Enantiomerisation of Tetrahedral Homochiral [M_4L_6] Clusters: Synchronised Four Bailar Twists and Six Atropenantiomerisation Processes Monitored by Temperature-Dependent Dynamic ^{1}H NMR Spectroscopy**

Rolf W. Saalfrank,*[a] Bernhard Demleitner,[a] Horst Glaser,[a] Harald Maid,[a] Daniela Bathelt,[a] Frank Hampel,[a] Walter Bauer,[a] and Markus Teichert[b]

Dedicated to Professor Karl Wieghardt on the occasion of his 60th birthday

Abstract: Temperature-dependent ^{1}H NMR studies prove homochiral, racemic $[(\Delta,\Delta,\Delta,\Delta)/(\Lambda,\Lambda,\Lambda,\Lambda)]$-$\{(NH_4)_4 \cap [Mg_4(L^1)_6]\}$ (**1**) to be kinetically stable on the NMR timescale. Due to steric reasons, rotation around the central C–C single bond in $(L^1)^{2-}$ is blocked, which prevents **1** from enantiomerisation. Most interestingly, however, the ^{1}H NMR spectrum of racemic **2a** reveals dynamic temperature dependence. This phenomenon can be explained by simultaneous Bailar twists at the four octahedrally coordinated magnesium centres, synchronised with the sterically unhindered atropenantiomerisation processes around the C–C single bonds of the six ligands $(L^2)^{2-}$, leading to the unprecedented enantiomerisation $(\Delta,\Delta,\Delta,\Delta)$-**2a** $\rightleftarrows$ $(\Lambda,\Lambda,\Lambda,\Lambda)$-**2a**. The profound nondissociative rearrangement occurs without the formation of diastereoisomers. Supplementary support for the interpretation of the temperature-dependent dynamic ^{1}H NMR spectra of **2a** is presented by additional studies of $[(\Delta,\Delta,\Delta,\Delta)/(\Lambda,\Lambda,\Lambda,\Lambda)]$-$\{(EtNH_3)_4 \cap [Mg_4(L^2)_6]\}$ (**2b**). In **2a** and **2b**, the ether methylene protons exhibit identical temperature dependence. However, with addition, the methylene protons of the ethyl ammonium groups of **2b** display similar temperature dependence as the ligand ether methylene protons.

Keywords: Bailar twist · cage compounds · enantiomerization · NMR spectroscopy · supramolecular chemistry

Introduction

In the last few years, enormous progress has been made in the synthesis of ordered assemblies, by using metal–ligand bonds.[1] There is currently much interest in the role of guest molecules in the self-assembly of metal–ligand clusters and their possible application as test tubes for chemical reactions.[2] Chiral voids principally should be able to induce asymmetry if chiral products are generated therein. For that reason, it is of fundamental interest to gain profound insight into the stereochemistry of three-dimensional metal clusters such as the tetrahedral [M_4L_6] species. For [M_4L_6] clusters, each vertex of the tetrahedron is a chiral metal centre of (Δ) or (Λ) configuration that generally may lead to diastereoisomers with T $[(\Delta,\Delta,\Delta,\Delta)/(\Lambda,\Lambda,\Lambda,\Lambda)]$, C_3 $[(\Delta,\Delta,\Delta,\Lambda)/(\Lambda,\Lambda,\Lambda,\Delta)]$ or S_4 $(\Delta,\Delta,\Lambda,\Lambda)$ symmetry. Their nearly equal stability explains the mix (T, C_3, S_4) of cluster isomers seen.[3] The self-assembly process requires reversibility of a series of connecting steps. Therefore, the rigidity of the bimodal ligand spacers, the nature of the metal and asymmetric induction seem crucial, accommodating either a mixture of diastereoisomers[3] or homoconfigured[4–6] and S_4-symmetric[7] M_4L_6 complexes.

The tetranuclear chelate complex $\{(NH_4)_4 \cap [Mg_4(L^1)_6]\}$ (**1**) is formed in a one-pot reaction from diethyl malonate,[4, 5] whereas the tetrahemispheraplexes $\{(NH_4)_4 \cap [Mg_4(L^2)_6]\}$ (**2a**)[8] and $\{(EtNH_3)_4 \cap [Mg_4(L^2)_6]\}$ (**2b**) are generated from diethyl ketipinate (Scheme 1). According to single-crystal X-ray analyses, **1**[4] and **2a**,**b**[9–12] are isostructural. In contrast, in solution **1** and **2a**,**b** differ considerably with respect to their dynamics. This was realised only recently and is subject of this communication.

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[a] Prof. Dr. R. W. Saalfrank, Dr. B. Demleitner, Dr. H. Glaser,
Dr. H. Maid, Dipl.-Chem. D. Bathelt, Dr. F. Hampel,
Priv.-Doz. Dr. W. Bauer
Institut für Organische Chemie
der Universität Erlangen-Nürnberg
Henkestrasse 42, 91054 Erlangen (Germany)
Fax: (+49) 9131-852-1165
E-mail: saalfrank@organik.uni-erlangen.de

[b] Dr. M. Teichert
Institut für Anorganische Chemie
der Universität Göttingen (Germany)

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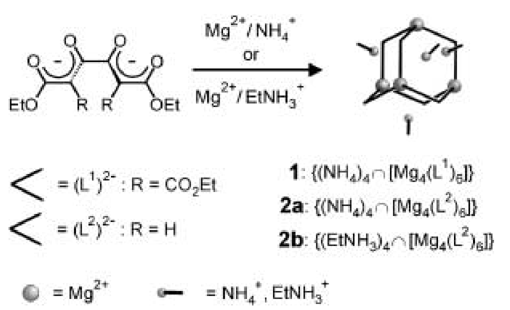

Scheme 1. Generation and schematic representation of **1** and **2a**,**b**.

Results and Discussion

X-ray analyses: The tetrahemispheraplexes **2a**,**b** display a common tetramagnesate(4$^-$) anionic core $(\mathbf{2})^{4-}$, representing an idealised tetrahedron composed of four magnesium cations. These ions are linked along each of the six edges of the tetrahedron by a doubly bidentate diethyl 2,3-dioxobutane-1,4-dicarboxylato(2$^-$) bridge, so that each of the four magnesium(II) ions is octahedrally coordinated by six oxygen donors. The anionic core $(\mathbf{2})^{4-}$ can be regarded as having nearly T symmetry (characterised by three C_2 and four C_3 axes). Accordingly, $(\mathbf{2})^{4-}$ is dissymmetric and thus chiral. The dissymmetry of this anion results from the atropisomerism of the six ligands and the four homoconfigured ($\Delta,\Delta,\Delta,\Delta$)-*fac* or ($\Lambda,\Lambda,\Lambda,\Lambda$)-*fac* metal centres. Charge compensation of $(\mathbf{2})^{4-}$ is achieved by a set of four ammonium or ethylammonium counter ions. Each set is hydrogen bonded to the oxygen donors of the tetrahedral faces of $(\mathbf{2})^{4-}$ to give **2a**,**b**. Each of the crystals of **2a** and **2b** represent a racemic mixture of homoconfigurational ($\Delta,\Delta,\Delta,\Delta$)-*fac* and ($\Lambda,\Lambda,\Lambda,\Lambda$)-*fac* stereoisomers. For graphical representation complex **2b** was chosen (Figure 1).

Abstract in German: *Temperaturabhängigen ^{1}H-NMR-Studien zufolge ist der homochirale, racemische Komplex [($\Delta,\Delta,\Delta,\Delta$)/($\Lambda,\Lambda,\Lambda,\Lambda$)]-$\{(NH_4)_4 \cap [Mg_4(L^1)_6]\}$ (**1**) auf der NMR-Zeitskala kinetisch stabil. Aufgrund sterischer Faktoren ist eine freie Rotation um die C–C-Einfachbindung in $(L^1)^{2-}$ blockiert, wodurch **1** nicht zur Enantiomerisierung befähigt ist. Interessanterweise zeigt das ^{1}H-NMR-Spektrum von racemischem **2** jedoch Temperaturabhängigkeit. Dieses Phänomen läßt sich durch die Synchronisation der an den vier oktaedrisch koordinierten Magnesiumzentren gleichzeitig ablaufenden Bailar-Twists mit den sterisch nicht behinderten Atropenantiomerisierungen um die C–C-Einfachbindungen der sechs Liganden $(L^2)^{2-}$ erklären, was zu der präzedenzlosen Enantiomerisierung ($\Delta,\Delta,\Delta,\Delta$)-**2a** ⇄ ($\Lambda,\Lambda,\Lambda,\Lambda$)-**2a** führt. Die tiefgreifende Umlagerung erfolgt nicht-dissoziativ und ohne das Auftreten von Diastereoisomeren. Die Interpretation der temperaturabhängigen dynamischen ^{1}H-NMR-Spektren von **2a** wird durch zusätzliche Studien an [($\Delta,\Delta,\Delta,\Delta$)/($\Lambda,\Lambda,\Lambda,\Lambda$)]-$\{(EtNH_3)_4 \cap [Mg_4(L^2)_6]\}$ (**2b**) gestützt. In **2a** und **2b** weisen die Ether-methylen-protonen identische Temperaturabhängigkeit auf. In Ergänzung dazu zeigen die Methylenprotonen der Ethylammonium-Gruppen von **2b** eine vergleichbare Temperaturabhängigkeit.*

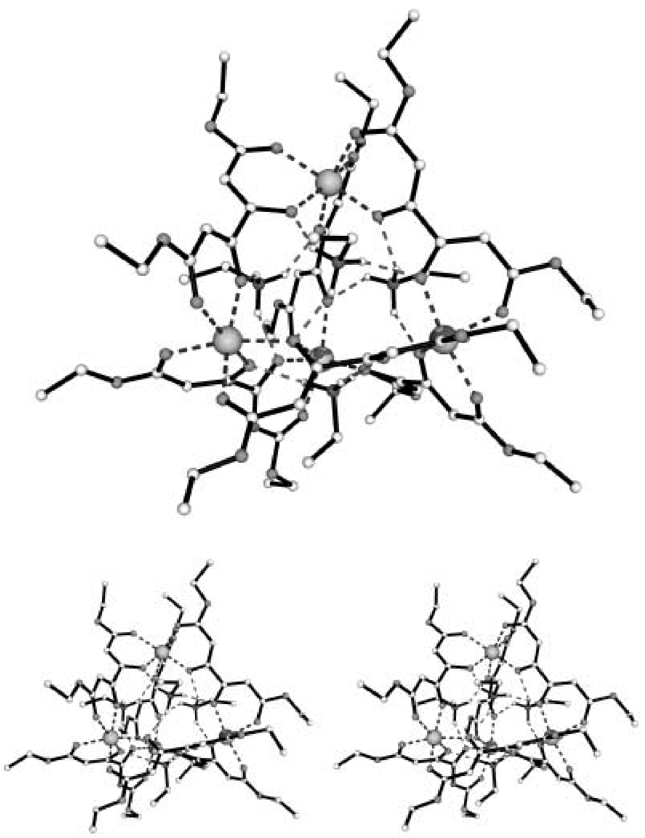

Figure 1. Top: Structure of $\{(EtNH_3)_4 \cap [Mg_4(L^2)_6]\}$ **2b** in the crystal. Bottom: Stereo representation of **2b**. Solvent molecules and hydrogen atoms (except ammonium hydrogens) are not depicted for clarity.

^{1}H NMR studies: Temperature-dependent ^{1}H NMR studies prove $\{(NH_4)_4 \cap [Mg_4(L^1)_6]\}$ (**1**) to be kinetically stable on the NMR timescale.[13] From 32 °C to −10 °C, the spectrum displays one triplet each for the ester and ether methyl groups and four multiplets for the corresponding diastereotopic methylene protons of racemic [($\Delta,\Delta,\Delta,\Delta$)/($\Lambda,\Lambda,\Lambda,\Lambda$)]-**1** (Figure 2, top).

Most interestingly, however, the ^{1}H NMR spectrum of racemic **2a** reveals temperature dependence. The spectrum presents one sharp triplet for the ether methyl groups at 32 °C, but only one unresolved broad signal for the diastereotopic methylene protons. The triplet remains sharp over a temperature range from 32 °C to −10 °C, whereas the methylene protons at 32 °C are recorded as one broad signal and at −10 °C as two poorly resolved quartets (Figure 2, centre). The unique dynamic temperature-dependent ^{1}H NMR spectroscopic behaviour of **2a** can be explained by the unprecedented enantiomerisation of ($\Delta,\Delta,\Delta,\Delta$)-**2a** ⇄ ($\Lambda,\Lambda,\Lambda,\Lambda$)-**2a** (Figure 3).

The enantiomerisation of ($\Delta,\Delta,\Delta,\Delta$)-**2a** ⇄ ($\Lambda,\Lambda,\Lambda,\Lambda$)-**2a** requires *four* synchronised Bailar twists and *six* atropenantiomerisation processes. The Bailar twist links octahedral and trigonal prismatic coordination environments in hexacoordi-

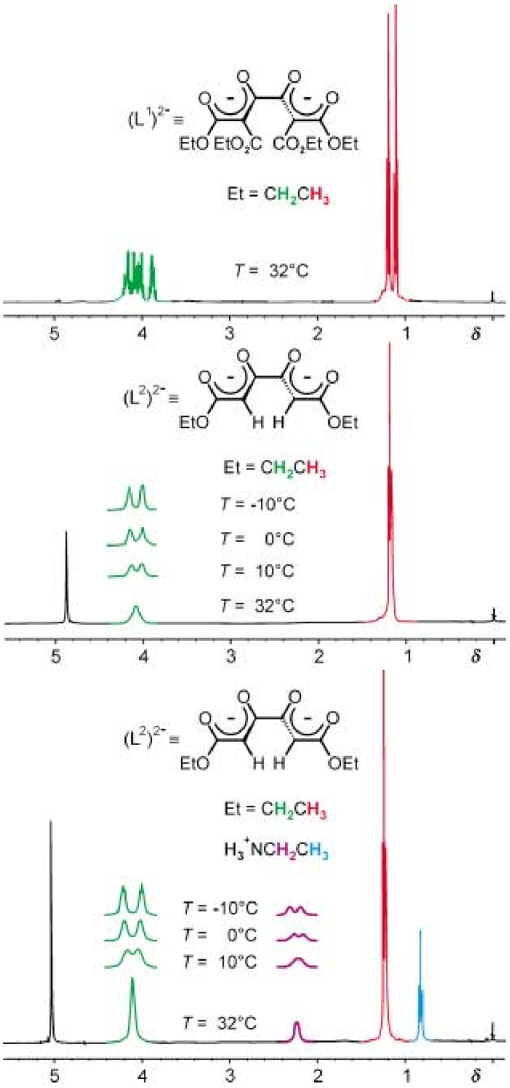

Figure 2. Temperature-dependent ^{1}H NMR spectra of $\{(NH_4)_4\cap[Mg_4(L^1)_6]\}$ (**1**: top), $\{(NH_4)_4\cap[Mg_4(L^2)_6]\}$ (**2a**; centre) and $\{(EtNH_3)_4\cap[Mg_4(L^2)_6]\}$ (**2b**; bottom).

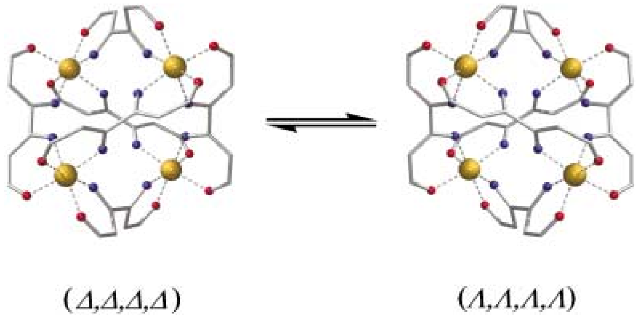

Figure 3. Enantiomerisation of **2a**.

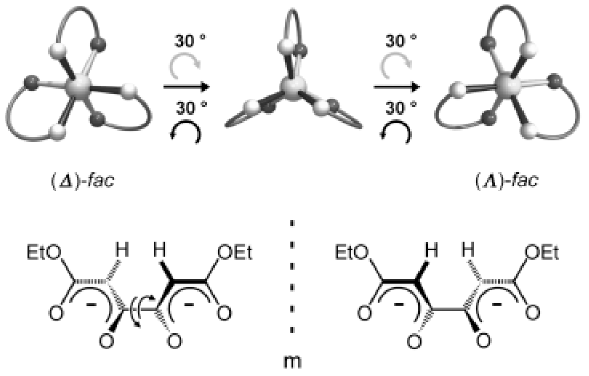

Figure 4. Inversion of configuration in hexacoordinate complexes by a trigonal twist about the C_3 axis through an achiral trigonal prismatic transition state (Bailar twist) (top), and atropenantiomerisation (back and forth twist around the central C–C bond) of ketipinate dianion (bottom).

nate complexes and thus facilitates *nondissociative inversion* of configuration at stereogenic metal centres (Figure 4, top).[14, 15]

A prerequisite for the performance of the Bailar twists in **2a** is its flexible $[Mg_4(L^2)_6]^{4-}$ scaffold. This is guaranteed, since the ketipinate dianion $(L^2)^{2-}$ allows sterically unhindered back and forth twists around the central C–C single bond and thus atropenantiomerisation of the ligands (Figure 4, bottom; Figure 5, top). Consequently, in (Δ,Δ,Δ,Δ)-**2a** the *six* atropenantiomeric ligands $(L^2)^{2-}$ are rocking in the same sense and simultaneously synchronous[16] with *four* Bailar twists to give mirror image (Λ,Λ,Λ,Λ)-**2a** (Figure 3). However, owing to steric reasons, torsion around the central C–C single bond in $(L^1)^{2-}$ is blocked (Figure 5, bottom), which prevents racemic [(Δ,Δ,Δ,Δ)/(Λ,Λ,Λ,Λ)]-**1** from enantiomerisation as is most impressively documented by the temperature-independent ^{1}H NMR spectrum of **1** (Figure 2, top).

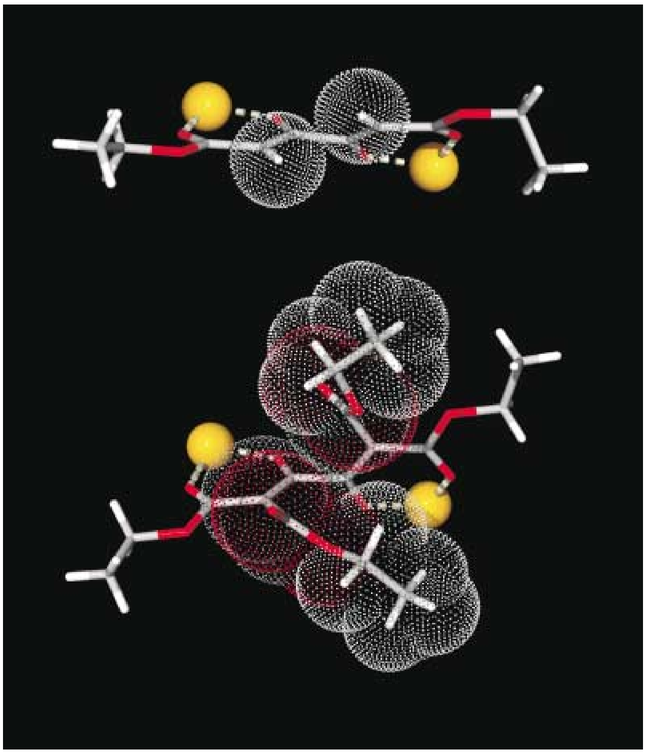

Figure 5. Ligands $(L^2)^{2-}\cdot 2Mg^{2+}$ (top) and $(L^1)^{2-}\cdot 2Mg^{2+}$ (bottom) highlighting the groups in 1,2-position that are responsible for unhindered and blocked rocking around the central C–C bond.

The enantiomerisation of **2a** occurs *nondissociative* without the formation of diastereoisomers, outlined by the sharp singlet at $\delta = 4.90$ ppm for the olefinic protons of **2a**, indicating the presence of only one product. The free activation enthalpy $\Delta G^{\ddagger}_{295}$ for the interconversion barrier of the enantiomerisation process of **2a** is 14.3 kcal mol^{-1}.[17]

Additional support for the interpretation of the temperature dependent dynamic ^{1}H NMR spectrum of **2a** is presented by racemic homochiral $[(\Delta,\Delta,\Delta,\Delta)/(\Lambda,\Lambda,\Lambda,\Lambda)]$-$\{(EtNH_3)_4\cap[Mg_4(L^2)_6]\}$ (**2b**).[10–12] In **2a** and **2b**, the ether methylene protons exhibit identical temperature-dependent ^{1}H NMR signals. In addition, the methylene protons of the face-centred ethyl ammonium groups of tetrahemispheraplex **2b** display similar temperature-dependent signals as the ether methylene protons (Figure 2, bottom). At low temperatures, the enantiomerisation of **2b** is slow on the NMR timescale. The ethyl ammonium methylene protons are in a chiral environment and display diastereotopicity. At higher temperatures, however, the diastereotopicity of the NCH_2 protons is lost because of rapid enantiomerisation of the $[Mg_4(L^2)_6]^{4-}$ core. The free activation enthalpy $\Delta G^{\ddagger}_{273}$ for the interconversion barrier of the enantiomerisation process of **2b** is 12.7 kcal mol^{-1}.

The ammonium counter ions in **1** and **2a** display only one set of protons in their ^{1}H NMR spectra over a temperature range of −50 °C to 50 °C and even at high pressure (1.5 kbar), outlined by singlets at $\delta = 7.21$ and 7.83 ppm (not depicted). This indicates, that the ammonium cations are *rolling* on the tetrahedral faces of **1** and **2a** and are not fixed by directed hydrogen bonds. In the case of directed bonding one ought to see two signals with an intensity ratio of 3:1 for the bonded and the free ammonium protons.

In summary, we have clearly demonstrated by temperature-dependent dynamic ^{1}H NMR spectroscopy that tetrahedral, tetrametallic chelate complexes may undergo multiple non-dissociative rearrangement processes, provided the bridging ligands are flexible. Four synchronised Bailar twists at hexacoordinate magnesium and six atropenantiomerisation processes around the central C–C bond of the dianionic ketipinate scaffold ligands lead to the enantiomerisation of the homoconfigured clusters.

Experimental Section

General methods: All reagents and solvents employed were commercially available high-grade purity materials (Fluka, Aldrich), which were used as supplied without further purification. Temperature-dependent ^{1}H NMR spectra of **2a**,**b** were recorded on a JEOL Alpha 500 spectrometer (500 MHz; 11.7 T) in $CDCl_3$ solutions. The residual solvent signal ($\delta =$ 7.27 ppm) was used as an internal standard. The numbers of the free activation enthalpies were derived by using standard equations for compounds **2a**,**b** or by complete lineshape analysis (software: gNMR, Cherwell scientific) for **2b**. The two methods yield similar results for $\Delta G^{\neq}$ within 0.1 kcal mol^{-1}.[18] Synthesis and spectroscopic data of **1** and **2a** were reported previously.[4, 8]

Compound 2b: A methyllithium solution (1.25 mL, 1.6 N in diethyl ether, 2 mmol) diluted with dry THF (25 mL) was added dropwise to a solution of diethyl ketipinate (230 mg, 1 mmol) in dry THF (50 mL, −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 allowed to warm up to room temperature over a period of 18 h and the resulting yellow solution was then treated for 5 min with 10 % aqueous ethyl ammonium chloride (50 mL). The two layers were separated, the aqueous layer was extracted three times with trichloromethane (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 trichloromethane (5 mL). The reaction product was crystallised by addition of *i*-hexane (50 mL). Yield: 155 mg (55 %) colourless microcrystals; m.p. 198 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.82$ (t, $^3J(H,H) = 7.4$ Hz, 12 H; 4 CH_3 (amine)), 1.23 (t, $^3J(H,H) = 7.0$ Hz, 36 H; 12 CH_3 (ligand)), 2.34 (br s, 8 H; 4 NCH_2), 4.10 (br s, 24 H; 12 OCH_2), 5.04 (s, 12 H; 12 CH), 8.83 ppm (br s, 12 H, 4 NH_3^+); ^{13}C NMR (100.5 MHz, $CDCl_3$): $\delta = 11.94$ (4 CH_3 (amine)), 14.26 (12 CH_3 (ligand)), 34.12 (4 NCH_2), 59.11 (12 OCH_2), 84.25 (12 CH), 172.81, 180.35 ppm (24 C=O); IR ($CHBr_3$): $\tilde{\nu} = 2940$ (CH), 1640 (C=O), 1540 cm^{-1} (C=C); elemental analysis calcd (%) for $C_{68}H_{104}O_{36}N_4Mg_4$ (1650.81): C 49.48 H 6.35 N 3.39; found C 49.21 H 6.45 N 3.09.

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[9] Crystal data for $\{(NH_4)_4 \cap [Mg_4(L^2)_6]\}$ (**2a**): $C_{60}H_{88}O_{36}N_4Mg_4 \cdot 2\,CH_2Cl_2$, $M_r = 1708.46$; crystal dimensions $0.32 \times 0.32 \times 0.09$ mm; cubic, space group $Fd\bar{3}c$, $a = b = c = 33.127(15)$ Å, $V = 36353$ Å^3; $Z = 16$; $F(000) = 14336$, $\rho_{calcd} = 1.248$ g cm^{-3}. Diffractometer: Stoe–Siemens–Huber four-circle diffractometer, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å); $T = 133(2)$ K; graphite monochromator; theta range [°] $3.01 < \Theta < 24.96$; section of the reciprocal lattice: $0 \le h \le 22$, $0 \le k \le 27$, $-2 \le l \le 39$; of 62999 measured reflections, 1340 were independent and 1340 observed with $I > 2\sigma(I)$; linear absorption coefficient 0.237 mm^{-1}. The structure was solved by direct methods using SHELXS-97 and refinement with all data (116 parameters) by full-matrix least-squares on F^2 using SHELXL-97;[11] all non-hydrogen atoms were refined anisotropically; $R1 = 0.0670$ for $I > 2\sigma(I)$ and $wR2 = 0.2103$ (all data); largest peak (0.738 e Å^{-3}) and hole (-0.325 e Å^{-3}).[11, 12]

[10] Crystal data for $\{(EtNH_3)_4 \cap [Mg_4(L^2)_6]\}$ (**2b**): $C_{68}H_{104}O_{36}N_4Mg_4 \cdot 1/2\,CHCl_3$, $M_r = 1710.49$; crystal dimensions $0{,}30 \times 0.30 \times 0.30$ mm; rhombohedral, space group $R\bar{3}$, $a = b = 19.8032(3)$ Å, $c = 39.0214(8)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 120°$, $V = 13252.7(4)$ Å^3; $Z = 6$; $F(000) = 5373$, $\rho_{calcd} = 1.286$ g cm^{-3}; Diffractometer: Nonius KappaCCD, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å); $T = 173(2)$ K; graphite monochromator; theta range [°] $2.40° < \Theta < 26.01$; section of the reciprocal lattice: $-24 \le h \le 18$, $-23 \le k \le 24$, $-48 \le l \le 46$; of 19778 measured reflections, 5800 were independent and 4239 observed with $I > 2\sigma(I)$; linear absorption coefficient 0.156 mm^{-1}. The structure was solved by direct methods using SHELXS-97 and refinement with all data (355 parameters) by full-matrix least-squares on F^2 by using SHELXL97;[11] all non-hydrogen atoms were refined anisotropically; $R1 = 0.0532$ for $I > 2\sigma(I)$ and $wR2 = 0.1626$ (all data); largest peak (0.779 e Å^{-3}) and hole (-0.444 e Å^{-3}).

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[12] CCDC-173862 (**2a**) and CCDC-173040 (**2b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

[13] A prerequisite for the formation of supramolecular species by self-assembly are repair mechanisms. Consequently, with respect to long term experiments, **1** was shown to be kinetically unstable. In **1**, magnesium can be substituted by cobalt, simply by stirring a solution of **1** in methylene chloride for several hours in the presence of an excess of cobalt ions. In contrast, rapid ligand dissociation was monitored for kinetically less-stable $[Ga_4(L^3)_6]$ (L^3 = dianion of tetra-*t*Bu-2,2′-terephthaloyldimalonate) at 20 °C by ^{1}H NMR spectroscopy. In this case, there is only one signal to be seen in the ^{1}H NMR spectrum for the *t*Bu groups due to successive dissociation and rotational equilibration of the ester and ether functions.

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[15] Principally, there are two mechanisms conceivable for the nondissociative enantiomerisation of triple bis-chelate compounds of type $M(A{-}B)_3$: the Bailar-twist and the Ray–Dutt mechanism. A (Δ)-*fac* configured $M(A{-}B)_3$-type compound is transformed into its (Λ)-*fac* stereoisomer by a Bailar twist, but into the (Λ)-*mer* stereoisomer by a Ray–Dutt mechanism. In the case of tetrametallic clusters like **2a**,**b**-*fac* for steric reasons a Ray–Dutt mechanism is excluded, since there is no way to generate **2a**,**b**-*mer* isomers.

[16] The ^{1}H NMR data do not allow to distinguish between a synchronous and a "laola" mechanism, respectively.

[17] See: B. P. Hay, D. A. Dixon, R. Vargas, J. Garza, K. N. Raymond, *Inorg. Chem.* **2001**, *40*, 3922–3935.

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