

Synthesis and Structure of Self-Complementary {2}-Metallacryptates and Their Linear or Meandering Infinite Arrangements in the Solid State^[‡]

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Dedicated to Professor Herbert Mayr on the occasion of his 60th birthday

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Reaction of bis(1,3-diketone) H_2L^1 in the presence of cesium acetate with magnesium acetate yielded crystalline one-dimensional coordination polymer *rac*-(2)_n. The {2}-metallacryptand core $[Mg_2(L^1)_3]^{2-}$ is composed of two magnesium centres linked through three bis(1,3-diketo) dianions $(L^1)^{2-}$. These {2}-metallacryptands are homochiral with either (Δ,Δ)-*fac* or (Λ,Λ)-*fac* stereochemistry at the magnesium centres, and they are capable to host a cesium ion in the cavity. Charge compensation of the thus formed {2}-metallacryptates $\{Cs[C[Mg_2(L^1)_3]]\}^-$ is achieved through extra external cesium ions to give the neutral self-complementary building blocks $[[CsC[(Δ,Δ)/(Λ,Λ)-Mg_2(L^1)_3]]Cs]$, which aggregate end-on across the external cesium ions to give the *homo-chiral* one-dimensional strings $[[CsC[(Δ,Δ)-Mg_2(L^1)_3]]Cs]_n$ $[(Δ,Δ)-(2)_n]$ and $[[CsC[(Λ,Λ)-Mg_2(L^1)_3]]Cs]_n$ $[(Λ,Λ)-(2)_n]$, which are packed in the crystal in alternating homochiral layers. However, reaction of bulkier phenyl-substituted bis(1,3-diketone)

H_2L^2 instead of methyl-substituted H_2L^1 with cesium or rubidium acetate and magnesium, cobalt or zinc acetate yielded the meandering polymer *meso*- $\{[[M^1C[(Δ,Δ)-M^2_2(L^2)_3]]M^1_{end}]\{[[M^1C[(Λ,Λ)-M^2_2(L^2)_3]]M^1_{side}]]\{[[M^1C[(Λ,Λ)-M^2_2(L^2)_3]]M^1_{end}]\{[[M^1C[(Δ,Δ)-M^2_2(L^2)_3]]M^1_{side}]]\}_n$ $[meso-(3)_n]$ ($M^1 = Cs^+, Rb^+$; $M^2 = Mg^{2+}, Co^{2+}, Zn^{2+}$). In this case, the {2}-metallacryptates $\{M^1C[(Δ,Δ)/(Λ,Λ)-M^2_2(L^2)_3]\}^-$ are linked by only one cesium ion end-on to give the fragments *meso*- $\{[[M^1C[(Δ,Δ)-M^2_2(L^2)_3]]M^1_{end}]\{[[M^1C[(Λ,Λ)-M^2_2(L^2)_3]]M^1_{side}]]\}$, which are connected by the second cesium ions side-on. The one-dimensional meander strands of isostructural *meso*-(3)_n are packed in the crystal in parallel. Reaction of 4 equiv. of zinc acetate and 1 equiv. of cesium or rubidium acetate with 2 equiv. of H_2L^2 afforded the $\{M^1C[Zn_2(L^2)_2OAc]\}$ cryptates **4a,b** ($M^1 = Cs^+, Rb^+$).

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Introduction

In earlier work, we demonstrated that hexacoordinate nickel(II) in the presence of cesium ions reacts with bis(1,3-diketo) dianion $(L^1)^{2-}$ to yield the neutral {2}-metallacryptate $\{[CsC[Ni_2(L^1)_3]]Cs\}$ with either (Δ,Δ)-*fac* or (Λ,Λ)-*fac* stereochemistry at the nickel centres. These building blocks are self-complementary and aggregate across the external cesium ions alternately *end-on* to yield in the solid state the one-dimensional coordination polymer *meso*- $\{[[CsC[(Δ,Δ)-Ni_2(L^1)_3]]Cs]\{[[CsC[(Λ,Λ)-Ni_2(L^1)_3]]Cs]\}_n$ $[meso-(1)_n]$ (Figure 1).^[2]

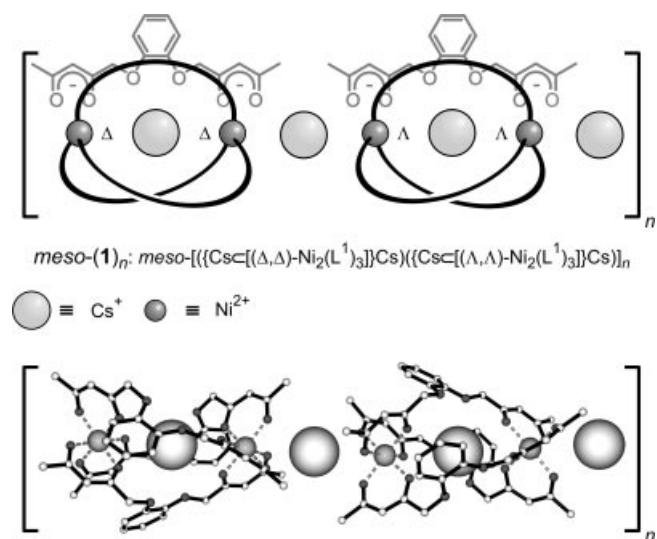


Figure 1. Schematic presentation of the repeating unit of crystalline 1D coordination polymer *meso*-(1)_n (top) and the POVray presentation of the repeating unit of the molecular structure of *meso*-(1)_n (bottom).

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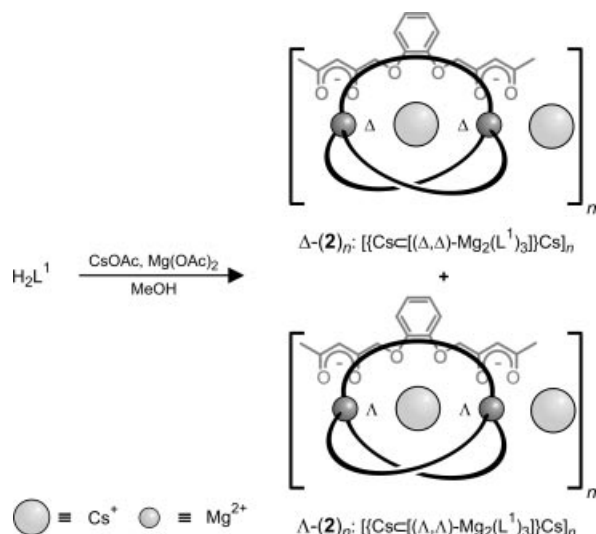
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Results and Discussion

In the course of our ongoing studies on supramolecular coordination chemistry with nickel(II)^[2] and copper(II),^[2–4] we focused on the development of new oligonuclear complexes by self-assembly^[5] with the bis(1,3-diketo) dianion (L^1)^{2–}. To this end, we treated H_2L^1 with magnesium acetate in the presence of cesium acetate in methanol. As in the nickel case, the cesium ions function as templates for the formation of crystalline one-dimensional coordination polymer *rac*-(**2**)_n (Scheme 1). Cuboids obtained by vapour diffusion of diethyl ether into a solution of the reaction product in acetonitrile were subjected to X-ray crystal analysis, which revealed that Δ/Λ -(**2**)_n crystallizes in the triclinic space group $P\bar{1}$ (Table 1).^[6] In Δ/Λ -(**2**)_n, the {2}-metallacryptand $[Mg_2(L^1)_3]^{2–}$ core is composed of two magnesium centres linked through three hexadentate catecholate-spacered bis(1,3-diketo) dianions (L^1)^{2–}. Therefore, each magnesium ion is coordinated octahedrally by six diketo oxygen donors. The resulting {2}-metallacryptands are homochiral with either (Δ,Δ)-*fac* or (Λ,Λ)-*fac* stereochemistry at the magnesium centres and capable to host a cesium ion in the cavity, which is coordinated by six carbonyl and six catecholate oxygen donors each. Charge compensation of the thus formed enantiomers $\{Cs\{[(\Delta,\Delta)/(\Lambda,\Lambda)-Mg_2(L^1)_3]\}^-\}$ is achieved through extra external cesium ions to give the neutral self-complementary building blocks $\{Cs\{[(\Delta,\Delta)/(\Lambda,\Lambda)-Mg_2(L^1)_3]\}Cs\}$. However, contrary to *meso*-(**1**)_n, these building blocks aggregate in the solid state end-on across the external cesium ions to give the *homochiral* strings $\{Cs\{[(\Delta,\Delta)-Mg_2(L^1)_3]\}Cs\}_n$ [Δ -(**2**)_n] and $\{Cs\{[(\Lambda,\Lambda)-Mg_2(L^1)_3]\}Cs\}_n$ [Λ -(**2**)_n],^[6] which are packed in the crystal in alternating homochiral layers (Figure 2). In Δ/Λ -(**2**)_n, the coupling external cesium ions are coordinated by two sets of three peripheral carbonyl oxygen donors and two acetonitrile molecules. An additional noncoordinating acetonitrile molecule per monomer unit, trapped in the crystal, leads to the final overall stoichiometry Δ/Λ -(**2**·3MeCN)_n. Therefore, the stereogenic metal centres are controlled, simply by varying hexacoordinate Ni^{II} in *meso*-(**1**)_n to Mg^{II} in Δ/Λ -(**2**)_n.

To suppress the formation of self-complementary monomers and their aggregation in the solid state by making the external pockets of the cryptates too small to host the external cesium ions, we used H_2L^2 with bulkier phenyl groups instead of H_2L^1 with methyl substituents at the end. For that purpose, the reaction of stoichiometric amounts of H_2L^2 , cesium or rubidium acetate and magnesium, cobalt or zinc acetate in acetonitrile was performed, and we isolated microcrystalline materials after vapour diffusion of diethyl ether into a solution of the reaction products (Scheme 2).

Single crystals obtained for *meso*-(**3b,e**)_n were subjected to X-ray crystal analyses (Table 1).^[6] According to these analyses, *meso*-(**3b,e**)_n are isostructural and crystallize in the monoclinic space group $P2_1/n$. Therefore, only the structure of *meso*-(**3e**)_n is discussed in detail. Contrary to our expectation, a strand *meso*-(**3e**)_n was obtained in the solid state.



Scheme 1. Synthesis and schematic presentation of the repeating units of the homochiral strings Δ -(**2**)_n and Λ -(**2**)_n [= *rac*-(**2**)_n].

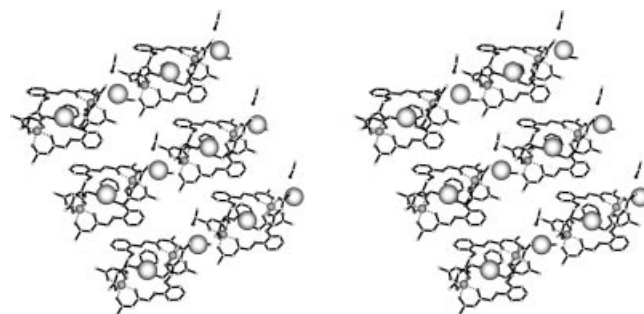
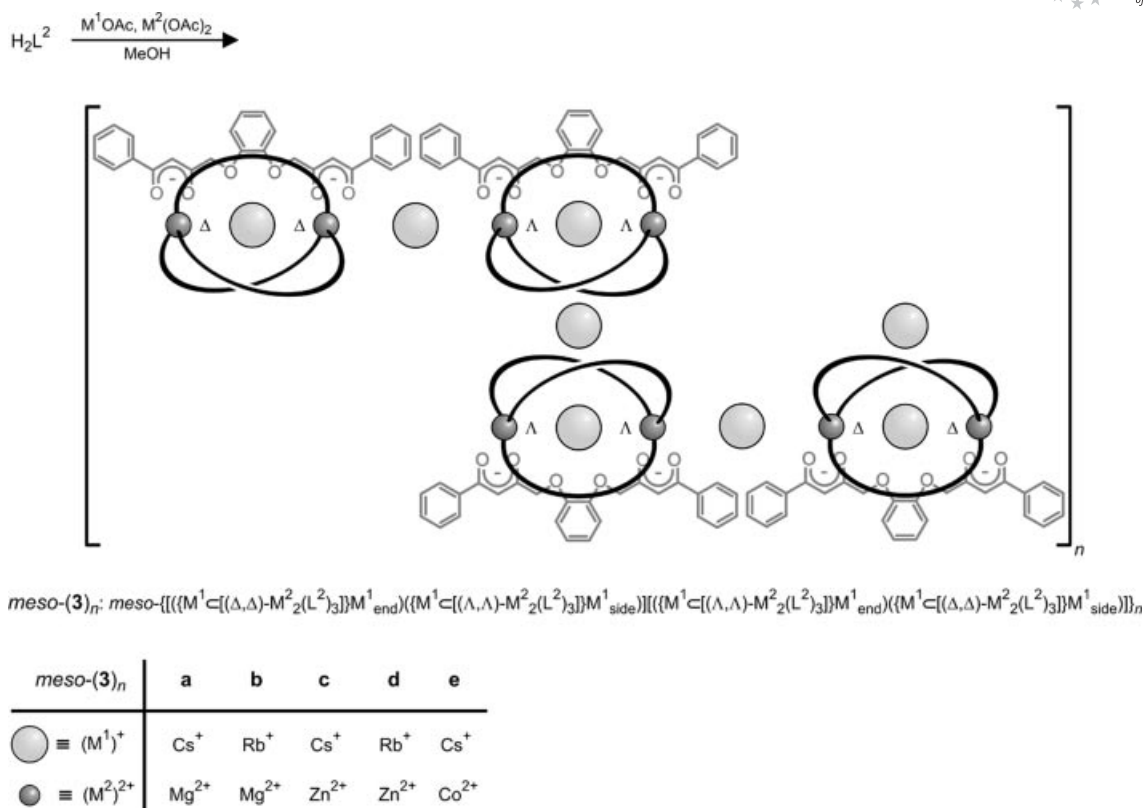


Figure 2. Stereo presentation (POVRAY) of a layer of Λ -(**2**)_n in the crystal together with the coordinating acetonitrile solvent molecules. Mg grey, Cs light grey.

In *meso*-(**3e**)_n, two enantiomers $\{Cs\{[(\Delta,\Delta/\Lambda,\Lambda)-Co_2(L^2)_3]\}^-\}$ are linked by only one cesium ion *end-on* and a second one is coordinated *side-on* to connect these units to finally give *meso*- $\{[(\{Cs\{[(\Delta,\Delta)-Co_2(L^2)_3]\}Cs_{end})-(\{Cs\{[(\Lambda,\Lambda)-Co_2(L^2)_3]\}Cs_{side})][(\{Cs\{[(\Lambda,\Lambda)-Co_2(L^2)_3]\}Cs_{end})-(\{Cs\{[(\Delta,\Delta)-Co_2(L^2)_3]\}Cs_{side})]\}_n$ [*meso*-(**3e**)_n]. Therefore, the Cs_{end} links two enantiomers $\{Cs\{[(\Delta,\Delta/\Lambda,\Lambda)-Co_2(L^2)_3]\}^-\}$, whereas the Cs_{side} links the *meso*- $\{[(\{Cs\{[(\Delta,\Delta)-Co_2(L^2)_3]\}Cs_{end})-(\{Cs\{[(\Lambda,\Lambda)-Co_2(L^2)_3]\}Cs_{side})]\}_n$ fragments across their homochiral {2}-metallacryptate halves. The explanation for the formation of this structure is the fact that when an external cesium splits the {2}-metallacryptate building block at one end, the pocket at the other end is compressed and incapable to host another Cs_{end} . The Cs_{side} ion is coordinated to eight oxygen donors of four ligands (L^2)^{2–} (one carbonyl oxygen donor of one ligand and one carbonyl oxygen donor together with two catecholate oxygen donors of another ligand of one cryptate each) and to two acetonitrile molecules. The meander strands of isostructural *meso*-(**3b,e**)_n are packed in the crystal in parallel. The repetitive unit of the structure in the crystal is therefore



Scheme 2. Synthesis and schematic presentation of the complex repeating unit of infinite one dimensional meander meso-(3)_n .

rather complex. Figure 3 exemplarily exhibits the stereo presentation of the repeating unit of meso-(3e)_n . The stereo view of Figure 4 presents only the metal centres of two strands of meso-(3e)_n .

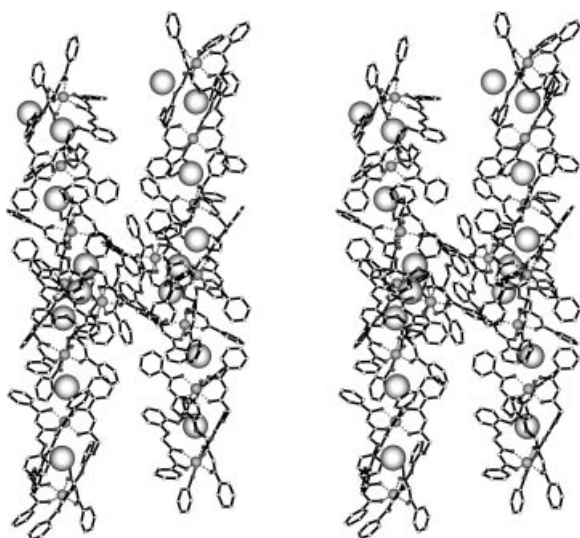


Figure 3. Stereo presentation (POVRAY) of the repeating unit of meso-(3e)_n in the crystal without solvent molecules. Co grey, Cs light grey.

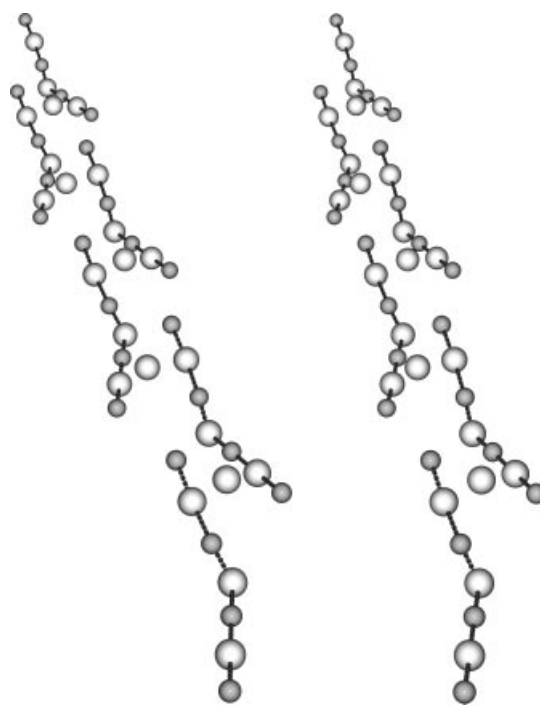
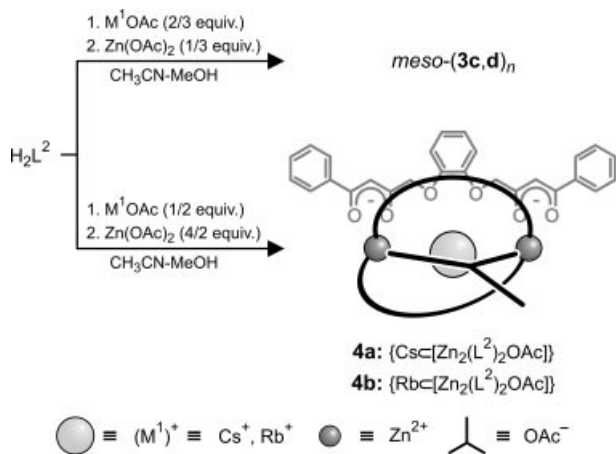


Figure 4. Simplified stereo presentation (POVRAY) of meander meso-(3e)_n . The CsC , Cs_{end} and Co centres are connected by lines and are arranged in angles, linked by the Cs_{side} ions. Co grey, Cs light grey.

Surprisingly, when stoichiometric amounts of H_2L^2 , zinc acetate and cesium acetate were combined, a mixture of two compounds was generated. However, both components can be synthesized separately by using the appropriate stoichiometry (Scheme 3). The reaction of 1 equiv. of zinc acetate and 2 equiv. of cesium acetate with 3 equiv. of H_2L^2 in a mixture of acetonitrile and methanol (3:1) yielded one-dimensional meander polymer *meso*-(**3c**)_n. In contrast, the reaction of 4 equiv. of zinc acetate and 1 equiv. of cesium acetate with 2 equiv. of H_2L^2 afforded {CsC[Zn₂(L²)₂OAc]} cryptate **4a**, which readily crystallized from a mixture of acetonitrile and methanol (3:1) (Scheme 3, Figure 5). Analogously, supramolecular *meso*-(**3d**)_n as well as metallacryptate **4b** are accessible with rubidium (Schemes 2 and 3). Metallacryptate **4a** crystallizes in space group $P2_1/c$ and has idealized C_{2v} molecule symmetry (Table 1).^[6] Two hexadentate bis(1,3-diketo) dianions (L²)²⁻ together with an encapsulated cesium ion formally create a {2}-metallacoronate that is folded by an acetate bridge. In the heteroleptic cryptate, one acetate oxygen atom functions as a μ_1 -donor to one zinc ion and the other as a μ_2 -donor to the other zinc ion, but also to the cesium ion. In **4a**, the cesium ion at one side is coordinatively unsaturated and, therefore, two molecules of **4a** form a dimer due to cation- π interaction of neighboring phenyl groups (Figure 5 bottom).^[7]



Scheme 3. Synthesis of one-dimensional meandering polymers *meso*-(**3c,d**)_n and heteroleptic {2}-cryptates **4** (schematic presentation).

To prove the existence of the supramolecular cryptate monomers of crystalline *rac*-(**2**)_n and *meso*-(**3**)_n also in solution, we carried out ¹H and ¹³C NMR spectroscopic studies of diamagnetic *rac*-(**2**)_n and *meso*-(**3a-d**)_n. It turned out that the spectra of all five compounds were not very significant [5 ¹H and 8 ¹³C NMR signals for *rac*-(**2**)_n and 7 ¹H and 11 ¹³C NMR signals for *meso*-(**3a-d**)_n]. We were unable to detect an AB pattern for the diastereotopic OCH₂ protons, even by using variable temperature techniques.^[8] The compounds *meso*-(**3a**)_n and *meso*-(**3c**)_n are identical except for the metal ions magnesium or zinc. Exemplarily, their spectra are discussed here in detail. They differ only slightly in their chemical shifts. To evaluate the intermolecular exchange processes, we also recorded a ¹³C NMR spectrum

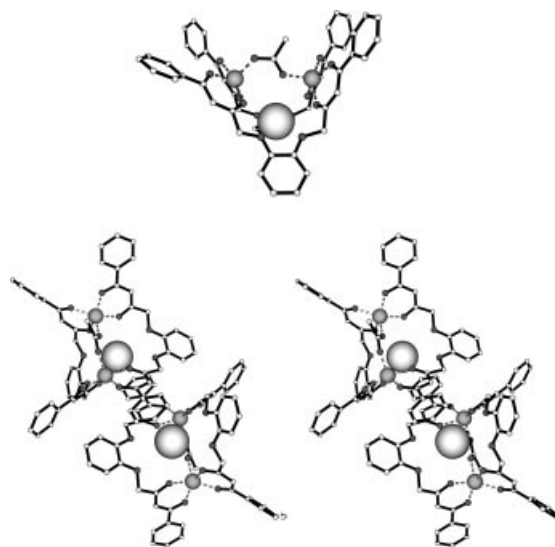


Figure 5. Structure of heteroleptic cryptate **4a** (top) and stereo presentation (POVRAY) of the dimer of **4a** (bottom). Zn grey, Cs light grey.

of a 1:1 mixture of *meso*-(**3a**)_n and *meso*-(**3c**)_n in [D₆]acetone. A total of 22 signals was detected, which is twice the number of signals for each individual compound. We thus concluded that any Mg/Zn exchange process must be extremely slow on the NMR timescale. Unequivocally, we observed intact cryptate monomers also in solution. For convenience, we present only the carbonyl ¹³C NMR signals for cryptates *meso*-(**3a**)_n and *meso*-(**3c**)_n and their 1:1 mixture in [D₆]acetone (Figure 6).

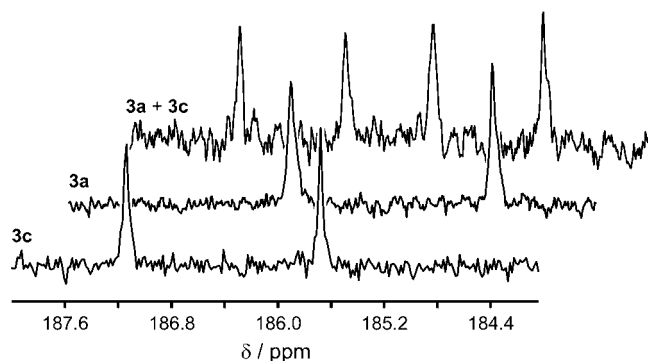


Figure 6. ¹³C NMR signals for the carbonyl atoms of *meso*-(**3a**)_n and *meso*-(**3c**)_n and their 1:1 mixture in [D₆]acetone at ca. 25 °C.

The number of ¹³C NMR signals found for *meso*-(**3a**)_n and *meso*-(**3c**)_n observed in solution (11 each) suggests that a homochiral ($\Delta,\Delta/\Lambda,\Lambda$) monomeric species exists as proposed from the X-ray data. However, the ¹³C NMR spectroscopic data would also match a heterochiral (Δ,Λ) monomeric species. The monomeric homochiral species represents the racemate, the heterochiral species is a monomeric *meso* compound. Therefore, provided that there are only minute chemical shift differences between the racemate and *meso* compounds, there might be a mixture of both diastereomers present. Normal ¹³C NMR spectroscopic pro-

cessing yields only a single set of signals. However, we are currently exploring whether these signals can be resolved further. This requires ^{13}C NMR spectroscopic data with very high signal-to-noise ratios and resolution enhancement techniques. We will report in forthcoming papers on these results.

Conclusions

We presented the synthesis of the homochiral linear one-dimensional polymers $[\{\text{Cs}[(\Delta, \Delta)\text{-Mg}_2(\text{L}^1)_3]\}\text{Cs}]_n$ $[\Delta\text{-}(2)_n]$ and $[\{\text{Cs}[(\Lambda, \Lambda)\text{-Mg}_2(\text{L}^1)_3]\}\text{Cs}]_n$ $[\Lambda\text{-}(2)_n]$ and the one dimensional meander polymers *meso*- $\{[(\text{M}^1\text{C}[(\Delta, \Delta)\text{-M}^2_2(\text{L}^2)_3])\text{M}^1_{\text{end}})(\text{M}^1\text{C}[(\Lambda, \Lambda)\text{-M}^2_2(\text{L}^2)_3])\text{M}^1_{\text{side}}]\}_n$ $[\text{meso}\text{-}(3)_n]$ ($\text{M}^1 = \text{Cs}^+, \text{Rb}^+$; $\text{M}^2 = \text{Mg}^{2+}, \text{Co}^{2+}, \text{Zn}^{2+}$). The structures of complexes **1–4** were solved by the combination of mass spectroscopy, single-crystal X-ray analyses and ^1H and ^{13}C NMR spectroscopy. Most importantly, the ^{13}C NMR spectrum of a mixture of *meso*-(**3a,c**) unequivocally proved the existence of the intact cryptates $\{\text{Cs}[(\text{Mg}_2(\text{L}^2)_3)]^-\}$ of *meso*-(**3a**) $_n$ and $\{\text{Cs}[\text{Zn}_2(\text{L}^2)_3)]^-\}$ of *meso*-(**3c**) $_n$ in solution.

Experimental Section

General Techniques: All solvents used were purified according to standard procedures. All reagents employed were commercially available, high-grade purity materials and used as supplied (Fluka, Aldrich and Acros). Melting points were determined with a WAGNER-MUNZ apparatus and are uncorrected. IR spectra were recorded as powder films with a ASI React IR-1000 spectrometer. NMR spectra were obtained from dilute solutions in CDCl_3 , unless stated otherwise, and recorded with a JEOL EX400 or a BRUKER Avance 300 spectrometer. The residual solvent signals were used as internal standards: CDCl_3 (^1H 7.27 ppm, ^{13}C 77.0 ppm); $[\text{D}_6]\text{acetone}$ (^1H 2.05 ppm; ^{13}C 29.85 ppm).^[9] The resonance multiplicity is indicated as s (singlet), d (doublet) and m (multiplet). MS (FAB) spectra were recorded with a Micromass ZAB-Spec (Cs^+) spectrometer with *m*-NBA as matrix. Elemental analyses were performed with a Carlo Erba EA1110 CHN instrument and with a HERAEUS CHN-Mikroautomat.

General Procedure for $\text{H}_2\text{L}^{1,2}$:^[2,10] To a suspension of sodium amide (7.8 g, 200 mmol) in THF (200 mL) was added a solution of the corresponding methyl ketone (100 mmol) in THF (20 mL) by a dropping funnel. After 15 min, a solution of ester 1,2-bis(methyl-acetoxy)benzene^[11] (12.71 g, 50 mmol) in THF (20 mL) was added. After heating at reflux for 4 h, cooling to room temp. and the addition of water (5 mL), the mixture was concentrated under reduced pressure. The residue was taken up in water (100 mL) and acidified with concentrated HCl (30 mL). Extraction of the aqueous phase with chloroform (3×100 mL), drying (over sodium sulfate) and evaporation of the combined organic phases yielded the crude reaction product, which was further purified by recrystallization. In solution, the ligands $\text{H}_2\text{L}^{1,2}$ are present as a tautomeric mixture of the diketo, monoenol and bisenol species. Below, only signals of the dominating bisenol form are listed.

H_2L^1 : Acetone (7.34 mL). Yield: 5.5 g (36%), bright-beige crystals (methanol). M.p. 92 °C. ^1H NMR (300.1 MHz): δ = 15.26 (br. s, 2

H, OH), 6.98–6.95 (m, 2 H, Ar-H), 6.89–6.86 (m, 2 H, Ar-H), 5.98 (s, 2 H, CH), 4.65 (s, 4 H, CH_2), 2.10 (s, 6 H, CH_3) ppm. ^{13}C NMR (75.5 MHz): δ = 191.88 (2 C=O), 190.50 (2 C=O), 148.04 (2 Ar-C-O), 122.57 (2 Ar-C-H, *m*- C_6H_4), 114.69 (2 Ar-C-H, *o*- C_6H_4), 97.44 (2 CH), 70.24 (2 CH_2), 24.47 (2 CH_3) ppm. IR: $\tilde{\nu}$ = 2922, 1609, 1589, 1509, 1225, 1124 cm^{-1} . MS: m/z (%) = 307 (100) $[\text{M} + \text{H}]^+$, 222 (9) $[\text{M} - \text{COCH}_2\text{COMe}]^+$. $\text{C}_{16}\text{H}_{18}\text{O}_6$ (306.32): calcd. C 62.74, H 5.92; found C 62.85, H 6.04.

H_2L^2 : Acetophenone (11.67 mL). Yield: 10.3 g (48%), colorless cotton-like crystals (methanol). M.p. 117 °C. ^1H NMR (300.1 MHz): δ = 15.87 (br. s, 2 H, OH), 7.78–7.76 (m, 4 H, Ar-H, *o*- C_6H_5), 7.41–7.36 (m, 2 H, Ar-H, *p*- C_6H_5), 7.30–7.25 (m, 4 H, Ar-H, *m*- C_6H_5), 6.93–6.86 (m, 4 H, Ar-H, C_6H_4), 6.66 (s, 2 H, CH), 4.72 (s, 4 H, CH_2) ppm. ^{13}C NMR (75.5 MHz): δ = 193.70 (2 C=O), 182.75 (2 C=O), 147.95 (2 Ar-C-O), 133.90 (2 Ar-C-C=O), 132.67 (2 Ar-C-H, *p*- C_6H_5), 128.62 (4 Ar-C-H, C_6H_5), 127.11 (4 Ar-C-H, C_6H_5), 122.54 (2 Ar-C-H, *m*- C_6H_4), 114.68 (2 Ar-C-H, *o*- C_6H_4), 93.44 (2 CH), 70.73 (2 CH_2) ppm. IR: $\tilde{\nu}$ = 3050, 2890, 2830, 1610, 1575, 1509, 1262, 1227, 1127 cm^{-1} . MS: m/z (%) = 431 (100) $[\text{M}]^+$. $\text{C}_{26}\text{H}_{22}\text{O}_6$ (430.46): calcd. C 72.55, H 5.15; found C 72.19, H 5.13.

$\Delta/\Lambda\text{-}(2)_n$: A solution of cesium acetate (25 mg, 131 μmol) in MeOH (1 mL) was added to a solution of ligand H_2L^1 (40 mg, 131 μmol) in MeOH (3 mL). The mixture was heated to boiling. Then a solution of $\text{Mg}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (19 mg, 87 μmol) in MeOH (1 mL) was prepared at boiling heat and added dropwise. After cooling and filtration of the resulting mixture, the crude product was obtained in the form of microcrystals by vapour diffusion of diethyl ether into the filtrate. Recrystallisation from acetonitrile by vapour diffusion of diethyl ether gave colourless crystals of $\Delta/\Lambda\text{-}(2\cdot 3\text{CH}_3\text{-CN})_n$, suitable for X-ray structure determination. Yield: 25 mg (47%) of $\Delta/\Lambda\text{-}(2)_n$ after drying for 8 h under reduced pressure (10^{-3} mbar). M.p. >260 °C (decomp). ^1H NMR (300.1 MHz, XXXX): δ = 6.76 (br. s, 6 H, Ar-H), 6.46 (br. s, 6 H, Ar-H), 4.75 (br. s, 6 H, CH), 4.03 (br. s, 12 H, CH_2), 1.78 (br. s, 18 H, CH_3) ppm. ^{13}C NMR (100.5 MHz, XXXX): δ = 191.66 (6 C=O), 183.23 (6 C=O), 146.42 (6 Ar-C-O), 120.67 (6 Ar-C-H), 111.67 (6 Ar-C-H), 95.11 (6 CH), 68.24 (6 CH_2), 28.21 (6 CH_3) ppm. IR: $\tilde{\nu}$ = 3065, 2910, 1613, 1521, 1235, 1127, 1054 cm^{-1} . MS: m/z (%) = 1359 (15) $[\text{Cs}[\text{Mg}_2\text{L}_3 + 2\text{Cs}]^+]$, 1227 (22) $[\text{Cs}[\text{Mg}_2\text{L}_3 + \text{Cs}]^+]$, 789 (100) $[\text{Mg}_2\text{L}_2 + \text{Cs}]^+$, 691 (16) $[\text{Mg}_2\text{L}_2 + \text{Cs} - \text{CH}_2\text{COCHCOCH}_3]^+$. $\text{C}_{48}\text{H}_{48}\text{Cs}_2\text{Mg}_2\text{O}_{18}$ (1227.40): calcd. C 46.97, H 3.95; found C 46.47, H 4.13.

General Procedure for *meso*-(3a,b,e**) $_n$:** A solution of cesium or rubidium acetate (77 μmol) in MeOH (1 mL) was added to a solution of ligand H_2L^2 (50 mg, 116 μmol) in acetonitrile (3 mL). The mixture was heated to boiling. Then a solution of $\text{M}^2(\text{OAc})_2 \cdot x\text{H}_2\text{O}$ (77 μmol) in MeOH (1 mL) was prepared at boiling heat and added dropwise. After cooling and filtration of the resulting mixture, the product was obtained in the form of crystals by vapour diffusion of diethyl ether into the filtrate.

***meso*-(**3a**) $_n$:** CsOAc (15 mg) and $\text{Mg}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (17 mg). Yield: 38 mg (62%), colorless crystals after drying for 8 h under reduced pressure (10^{-3} mbar). M.p. >220 °C (decomp). ^1H NMR (300.1 MHz, $[\text{D}_6]\text{acetone}$): δ = 7.88–7.85 (m, 12 H, Ar-H, *o*- C_6H_5), 7.41–7.31 (m, 18 H, Ar-H, *m*- and *p*- C_6H_5), 6.61–6.58 (m, 6 H, Ar-H, C_6H_4), 6.33–6.30 (m, 6 H, Ar-H, C_6H_4), 5.63 (br. s, 6 H, CH), 4.33 (br. s, 12 H, CH_2) ppm. ^{13}C NMR (75.5 MHz, $[\text{D}_6]\text{acetone}$): δ = 186.32 (6 C=O), 184.80 (6 C=O), 147.65 (6 Ar-C-O), 142.54 (6 Ar-C-C=O), 130.71 (6 Ar-C-H, *p*- C_6H_5), 128.64 (12 Ar-C-H, C_6H_5), 128.16 (12 Ar-C-H, C_6H_5), 121.41 (6 Ar-C-H, *m*- C_6H_4), 112.57 (6 Ar-C-H, *o*- C_6H_4), 92.30 (6 CH), 69.60 (6 CH_2) ppm. IR:

$\tilde{\nu}$ = 3065, 2918, 1610, 1575, 1502, 1247, 1127, 1042 cm⁻¹. MS: m/z (%) = 1732 (83) [CsC≡Mg₂L₃ + 2Cs]⁺, 1601 (23) [CsC≡Mg₂L₃ + Cs]⁺, 1038 (100) [Mg₂L₂ + Cs]⁺, 877 (32) [Mg₂L₂ + Cs – CH₂COCHCOC₆H₅]⁺, 718 (21) [Mg₂L₂ + Cs – 2CH₂COCHCOC₆H₅]⁺. C₇₈H₆₀O₁₈Cs₂Mg₂ (1599.82): calcd. C 58.56, H 3.79; found C 57.71, H 3.93.

meso-(3b)_n: RbOAc (11 mg) and Mg(OAc)₂·4H₂O (17 mg), colorless crystals of **meso-(3b)·2CH₃CN**_n suitable for X-ray structure determination. Yield: 21 mg (36%) of **meso-(3b)_n** after drying for 8 h under reduced pressure (10⁻³ mbar). M.p. >190 °C (decomp). ¹H NMR (300.1 MHz, [D₆]acetone): δ = 7.88–7.85 (br. s, 12 H, Ar-*H*, *o*-C₆H₅), 7.40–7.30 (m, 18 H, Ar-*H*, *m*- and *p*-C₆H₅), 6.57 (br. s, 6 H, Ar-*H*, C₆H₄), 6.26 (br. s, 6 H, Ar-*H*, C₆H₄), 5.60 (br. s, 6 H, CH), 4.28 (br. s, 12 H, CH₂) ppm. ¹³C NMR (75.5 MHz, [D₆]acetone): δ = 185.79 (6 C=O), 184.40 (6 C=O), 147.34 (6 Ar-C-O), 141.86 (6 Ar-C-C=O), 130.15 (6 Ar-C-H, *p*-C₆H₅), 128.03 (12 Ar-C-H, C₆H₅), 127.63 (12 Ar-C-H, C₆H₅), 120.85 (6 Ar-C-H, *m*-C₆H₄), 112.07 (6 Ar-C-H, *o*-C₆H₄), 92.12 (6 CH), 69.24 (6 CH₂) ppm. IR: $\tilde{\nu}$ = 3065, 2922, 1606, 1575, 1502, 1247, 1127, 1038 cm⁻¹. MS: m/z (%) = 1590 (27) [RbC≡Mg₂L₃ + 2 Rb]⁺, 1505 (28) [RbC≡Mg₂L₃ + Rb]⁺, 991 (100) [Mg₂L₂ + Rb]⁺, 831 (25) [Mg₂L₂ + Rb – CH₂COCHCOC₆H₅]⁺. C₇₈H₆₀O₁₈Mg₂O₁₈Rb₂ (1504.94): calcd. C 62.26, H 4.02; found C 63.00, H 3.89.

meso-(3e)_n: CsOAc (15 mg) and Co(OAc)₂·4H₂O (19 mg), red crystals of **meso-(3e)·10CH₃CN·18CH₃OH**_n suitable for X-ray structure determination. Yield: 45 mg (70%) of **meso-(3e)_n** after drying for 8 h under reduced pressure (10⁻³ mbar). M.p. >220 °C (decomp). IR: $\tilde{\nu}$ = 3061, 2918, 1598, 1571, 1502, 1243, 1127, 1038 cm⁻¹. MS: m/z (%) = 1799 (42) [CsC≡Co₂L₃ + 2Cs]⁺, 1669 (74) [CsC≡Co₂L₃ + Cs]⁺, 1536 (31) [CsC≡Co₂L₃]⁺, 1107 (100) [Co₂L₂ + Cs]⁺, 947 (27) [Co₂L₂ + Cs – CH₂COCHCOC₆H₅]⁺. C₇₈H₆₀O₁₈Co₂Cs₂ (1669.06): calcd. C 56.13, H 3.63; found C 56.68, H 3.81.

General Procedure for meso-(3c,d)_n: A solution of cesium or rubidium acetate (116 μmol) in MeOH (1 mL) was added to a solution of ligand H₂L² (75 mg, 174 μmol) in acetonitrile (5 mL). The mixture was heated to boiling. Then a solution of Zn(OAc)₂·2H₂O (13 mg, 58 μmol) in MeOH (1 mL) was prepared at boiling heat and added dropwise. After cooling and filtration of the resulting mixture, the product precipitated from the filtrate during 12 h in the form of crystals.

meso-(3c)_n: CsOAc (22 mg). Yield: 32 mg (66%), colorless crystals of **meso-(3c)_n** after drying for 8 h under reduced pressure (10⁻³ mbar). M.p. >190 °C (decomp). ¹H NMR (300.1 MHz, [D₆]acetone): δ = 7.85–7.83 (m, 12 H, Ar-*H*, *o*-C₆H₅), 7.31–7.41 (m, 18 H, Ar-*H*, *m*- and *p*-C₆H₅), 6.57 (br. s, 6 H, Ar-*H*, C₆H₄), 6.35 (br. s, 6 H, Ar-*H*, C₆H₄), 5.56 (br. s, 6 H, CH), 4.27 (br. s, 12 H, CH₂) ppm. ¹³C NMR (100.5 MHz, [D₆]acetone): δ = 187.14 (6 C=O), 185.68 (6 C=O), 147.65 (6 Ar-C-O), 142.61 (6 Ar-C-C=O), 130.74 (6 Ar-C-H, *p*-C₆H₅), 128.68 (12 Ar-C-H, C₆H₅), 128.10 (12 Ar-C-H, C₆H₅), 121.43 (6 Ar-C-H, *m*-C₆H₄), 112.57 (6 Ar-C-H, *o*-C₆H₄), 92.11 (6 CH), 69.58 (6 CH₂) ppm. IR: $\tilde{\nu}$ = 3065, 2918, 1598, 1571, 1502, 1243, 1127, 1038 cm⁻¹. MS: m/z (%) = 1813 (33) [CsC≡Zn₂L₃ + 2Cs]⁺, 1683 (11) [CsC≡Zn₂L₃ + Cs]⁺, 1121 (100) [Zn₂L₂ + Cs]⁺, 961 (16) [Zn₂L₂ + Cs – CH₂COCHCOC₆H₅]⁺. C₇₈H₆₀O₁₈Cs₂Zn₂ (1681.98): calcd. C 55.70, H 3.60; found C 55.56, H 3.69.

meso-(3d)_n: RbOAc (17 mg). Yield: 14 mg (45%), colorless crystals of **meso-(3d)_n** after drying for 8 h under reduced pressure (10⁻³ mbar). M.p. >180 °C (decomp). ¹H NMR (300.1 MHz, [D₆]acetone): δ = 7.81 (br. s, 12 H, Ar-*H*, *o*-C₆H₅), 7.38–7.32 (m, 18 H, Ar-*H*, *m*- and *p*-C₆H₅), 6.56 (br. s, 6 H, Ar-*H*, C₆H₄), 6.30 (br. s, 6 H, Ar-*H*, C₆H₄), 5.52 (br. s, 6 H, CH), 4.24 (br. s, 12 H, CH₂) ppm. ¹³C NMR (75.5 MHz, [D₆]acetone): δ = 186.70 (6 C=O), 185.30 (6

C=O), 147.33 (6 Ar-C-O), 141.95 (6 Ar-C-C=O), 130.21 (6 Ar-C-H, *p*-C₆H₅), 128.11 (12 Ar-C-H, C₆H₅), 127.60 (12 Ar-C-H, C₆H₅), 120.87 (6 Ar-C-H, *m*-C₆H₄), 112.15 (6 Ar-C-H, *o*-C₆H₄), 92.02 (6 CH), 69.22 (6 CH₂) ppm. IR: $\tilde{\nu}$ = 3065, 2918, 1598, 1571, 1513, 1247, 1127, 1038 cm⁻¹. MS: m/z (%) = 1671 (32) [RbC≡Zn₂L₃ + 2Rb]⁺, 1587 (17) [RbC≡Zn₂L₃ + Rb]⁺, 1073 (100) [Zn₂L₂ + Rb]⁺, 913 (27) [Zn₂L₂ + Rb – CH₂COCHCOC₆H₅]⁺. C₇₈H₆₀O₁₈Rb₂Zn₂ (1587.10): calcd. C 59.02, H 3.82; found C 58.76, H 3.97.

General Procedure for 4a,b: A solution of cesium or rubidium acetate (29 μmol) in MeOH (1 mL) was added to a solution of ligand H₂L² (25 mg, 58 μmol) in acetonitrile (3 mL). The mixture was heated to boiling. Then a solution of Zn(OAc)₂·2H₂O (25 mg, 116 μmol) in MeOH (1 mL) was prepared at boiling heat and added dropwise. After cooling and filtration of the resulting mixture, the product precipitated from the filtrate during 12 h in the form of crystals.

4a: CsOAc (6 mg). Colorless crystals of **4a·3CH₃CN** suitable for X-ray structure determination by vapour diffusion of diethyl ether into a mother liquor of **4a** in acetonitrile. Yield: 59 mg (86%) of **4a** after drying for 8 h under reduced pressure (10⁻³ mbar). M.p. >210 °C (decomp). ¹H NMR (300.1 MHz): δ = 7.93–7.91 (m, 8 H, Ar-*H*, *o*-C₆H₅), 7.42–7.31 (m, 12 H, Ar-*H*, *m*- and *p*-C₆H₅), 6.95 (*ps*-s, 8 H, Ar-*H*, C₆H₄), 5.97 (s, 4 H, CH), 4.71 (d, ²*J* = 12.0 Hz, 4 H, CH₂), 4.36 (d, ²*J* = 12.0 Hz, 4 H, CH₂), 2.20 (s, 3 H, CH₃) ppm. ¹³C NMR (75.5 MHz): δ = 188.30 (4 C=O), 186.51 (4 C=O), 180.38 (H₃C-CO₂), 148.46 (4 Ar-C-O), 139.72 (4 Ar-C-C=O), 131.05 (2 Ar-C-H, *p*-C₆H₅), 128.03 (4 Ar-C-H, C₆H₅), 127.57 (8 Ar-C-H, C₆H₅), 122.82 (4 Ar-C-H, *m*-C₆H₄), 115.95 (4 Ar-C-H, *o*-C₆H₄), 93.79 (4 CH), 73.90 (4 CH₂), 24.56 (CH₃-CO₂) ppm. IR: $\tilde{\nu}$ = 3065, 2903, 2849, 1598, 1567, 1521, 1254, 1119, 1034 cm⁻¹. MS: m/z (%) = 1121 (84) [CsC≡Zn₂L₂]⁺, 959 (11) [CsC≡Zn₂L₂ – CH₂COCHCOC₆H₅]⁺, 625 (17) [ZnL + Cs]⁺. C₅₄H₄₃O₁₄CsZn₂ (1179.66): calcd. C 54.98, H 3.68; found C 54.81, H 3.69.

4b: RbOAc (4 mg). Colorless crystals of **4b·2CH₃CN·CH₃OH** suitable for X-ray structure determination by vapour diffusion of diethyl ether into a mother liquor of **4b** in acetonitrile. Yield: 47 mg (72%) of **4b** after drying for 8 h under reduced pressure (10⁻³ mbar). M.p. >210 °C (decomp). ¹H NMR (300.1 MHz): δ = 7.94–7.91 (m, 8 H, Ar-*H*, *o*-C₆H₅), 7.43–7.32 (m, 12 H, Ar-*H*, *m*- and *p*-C₆H₅), 6.99 (*ps*-s, 8 H, Ar-*H*, C₆H₄), 5.94 (s, 4 H, CH), 4.71 (d, ²*J* = 12.6 Hz, 4 H, CH₂), 4.37 (d, ²*J* = 12.6 Hz, 4 H, CH₂), 2.25 (s, 3 H, CH₃) ppm. ¹³C NMR (75.5 MHz): δ = 188.10 (4 C=O), 186.79 (4 C=O), 180.67 (H₃C-CO₂), 148.76 (4 Ar-C-O), 139.69 (4 Ar-C-C=O), 131.05 (2 Ar-C-H, *p*-C₆H₅), 128.04 (4 Ar-C-H, C₆H₅), 127.53 (8 Ar-C-H, C₆H₅), 123.07 (4 Ar-C-H, *m*-C₆H₄), 116.71 (4 Ar-C-H, *o*-C₆H₄), 93.31 (4 CH), 73.78 (4 CH₂), 24.74 (CH₃-CO₂) ppm. IR: $\tilde{\nu}$ = 3065, 2903, 2845, 1594, 1563, 1521, 1254, 1119, 1034 cm⁻¹. MS: m/z (%) = 1073 (100) [RbC≡Zn₂L₂]⁺, 913 (23) [RbC≡Zn₂L₂ – CH₂COCHCOC₆H₅]⁺, 579 (39) [ZnL + Rb]⁺. C₅₄H₄₃O₁₄RbZn₂ (1132.22): calcd. C 57.28, H 3.84; found C 56.82, H 3.91.

Single Crystal X-ray Structure Analyses: Details of crystal data, data collection and refinement are given in Table 1. X-ray data for **Δ/Λ-(2)_n**, **meso-(3e)_n**, **4a** and **4b** were collected with a Nonius Kappa CCD area detector by using Mo-*K*_α radiation (λ = 0.71073 Å). The structures were solved by direct methods with SHELXS-97^[12] and refined with full-matrix least-squares against *F*² using the SHELXL-97 program system.^[13] All non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were fixed in ideal positions (riding model) and were included without refinement and with fixed isotropic *U*. Data for **meso-(3b)_n** were collected with a Bruker-Nonius KappaCCD dif-

Table 1. Crystal and structure refinement data for complexes Δ/Λ -(**2**)_n, *meso*-(**3b**)_n, *meso*-(**3e**)_n, **4a** and **4b**.

	Δ/Λ -(2) _n	<i>meso</i> -(3b) _n	<i>meso</i> -(3e) _n
Empirical formula	C ₄₈ H ₄₈ CS ₂ Mg ₂ O ₁₈ ·3CH ₃ CN	C ₁₅₆ H ₁₂₀ Mg ₄ O ₃₆ Rb ₄ ·2CH ₃ CN	C ₃₁₂ H ₂₄₀ Co ₈ CS ₈ O ₇₂ ·10CH ₃ CN·18CH ₃ OH
<i>M</i> _r [g mol ⁻¹]	1350.47	3091.84	7663.06
Crystal size [mm]	0.35 × 0.20 × 0.15	0.18 × 0.16 × 0.13	0.25 × 0.20 × 0.20
Crystal system	triclinic	monoclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> [Å]	11.9122(3)	25.643(2)	25.9749(3)
<i>b</i> [Å]	16.1944(2)	21.655(2)	21.6357(2)
<i>c</i> [Å]	17.7467(3)	29.756(2)	30.2700(3)
α [°]	114.852(1)		
β [°]	96.960(1)	90.502(6)	90.077(3)
γ [°]	95.055(1)		
<i>V</i> [Å ³]	3046.65(10)	16523(2)	17011.3(3)
<i>Z</i>	2	4	2
$\rho_{\text{calcd.}}$ [Mg m ⁻³]	1.472	1.243	1.496
<i>T</i> [K]	173(2)	100(2)	173(2)
Absorption coeff. [mm ⁻¹]	1.286	1.263	1.308
<i>F</i> (000)	1360	6336	7776
θ range [°]	1.74 to 27.50	3.38 to 27.00	1.03 to 26.01
Index ranges	−15 ≤ <i>h</i> ≤ 15 −21 ≤ <i>k</i> ≤ 21 −23 ≤ <i>l</i> ≤ 23	−32 ≤ <i>h</i> ≤ 32 −27 ≤ <i>k</i> ≤ 27 −37 ≤ <i>l</i> ≤ 37	−31 ≤ <i>h</i> ≤ 32 −24 ≤ <i>k</i> ≤ 26 −37 ≤ <i>l</i> ≤ 37
Reflections collected	26391	166961	88290
Independent reflections	13968	35804	31901
Refl. observed [<i>I</i> ≥ 2σ(<i>I</i>)]	10176	22949	19074
Absorption correction	Scalepack	SADABS	Scalepack
Refinement method	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²
Max./Min. transm.	0.8305/0.6617	0.850/0.783	0.7799/0.7357
[<i>R</i> _{int}]	0.0226	0.0699	0.0705
Data/parameters	13968/732	35804/1922	31901/2093
Goodness-of-fit on <i>F</i> ²	0.983	1.067	0.929
Final <i>R</i> ₁ [<i>I</i> ≥ 2σ(<i>I</i>)]	0.0430	0.0537	0.0484
<i>wR</i> ₂ (all data)	0.1470	0.1425	0.1520
Largest residuals [e Å ⁻³]	2.019/−1.330	2.913/−1.162	1.263/−1.252
	4a	4b	
Empirical formula	C ₅₄ H ₄₃ CSO ₁₄ Zn ₂ ·3CH ₃ CN	C ₅₄ H ₄₃ O ₁₄ RbZn ₂ ·2CH ₃ CN·CH ₃ OH	
<i>M</i> _r [g mol ⁻¹]	1302.70	1246.24	
Crystal size [mm]	0.30 × 0.30 × 0.30	0.20 × 0.20 × 0.20	
Crystal system	monoclinic	monoclinic	
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	
<i>a</i> [Å]	19.0036(3)	18.7116(4)	
<i>b</i> [Å]	14.4150(2)	14.6150(3)	
<i>c</i> [Å]	20.5309(3)	20.3408(4)	
α [°]			
β [°]	103.511(1)	103.419(1)	
γ [°]			
<i>V</i> [Å ³]	5468.52(14)	5410.73(19)	
<i>Z</i>	4	4	
$\rho_{\text{calcd.}}$ [Mg m ⁻³]	1.582	1.530	
<i>T</i> [K]	173(2)	173(2)	
Absorption coeff. [mm ⁻¹]	1.605	1.852	
<i>F</i> (000)	2640	2552	
θ range [°]	1.10 to 27.49	2.06 to 27.48	
Index ranges	−24 ≤ <i>h</i> ≤ 24 −18 ≤ <i>k</i> ≤ 17 −26 ≤ <i>l</i> ≤ 26	−24 ≤ <i>h</i> ≤ 24 −18 ≤ <i>k</i> ≤ 17 −26 ≤ <i>l</i> ≤ 26	
Reflections collected	23739	22634	
Independent reflections	12546	12355	
Refl. observed [<i>I</i> ≥ 2σ(<i>I</i>)]	9906	7781	
Absorption correction	Scalepack	Scalepack	
Refinement method	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²	
Max./Min. transm.	0.6446/0.6446	0.7083/0.7083	
[<i>R</i> _{int}]	0.0247	0.0417	
Data/parameters	12546/721	12355/712	
Goodness-of-fit on <i>F</i> ²	1.022	1.000	
Final <i>R</i> ₁ [<i>I</i> ≥ 2σ(<i>I</i>)]	0.0328	0.0479	
<i>wR</i> ₂ (all data)	0.1049	0.1321	
Largest residuals [e Å ⁻³]	0.745/−0.841	1.149/−0.583	

fractometer by using Mo- K_α radiation ($\lambda = 0.71073 \text{ \AA}$), and a graphite monochromator. The structure was solved by direct methods; full-matrix least-squares refinements were carried out on F^2 using SHELXTL NT 6.12.^[14] A semiempirical absorption correction based on multiple scans (SADABS)^[15] was performed. All non-hydrogen atoms were refined anisotropically. The H atoms were geometrically positioned with isotropic displacement parameters being either 1.2 U(eq) or 1.5 U(eq) of the preceding C atom. Disorder: Two of the aromatic rings (C99–C104 and C125–C130) are disordered with 42.6(5) and 57.4(5)% and 47.8(4) and 52.2(4)%, respectively. In the crystal structure two huge cavities are present that are occupied by different disordered solvent molecules. Attempts to solve this disorder did not lead to reasonable results and therefore the SQUEEZE algorithm was employed to treat the rest electron density in this part of the structure.^[16]

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