

# Metal-Directed Formation of Tetra-, Hexa-, Octa-, and Nonanuclear Complexes of Magnesium, Calcium, Manganese, Copper, and Cadmium\*\*

Rolf W. Saalfrank,\* Norbert Löw, Bernhard Demleitner, Dietmar Stalke, and Markus Teichert

Dedicated to Professor Achim Müller on the occasion of his 60th birthday

**Abstract:** Reactions of bis-1,3-dicarbonyl compounds  $H_2L$  (**1**) with metal dichlorides of cadmium, manganese and calcium in the presence of aqueous ammonia affords octanuclear supramolecular coordination complexes  $[M_8L_8] \cdot 4Y$  (**2–5**), whereas reaction with magnesium dichloride yields an adamantanoid tetranuclear cluster  $[(4NH_4) \cap (Mg_4L_6^a)]$  (**6**). Treatment of

copper dichloride with diethyl ketipinate **1a** and sodium hydroxide furnishes the double-/triple-decker metalla-coronates  $[[[Na \cap (Cu_3L_3^a)BF_4] \cdot THF \cdot H_2O]_2]$  (**7**) and  $[[Na \cap (Cu_3L_3^a)BF_4]_3 \cdot$

$2THF]$  (**8**) with an encapsulated sodium ion. Since the  $^1H$  and  $^{13}C$  NMR spectra of diamagnetic **2** and **5** and paramagnetic **4**, **7** and **8** do not unambiguously establish the exact structure of these compounds, exemplary X-ray diffraction analyses of **4**, **7** and **8** were carried out.

**Keywords:** metal(II) compounds · metallacycles · self-assembly · structure elucidation · tetraketones

## Introduction

There is considerable interest in the design of metallo-supramolecular oligomers that contain a defined number of metal ions in determined spatial arrangements. Therefore metal-directed multicomponent self-assembly is currently attracting great attention as a strategy for the synthesis of polynuclear metal complexes, in order to develop new materials with novel properties and structural features.<sup>[1]</sup> Over the last few years we have devised and described a versatile procedure for the synthesis of numerous bis-,<sup>[2]</sup> tris-,<sup>[3]</sup> tetra-,<sup>[4]</sup> hexa-<sup>[5]</sup> and octanuclear<sup>[5, 6]</sup> chelate complexes. The metal-directed self-assembly of polydentate ligands with transition metal ions leads to metalla-crown ethers,<sup>[7]</sup> which are topological analogues of crown ethers.<sup>[8]</sup> Based on the cavity size of the metalla-crown ethers and the radii of the ions to be encapsulated, they display cation-binding selectivities

similar to those known for the classical crown ethers. The readiness of metalla-crown ethers of copper(II) and dialkyl-ketipinate dianions to *coronate* is highlighted in the formation of metalla-coronates<sup>[9]</sup> and metalla-crown ether sandwich complexes.<sup>[9, 10]</sup> A few of our notable advances in this area are detailed below. Herein we describe a convenient procedure for the synthesis of dialkyl ketipinates and tetraketones  $H_2L$  **1**,<sup>[11]</sup> and we also outline the potential of  $L^{2-}$  as tetradentate binucleating ligands for various metal(II) ions; this leads to octanuclear complexes  $[M_8L_8] \cdot 4Y$  (**2–5**), tetrahemispheraplex  $[(4NH_4) \cap (Mg_4L_6^a)]$  (**6**), and double/triple-decker metalla-coronates  $[[[Na \cap (Cu_3L_3^a)BF_4] \cdot THF \cdot H_2O]_2]$  (**7**) and  $[[Na \cap (Cu_3L_3^a)BF_4]_3 \cdot 2THF]$  (**8**).

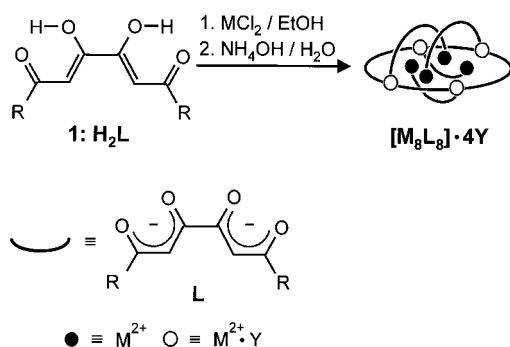
## Results and Discussion

Claisen condensation of alkyl acetates or methyl ketones with dialkyl oxalates followed by acidic workup yields the ketipinates and tetraketones  $H_2L$  **1**.<sup>[11]</sup> Reaction of **1** with cadmium or manganese dichloride in methanol in the presence of aqueous ammonia affords the octanuclear complexes  $[M_8L_8] \cdot 4H_2O$  **2** and **3** ( $M = Cd, Mn$ ) (Scheme 1). The cadmium complexes **2** were obtained as yellow microcrystals, the manganese complexes **3** as orange ones. The  $^1H$  and  $^{13}C$  NMR spectra of the diamagnetic cadmium compounds **2** ( $S_4$  symmetry, e.g., **2c**: nine  $^1H$  and twenty  $^{13}C$  NMR signals)<sup>[12]</sup> indicate that in each case four ligands in these complexes are identical and the two halves of each ligand have to be in

[\*] Prof. Dr. R. W. Saalfrank, Dr. N. Löw, Dipl.-Chem. B. Demleitner  
Institut für Organische Chemie der Universität Erlangen-Nürnberg  
Henkestrasse 42, D-91054 Erlangen (Germany)  
Fax: (+49)9131-85-1165  
E-mail: saalfrank@organik.uni-erlangen.de

Prof. Dr. D. Stalke  
Institut für Anorganische Chemie der Universität Würzburg  
D-97074 Würzburg (Germany)  
Dipl.-Chem. M. Teichert  
Institut für Anorganische Chemie der Universität Göttingen  
D-37077 Göttingen (Germany)

[\*\*] Chelate Complexes, Part 12. Part 11, see ref. [16]



Scheme 1. Reaction scheme for the formation of  $[M_8L_8] \cdot 4Y$ : **1a–e**: R = OEt, OtBu, Me, C<sub>6</sub>H<sub>5</sub>, C<sub>7</sub>H<sub>7</sub>; **2a–e**: M = Cd<sup>2+</sup>, Y = H<sub>2</sub>O, R = OEt, OtBu, Me, C<sub>6</sub>H<sub>5</sub>, C<sub>7</sub>H<sub>7</sub>, respectively; **3a–e**: M = Mn<sup>2+</sup>, Y = H<sub>2</sub>O, R = OEt, OtBu, Me, C<sub>6</sub>H<sub>5</sub>, C<sub>7</sub>H<sub>7</sub>, respectively; **4**: M = Mn<sup>2+</sup>, Y = HOPr, R = OEt; **5a–c**: M = Ca<sup>2+</sup>, R = OEt, Y = HOEt, HOiPr, HOtBu, respectively.

different magnetic environments. For unambiguous characterisation of the molecular structure of these octanuclear metal chelates, we tried to grow single crystals suitable for X-ray analysis. This proved to be extremely difficult, but we were successful in crystallising the manganese complex  $[Mn_8L_8] \cdot 4H_2O$  (**3a**) from hot propanol. This leads to complete exchange of the coordinated water molecules by propanol and the formation of dark yellow single crystals of **4** suitable for X-ray analysis. The results show that **4** exists in the crystal as an octanuclear manganese(II) chelate complex  $[Mn_8L_8] \cdot 4HOPr$  with four coordinated propanol molecules (Figure 1). Each of the eight manganese ions form the corners of one of two squares of different sizes, but with the same centre. The smaller square is turned 45° relative to the larger one. The four outer manganese ions are linked in a  $\mu_1$  fashion through the two ester carbonyl oxygen atoms of a set of four ketipinic acid diester dianions ( $\bar{d}_{Mn-O} = 220.1$  pm), which lie almost in a plane ( $E^1$ ). The two keto oxygen atoms of these four ligands are  $\mu_2$ -bound and bridge inner and outer manganese ions. Furthermore, a propanol molecule is coordinated to each of the four outer manganese ions ( $\bar{d}_{Mn-O} = 224.4$  pm) alternately above and below  $E^1$ . In two sets of parallel planes above and below  $E^1$  and perpendicular to it lie four ligands, which are

shifted in pairs relative to each other such that  $[(E^2 || E^3) \perp (E^4 || E^5)]$ . These four ketipinic acid diester dianions are each bound in a  $\mu_1$  fashion through the ester-carbonyl oxygen atoms to one outer and one inner manganese ion ( $\bar{d}_{Mn-O} = 228.7$  pm). One of the keto oxygen atoms forms a  $\mu_2$  bridge between two inner manganese ions, and the other forms a  $\mu_3$  bridge to two inner and an outer manganese ion. Thus all eight manganese ions are sevenfold coordinated.

Deprotonation of diethyl ketipinate  $H_2L^a$  **1a** with aqueous ammonia in ethanol in the presence of calcium chloride furnishes the octanuclear calcium chelate  $[Ca_8L_8] \cdot 4HOEt$  (**5a**), which is isostructural to the cadmium and manganese complexes mentioned above. The coordinated ethanol in **5a** is exchanged on crystallisation from hot alcohols to give  $[Ca_8L_8] \cdot 4Y$  (**5b** and **5c**; Y = HOiPr, HOtBu, respectively), the formation of which can be easily monitored by NMR spectroscopy. The <sup>1</sup>H NMR spectrum of **5b** exhibits a quadruple set of peaks indicating two different groups of ketipinic acid diethylester dianion ligands, with the two halves of each ligand in a different magnetic environment. Thus four singlets at  $\delta = 5.05, 5.11, 5.21$  and  $5.35$  are recorded for the sixteen chelate CH groups. In addition, the coordinated isopropanol accounts for peaks at  $\delta = 1.02$  (d, CH<sub>3</sub>),  $1.80$  (d, -OH) and  $3.86$  (sept, CH).<sup>[12]</sup>

Tetranuclear adamantanoid chelate complexes are formed in a one-pot reaction from dimethyl malonate, methyl lithium, metal(II) chlorides and oxalylchloride at  $-78^\circ C$  in tetrahydrofuran (THF) and subsequent workup with aqueous ammonium chloride.<sup>[4]</sup> However, this methodology does not work in the case of ethyl acetate and oxalylchloride. Instead, double deprotonation of free  $H_2L^a$  (**1a**) with methyl lithium at  $-78^\circ C$  in THF and addition of magnesium chloride, followed by workup with aqueous ammonium chloride, furnishes the tetrahemispheraplex  $[(4NH_4) \cap (Mg_4L_8^a)]$  (**6**, Scheme 2). Evidence for the formation of complex **6** stems from an intense peak at  $m/z = 1537$  in the FAB-MS spectrum (FAB = fast atom bombardment). This hypothesis is confirmed by the <sup>13</sup>C NMR spectrum of **6**,<sup>[12]</sup> which is almost superimposable with the spectra of similar magnesium complexes previously synthesized in our laboratory.<sup>[4]</sup> Compound **6** is not a salt in the usual sense, but a tetrahemispheraplex. This is confirmed by X-ray crystal structures of analogous complexes and by the downfield shift of the ammonium protons in the <sup>1</sup>H NMR spectrum of **6**. On each face of the imaginary tetrahedron constituted by the four magnesium ions, three oxygen atoms are in ideal positions to bind an ammonium ion through three hydrogen bonds.<sup>[6]</sup>

Recently we pointed out the structural analogy between the classical crown ethers, cryptands, spherands and their inclusion complexes, and the class of topologically analogous metalla-crown ethers (MC),<sup>[9,10]</sup> metalla-cryptands,<sup>[12]</sup> and metalla-spherands<sup>[4]</sup> and their inclusion compounds. If one applies the knowledge about crown ethers to the chemistry of metalla-crown ethers, then the complexation of different sized cations by metalla-crown ethers should lead to metalla-coronates of different structures. Since the ionic radii of alkaline and alkaline earth metal cations differ remarkably in size, whereas the diameter of a given metalla-crown ether essentially remains the same, the inclusion of small cations

**Abstract in German:** Die Umsetzung von Bis-1,3-dicarbonylverbindungen  $H_2L$  **1** mit Cadmium-, Mangan- und Calciumdichlorid liefert in Gegenwart von Ammoniakwasser acht-kernige supramolekulare Komplexe  $[M_8L_8] \cdot 4Y$  (**2–5**), während man mit Magnesiumdichlorid den adamantanoiden Cluster  $[(4NH_4) \cap (Mg_4L_8^a)]$  (**6**) erhält. Im Gegensatz dazu entstehen bei der Umsetzung von Kupferdichlorid mit Ketipinsäurediethylester **1a** und Natriumhydroxid die Doppel-/Tripeldecker metalla-Coronate  $[[Na \cap (Cu_3L_3^a)BF_4] \cdot THF \cdot H_2O]_2$  (**7**) und  $[[Na \cap (Cu_3L_3^a)BF_4]_3 \cdot 2THF]$  (**8**) mit eingeschlossenem Natriumion. Da die exakten Strukturen der diamagnetischen Komplexe **2** und **5** bzw. der paramagnetischen Komplexe **4**, **7** und **8** durch <sup>1</sup>H- und <sup>13</sup>C-NMR Spektroskopie nicht eindeutig zu lösen waren, wurden exemplarisch von **4**, **7** und **8** röntgenographische Kristallstrukturanalysen angefertigt.

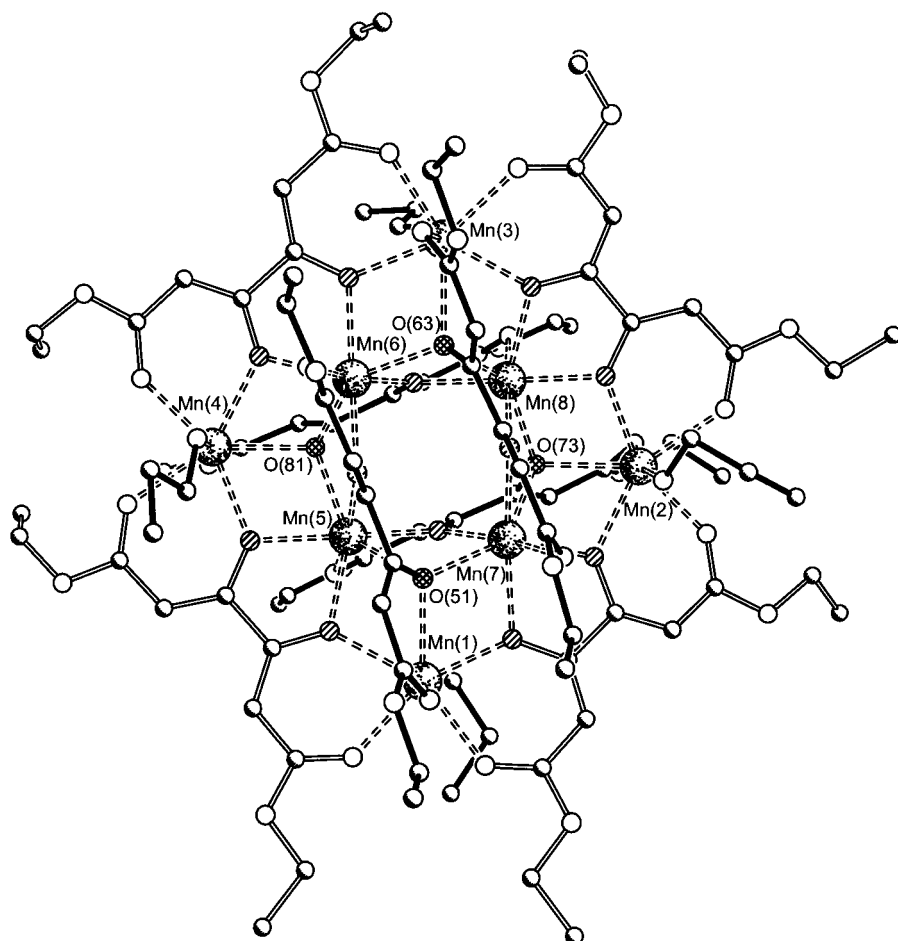
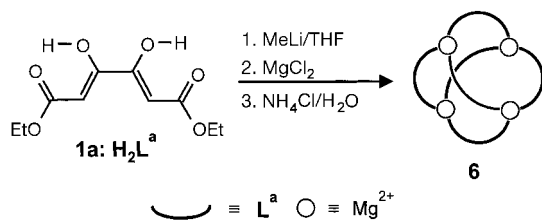


Figure 1. Structure of  $[\text{Mn}_8\text{L}_8] \cdot 4\text{HOPr}$  (**4**) in the crystal.  $\mu_1$ -bound ester carbonyl atoms shown open,  $\mu_2$ -bound keto oxygen atoms hatched,  $\mu_3$ -bound oxygen atoms double hatched, manganese ions dotted. For clarity the H atoms are omitted.



Scheme 2. Reaction scheme for the formation of  $[(4\text{NH}_4)\text{O}(\text{Mg}_4\text{L}_8)]$  (**6**).

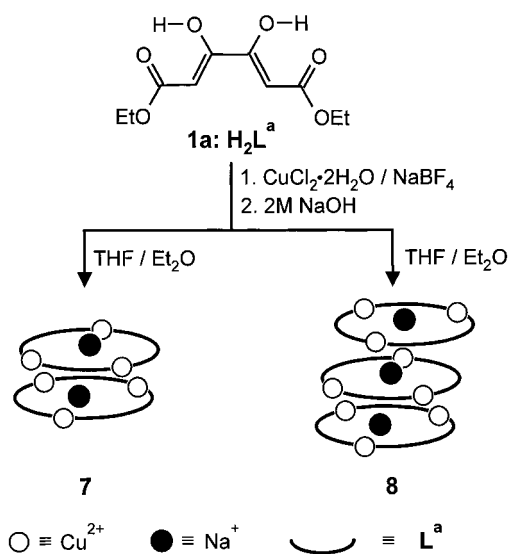
such as  $\text{Na}^+$  or  $\text{Ca}^{2+}$  leads to metalla-coronates with 1:1 stoichiometry. In contrast, encapsulation of the larger  $\text{K}^+$  ion leads to the formation of a metalla-crown ether sandwich complex ( $\text{K}^+:\text{MC}=1:2$ ).<sup>[9]</sup>

Double deprotonation of diethyl ketipinate **1a** with potassium hydroxide in a methanolic sodium tetrafluoroborate solution (0.1M) and treatment with copper(II) chloride dihydrate leads to a dark green crude product. Based on the microanalytical data and FAB-MS spectra ( $m/z=898$ ) the product isolated is a trinuclear copper-crown ether with an encapsulated sodium ion, of the general composition  $[\text{Na} \subset (\text{Cu}_3\text{L}_3)\text{BF}_4]$ . For unambiguous characterization of this metalla-coronate we grew single crystals suitable for X-ray analysis from THF and isolated two types of crystals:

the double-decker metalla-coronate  $[[\text{Na} \subset (\text{Cu}_3\text{L}_3)\text{BF}_4] \cdot \text{THF} \cdot \text{H}_2\text{O}]_2$  (**7**) and the triple-decker metalla-crown ether complex  $[[\text{Na} \subset (\text{Cu}_3\text{L}_3)\text{BF}_4]_3 \cdot 2\text{THF}]$  (**8**) (Scheme 3).

A common feature of **7** and **8** is the neutral, 15-membered tri-metalla-crown-6 (15-MC-6) building block (Figure 2, left). Formal replacement of the three copper(II) centres in the 15-MC-6 fragments of **7** or **8** by ethano bridges leads to the topologically equivalent crown ether 18-C-6. The three copper(II) atoms in the 15-MC-6 fragments are linked across the triangular edges by bis(bidentate) diethyl ketipinate dianions  $\text{L}^{2-}$  ( $d_{\text{Cu-O}}=193.2$  pm). A sodium ion is encapsulated in the centre of the 15-MC-6 fragment ( $d_{\text{Na-O}}=256.4$  pm) and charge neutrality is achieved by  $\text{BF}_4^-$  counterions ( $d_{\text{Na-F}}=223.5$  pm).

In order to accomplish eightfold coordination of the sodium ions, aggregation of the  $[\text{Na} \subset (\text{Cu}_3\text{L}_3)]^+$  monomers furnishes double- and triple-decker metalla-coronates **7** and **8**. The stacking features are governed by the coordination of water molecules. The coordination of water leads to the formation of the dimeric complex **7**. In **7** both sides of the stack are totally coordinatively blocked by solvent molecules (THF,  $\text{H}_2\text{O}$ ) or counterions ( $\text{BF}_4^-$ ) (Figure 2, right). However, without coordination of water, the most suitable ligation around copper(II) and sodium is achieved by the formation of the triple-decker metalla-coronate **8** (Figure 3).



Scheme 3. Reaction scheme for the formation of  $[[\text{Na} \subset (\text{Cu}_3\text{L}_3)\text{BF}_4] \cdot \text{THF} \cdot \text{H}_2\text{O}]_2$  (**7**) and  $[[\text{Na} \subset (\text{Cu}_3\text{L}_3)\text{BF}_4]_3 \cdot 2\text{THF}]$  (**8**).

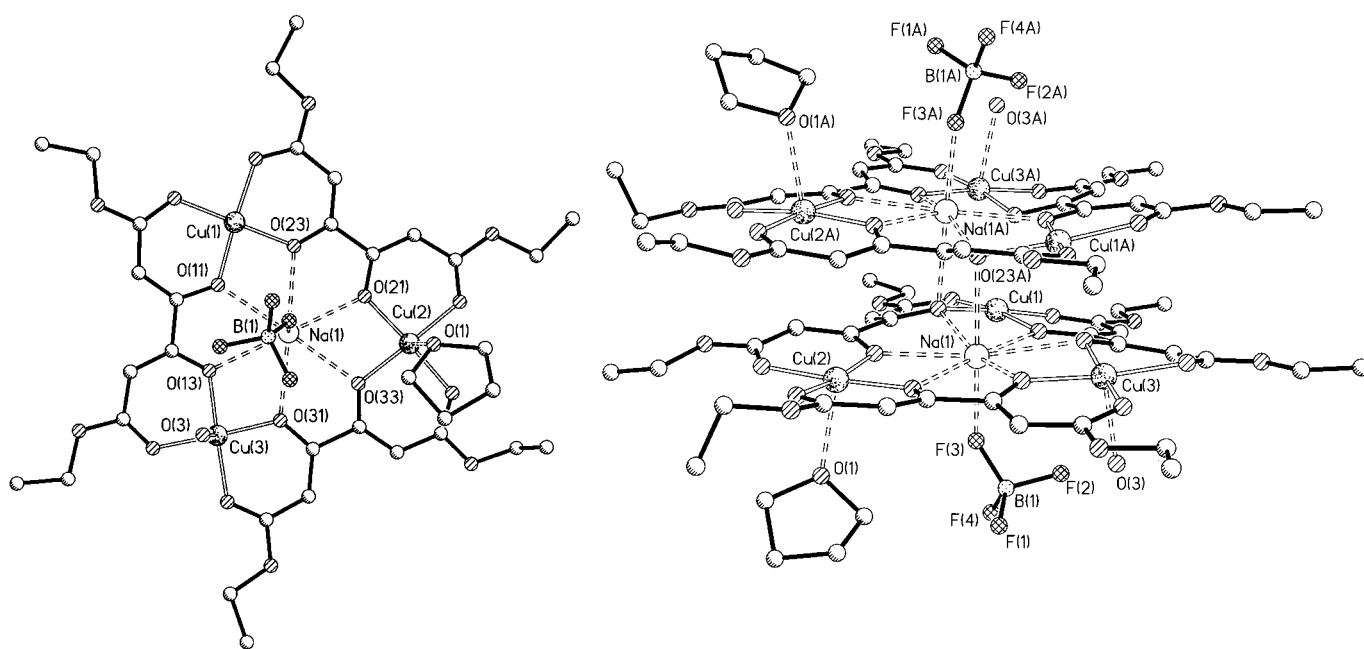


Figure 2. Left: Structure of one 15-membered tri-metalla-crown-6 unit of double-decker metalla-coronate **7**, including the encapsulated sodium ion, the  $\text{BF}_4^-$  counterion and the coordinated solvent molecules, water and THF. Right: Structure of double-decker metalla-coronate **7** (side view with counterions and solvent molecules;  $d_{\text{Na}(1)-\text{O}(23\text{A})} = 258.1$  pm).

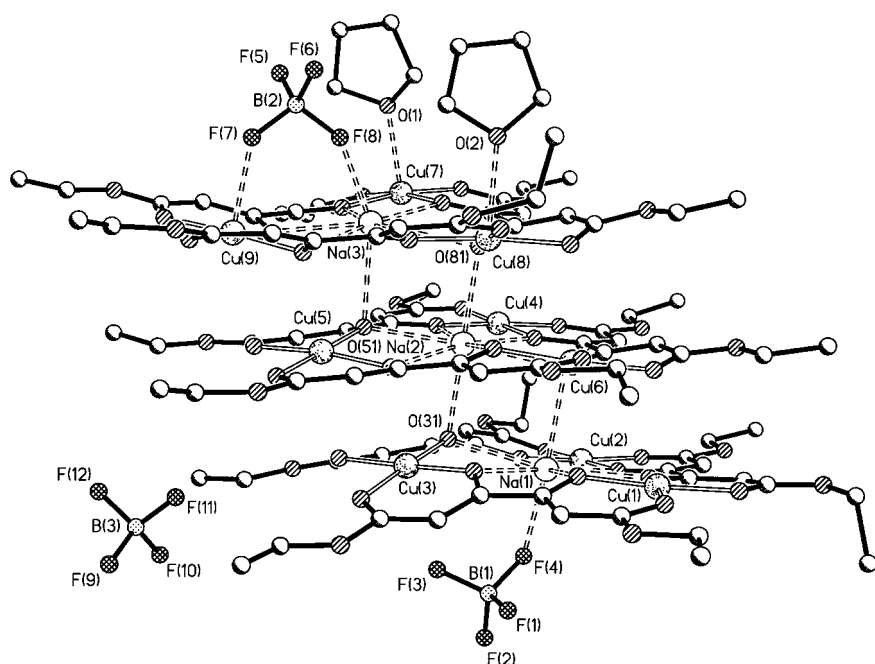


Figure 3. Structure of triple-decker metalla-coronate **8** (side view with counterions and solvent molecules;  $\bar{d}_{\text{Na}(1)-\text{O}} = 256.9$  pm,  $\bar{d}_{\text{Na}(2)-\text{O}} = 255.3$  pm,  $\bar{d}_{\text{Na}(3)-\text{O}} = 257.3$  pm,  $d_{\text{Na}(1)-\text{O}(11)} = 258.7$  pm,  $d_{\text{Na}(2)-\text{O}(31)} = 248.8$  pm,  $d_{\text{Na}(2)-\text{O}(81)} = 248.2$  pm,  $d_{\text{Na}(3)-\text{O}(51)} = 266.9$  pm).

## Conclusions

The dianions of 1,3-dicarbonyl compounds  $\text{H}_2\text{L}$  **1** are powerful binucleating ligands for the synthesis of polynuclear metal complexes from divalent metal ions in one-pot reactions by spontaneous self-assembly. Cadmium-, manganese- or calcium dichloride and  $\text{L}^{2-}$  yield supramolecular architectures  $[\text{M}_8\text{L}_8] \cdot 4\text{Y}$  (**2–5**) of octameric nuclearity. The diamagnetic complexes of cadmium **2** and calcium **5** can be characterized

by NMR. For unambiguous determination of the structures of **2–5**, we carried out an exemplary X-ray crystallographic analysis of the manganese complex **4**. The results testify that the reaction of  $\text{L}^{2-}$  with metal(II) ions with similar ion radii and coordination mode such as Ca, Mn and Cd furnishes isostructural supramolecular assemblies. However,  $\text{L}^{2-}$  and magnesium ions, which prefer octahedral coordination, yield the adamantanoid exohedral tetraammonium tetramagnesate(4-) chelate **6**. There is still a long way to go in order to be able to predict supramolecular structures, as shown by the unforeseen formation of **7** and **8** starting from  $\text{H}_2\text{L}^a$  **1a**, copper dichloride and sodium hydroxide.

## Experimental Section

**Materials and methods:** All preparations were carried out under an atmosphere of dry nitrogen. All common reagents and solvents were purchased from commercial suppliers and used without further purification unless otherwise indicated. Melting points were determined on a Wagner–Munz apparatus and are uncorrected. Infrared spectra were recorded on a Beckman Acculab or on a Perkin–Elmer 1420 Ratio Recording Infrared Spectrophotometer.  $^1\text{H}$  NMR spectra were recorded on JEOL JNM-PMX-60 (60 MHz) or JNM-GX-400 (400 MHz) spectrometers.  $^{13}\text{C}$  NMR spectra were recorded on a JEOL JNM-GX-400 (100 MHz) spectrometer. The assignment of the carbon atoms was achieved by DEPT technique. All chemical shifts are based on the  $\delta$  scale with TMS as an internal standard. Mass spectra were recorded on a Varian MAT 311A (EIMS) or on a Finnigan MATTSQ 70 spectrometer ( $m/z \leq 1500$ ; ion source temperature:  $50^\circ\text{C}$ ; ion desorption from *m*-nitrobenzyl

alcohol matrix: 10 keV Xenon atoms, FAB-MS) or on a Finnigan MAT711 A (AMD Intectra modified,  $m/z > 1500$ , ion source temperature: 35 °C, ion desorption: 12 keV Cs<sup>+</sup> ions, LSIMS).

**General procedure for the synthesis of dialkyl ketipinates 1a and 1b:** Ethyl acetate (2.3 mL, 24 mmol) or *tert*-butyl acetate (3.2 mL, 24 mmol) and the corresponding dialkyl oxalate (1.6 mL, 2.4 g, 12 mmol) in dry THF (50 mL) were placed in a three-necked, round-bottom flask fitted with a condenser. The solution was agitated with a magnetic stirrer, while sodium or potassium alkoxide (1.6 g or 2.9 g, respectively, 24 mmol) was added slowly. Stirring at 20 °C was continued for 30 min and the suspension was refluxed gently for 3–6 h, then cooled. To achieve complete precipitation of the yellow alkali salt, petroleum ether (200 mL) was added. The salt was collected by filtration, washed with petroleum ether (3 × 25 mL), dried under vacuum (oil pump) and added to hydrochloric acid (1N, 50 mL, 20 °C). Thereafter the product was collected by filtration, washed with water (50 mL, 20 °C), dried under vacuum and crystallized from ethanol. **Diethyl ketipinate (1a):** Yield: 0.50 g (18%) yellow needles from ethanol; m.p. 76 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ = 1.32 (t, <sup>3</sup>J(H,H) = 7.0 Hz, 6H; 2CH<sub>3</sub>), 4.26 (q, <sup>3</sup>J(H,H) = 7.0 Hz, 4H; 2OCH<sub>2</sub>), 5.86 (s, 2H; 2=CH), 11.73 (s, 2H; 2=C–OH); <sup>13</sup>C NMR (100.5 MHz, CDCl<sub>3</sub>, 25 °C): δ = 14.16 (2CH<sub>3</sub>), 60.91 (2OCH<sub>2</sub>), 92.21 (2=CH), 163.32 (2=C–OH), 172.45 (2C=O); IR (CHBr<sub>3</sub>):  $\tilde{\nu}$  = 3480 (OH), 2970 (CH), 1660 (C=O), 1630 cm<sup>-1</sup> (C=C); MS (70 eV, EI):  $m/z$  (%): 230 (20) [M<sup>+</sup>].

**Di-*tert*-butyl ketipinate (1b):** The <sup>1</sup>H NMR spectrum indicates the presence of three keto–enol tautomers. Herein we describe only the main tautomer (50%), the bis(keto–enol) system. Yield: 0.30 g (9%) colourless needles from ethanol; m.p. 120 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ = 1.52 (s, 18H; 6CH<sub>3</sub>), 5.75 (s, 2H; 2=CH), 11.84 (s, 2H; 2=C–OH); <sup>13</sup>C NMR (100.5 MHz, CDCl<sub>3</sub>, 25 °C): δ = 28.17 (6CH<sub>3</sub>), 45.93 (2Me<sub>3</sub>C–), 93.36 (2=CH), 163.11 (2=C–OH), 172.26 (2C=O); IR (CHBr<sub>3</sub>):  $\tilde{\nu}$  = 3390 (OH), 2995 (CH), 1650 (C=O), 1590 cm<sup>-1</sup> (C=C); MS (70 eV, EI):  $m/z$  (%): 286 (4) [M<sup>+</sup>].

#### General procedure for the synthesis of tetraketones 1c–e:

A suspension of sodium ethoxide (3.0 g, 44 mmol) in dry diethyl ether (50 mL) was stirred at 20 °C in a three-necked, round-bottom flask fitted with a condenser and a dropping funnel. A mixture of diethyl oxalate (3.0 mL, 22 mmol), acetone, acetophenone or 4-methyl-acetophenone (3.2 mL, 5.2 mL or 5.9 mL, respectively, 44 mmol) was then added dropwise. After stirring the reaction mixture for 3 d, the precipitated sodium salt was collected by filtration, washed with petroleum ether (3 × 50 mL), dried under vacuum, added to acetic acid (15%, 50 mL), collected by filtration and crystallized.

**Octane-2,4,5,7-tetraone (1c):** Yield: 0.38 g (10%) colourless needles from methanol; m.p. 116 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ = 2.26 (s, 6H; 2CH<sub>3</sub>), 6.35 (s, 2H; 2=CH), 14.57 (br s, 2H; 2=C–OH); <sup>13</sup>C NMR (100.5 MHz, CDCl<sub>3</sub>, 25 °C): δ = 28.01 (2CH<sub>3</sub>), 99.66 (2=CH), 170.59 (2=C–OH), 200.71 (2C=O); IR (CHBr<sub>3</sub>):  $\tilde{\nu}$  = 3430 (OH), 2920 (CH), 1595 (C=O), 1570 cm<sup>-1</sup> (C=C); MS (70 eV, EI):  $m/z$  (%): 170 (8) [M<sup>+</sup>].

**1,6-Bisphenyl-1,3,4,6-hexanetetraone (1d):** Yield: 3.50 g (54%) yellow needles from chloroform; m.p. 180 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ = 7.15 (s, 2H; =CH), 7.52 (t, <sup>3</sup>J(H,H) = 7.3 Hz, 4H; 3,5-Ph–CH), 7.61 (t, <sup>3</sup>J(H,H) = 7.3 Hz, 2H; 4-Ph–CH), 8.04 (d, <sup>3</sup>J(H,H) = 7.3 Hz, 4H; 2,6-Ph–CH), 15.61 (s, 2H; 2=C–OH); <sup>13</sup>C NMR (100.5 MHz, CDCl<sub>3</sub>, 25 °C): δ = 95.52 (2=CH), 127.93, 128.86, 133.57, 135.54 (6C; Ph–C), 173.86 (2=C–OH), 191.36 (2C=O); IR (CHBr<sub>3</sub>):  $\tilde{\nu}$  = 3420 (OH), 3120 (=CH), 1550 (C=O), 1590 cm<sup>-1</sup> (C=C); MS (70 eV, EI):  $m/z$  (%): 294 (8) [M<sup>+</sup>].

**1,6-Bis(4-methylphenyl)-1,3,4,6-hexanetetraone (1e):** Yield: 4.40 g (62%) yellow needles from 1,2-dimethylbenzene; m.p. 200 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ = 2.44 (s, 6H; 2CH<sub>3</sub>), 7.11 (s, 2H; 2=CH), 7.30 (d, <sup>3</sup>J(H,H) = 8.0 Hz, 4H; 2,6-Ar–CH), 7.94 (d, <sup>3</sup>J(H,H) = 8.0 Hz, 4H; 3,5-Ar–CH), 15.69 (s, 2H; 2=C–OH); <sup>13</sup>C NMR (100.5 MHz, CDCl<sub>3</sub>, 25 °C): δ = 21.78 (2CH<sub>3</sub>), 95.35 (2=CH), 128.04, 129.57, 132.99, 144.64 (6C; Ar–C), 173.45 (2=C–OH), 191.32 (2C=O); IR (CHBr<sub>3</sub>):  $\tilde{\nu}$  = 3440 (OH), 2920 (CH), 1660 (C=O), 1590 cm<sup>-1</sup> (C=C); MS (70 eV, EI):  $m/z$  (%): 322 (20) [M<sup>+</sup>].

**General procedure for the synthesis of octameric cadmium- (2a–e) manganese- (3a–e, 4) and calcium complexes (5a–c):** Aqueous ammonia (2 mL, 12%) was added dropwise to a stirred solution of cadmium, manganese(II) or calcium chloride (184 mg, 126 mg or 111 mg, respectively, 1.0 mmol) and the appropriate bis-1,3-dioxo-ligand **1** (1.0 mmol) in ethanol (100 mL). Thereafter water (100 mL) was added to achieve complete

precipitation of the products, which were filtered off, dried under vacuum (oil pump) and crystallized.

[Cd<sub>8</sub>L<sub>8</sub>]<sup>4+</sup>·4H<sub>2</sub>O (**2a**): Yield: 290 mg (84%) yellow needles from ethanol; m.p. 210 °C (decomp); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ = 1.11, 1.19, 1.28, 1.39 (t, <sup>3</sup>J(H,H) = 7.2 Hz, each 12H; 4CH<sub>3</sub>), 2.47 (brs, 8H; 4H<sub>2</sub>O), 3.80 (q, <sup>3</sup>J(H,H) = 7.2 Hz, 8H; 4OCH<sub>2</sub>), 3.94–4.07 (m, 8H; 4OCH<sub>2</sub>), 4.21 (q, <sup>3</sup>J(H,H) = 6.9 Hz, 8H; 4OCH<sub>2</sub>), 4.07–4.27 (m, 8H; 4OCH<sub>2</sub>), 4.95, 5.10, 5.30, 5.43 (s, each 4H; 4=CH); <sup>13</sup>C NMR (100.5 MHz, CDCl<sub>3</sub>, 25 °C): δ = 14.20, 14.32, 14.54, 14.63 (16CH<sub>3</sub>), 59.27, 59.38, 59.60, 59.96 (16OCH<sub>2</sub>), 83.75, 84.92, 88.34, 88.74 (16=CH), 172.47, 173.16, 173.84, 174.26, 175.21, 177.06, 177.99 (32C=O, two signals overlap); IR (KBr):  $\tilde{\nu}$  = 3400 (OH), 2975 (CH), 1620 (C=O), 1515 cm<sup>-1</sup> (C=C); MS (FAB):  $m/z$  (%): 2724 (20) [M<sup>+</sup>–4H<sub>2</sub>O].

[Cd<sub>8</sub>L<sub>8</sub>]<sup>4+</sup>·4H<sub>2</sub>O (**2b**): Yield: 252 mg (62%) colourless microcrystals from ethanol; m.p. 230 °C (decomp); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ = 1.26, 1.32, 1.44, 1.58 (s, each 36H; 18CH<sub>3</sub>), 2.36 (brs, 8H; 4H<sub>2</sub>O), 5.10, 5.25, 5.40, 5.75 (s, each 4H; 4=CH); <sup>13</sup>C NMR (100.5 MHz, CDCl<sub>3</sub>, 25 °C): δ = 28.12, 28.21, 28.30, 28.68 (48CH<sub>3</sub>), 78.51, 78.78, 79.36, 79.95 (16C; CMe<sub>3</sub>), 85.12, 85.91, 89.83, 90.09 (16=CH), 172.56, 173.27, 173.51, 173.87, 173.97, 175.37, 177.13, 177.38 (32C=O); IR (KBr):  $\tilde{\nu}$  = 3450 (OH), 2995 (CH), 1635 (C=O), 1540 cm<sup>-1</sup> (C=C); MS (FAB):  $m/z$  (%): 3173 (40) [M<sup>+</sup>–4H<sub>2</sub>O].

[Cd<sub>8</sub>L<sub>8</sub>]<sup>4+</sup>·4H<sub>2</sub>O (**2c**): Yield: 125 mg (43%) yellow microcrystals from ethanol; m.p. 245 °C (decomp); <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD, 25 °C): δ = 1.90, 1.95, 2.10, 2.19 (s, each 12H; 4CH<sub>3</sub>), 3.28 (s, 8H; 4H<sub>2</sub>O), 5.53, 5.64, 5.90, 6.05 (s, each 4H; 4=CH); <sup>13</sup>C NMR (100.5 MHz, CDCl<sub>3</sub>, 25 °C): δ = 29.62, 29.67, 29.73, 29.78, 29.82, 29.89, 30.09, 30.15 (eight signals caused by slight distortion of the S<sub>4</sub> symmetry, 16CH<sub>3</sub>), 96.37, 97.60, 100.23, 100.58 (16=CH), 176.58, 177.29, 180.53, 180.80, 200.07, 200.53, 201.48, 201.65 (32C=O); IR (CHBr<sub>3</sub>):  $\tilde{\nu}$  = 3400 (OH), 2950 (CH), 1590 (C=O), 1480 cm<sup>-1</sup> (C=C); MS (FAB):  $m/z$  (%): 2247 (100) [M<sup>+</sup>–4H<sub>2</sub>O].

[Cd<sub>8</sub>L<sub>8</sub>]<sup>4+</sup>·4H<sub>2</sub>O (**2d**): Yield: 400 mg (97%) yellow microcrystals from ethanol; m.p. 165 °C (decomp); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ = 2.58 (brs, 8H; 4H<sub>2</sub>O), 6.08, 6.39, 6.65, 6.85 (s, each 4H; 4=CH), 7.04, 7.18, 7.52, 7.55 (t, <sup>3</sup>J(H,H) = 7.7 Hz, each 8H; Ar–H), 7.33–7.59 (m, 16H; Ar–H), 7.41, 7.56, 8.02, 8.14 (d, <sup>3</sup>J(H,H) = 7.7 Hz, each 8H; Ar–H); <sup>13</sup>C NMR (100.5 MHz, CDCl<sub>3</sub>, 25 °C): δ = 94.01, 94.48, 97.15, 97.27 (16=CH), 125.20, 127.93, 128.10, 128.18, 128.28, 128.38, 128.59, 128.78 (32C; Ar–C), 131.67, 131.99, 132.22, 132.25 (16C; Ar–C), 139.44, 139.93, 141.17, 141.26 (16C; Ar–C), 177.49, 178.78, 180.96, 191.96, 192.43, 192.75, 193.33 (32C=O, two signals overlap); IR (CHBr<sub>3</sub>):  $\tilde{\nu}$  = 3420 (OH), 3050 (=CH), 1590 (C=O), 1480 cm<sup>-1</sup> (C=C); MS (FAB):  $m/z$  (%): 3237 (100) [M<sup>+</sup>–4H<sub>2</sub>O].

[Cd<sub>8</sub>L<sub>8</sub>]<sup>4+</sup>·4H<sub>2</sub>O (**2e**): Yield: 315 mg (71%) yellow microcrystals from ethanol; m.p. 165 °C (decomp); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ = 1.93 (brs, 8H; 4H<sub>2</sub>O), 2.25, 2.32, 2.42, 2.44 (s, each 12H; 4CH<sub>3</sub>), 5.95, 6.21, 6.50, 6.72 (s, each 4H; 4=CH), 6.77, 6.90, 7.15, 7.23 (d, <sup>3</sup>J(H,H) = 7.8 Hz, each 8H; Ar–H), 7.27, 7.40, 7.88, 8.02 (d, <sup>3</sup>J(H,H) = 7.8 Hz, each 8H; Ar–H); <sup>13</sup>C NMR (100.5 MHz, CDCl<sub>3</sub>, 25 °C): δ = 22.14, 22.19, (8CH<sub>3</sub>, each two signals overlap), 93.95, 94.30, 96.93, 97.26 (16=CH), 128.47, 128.63, 128.70, 128.76, 129.05, 129.23, 129.29, 129.45 (32C; Ar–C), 137.29, 137.35, 137.91, 139.19 (16C; Ar–C), 139.28, 141.73, 142.15, 142.42 (16C; Ar–C), 177.78, 178.89, 180.88, 181.16, 191.61, 191.95, 192.21, 192.94 (32C=O); IR (CHBr<sub>3</sub>):  $\tilde{\nu}$  = 3430 (OH), 2920 (CH), 1595 (C=O), 1470 cm<sup>-1</sup> (C=C); MS (FAB):  $m/z$  (%): 3462 (40) [M<sup>+</sup>–4H<sub>2</sub>O].

[Mn<sub>8</sub>L<sub>8</sub>]<sup>4+</sup>·4H<sub>2</sub>O (**3a**): Yield: 190 mg (59%) orange microcrystals obtained by filtration; m.p. 275 °C (decomp); IR (KBr):  $\tilde{\nu}$  = 3440 (OH), 2970 (CH), 1660 (C=O), 1540 cm<sup>-1</sup> (C=C); MS (FAB):  $m/z$  (%): 2265 (100) [M<sup>+</sup>–4H<sub>2</sub>O].

[Mn<sub>8</sub>L<sub>8</sub>]<sup>4+</sup>·4H<sub>2</sub>O (**3b**): Yield: 91 mg (26%) orange microcrystals obtained by filtration; m.p. 245 °C (decomp); IR (CHBr<sub>3</sub>):  $\tilde{\nu}$  = 3380 (OH), 2970 (CH), 1595 (C=O), 1520 cm<sup>-1</sup> (C=C); MS (FAB):  $m/z$  (%): 2714 (40) [M<sup>+</sup>–4H<sub>2</sub>O].

[Mn<sub>8</sub>L<sub>8</sub>]<sup>4+</sup>·4H<sub>2</sub>O (**3c**): Yield: 125 mg (43%) orange microcrystals obtained by filtration; m.p. 245 °C (decomp); IR (CHBr<sub>3</sub>):  $\tilde{\nu}$  = 3400 (OH), 2950 (CH), 1590 (C=O), 1480 cm<sup>-1</sup> (C=O); MS (FAB):  $m/z$  (%): 1785 (40) [M<sup>+</sup>–4H<sub>2</sub>O].

[Mn<sub>8</sub>L<sub>8</sub>]<sup>4+</sup>·4H<sub>2</sub>O (**3d**): Yield: 320 mg (90%) orange microcrystals obtained by filtration; m.p. 283 °C (decomp); IR (KBr):  $\tilde{\nu}$  = 3420 (OH), 3060 (=CH), 1595 (C=O), 1470 cm<sup>-1</sup> (C=C); MS (FAB):  $m/z$  (%): 2777 (100) [M<sup>+</sup>–4H<sub>2</sub>O].

[Mn<sub>8</sub>L<sub>8</sub>]<sup>4+</sup>·4H<sub>2</sub>O (**3e**): Yield: 264 mg (69%) orange microcrystals obtained by filtration; m.p. 310 °C (decomp); IR (KBr):  $\tilde{\nu}$  = 3420 (OH), 2970 (CH),

1560 (C=O), 1475 cm<sup>-1</sup> (C=C); MS (FAB): *m/z* (%): 3001 (60) [*M*<sup>+</sup> - 4H<sub>2</sub>O].

[Mn<sub>8</sub>L<sub>8</sub>]<sup>+</sup>·4HOPr (**4**): Crystallization of [Mn<sub>8</sub>L<sub>8</sub>]<sup>+</sup>·4H<sub>2</sub>O **3a** from hot propanol leads to the complete exchange of the coordinated water molecules and the formation of dark yellow single crystals.<sup>[13]</sup>

[Ca<sub>8</sub>L<sub>8</sub>]<sup>+</sup>·4EtOH (**5a**): Yield: 280 mg (96%) colourless needles from ethanol; m.p. > 300 °C (decomp); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ = 1.06 (t, <sup>3</sup>J(H,H) = 6.9 Hz, 12H; 4CH<sub>3</sub>/EtOH), 1.14, 1.15, 1.25, 1.27 (t, each 12H; 4CH<sub>3</sub>), 2.10 (brs, 4H; 4OH/EtOH), 3.48 (quintett, <sup>3</sup>J(H,H) = 6.9 Hz, 8H; 4OCH<sub>2</sub>/EtOH), 3.92, 3.98, 4.02, 4.05, 4.13, 4.15, 4.17, 4.19 (q, each 4H; 2OCH<sub>2</sub>), 5.06, 5.13, 5.22, 5.34 (s, each 4H; 4=CH); <sup>13</sup>C NMR (100.5 MHz, CDCl<sub>3</sub>, 25 °C): δ = 14.27, 14.31, 14.67, 14.73 (16CH<sub>3</sub>), 17.48 (4CH<sub>3</sub>/EtOH), 58.63, 58.89, 59.14, 59.29, 59.63 (16OCH<sub>2</sub> and 4OCH<sub>2</sub>/EtOH), 82.84, 84.15, 87.24, 88.06 (16=CH), 171.52, 172.25, 172.34, 172.54, 175.94, 178.84, 179.19, 179.37 (32C=O); IR (KBr):  $\tilde{\nu}$  = 3400 (OH), 2980 (CH), 1675 (C=O), 1550 cm<sup>-1</sup> (C=C); MS (FAB): *m/z* (%): 2145 (25) [*M*<sup>+</sup> + H - 4H<sub>2</sub>O].

[Ca<sub>8</sub>L<sub>8</sub>]<sup>+</sup>·4*i*PrOH (**5b**): Yield: 150 mg (50%) yellow needles from isopropanol; m.p. > 350 °C (decomp); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ = 1.02 (d, <sup>3</sup>J(H,H) = 5.8 Hz, 24H; 8CH<sub>3</sub>/*i*PrOH), 1.14, 1.15, 1.25, 1.26 (t, each 12H; 4CH<sub>3</sub>), 1.79 (d, <sup>3</sup>J(H,H) = 5.8 Hz, 4H; 4OH/*i*PrOH), 2.71 (brs, 2H; H<sub>2</sub>O), 3.86 (sept, J = 5.8 Hz, 4H; 4Me<sub>2</sub>CH-*i*PrOH), 3.91, 3.94, 3.98, 4.02, 4.05, 4.13, 4.15, 4.17 (q, each 4H; 2OCH<sub>2</sub>), 5.05, 5.11, 5.21, 5.35 (s, each 4H; 4=CH); <sup>13</sup>C NMR (100.5 MHz, CDCl<sub>3</sub>, 25 °C): δ = 14.31, 14.71 (16CH<sub>3</sub>, each two signals overlap), 24.43 (8CH<sub>3</sub>/*i*PrOH), 58.37, 58.79, 59.09, 59.62 (16OCH<sub>2</sub>), 65.70 (4Me<sub>2</sub>CH-*i*PrOH), 82.69, 84.08, 87.57, 87.95 (16=CH), 171.50, 172.10, 172.30, 172.43, 176.07, 178.72, 179.10, 179.34 (32C=O); IR (KBr):  $\tilde{\nu}$  = 3444 (OH), 2977 (CH), 1651 (C=O), 1537 cm<sup>-1</sup> (C=C); MS (FAB): *m/z* (%): 2144 (100) [*M*<sup>+</sup> - 4*i*PrOH].

[Ca<sub>8</sub>L<sub>8</sub>]<sup>+</sup>·4*t*BuOH (**5c**): Yield: 150 mg (49%) colourless microcrystals from *tert*-butanol; m.p. > 350 °C (decomp); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ = 1.16 (s, 36H; 12CH<sub>3</sub>/*t*BuOH), 1.13, 1.15, 1.24, 1.26 (t, each 36H; 12CH<sub>3</sub>), 1.81 (brs, 4H; 4OH/*t*BuOH), 2.70 (brs, 2H; H<sub>2</sub>O), 3.89 - 4.22 (m, 32H; 16OCH<sub>2</sub>), 5.06, 5.11, 5.21, 5.35 (s, each 4H; 4=CH); <sup>13</sup>C NMR (100.5 MHz, CDCl<sub>3</sub>, 25 °C): δ = 14.21, 14.32, 14.69, 14.73 (16CH<sub>3</sub>), 30.55 (12CH<sub>3</sub>/*t*BuOH), 58.61, 58.79, 59.05, 59.62 (16OCH<sub>2</sub>), 70.80 (4(CH<sub>3</sub>)<sub>3</sub>COH), 82.82, 84.32, 87.99, 88.06 (16=CH), 171.46, 172.18, 172.23, 172.43, 176.10, 178.61, 179.34, 179.45 (32C=O); IR (KBr):  $\tilde{\nu}$  = 3410 (OH), 2950 (CH), 1635 (C=O), 1520 cm<sup>-1</sup> (C=C); MS (FAB): *m/z* (%): 2144 (100) [*M*<sup>+</sup> - 4*t*BuOH].

**Synthesis of [(4NH<sub>4</sub>)<sub>2</sub>(Mg<sub>2</sub>L<sub>2</sub>)] (6):** Methyllithium solution (1.25 mL, 1.6 M in diethyl ether, 2 mmol) diluted with dry THF (25 mL) was added dropwise to a solution of diethyl ketipinate **1a** (230 mg, 1 mmol) in dry THF (50 mL, N<sub>2</sub>, -78 °C) over 30 min. The mixture was stirred for 1 h at -78 °C and magnesium chloride (64 mg, 0.67 mmol) was added. The mixture was then warmed to 20 °C during 18 h and the resulting clear yellow solution was treated with saturated aqueous ammonium chloride solution (50 mL). The two phases were separated, the aqueous layer extracted with trichloromethane (3 × 50 mL) and the combined organic phases dried over anhydrous sodium sulfate. After concentration to a small volume (5 mL), the reaction product was crystallized by addition of hexane (50 mL, 0 °C). Occasionally yellow microcrystals are formed. Yield: 300 mg (78%) yellow microcrystals from chloroform/hexane; m.p. 120 °C (decomp); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ = 1.23 (t, <sup>3</sup>J(H,H) = 7.1 Hz, 36H; 12CH<sub>3</sub>), 4.09 (brs, 24H; 12OCH<sub>2</sub>), 5.30 (s, 12H; 12=CH), 7.56 (brs, 16H; 4NH<sub>4</sub><sup>+</sup>); <sup>13</sup>C NMR (100.5 MHz, CDCl<sub>3</sub>, 25 °C): δ = 14.40 (12CH<sub>3</sub>), 59.43 (12OCH<sub>2</sub>), 84.17 (12=CH), 172.96, 180.71 (24C=O); IR (KBr):  $\tilde{\nu}$  = 3350 (NH), 1640 (C=O), 1590 cm<sup>-1</sup> (C=C); MS (FAB): *m/z* (%): 1537 (45) [*M*<sup>+</sup> - 2H].

**General procedure for the synthesis of oligomeric metalla-coronates (7 and 8):** Aqueous sodium hydroxide (2 mL, 2 N) was added dropwise to a solution of copper(II) chloride dihydrate (1.0 mmol, 171 mg) and diethyl ketipinate **1a** (1.0 mmol, 230 mg) in a methanolic solution of NaBF<sub>4</sub> (100 mL, 0.1 M). To achieve complete precipitation of the products, water (100 mL) was added. The crude product was filtered off, dried under vacuum (oil pump) and crystallized.

[Na(Cu<sub>3</sub>L<sub>3</sub>)BF<sub>4</sub>]·THF·H<sub>2</sub>O<sub>2</sub> (**7**): Yield (crude product): 265 mg (84%) green microcrystals from moist THF/diethyl ether; m.p. 230 °C (decomp); IR (CHBr<sub>3</sub>):  $\tilde{\nu}$  = 3596 (OH), 2985 (CH), 1605 (C=O), 1546 cm<sup>-1</sup> (C=C); MS (FAB): *m/z* (%): 898 (100) [Na(Cu<sub>3</sub>L<sub>3</sub>)]<sup>+</sup>.

[Na(Cu<sub>3</sub>L<sub>3</sub>)BF<sub>4</sub>]·2THF (**8**): Yield (crude product): 265 mg (84%) green microcrystals from water free THF/diethyl ether; m.p. 220 °C

(decomp); IR (CHBr<sub>3</sub>):  $\tilde{\nu}$  = 2975 (CH), 1615 (C=O), 1554 cm<sup>-1</sup> (C=C); MS (FAB): *m/z* (%): 898 (100) [Na(Cu<sub>3</sub>L<sub>3</sub>)]<sup>+</sup>.

**Crystal structure determination of compound 4:** C<sub>92</sub>H<sub>128</sub>Mn<sub>8</sub>O<sub>52</sub>, *M<sub>r</sub>* = 2505.46, triclinic, space group *P* $\bar{1}$ , *a* = 1617.3(2) pm, *b* = 1720.8(3) pm, *c* = 2201.8(2) pm,  $\alpha$  = 87.37(1)°,  $\beta$  = 77.51(2)°,  $\gamma$  = 68.53(1)°, *V* = 5.5638(13) nm<sup>3</sup>, *Z* = 2,  $\rho_{\text{calcd}}$  = 1.496 Mg m<sup>-3</sup>, *F*(000) = 2592,  $\lambda$  = 71.073 pm, *T* = 133(2) K,  $\mu(\text{MoK}\alpha)$  = 0.970 mm<sup>-1</sup>, min/max transmission: 0.698/0.794, crystal dimensions 0.40 × 0.35 × 0.25 mm<sup>3</sup>, 3.28° ≤ 2 $\theta$  ≤ 52.74°; 119230 measured reflections of which 22616 were independent (*R*<sub>int</sub> = 0.0516) and employed in the structure refinement (1630 parameters, 677 restraints). The *R* values are *R*<sub>1</sub> =  $\Sigma |F_o - F_c| / \Sigma F_o$  = 0.0543 (*I* 2 $\sigma$ (*I*)) and *wR*<sub>2</sub> =  $[\Sigma w(F_o^2 - F_c^2)^2 / \Sigma wF_o^4]^{1/2}$  = 0.1300 (all data); min/max residual electron density: 1384/1118 e nm<sup>-3</sup>. The hydrogen atoms of the hydroxyl groups were refined freely with isotropic displacement parameters. OH distances were restrained to a fixed value. The hydrogen atom bound to the minor part of the disordered *n*-propanol could not be located in the difference Fourier synthesis. Two ethyl and one propyl group of the *n*-propanol molecules are disordered over two sites. Two methyl and two ethyl groups and the parts of the ligands containing C(21)–C(27) and C(74)–C(79) are disordered over two sites.

**Crystal structure determination of compound 7:** C<sub>68</sub>H<sub>92</sub>B<sub>2</sub>Cu<sub>6</sub>F<sub>8</sub>Na<sub>2</sub>O<sub>40</sub>·C<sub>4</sub>H<sub>10</sub>O, *M<sub>r</sub>* = 2150.32 + 74.12, monoclinic, space group *C*2/*c*, *a* = 1789.2(3) pm, *b* = 1894.7(3) pm, *c* = 2624.3(1) pm,  $\beta$  = 96.03(2)°, *V* = 8.847(2) nm<sup>3</sup>, *Z* = 4,  $\rho_{\text{calcd}}$  = 1.670 Mg m<sup>-3</sup>, *F*(000) = 4560,  $\lambda$  = 71.073 pm, *T* = 133(2) K,  $\mu(\text{MoK}\alpha)$  = 1.535 mm<sup>-1</sup>, min/max transmission: 0.579/0.700, crystal dimensions 0.40 × 0.30 × 0.25 mm<sup>3</sup>, 4.26° ≤ 2 $\theta$  ≤ 52.32°; 27244 measured reflections of which 8044 were independent (*R*<sub>int</sub> = 0.0307) and employed in the structure refinement (675 parameters, 282 restraints). The *R* values were *R*<sub>1</sub> = 0.0330 (*I* > 2 $\sigma$ (*I*)) and *wR*<sub>2</sub> = 0.0768 (all data); min/max residual electron density: 575/293 e nm<sup>-3</sup>. The tetrafluoroborate anion is disordered over two sites. The diethyl ether solvent molecule in **7** is disordered around a twofold axis. The hydrogen atoms of the water molecule were refined freely with isotropic displacement parameters. OH distances were restrained to a fixed value.

**Crystal structure determination of compound 8:** C<sub>98</sub>H<sub>124</sub>B<sub>3</sub>Cu<sub>9</sub>F<sub>12</sub>Na<sub>3</sub>O<sub>56</sub>·2.75 C<sub>4</sub>H<sub>10</sub>O·1.25 C<sub>4</sub>H<sub>8</sub>O, *M<sub>r</sub>* = 3099.32 + 2.75 × 74.12 + 1.25 × 72.11, monoclinic, space group *C*2/*c*, *a* = 6139.3(8) pm, *b* = 1556.0(2) pm, *c* = 3220.2(2) pm,  $\beta$  = 109.08(3)°, *V* = 29.072(6) nm<sup>3</sup>, *Z* = 8,  $\rho_{\text{calcd}}$  = 1.551 Mg m<sup>-3</sup>, *F*(000) = 13940,  $\lambda$  = 71.073 pm, *T* = 133(2) K,  $\mu(\text{MoK}\alpha)$  = 1.403 mm<sup>-1</sup>, min/max transmission: 0.440/0.873, crystal dimensions 0.70 × 0.30 × 0.10 mm<sup>3</sup>, 3.86° ≤ 2 $\theta$  ≤ 46.52°; 77485 measured reflections of which 20723 were independent (*R*<sub>int</sub> = 0.0631) and employed in the structure refinement (2218 parameters, 1836 restraints). The *R* values are *R*<sub>1</sub> = 0.0827 (*I* > 2 $\sigma$ (*I*)) and *wR*<sub>2</sub> = 0.1934 (all data); min/max residual electron density: 788/787 e nm<sup>-3</sup>. The uncoordinated tetrafluoroborate, two methyl and three ethyl groups and the part of the ligand containing C(23)–C(29) are disordered over two sites. Three solvent molecule positions are disordered. One site is occupied by diethyl ether at two positions, a second by a mixture of diethyl ether and tetrahydrofuran disordered around a twofold axis and a third by tetrahydrofuran at two positions and by diethyl ether at the third position.

Crystallographic data for **4**, **7** and **8** were collected on a Stoe–Siemens–Huber four circle diffractometer with Siemens CCD area detector by use of  $\varphi$  and  $\omega$  scans on a shock cooled crystal in an oil drop.<sup>[13]</sup> Data integration was performed with the program SAINT. A semiempirical absorption correction was applied. The structures were solved by direct methods (SHELXS-97)<sup>[14]</sup> and refined against *F*<sup>2</sup> by least-squares.<sup>[15]</sup> All non-hydrogen atoms were refined anisotropically. For the hydrogen atoms a riding model was employed. Ligand as well as solvent molecule disorder was successfully modelled by employing 1,2- and 1,3-distance- and ADP-similarity restraints. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101000. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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- [1] D. Philp, J. F. Stoddart, *Angew. Chem.* **1996**, *108*, 1243–1286; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1154–1196; J.-M. Lehn, B. O. Kneisel, G. Baum, D. Fenske, *ibid.* **1996**, *108*, 1987–1990 and **1996**, *35*, 1838–1840; J.-M. Lehn, *ibid.* **1990**, *102*, 1347–1362 and **1990**, *29*, 1304–1319; I. Cragg-Hine, M. G. Davidson, O. Kocian, F. S. Mair, E. Pohl, P. R. Raithby, R. Snaith, N. Spencer, J. F. Stoddart, *ibid.* **1993**, *105*, 1254–1256 and **1993**, *32*, 1182–1184; M. Simard, D. Su, J. D. Wuest, *J. Am. Chem. Soc.* **1991**, *113*, 4696–4698.
- [2] R. W. Saalfrank, A. Dresel, V. Seitz, S. Trummer, F. Hampel, M. Teichert, D. Stalke, C. Stadler, J. Daub, V. Schünemann, A. X. Trautwein, *Chem. Eur. J.* **1997**, *3*, 2058–2062.
- [3] R. W. Saalfrank, S. Trummer, H. Krautscheid, V. Schünemann, A. X. Trautwein, S. Hien, J. Daub, *Angew. Chem.* **1996**, *108*, 2352–2350; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2206–2208.
- [4] R. W. Saalfrank, R. Burak, A. Breit, D. Stalke, R. Herbst-Irmer, J. Daub, M. Porsch, E. Bill, M. Mütther, A. X. Trautwein, *Angew. Chem.* **1994**, *106*, 1697–1699; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1621–1623; R. W. Saalfrank, T. Lutz, *ibid.* **1990**, *102*, 1064–1065 and **1990**, *29*, 1041–1042; R. W. Saalfrank, A. Stark, M. Bremer, H.-U. Hummel, *ibid.* **1990**, *102*, 292–295 and **1990**, *29*, 311–314; R. W. Saalfrank, A. Stark, K. Peters, H. G. von Schnering, *ibid.* **1988**, *100*, 878–880 and **1988**, *27*, 851–853.
- [5] R. W. Saalfrank, I. Bernt, F. Hampel, E. Uller, *Angew. Chem.* **1997**, *109*, 2596–2599; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2482–2485.
- [6] R. W. Saalfrank, R. Burak, S. Reihls, N. Löw, F. Hampel, H.-D. Stachel, J. Lentmaeier, K. Peters, E. M. Peters, H. G. von Schnering, *Angew. Chem.* **1995**, *107*, 1085–1087; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 993–995.
- [7] V. L. Pecoraro, A. J. Stemmler, B. R. Gibney, J. J. Bodwin, H. Wang, J. W. Kampf, A. Barwinski, *Prog. Inorg. Chem.* **1997**, *45*, 83–177; A. J. Stemmler, J. W. Kampf, V. L. Pecoraro, *Angew. Chem.* **1996**, *108*, 3011–3013; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2841–2843; A. J. Stemmler, A. Barwinski, M. J. Baldwin, V. Young, V. L. Pecoraro, *J. Am. Chem. Soc.* **1996**, *118*, 11962–11963; I. Haiduc, R. B. King, *Large Ring Molecules* (Ed.: J. A. Semlyen), Wiley, New York, **1996**, p. 525; W. Hayes, J. F. Stoddart, *ibid.* p. 433; A. J. Blake, R. O. Gould, C. M. Grand, P. E. Y. Milne, D. Reed, R. E. P. Winpenny, *Angew. Chem.* **1994**, *106*, 208–210; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 195–197; J. Blake, R. O. Gould, P. E. Y. Milne, R. E. P. Winpenny, *J. Chem. Soc. Chem. Commun.* **1991**, 1453–1454; A. Caneschi, A. Cormia, S. J. Lippard, *Angew. Chem.* **1995**, *107*, 511–513; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 467–469.
- [8] C. J. Pedersen, *J. Am. Chem. Soc.* **1967**, *89*, 2495–3496; J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, **1995**, p. 17; G. Gokel, *Crown Ethers and Cryptands in Monographs in Supramolecular Chemistry* (Ed.: J. F. Stoddart), Black Bear, Cambridge, **1991**, p. 64; F. Vögtle, *Supramolekulare Chemie*, Teubner, Stuttgart, **1992**, p. 45; E. Weber, F. Vögtle, *Crown-Type Compounds—An Introductory Overview in Topics in Current Chemistry*, Springer, Berlin, **1981**, p. 1–41.
- [9] R. W. Saalfrank, N. Löw, S. Kareth, V. Seitz, F. Hampel, D. Stalke, M. Teichert, *Angew. Chem.* **1998**, *110*, 182–184; *Angew. Chem. Int. Ed.* **1998**, *37*, 172–174.
- [10] R. W. Saalfrank, N. Löw, F. Hampel, H.-D. Stachel, *Angew. Chem.* **1996**, *108*, 2353–2354; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2209–2210.
- [11] For the synthesis of dialkyl ketipinates we found the procedure described herein (see experimental section) most convenient: J. L. Finar, *J. Chem. Soc.* **1955**, 1205–1208; P. Andrejczyk, R. L. Lintvedt, *J. Am. Chem. Soc.* **1972**, *94*, 8633–8634; H.-D. Stachel, *Arch. Pharm. Ber. Dtsch. Pharm. Ges.* **1962**, *295*, 735–744; H.-D. Stachel, M. Jungkenn, C. Kosergnoss, H. Poschenrieder, J. Redlin, *Liebigs Ann. Chem.* **1994**, 961–964.
- [12] For more details see Experimental Section.
- [13] T. Kottke, D. Stalke, *J. Appl. Crystallogr.* **1993**, *26*, 615T. Kottke, R. Lagow, D. Stalke, *J. Appl. Crystallogr.* **1996**, *29*, 465.
- [14] G. M. Sheldrick, SHELXS-97, Program for structure solution, *Acta Crystallogr. A* **1990**, *46*, 467.
- [15] G. M. Sheldrick, SHELXL-97, Program for structure refinement, University of Göttingen **1997**.
- [16] R. W. Saalfrank, N. Löw, S. Trummer, G. M. Sheldrick, M. Teichert, D. Stalke, *Eur. J. Inorg. Chem.* **1998**, 559–563.