Synthesis of Tetrahemispheraplexes with Ammonium, Alkylammonium or Alkaline Metal Ions as Exohedral Guests via Self-Assembly or Guest Exchange[‡]

Rolf W. Saalfrank,*[a] Bernhard Demleitner,[a] Horst Glaser,[a] Harald Maid,[a] Stefan Reihs,[a] Walter Bauer,[a] Monica Maluenga,[a] Frank Hampel,[a] Markus Teichert,[b] and Harald Krautscheid[c]

Dedicated to Prof. Dr. Horst Kisch on the occasion of his 60th birthday

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To study the interplay between the steric demand of the guest and the space available at the host, we have prepared the tetraammonium complexes $\{(NH_4)_4\cap[Mg_4(L^{1/2})_6]\}$ **1**, tetrakis(methylammonium) complexes $\{(Me\text{-}NH_3)_4\cap[Mg_4(L^{1/2})_6]\}$ **2**, tetrakis(ethylammonium) complex $\{(Et\text{-}NH_3)_4\cap[Mg_4(L^1)_6]\}$ **3**, and mixed sodium tris(ethylammonium) complex $\{Na(Et\text{-}NH_3)_3\cap[Mg_4(L^2)_6]\}$ **4**. The tetrahemispheraplexes **1–4** were available in one-pot syntheses. The tetrakis(alkylammonium) clusters $\{(R^1\text{–}NH_3)_4\cap[Mg_4(L^1)_6]\}$ **5** and the mixed diammonium-bis(*p*-methoxybenzylammonium) cluster $\{(NH_4)_2(R^2\text{–}NH_3)_2\cap[Mg_4(L^1)_6]\}$ **6**, however, were prepared by exchange of the ammonium ions of **1a** by alkylammonium ions. Similarly, exchange of the four ammonium ions of **1b** by alkaline metal cations afforded the tetraalkaline metal tetrahemispheraplexes $\{M_4\cap[Mg_4(L^2)_6]\}$ **7**.

Introduction

Following the considerable progress made towards predicting ordered supramolecular assemblies on the basis of coordinative metal/ligand bonds,[1] great attention is being paid to the role guest molecules play in the self-assembly of metal/ligand clusters. The inner voids of supramolecular metal/ligand cages are possible sites for encapsulated anionic,[2] electronically neutral[3] and cationic species.[4] Kinetic data for the equilibria of guest exchange reactions have been determined.[5] In special cases, the nature of the encapsulated guest was shown to be the crucial factor for the nuclearity of the compound formed.[6] However, there are far fewer examples of host/guest interactions at the surface of supramolecular coordination polygons.[7–9] The synthesis of novel tetrahemispheraplexes that contain alkylammonium and alkaline-metal cations has been achieved by an advanced one-pot procedure or by host/guest exchange reactions and is subject of this paper.

Results and Discussion

One-Pot Syntheses of Tetraammonium Complexes 1 and Tetrakis(methylammonium) Complexes 2

We have previously reported the gram-scale synthesis of tetraammonium tetramagnesium chelate complexes $\{(NH_4)_4\cap[Mg_4(L^{1/2})_6]\}$ **1a,b** in high yields by deprotonation of dialkyl malonates with methyllithium in tetrahydrofuran, subsequent addition of magnesium chloride and oxalyl chloride followed by workup with aqueous ammonium chloride solution (Scheme 1).[8] The doubly bidentate bridging ligands $(L^{1/2})^{2-}$ (R = Me, Et) are formally obtained by template coupling of two malonate monoanions with oxalyl chloride and spontaneous double deprotonation of the bisenol intermediates. Replacement of the aqueous ammonium chloride solution of this one-pot reaction by a solution of methylammonium chloride yielded the corresponding tetrahemispheraplexes $\{(Me{-}NH_3)_4\cap[Mg_4(L^{1/2})_6]\}$ **2a,b** (Scheme 1).

The NMR spectra of the tetrahemispheraplexes **1** and **2** are surprisingly simple. For example, despite there being four stereogenic metal centers and six C_2-symmetric ligands, the ^{13}C NMR spectrum of **2a** displays only six signals, representing the atropisomeric ligands, and only one for the four exohedrally bonded methylammonium ions. The low number of signals is explained by approximate molecular T symmetry of **2a** (characterised by three C_2 and four C_3 axes). To further support the proposed structure of

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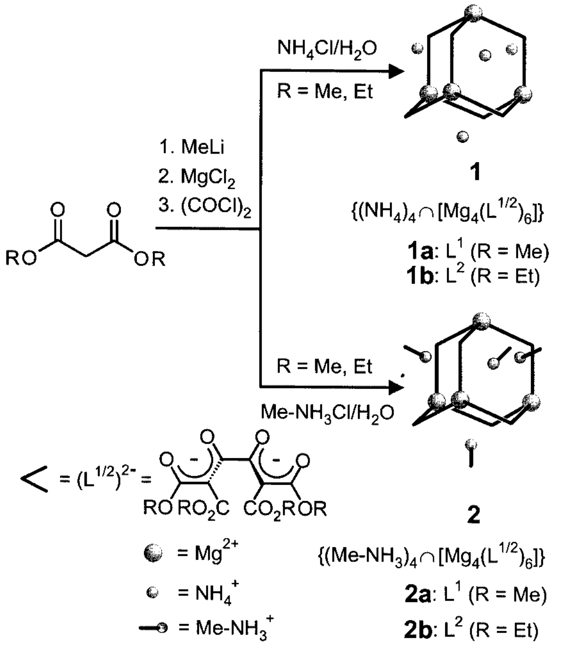
[‡] Chelate complexes (metalla-coronates), 24. Part 23: Ref.[16]

[a] Institut für Organische Chemie der Universität Erlangen-Nürnberg,
Henkestrasse 42, 91054 Erlangen, Germany
Fax: (internat.) + 49-(0)9131/852−1165
E-mail: saalfrank@chemie.uni-erlangen.de

[b] Institut für Anorganische Chemie der Universität Göttingen,
Göttingen, Germany

[c] Institut für Anorganische Chemie der Universität Leipzig,
Leipzig, Germany

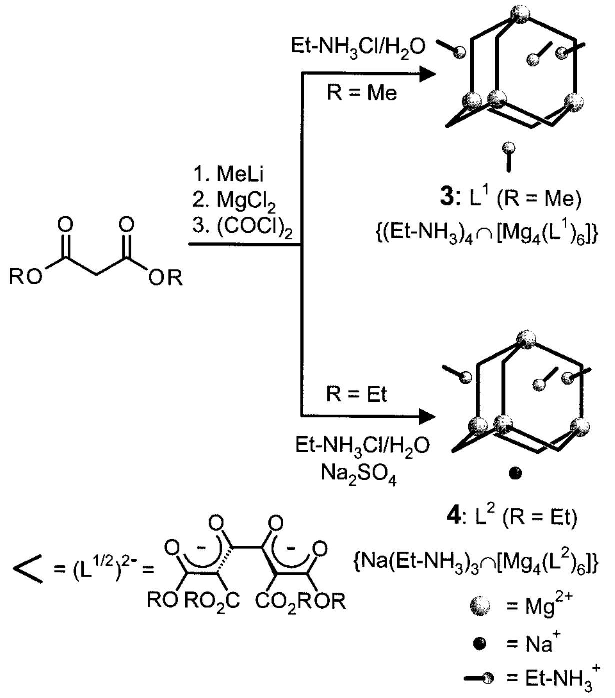


Scheme 1. Synthesis of tetraammonium tetrahemispheraplexes **1** and tetrakis(methylammonium) tetrahemispheraplexes **2**

2a, we carried out a single crystal X-ray structure determination.[11-13] According to this analysis, **2a** crystallises in the monoclinic space group $P2_1/c$ with four molecules per unit cell. The four magnesium cations of the tetraanionic core $[Mg_4(L^1)_6]^{4-}$ of tetrahemispheraplex **2a** frame the corners of an idealised tetrahedron and are linked along each of the six edges by doubly bidentate tetramethyl-2,3-dioxobutane-1,1,4,4-tetracarboxylato(2$^-$) bridges. Consequently, each of the four magnesium ions is octahedrally coordinated by six oxygen donors. Charge compensation of $[Mg_4(L^1)_6]^{4-}$ is achieved by a set of four methylammonium counterions, which are hydrogen bonded to the oxygen donors of the triangular faces of the tetraanionic core to give **2a**. The crystals of **2a** consist of a racemic mixture of homochiral stereoisomers with (Δ,Δ,Δ,Δ)-*fac* or (Λ,Λ,Λ,Λ)-*fac* configuration at the magnesium centers and with six atropisomeric ligands each, twisted clockwise or counter-clockwise.

One-Pot Synthesis of Tetrakis(ethylammonium) Complex 3 and Mixed Sodium Tris(ethylammonium) Complex 4

To study the effect of the steric demand of the ligands $(L^{1/2})^{2-}$ (R = Me, Et) on the packing density at the surfaces of the tetraanionic $[Mg_4(L^{1/2})_6]^{4-}$ cores, unlike the synthesis of **2**, an aqueous *ethyl*ammonium instead of an *methyl*ammonium chloride solution was used for workup. Starting from *dimethyl* malonate, tetrakis(ethylammonium) complex $\{(Et-NH_3)_4\cap[Mg_4(L^1)_6]\}$ **3** was formed, whereas sodium tris(ethylammonium) complex $\{Na(Et-NH_3)_3\cap[Mg_4(L^2)_6]\}$ **4** was isolated with *diethyl* malonate as starting material and the reaction mixture dried over sodium sulfate (Scheme 2).



Scheme 2. Synthesis of tetrakis(ethylammonium) tetrahemispheraplex **3** and mixed sodium tris(ethylammonium) tetrahemispheraplex **4**

The NMR spectra of **3**, as with **1** and **2**, originate from the molecular T symmetry of the tetrahemispheraplex in solution. However, the ^{1}H and ^{13}C NMR spectra of **4** were more complex. Two signals in the ^{13}C NMR spectrum confirm magnetically equivalent exohedral ethylammonium guests. Integration of the ^{1}H NMR signals provide an ethylammonium-to-ligand ratio of 1:2, indicating that only three of the four triangular faces of the compound are occupied by ethylammonium ions. Compared to the higher symmetric analogue **3**, the ^{13}C NMR spectrum of C_3-symmetric **4** displayed a total of 32 signals due to two sets of three C_1-symmetric ligands $(L^2)^{2-}$ (R = Et). The structure proposed for **4** is further supported by a single crystal X-ray structure determination,[11-13] which shows that $\{Na(Et-NH_3)_3\cap[Mg_4(L^2)_6]\}\cdot 2H_2O$ **4** crystallises in the monoclinic space group $P2_1/n$ with four molecules per unit cell. The crystals of **4** consist of a racemic mixture of homochiral stereoisomers with a (Δ,Δ,Δ,Δ)-*fac* or (Λ,Λ,Λ,Λ)-*fac* configuration at the metal centers and with two sets of three atropisomeric ligands each, twisted clockwise or counterclockwise. Unlike to the tetrahedral core $[Mg_4(L^1)_6]^{4-}$ of **2a**, in **4** the $[Mg_4(L^2)_6]^{4-}$ framework is stretched along the C_3 axis. This results in an overall trigonal pyramidal scaffold for **4**. Each of the three isosceles triangular faces of the pyramid are occupied by one ethylammonium ion hydrogen bonded to three oxygen donors of the adjacent ligands. Charge compensation of the resulting $\{(Et-NH_3)_3\cap[Mg_4(L^2)_6]\}^-$ framework is achieved by the sterically less demanding sodium ion, which is coordinated by two carbonyl oxygen donors of each of the three ligands, establishing the basic equilateral triangle. The sodium coordination sphere is completed by two water molecules. Remarkably, one water molecule is located *in* the void and the other one *outside* the trigonal pyramid (Figure 1).[10]

Exchange of Ammonium Ions of 1a,b by Alkylammonium Ions to give the Tetrakis(alkylammonium) Clusters 5 and the Mixed Diammonium-bis(*p*-methoxybenzylammonium) Cluster 6

To tune the physical and chemical properties of the spherical surface of $\{(NH_4)_4\cap[Mg_4(L^1)_6]\}$ **1a** we extended the *direct method* described above by replacing the four ammonium ions with *n*-alkylammonium ions. The exchange of the ammonium ions in **1a** (R = Me) for *n*-alkylammonium ions to form the tetrakis(alkylammonium) tetrahemispheraplexes $\{(R^1{-}NH_3)_4\cap[Mg_4(L^1)_6]\}$ **5** is achieved by addition of *n*-alkylamines $R^1{-}NH_2$ in excess. Ammonia is liberated during this exchange process.[9,14] The NMR spectra of **5** are consistent with the predicted structures (see the Exp. section for data).

However, when **1a** (R = Me) was allowed to react with an excess of bulky *p*-methoxybenzylamine R^2-NH_2, only two ammonium ions were exchanged by *p*-methoxybenzylammonium groups to give diammonium bis(*p*-methoxybenzylammonium) tetrahemispheraplex $\{(NH_4)_2(R^2{-}NH_3)_2\text{-}\cap[Mg_4(L^1)_6]\}$ **6** (Scheme 3).

The ^1H and ^{13}C NMR spectra of **6** were rather complex. Six signals in the ^{13}C NMR spectrum confirmed magnetically equivalent exohedral *p*-methoxybenzylammonium guests. Integration of the ^1H NMR signals provided a *p*-methoxybenzylammonium-to-ligand ratio of 1:3, indicating that only two of the four triangular faces of **6** are occupied by *p*-methoxybenzylammonium ions. Whereas the ^{13}C NMR spectrum for the *T*-symmetric precursor **1a** shows six signals, that of the C_2 symmetric core of **6** displays 36 signals. In **6**, the ligands are subdivided into four types: two different C_2-symmetric ligands and two sets of two identical C_1-symmetric ligands. Accordingly, thirteen discrete singlets are expected, representing the methoxy groups of the ligands and the guests; twelve (two signals are superimposed) were recorded.

A single crystal X-ray structure determination of **6**[11−13,15] is consistent with the proposal that **6** crystallises in the monoclinic space group *P*2/*c* with four molecules per unit cell. A common feature of **1a**, **5** and **6** is the tetrahedral module $[Mg_4(L^1)_6]^{4-}$. However, they differ markedly due to their exohedral guests. In **6**, charge compensation is achieved by two ammonium and two *p*-methoxybenzylammonium counterions, which are hydrogen-bonded to the

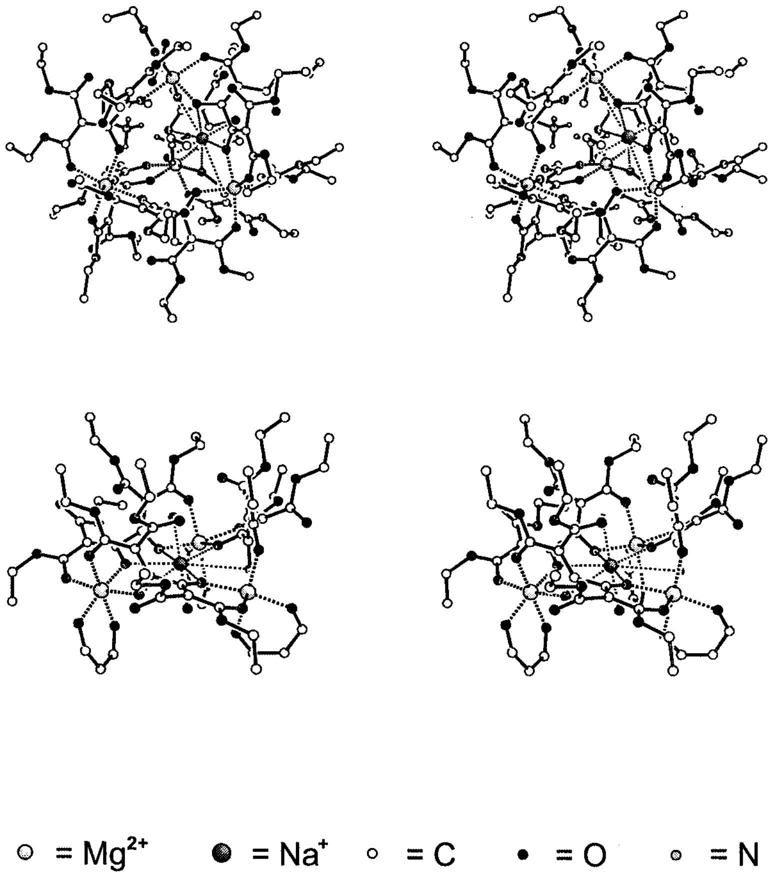
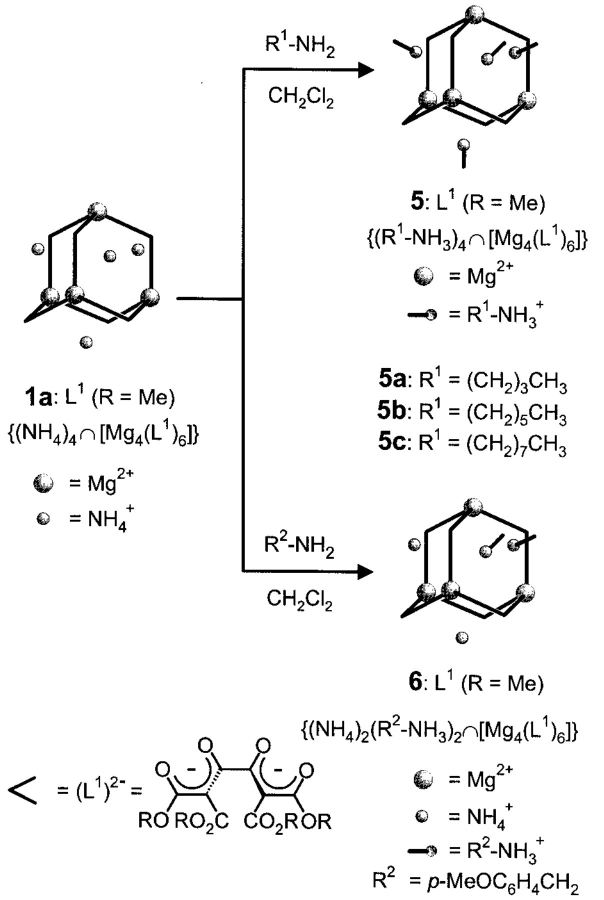
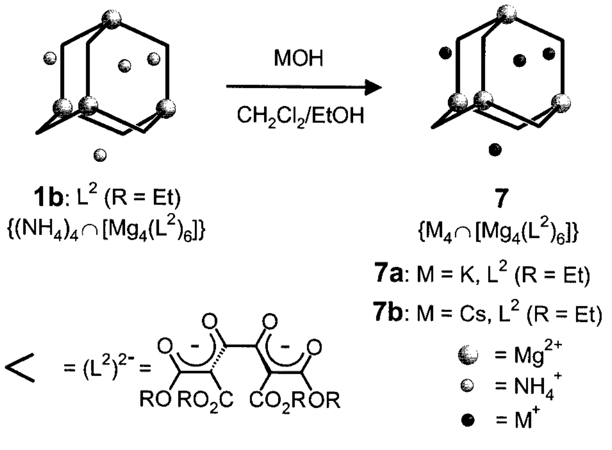


Figure 1. (Stereo view): Top: Structure of $\{Na(Et\text{-}NH_3)_3\cap[Mg_4(L^2)_6]\}$ **4** (L^2: R = Et) in the crystal. Bottom: Selected tetrahedral face highlighting its metalla-coronate character. Solvent molecules and hydrogen atoms except ammonium hydrogens are not depicted for clarity



Scheme 3. Ammonium ion exchange of **1a**: Synthesis of tetrakis(alkylammonium) tetrahemispheraplexes **5** and diammonium-bis(*p*-methoxybenzylammonium) tetrahemispheraplex **6**



Scheme 4. Ammonium ion exchange of **1b**: Synthesis of tetraalkaline metal tetrahemispheraplexes **7**

oxygen donors of the ligands of the triangular faces (Figure 2).[10]

Exchange of the Four Ammonium Ions of 1b by Alkaline Cations to Give the Tetraalkaline Metal Complexes 7

Reaction of a solution of tetraammonium tetrahemispheraplex **1b** in dichloromethane with a solution of potassium or caesium hydroxide in dichloromethane/ethanol afforded the alkaline metal complexes $\{M_4\cap[Mg_4(L^2)_6]\}$ **7** [(M = K, Cs; L^2 (R = Et)] in excellent yields (Scheme 4).

The NMR spectra of the tetrahemispheraplexes $\{M_4\cap[Mg_4(L^2)_6]\}$ **7a**,**b** are principally identical to those of **1b**, except for the missing ^1H NMR signals characteristic of the ammonium protons of **1b**. According to a single crystal X-ray structure determination, $\{K_4\cap[Mg_4(L^2)_6]\}\cdot4H_2O$ **7a** crystallises in the monoclinic space group $P2_1$ with two molecules per unit cell.[11–13] Charge compensation of the tetrahedral $[Mg_4(L^2)_6]^{4-}$ core is achieved by a set of four potassium counterions. The idealised structure of **7a** consists of four fused [15]metalla-crown-6 systems that encapsulate one potassium cation, each (Figure 3, top).[10] However, careful consideration revealed different coordination spheres at the potassium ions. Remarkably, the coordination number at the most symmetrically ligated potassium cation is eight. Its coordination sphere is composed of six carbonyl oxygen donors, one oxygen donor of a water molecule at the periphery and one oxygen donor of a water molecule encapsulated in the void of the tetrahedron (Figure 3, bottom). As with **1b**, the crystals of **7a** consist of a racemic mixture of homochiral stereoisomers.

Conclusions

The present study has shown that the space available at the surface of the self-assembled tetrahedral tetraanionic cores $[Mg_4(L^{1/2})_6]\}^{4-}$ depends on the steric demand of the ligands $(L^{1/2})^{2-}$. Whereas $[Mg_4(L^1)_6]\}^{4-}$ (L^1: R = Me) is able to host four $Et{-}NH_3^+$ cations, the more crowded $[Mg_4(L^2)_6]\}^{4-}$ (L^2: R = Et) is apt to only host four of the smaller NH_4^+-, $Me{-}NH_3^+$- or alkaline metal cations. However, tetrahemispheraplexes of $[Mg_4(L^2)_6]\}^{4-}$ (L^2: R = Et) with $Et{-}NH_3^+$ are conceivable in combination with the smaller Na^+ cation, and of $[Mg_4(L^1)_6]\}^{4-}$ (L^1: R = Me) with p-$MeOC_6H_4CH_2{-}NH_3^+$ together with NH_4^+ cations. In $\{(NH_4)_4\cap[Mg_4(L^2)_6]\}$ **1b** the four ammonium ions could be exchanged by potassium or caesium ions.

Experimental Section

General Methods: NMR spectra were recorded on a JEOL EX 400 and on a JEOL ALPHA 500 in $CDCl_3$ solutions. The residual solvent signal (δ = 7.27 ppm) was used as an internal standard. IR spectra were performed on a Bruker IFS 25 spectrometer. Elemental analyses were carried out on an EA 1110 CHNS-Microautomat.

Materials: All reagents and solvents employed were commercially available, high-grade purity materials (Fluka, Aldrich), used as supplied.

General Procedure. Direct Synthesis: A methyllithium solution (18.75 mL, 1.6 M in diethyl ether, 30 mmol) diluted with dry THF (10 mL) was added dropwise to a solution of dialkyl malonate (30 mmol) in dry THF (50 mL) (N_2, −78 °C) over 30 min. After stirring for 1 h, $MgCl_2$ (2.86 g, 30.0 mmol) was added and 1 h later a solution of oxalyl chloride (0.95 g, 7.5 mmol) in dry THF (20 mL)

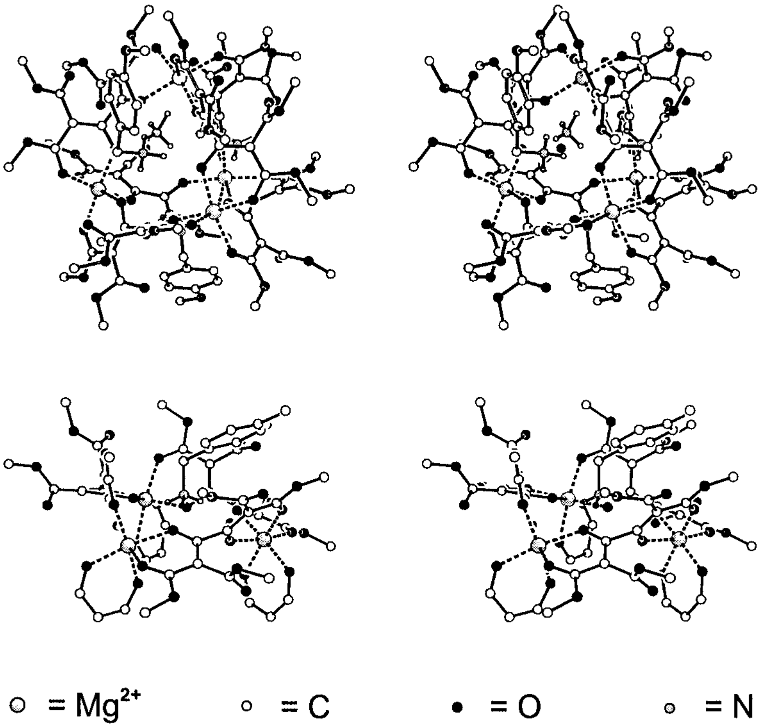


Figure 2. (Stereo view): Top: Structure of $\{(NH_4)_2(R^2-NH_3)_2\cap[Mg_4(L^1)_6]\}$ **6** (L^1: R = Me; R^2 = *p*-$MeOC_6H_4CH_2$) in the crystal. Bottom: Selected tetrahedral face hosting *p*-methoxybenzylammonium. Solvent molecules and hydrogen atoms except ammonium hydrogens are not depicted for clarity

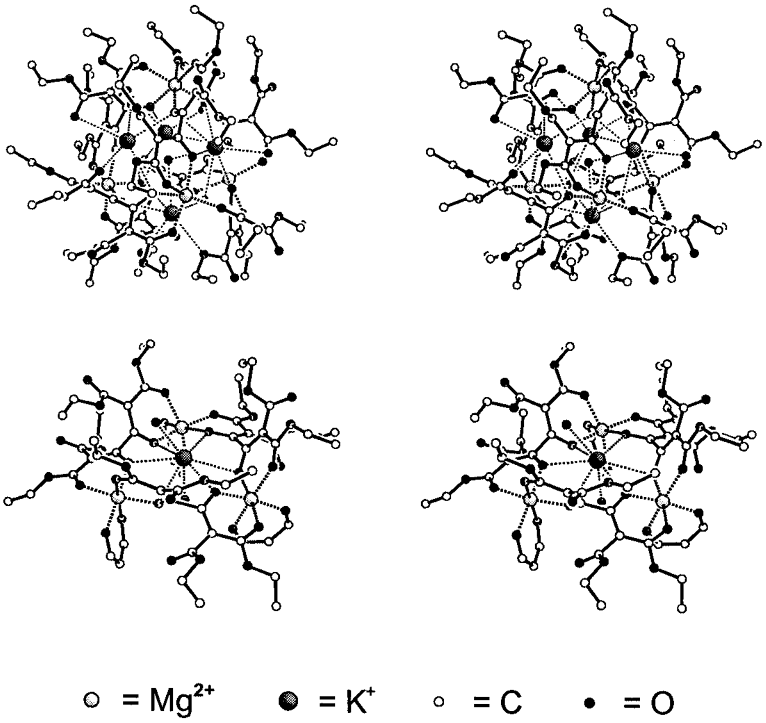


Figure 3. (Stereo view): Top: Structure of $\{K_4\cap[Mg_4(L^2)_6]\}$ **7a** (L^2: R = Et) in the crystal. Bottom: Selected tetrahedral face highlighting its metalla-coronate character. Solvent molecules and hydrogen atoms are not depicted for clarity

was added dropwise into the suspension within 2 h. The mixture was then allowed to warm to 20 °C during 18 h and the resulting yellow solution treated for 5 min with 10% aqueous alkyl ammonium chloride (50 mL). The two layers present were separated, the aqueous layer was extracted three times with chloroform (50 mL), and the combined organic phases were dried over anhydrous sodium sulfate. The solvent was removed in vacuo and the remaining yellow oil was diluted in chloroform (5 mL). The reaction product was crystallised by addition of isohexane (50 mL).

Compound 1a: Yield: 2.23 g (86%) colourless powder; m.p. 181 °C (decomp.). ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 3.57, 3.78$ (each s, 72 H, 24 OCH$_3$), 7.30 ppm (br. s, 16 H, 4 NH$_4^+$). ^{13}C NMR (100.5 MHz, CDCl$_3$): $\delta = 51.39, 52.05$ (24 OCH$_3$), 94.29 (12 =C), 167.97, 170.82 (24 C=O, ester), 184.25 ppm (12 C=O, keto). IR (CHBr$_3$): $\tilde{\nu} = 3180$ (NH), 1680 (C=O), 1630 cm^{-1} (C=C). $C_{72}H_{88}Mg_4N_4O_{60}$ (2066.71): calcd. C 41.84, H 4.29, N 2.71; found C 41.29, H 4.63, N 2.66.

Compound 1b: See ref.[8]

Compound 2a: Yield: 1.80 g (68%) colourless microcrystals; m.p. 161 °C (decomp.). ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 2.20$ (s, 12 H, 4 CH$_3$), 3.55, 3.81 (each s, 72 H, 24 OCH$_3$), 8.09 ppm (br. s, 12 H, 4 NH$_3^+$). ^{13}C NMR (100.5 MHz, CDCl$_3$): $\delta = 25.92$ (4 CH$_3$), 51.26, 52.26 (24 OCH$_3$), 94.56 (12 =C), 167.30, 170.88 (24 C=O, ester), 184.34 ppm (12C=O, keto). IR (CHBr$_3$): $\tilde{\nu} = 1710$ (C=O), 1640 cm^{-1} (C=C). $C_{76}H_{96}Mg_4N_4O_{60}$ (2122.82): calcd. C 43.00, H 4.56, N 2.64; found C 42.64, H 4.68, N 2.43.

Compound 2b: Yield: 1.65 g (54%) colourless powder; m.p. 202 °C (decomp.). ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 1.15, 1.27$ (each t, $J = 7.08$ Hz, 72 H, 24 CH$_3$), 2.25 (br. s, 12 H, 4 NCH$_3$), 3.95, 4.06, 4.18, 4.29 (each m, 48 H, 24 OCH$^{A/B}$), 8.16 ppm (br. s, 12 H, 4 NH$_3^+$). ^{13}C NMR (100.5 MHz, CDCl$_3$): $\delta = 14.03, 14.08$ (24 CH$_3$), 26.00 (4 NCH$_3$), 59.76, 60.73 (24 OCH$_2$), 95.40 (12 =C), 166.71, 170.59 (24 C=O, ester), 184.24 ppm (12 C=O, keto). IR (CHBr$_3$): $\tilde{\nu} = 1700$ (C=O), 1640 cm^{-1} (C=C). $C_{100}H_{144}Mg_4N_4O_{60}$ (2459.46): calcd. C 48.84, H 5.90, N 2.28; found C 48.94, H 5.90, N 2.23.

Compound 3: Yield: 1.25 g (46%) colourless powder; m.p. 182 °C (decomp.). ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 0.89$ (t, $J = 7.08$ Hz, 12 H, 4 CH$_3$), 2.65, 2.82 (each br. m, 8 H, 4 NCH$^{A/B}$), 3.56, 3.78 (each s, 72 H, 36 OCH$_3$), 7.67 ppm (br. s, 12 H, 4 NH$_3^+$). ^{13}C NMR (100.5 MHz, CDCl$_3$): $\delta = 11.80$ (4 CH$_3$), 36.50 (4 NCH$_2$), 51.26, 52.01 (24 OCH$_3$), 95.15 (12 =C), 167.39, 170.80 (24 C=O, ester), 184.56 ppm (12 C=O, keto). IR (CHBr$_3$): $\tilde{\nu} = 1730$ (C=O), 1650 cm^{-1} (C=C). $C_{80}H_{104}Mg_4N_4O_{60}$ (2178.95): calcd. C 44.10, H 4.81, N 2.57; found C 42.84, H 4.64, N 1.80.

Compound 4: Yield: 2.83 g (91%) colourless prisms, from dichloromethane/isohexane; m.p. 186 °C (decomp.). ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 0.92$ (t, $J = 7.4$ Hz, 9 H, 3 CH$_3$), 1.08−1.27 (m, 72 H, 24 CH$_3$), 2.61, 2.81 (each br. m, 6 H, 3 NCH$^{A/B}$), 3.85−4.31 (m, 48 H, 24 OCH$_2$), 7.50 ppm (br. s, 9 H, 3 NH$_3^+$). ^{13}C NMR (100.5 MHz, CDCl$_3$): $\delta = 11.91$ (3 CH$_3$), 13.67, 13.83, 13.93, 13.98, 14.19, 14.22, 14.36, two superimposed signals (24 CH$_3$), 36.12 (3 NCH$_2$), 59.74, 59.88, 60.09, 60.12, 60.20, 60.42, 60.55, 60.60 (24 OCH$_2$), 94.38, 94.91, 95.09, 95.59 (12 =C), 167.07, 167.27, 167.56, 168.99, 170.34, 170.58, 170.76, two superimposed signals (24 C=O, ester), 184.54, 184.74, 185.23, 185.67 ppm (12 C=O, keto); When the NMR spectra of C_3-symmetric **4** were carried out in CD$_3$CN/CDCl$_3$ instead of CDCl$_3$ alone, the spectra of **4** revealed molecular T symmetry due to the core $[Mg_4(L^2)_6]^{4-}$. This is explained by fast exchange of Na$^+$ and $[H_3NC_2H_5]^+$. ^{1}H NMR (400 MHz, CDCl$_3$/CD$_3$CN): $\delta = 0.92$ (t, $J = 7.4$ Hz, 9 H, 3 CH$_3$); 1.13, 1.22 (t, $J = 7.1$ Hz, 72 H, 24 CH$_3$); 2.22, 2.70 (each br. s, 6 H, 3 CH$_2$); 3.88, 3.99, 4.09, 4.17 (each m, 48 H, 24 OCH$_2$); 7.51 (br. s, 9 H, 3 NH$_3^+$) ppm. ^{13}C NMR (100.5 MHz, CDCl$_3$/CD$_3$CN): $\delta = 12.26$ (3 CH$_3$); 14.26, 14.48 (24 CH$_3$); 36.75 (3 NCH$_2$); 60.45, 61.06 (24 OCH$_2$); 95.71 (12 =C); 167.95, 171.28 (24 C=O, ester); 185.56 (12 C=O, keto). IR (CHBr$_3$): $\tilde{\nu} = 1700$ (C=O), 1640 cm^{-1} (C=C). $C_{102}H_{144}Mg_4N_3NaO_{60}$ (2492.47): calcd. C 49.15, H 5.82, N 1.69; found C 48.09, H 6.02, N 1.60.

General Procedure. Ammonium/Alkylammonium Cation-Exchange: A solution of the corresponding primary amine (5 mmol, 1 mmol for **6**) in dichloromethane (5 mL) was added dropwise to a solution of the corresponding tetrahemispheraplex **1a** (1.03 g, 0.5 mmol) in dichloromethane (50 mL) over 5 min. The mixture was then stirred for 20 min (5 min for **6**) at 0 °C. Subsequently, the volatile components were removed in vacuo and the resulting colourless solid was washed three times with hexane (30 mL), dried and crystallised from dichloromethane/diethyl ether.

Compound 5a: Yield: 0.49 g (43%) colourless powder; m.p. 186 °C (decomp.). ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 0.65$ (t, $J = 7.1$ Hz, 12 H, 4 CH$_3$), 0.93, 1.30 (each m, 16 H, 8 CH$_2$), 2.47, 2.73 (each br. m, 8 H, 4 NCH$^{A/B}$), 3.56, 3.79 (each s, 72 H, 24 CH$_3$), 7.68 ppm (br. s, 12 H, 4 NH$_3^+$). ^{13}C NMR (100.5 MHz, CDCl$_3$): $\delta = 12.89$ (4 CH$_3$), 20.00, 28.18 (8 CH$_2$), 41.58 (4 NCH$_2$), 51.15, 51.93 (24 OCH$_3$), 95.36 (12 =C), 167.16, 170.78 (24 C=O, ester), 184.38 ppm (12 C=O, keto). IR (CHBr$_3$): $\tilde{\nu} = 1720$ (C=O), 1650 cm^{-1} (C=C). $C_{88}H_{120}Mg_4N_4O_{60}$ (2291.17): calcd. C 46.13, H 5.28, N 2.45; found C 46.06, H 5.56, N 2.51.

Compound 5b: Yield: 0.47 g (49%) colourless powder; m.p. 194 °C (decomp.). ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 0.79$ (t, $J = 7.3$ Hz, 12 H, 4 CH$_3$), 0.89, 0.98, 1.12, 1.30 (each m, 32 H, 16 CH$_2$), 2.45, 2.74 (each br. m, 8 H, 4 NCH$^{A/B}$), 3.55, 3.78 (each s, 72 H, 24 CH$_3$), 7.70 ppm (br. s, 12 H, 4 NH$_3^+$). ^{13}C NMR (100.5 MHz, CDCl$_3$): $\delta = 13.88$ (4 CH$_3$), 22.06, 25.99, 26.34, 30.61 (16 CH$_2$), 41.50 (4 NCH$_2$), 51.16, 51.95 (24 OCH$_3$), 95.26 (12 =C), 167.18, 170.78 (24 C=O, ester), 184.30 ppm (12 C=O, keto). IR (CHBr$_3$): $\tilde{\nu} = 1725$ (C=O), 1640 cm^{-1} (C=C). $C_{96}H_{136}Mg_4N_4O_{60}$ (2403.36): calcd. C 47.98, H 5.70, N 2.33; found C 48.07, H 6.13, N 2.22.

Compound 5c: Yield: 0.48 g (38%) colourless powder; m.p. 187 °C (decomp.). ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 0.86$ (t, $J = 7.1$ Hz, 12 H, 4 CH$_3$), 0.98, 1.00, 1.13, 1.15, 1.24, 1.26 (each m, 48 H, 24 CH$_2$), 2.45, 2.73 (each br. m, 8 H, 4 NCH$^{A/B}$), 3.55, 3.78 (each s, 72 H, 24 CH$_3$), 7.69 ppm (br. s, 12 H, 4 NH$_3^+$). ^{13}C NMR (100.5 MHz, CDCl$_3$): $\delta = 14.12$ (4 CH$_3$), 22.51, 26.25, 26.89, 28.59, 28.99, 31.86 (24 CH$_2$), 41.56 (4 NCH$_2$), 51.21, 51.98 (24 OCH$_3$), 95.35 (12 =C), 167.22, 170.82 (24 C=O, ester), 184.36 ppm (12 C=O, keto). IR (CHBr$_3$): $\tilde{\nu} = 1720$ (C=O), 1645 cm^{-1} (C=C). $C_{104}H_{152}Mg_4N_4O_{60}$ (2515.57): calcd. C 49.66, H 6.09, N 2.23; found C 49.26, H 6.54, N 2.41.

Compound 6: Yield: 0.73 g (63%) colourless microcrystals; m.p. 182 °C (decomp.). ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 3.43$, 3.50, 3.51, 3.55, 3.56, 3.64, 3.67, 3.71, 3.72, 3.77, 3.79, 3.87, two times two superimposed signals (each s, 80 H, 26 OCH$_3$, 2 CH^A), 4.06 (br. m, 2 H, 2 CH^B, the corresponding H^A was identified by HETCOR), 6.55 (d, $J = 8.6$ Hz, 4 H, Ar-H), 6.96 (d, $J = 8.6$ Hz, 4 H, 4 Ar-H), 7.03 (br. s, 8 H, 2 NH$_4^+$), 8.05 (br. s, 6 H, 2 NH$_3^+$). ^{13}C NMR (100.5 MHz, CDCl$_3$): $\delta = 43.66$ (2 CH$_2$), 50.47, 50.86, 51.29, 51.32, 51.62, 51.70, 51.75, 51.98, 52.09, three times two superimposed signals (24 OCH$_3$), 54.86 (2 OCH$_3$), 94.05, 94.32, 94.45, 95.22, 95.25, two superimposed signals (12 =C), 113.56 (4 Ar-CH), 124.41 (2 Ar-C), 131.05 (4 Ar-CH), 159.71 (2 Ar-C), 166.18, 166.73, 166.99, 168.09, 169.54, 169.58, 170.35, 170.39, 170.67, 170.87, 170.93, 171.09 (24 C=O, ester), 183.83, 184.10, 184.22, 184.36, 185.33, 185.44 (12 C=O, keto); When the NMR spectra of C_2-symmetric **6** were recorded in CD$_3$CN/CDCl$_3$ instead of CDCl$_3$ alone, the spectra of **6** revealed molecular T symmetry due to the core $[Mg_4(L^1)_6]^{4-}$. This is explained by fast exchange of $[NH_4]^+$ and $[H_3NCH_2C_6H_4OMe]^+$. At lower temperatures, the NMR signals characteristic of C_2-symmetric **6** reappeared. ^{1}H NMR (500 MHz, CDCl$_3$/CD$_3$CN): $\delta = 3.44$ (s, 36 H, 12 CH$_3$);

Table 1. Details of X-ray structure determinations

	2a	**4**	**6**	**7a**
Empirical formula	$C_{76}H_{96}Mg_4N_4O_{60}$ $\cdot$ 6 $CHCl_3$	$C_{102}H_{144}Mg_4N_3NaO_{60}$ $\cdot$ 2 H_2O $\cdot$ CH_2Cl_2	$C_{88}H_{104}Mg_4N_4O_{62}$ $\cdot$ 6 $CHCl_3$	$C_{96}H_{120}K_4Mg_4O_{60}$ $\cdot$ 4 H_2O
Molecular mass	2839.08	2613.39	3023.28	2555.59
Crystal size [mm]	0.70 × 0.65 × 0.30	0.35 × 0.35 × 0.30	0.40 × 0.35 × 0.15	0.30 × 0.30 × 0.25
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$C2/c$	$P2_1$
T [K]	133(2)	173(2)	200(2)	173(2)
a [Å]	14.763(3)	20.9857(2)	22.412(6)	15.6360(2)
b [Å]	29.130(6)	22.9751(2)	19.277(4)	15.6507(3)
c [Å]	28.872(6)	26.6598(3)	29.950(9)	26.1277(4)
α [°]				
β [°]	90.15	98.8370(10)	90.97(3)	93.4160(10)
γ [°]				
V [Å^3]	12420(4)	12701.4(2)	12938(6)	6382.46(18)
Z	4	4	4	2
$P_{calcd.}$ [Mg·m^{-3}]	1.519	1.367	1.552	1.330
θ range [°]	1.70 to 25.00	2.19 to 24.42	3.87 to 24.00	1.30 to 24.10
reflections collected	187866	38797	24503	18804
independent reflections	21582	20881	10011	18804
parameters	1873	1576	845	1513
final $R1$ [$I > 2\sigma(I)$]	0.0541	0.0666	0.0967	0.0611
$wR2$ (all data)	0.1304	0.2017	0.2934	0.1761
largest residuals [e·Å^{-3}]	0.966/−0.772	0.988/−0.667	0.960/−1.365	1.348/−0.596

3.73 (s, 6 H, 2 CH_3); 3.74 (s, 38 H, 12 CH_3, 2 CH^B); 3.99 (br. s, 2 H, 2 CH^A); 6.65 (d, J = 8.5 Hz 4 H, Ar-H); 6.98 (d, J = 8.5 Hz, 4 H, 4 Ar-H; 7.00 (br. s, 8 H, 2 NH_4^+); 7.94 (br. s, 6 H, 2 NH_3^+).^{13}C NMR (125.7 MHz, $CDCl_3/CD_3CN$): δ = 44.16 (2 CH_2); 51.60, 52.38 (24 OCH_3); 55.60 (2 OCH_3); 95.69 (12 =C); 114.62 (4 Ar-CH); 125.10 (2 Ar-C); 131.64 (4 Ar-CH); 160.61 (2 Ar-C); 168.21, 171.68 (24 C=O, ester); 185.60 (12 C=O, keto). ^{13}C NMR (125.7 MHz, $CD_3CN/CDCl_3$): δ = 44.16 (2 CH_2), 51.60, 52.38 (24 OCH_3), 55.60 (2 OCH_3), 95.69 (12 =C), 114.61 (2 Ar-C), 125.10 (4 Ar-CH), 131.64 (4 Ar-CH), 160.61 (2 Ar-C), 168.21, 171.68 (24 C=O, ester), 185.60 (12 C=O, keto). IR ($CHBr_3$): $\tilde{\nu}$ = 1710 (C=O), 1640 cm^{-1} (C=C). $C_{88}H_{104}Mg_4N_4O_{62}$ (2307.01): calcd. C 45.82, H 4.54, N 2.43; found C 46.25, H 4.71, N 2.41.

General Procedure. Ammonium/Alkali Cation-Exchange: A solution of potassium hydroxide or caesium hydroxide hydrate (1.7 mmol) in a dichloromethane/ethanol mixture (1:1, 12 mL) was added dropwise to a solution of tetrahemispheraplex **1b** (0.96 g, 0.4 mmol) in dichloromethane (12 mL) over a period of 10 min. The mixture was stirred for 48 h at room temperature and concentrated to ca. 10 mL. The products were then obtained by addition of a mixture of diethyl ether/hexane (1:1, 100 mL), filtered off, washed three times with hexane and dried in vacuo.

Compound 7a: Yield: 0.94 g (94%) colourless microcrystals; m.p. >250 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94, 0.98 (each t, J = 7.0 Hz, 72 H, 24 CH_3), 3.55, 3.78, 4.11, 4.24 (each m, 48 H, 24 $OCH^{A/B}$). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 13.79, 14.02 (24 CH_3), 60.01, 60.23 (24 OCH_2), 93.99 (12 =C), 166.61, 170.14 (24 C=O, ester), 185.38 ppm (12 C=O, keto). IR ($CHBr_3$): $\tilde{\nu}$ = 1640 (C=O), 1480 cm^{-1} (C=C). $C_{96}H_{120}K_4Mg_4O_{60}$ (2487.60): calcd. C 46.35, H 4.86; found C 45.32, H 5.23.

Compound 7b: Yield: 1.03 g (91%) colourless microcrystals; m.p. 224 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.17, 1.21 (each t, J = 7.2 Hz, 72 H, 24 CH_3), 3.93, 3.98, 4.05, 4.14 (each m, 48 H, 24 $CH^{A/B}$). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 13.90, 14.14 (24 CH_3), 60.03, 60.24 (24 OCH_2), 94.00 (12 =C), 168.88, 170.14 (24 C=O, ester), 185.30 ppm (12 C=O, keto). IR ($CHBr_3$): $\tilde{\nu}$ = 1640 (C=O), 1480 cm^{-1} (C=C). $C_{96}H_{120}Cs_4Mg_4O_{60}$ (2862.82): calcd. C 40.28, H 4.22; found C 41.57, H 4.41.

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[10] To facilitate comparison of structures of **4**, **6**, and **7a** (Figures 1−3), identical projections are presented.

[11] Single crystal X-ray structure analyses: Details for crystal data, data collection and refinement are given in Table 1. X-ray data for **2a** were collected on a Stoe−Siemens−Huber Vierkreisdiffraktometer, for **4** and **7a** on a Nonius Kappa CCD area detector, and for **6** on a Stoe IPDS using Mo-K_{α} radiation (λ = 0.71073 Å). Semiempirical absorption corrections were employed. The structures were solved by direct methods with SHELXS-97[12] and refined with full-matrix least-squares against F^2 with SHELXL-97[12] (**2a**, **4** and **7a**) and SHELXL-93[12] (**6**).

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[13] CCDC-185489 (**2a**), CCDC-185404 (**4**), CCDC-186843 (**6**)[15] and CCDC-185405 (**7a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223−336−033; or E-mail: deposit@ccdc.cam.ac.uk).

[14] Because of the low boiling points of methyl- and ethylamine it is more convenient to use the procedure as described for **2a,b** and **3**.

[15] Compound **6** features polymorphism. For supplementary data see CCDC-186844.

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