissolved under reflux in 120 mL of a water/ethanol (1:5) mixture. Aqueous formaldehyde (37%, 8.0 mL) was added dropwise over 1 h, and the mixture was refluxed for an additional 24 h and then cooled, filtered, and sorbed onto an SP-Sephadex C-25 cation exchange column (Na$^+$ form). The column was washed with water (1 L), and the macrocyclic products were eluted with aqueous solutions containing different concentrations of NaClO$_4$ or NaNO$_3$. The mono(macrocyclic) ligand complex [Cu(L^1)]$^{2+}$ was eluted with 0.2 mol L^{-1} NaClO$_4$ as the second band, after unchanged [Cu(2,3,2-tet)]$^{2+}$. For [Cu(L^1)(OClO$_3$)$_2$]·H$_2$O (**1**), the eluate was concentrated to 25 mL and cooled to room temperature. The purple precipitate of **1** was filtered off, washed with ethanol, and dried in air (yield 0.25 g, 9%). C$_{12}$H$_{28}$Cl$_2$CuN$_{10}$O$_9$ (590.87): calcd. C 24.39, H 4.78, N 23.71; found C 24.15, H 4.63, N 23.66. Electronic absorption spectrum (H$_2$O, 0.1 mol L^{-1} NaNO$_3$): λ_{max} (ε [L mol^{-1} cm^{-1}]) = 515 (87), 253 (8500), 209 nm (51000). Crystals of **1** suitable for X-ray analysis were grown by slow cooling of its basic (pH ≈ 10) aqueous solution, in the presence of NaClO$_4$. [Cu(HL^1)(OClO$_3$)$_2$](ClO$_4$)·H$_2$O (**2**) and {[Cu(HL^1)(OH$_2$)(Cl)]-[Cu(HL^1)(OClO$_3$)(Cl)]}(ClO$_4$)$_3$ (**3**) were obtained by recrystallization of **1** from 0.1 mol L^{-1} HClO$_4$ or HCl, respectively. The yields were nearly quantitative. **2**: C$_{12}$H$_{29}$Cl$_3$CuN$_{10}$O$_{13}$ (691.33): calcd. C 20.85, H 4.23, N 20.26; found C 20.86, H 4.42, N 20.00. **3**: C$_{12}$H$_{29}$N$_{10}$Cl$_3$CuO$_{8.5}$ (619.33): calcd. C 23.31, H 4.56, N 22.65; found C 23.35, H 4.94, N 22.75. The electronic spectra of both complexes in aqueous solution were identical to that of **1**. Crystals suitable for X-ray analysis were selected from precipitates formed after reaction. The bis(macrocyclic) ligand copper(II) complex [Cu$_2$(L^2)]$^{4+}$ was eluted with 0.4 mol L^{-1} NaClO$_4$. Cooling of concentrated (approx. 25 mL) eluate resulted in a purple precipitate with the stoichiometry [Cu$_2$(L^2)](ClO$_4$)$_4$·2.5H$_2$O. This was collected on a filter, washed with aqueous NaClO$_4$ (0.6 mol L^{-1}) and then ethanol, and dried in air (yield 0.34 g, 13%). C$_{21}$H$_{51}$Cl$_4$Cu$_2$N$_{14}$O$_{18.5}$ (1064.63): calcd. C 23.69, H 4.83, N 18.42; found C 23.91, H 4.74, N 18.24. An additional crop of [Cu$_2$(L^2)]$^{4+}$ in the form of the protonated ligand complex [Cu$_2$(HL^2)](ClO$_4$)$_5$·3H$_2$O (up to 0.02 g) was obtained upon acidification of the filtrate with HClO$_4$ to pH ≈ 1. C$_{21}$H$_{53}$Cl$_5$Cu$_2$N$_{14}$O$_{23}$ (1174.09): calcd. C 21.48, H 4.55, N 16.70; found C 21.42, H 4.42, N 16.51. The electronic absorption spectra of the two complexes were identical (H$_2$O, 0.1 mol L^{-1} NaNO$_3$): λ_{max} (ε [L mol^{-1} cm^{-1}]) = 515 (176), 253 (16500), 213 nm (57600).

Table 2. Crystallographic data for the copper(II) complexes of the melamine-based ligands L^1, L^2 and L^3

	1	2	3	4	5	6	7
Empirical formula	$C_{12}H_{28}N_{10}$- Cl_2CuO_9	$C_{12}H_{29}$- $Cl_3CuN_{10}O_{13}$	$C_{24}H_{56}$- $Cl_6Cu_2N_{20}O_{17}$	$C_{22}H_{52}$- $Cl_4Cu_2N_{14}O_{18}$	$C_{30}H_{72}$- $Cl_3Cu_3N_{21}O_{24}$	$C_{70}H_{215}$- $Cu_6Fe_2N_{52}O_{46}$	$C_{48}H_{162}$- $Cu_3N_{18}O_{57}$
Formula mass	590.88	691.34	1236.64	1069.66	1408.02	3014.88	2094.58
Crystal system	triclinic	triclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$C2/m$	$P\bar{1}$	$P2_1/n$
a [Å]	8.225(1)	8.5253(17)	9.674(4)	8.3734(9)	15.970(3)	16.262(3)	15.603(1)
b [Å]	8.726(1)	8.6380(14)	38.42(2)	16.376(2)	25.576(5)	17.534(3)	33.792(2)
c [Å]	17.851(2)	19.654(3)	12.748(4)	29.259(3)	14.599(2)	26.257(7)	19.671(1)
α [°]	78.99(1)	78.509(11)	90.00	90.00	90.00	80.17(2)	90.00
β [°]	77.92(1)	89.896(13)	91.44(3)	97.383(2)	101.65(1)	74.29(2)	100.865(1)
γ [°]	68.46(1)	67.841(12)	90.00	90.00	90.00	67.61(2)	90.00
V [Å^3]	1156.1(2)	1309.3(4)	4737(4)	3978.7(8)	5840.30(18)	6645(2)	10186
Z	2	2	4	4	4	2	4
T [°C]	293	293	293	-100	293	-83	-100
D [g cm^{-3}]	1.697	1.754	1.728	1.786	1.601	1.51	1.37
Refl., meas./ unique	4808/4487	4910/4576	11062/10552	31441/8106	5279/5084	45394/13836	67391/24571
$R1$ [$I > 2\sigma(I)$]	0.052	0.072	0.071	0.084	0.081	0.115	0.056
$wR2$ (all)	0.149	0.212	0.218	0.217	0.209	0.380	0.167
GOF	1.035	1.042	1.040	1.163	1.016	1.047	1.025

X-ray quality crystals of $[Cu_2(L^2)(OClO_3)_4]\cdot H_2O\cdot CH_3OH$ (**4**) were grown by vapor diffusion of diethyl ether in a methanol/water (2:1) solution of $[Cu_2(L^2)](ClO_4)_4\cdot 2.5H_2O$. The tris(macrocyclic) ligand complex $[Cu_3(L^3)]^{6+}$ was eluted with 0.8 mol L^{-1} NaNO$_3$. $[Cu_3$-$(L^3)(OH_2)_3](NO_3)_3(ClO_4)_3$ (**5**) precipitated on concentration of the eluate to 25 mL, followed by the addition of 0.5 g of NaClO$_4$ (yield 0.15 g, 7%). **5**: $C_{30}H_{72}Cl_3Cu_3N_{21}O_{24}$ (1217.39): calcd. C 25.59, H 5.15, N 20.89; found C 25.82, H 5.20, N 21.11. Electronic absorption spectrum (H$_2$O, 0.1 mol L^{-1} NaNO$_3$): λ_{max} (ε [L mol^{-1} cm^{-1}]) = 515 (260), 253 (24400), 214 nm (87000). Purple crystals of **5** suitable for X-ray analysis were grown by slow cooling of an NaNO$_3$-saturated aqueous solution containing 10% of NaClO$_4$. Other salts of the tris(macrocyclic) ligand complex were also obtained. $[Cu_3(L^3)](ClO_4)_6\cdot 4H_2O$ was precipitated from an aqueous solution of **5** by addition of NaClO$_4$. The yield was nearly quantitative. $C_{30}H_{74}Cl_6Cu_3N_{18}O_{28}$ (1538.11): calcd. C 23.42, H 4.85, N 16.39; found C 23.28, H 4.98, N 16.68. Concentration of the initial eluate until the beginning of the precipitation of NaNO$_3$ yielded a purple compound, which was filtered, washed with small quantities of ice-cold water and ethanol, and dried in air (yield 0.03 g, 0.1%). According to its microanalytical data, the stoichiometry of the complex is $[Cu_3(L^3)](NO_3)_6\cdot 6H_2O$. $C_{30}H_{78}Cu_3N_{24}O_{24}$ (1349.47): calcd. C 26.70, H 5.82, N 24.91; found C 26.87, H 5.70, N 24.83. The absorption spectra of the two derivatives in aqueous solution were identical to that of **5**. The host-guest complex $\{[Cu_3(L^3)]_2[Fe_2(CN)_{11}]\}(CN)(NO_3)_4\cdot 34H_2O$ (**6**) was obtained by addition of an aqueous solution (5 mL) of $K_4[Fe(CN)_6]\cdot 3H_2O$ (0.0055 g, 0.013 mmol) to a hot aqueous solution (10 mL, 1 mol L^{-1} NaNO$_3$) of **5** (0.018 g, 0.013 mmol). The mixture was cooled very slowly. After several days, dark violet crystals were collected, washed with a small amount of ice-cold water and ethanol, and dried in air (yield 0.014 g, 72%). $C_{72}H_{200}Cu_6Fe_2N_{52}O_{46}$ (3023.13): calcd. C 28.60, H 6.67, N 24.09; found C 28.56, H 6.44, N 23.99. The CN stretching vibrations were observed as a single broad and intensive band, centered at 2032 cm^{-1}. Violet single crystals of **6** suitable for X-ray analysis were selected from the precipitate. The complex $[Cu_3(L^3)(OH_2)_6](C_9H_3O_6)_2\cdot 40H_2O$ (**7**) was prepared by addition of $C_6H_3(COONa)_3$ (0.01 g, 0.04 mmol) to a solution of $[Cu_3(L^3)](NO_3)_6\cdot 6H_2O$ (0.05 g, 0.04 mmol) in hot water (3 mL).

The mixture was placed in a Dewar vessel filled with hot water and allowed to cool very slowly. Purple needles formed over a few days and were collected on a filter; single crystals suitable for X-ray analysis were then selected. The remaining crystals were washed with a small amount of ice-cold water, and dried in air, producing a purple powder (yield 0.026 g, 92% based on the carboxylate salt). According to its microanalytical data, the composition of the complex is $[Cu_3(L^3)](C_9H_3O_6)_2\cdot 15H_2O$: $C_{48}H_{99}Cu_3N_{18}O_{27}$ (1550.65): calcd. C 37.17, H 6.43, N 16.25; found C 37.10, 6.61, N 16.09.

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