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

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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  $(\Delta, \Delta)$ fac or  $(\Lambda,\Lambda)$ -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  $\{Cs \subset [Mg_2(L^1)_3]\}^-$  is achieved through extra external cesium ions to give the neutral self-complementary building blocks  $[{Cs \subset [(\Delta, \Delta)/(\Lambda, \Lambda)-Mg_2(L^1)_3]}Cs]$ , which aggregate end-on across the external cesium ions to give the homo*chiral* one-dimensional strings  $[{Cs \subset [(\Delta, \Delta) - Mg_2(L^1)_3]}]Cs]_n [\Delta - Mg_2(L^1)_3]$  $(2)_n$  and  $[{Cs \subset [(\Lambda,\Lambda)-Mg_2(L^1)_3]}Cs]_n [\Lambda-(2)_n]$ , which are packed in the crystal in alternating homochiral layers. However, reaction of bulkier phenyl-substituted bis(1,3-diketone) H<sub>2</sub>L<sup>2</sup> instead of methyl-substituted H<sub>2</sub>L<sup>1</sup> with cesium or rubidium acetate and magnesium, cobalt or zinc acetate yielded the meandering polymer *meso*-{[({M<sup>1</sup>⊂[(Δ,Δ)-M<sup>2</sup><sub>2</sub>-(L<sup>2</sup>)<sub>3</sub>]}M<sup>1</sup><sub>end</sub>)({M<sup>1</sup>⊂[(Δ,Δ)-M<sup>2</sup><sub>2</sub>(L<sup>2</sup>)<sub>3</sub>]}M<sup>1</sup><sub>side</sub>)][({M<sup>1</sup>⊂[(Δ,Δ)-M<sup>2</sup><sub>2</sub>(L<sup>2</sup>)<sub>3</sub>]}M<sup>1</sup><sub>end</sub>)({M<sup>1</sup>⊂[(Δ,Δ)-M<sup>2</sup><sub>2</sub>(L<sup>2</sup>)<sub>3</sub>]}M<sup>1</sup><sub>side</sub>)]]<sub>n</sub> [*meso*-(**3**)<sub>n</sub>] (M<sup>1</sup> = Cs<sup>+</sup>, Rb<sup>+</sup>; M<sup>2</sup> = Mg<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup>). In this case, the {2}-metallacryptates {M<sup>1</sup>⊂[(Δ,Δ/Λ,Λ)-M<sup>2</sup><sub>2</sub>(L<sup>2</sup>)<sub>3</sub>]}<sup>−</sup> are linked by only one cesium ion end-on to give the fragments *meso*-[({M<sup>1</sup>⊂[(Δ,Δ)-M<sup>2</sup><sub>2</sub>(L<sup>2</sup>)<sub>3</sub>]}M<sup>1</sup><sub>end</sub>)({M<sup>1</sup>⊂[(Δ,Λ)-M<sup>2</sup><sub>2</sub>(L<sup>2</sup>)<sub>3</sub>]}M<sup>1</sup><sub>side</sub>)], which are connected by the second cesium ions side-on. The one-dimensional meander strands of isostructural *meso*-(**3**)<sub>n</sub> 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<sub>2</sub>L<sup>2</sup> afforded the {M<sup>1</sup>⊂[Zn<sub>2</sub>(L<sup>2</sup>)<sub>2</sub>OAc]} cryptates **4a,b** (M<sup>1</sup> = Cs<sup>+</sup>, Rb<sup>+</sup>).

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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 [{Cs $\subset$ [Ni<sub>2</sub>(L<sup>1</sup>)<sub>3</sub>]}Cs] with either ( $\Delta$ , $\Delta$ )-*fac* or ( $\Lambda$ , $\Lambda$ )-*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*-[({Cs $\subset$ [( $\Delta$ , $\Delta$ )-Ni<sub>2</sub>(L<sup>1</sup>)<sub>3</sub>]}Cs)({Cs $\subset$ [( $\Lambda$ , $\Lambda$ )-Ni<sub>2</sub>(L<sup>1</sup>)<sub>3</sub>]}Cs)]<sub>n</sub> [*meso*-(1)<sub>n</sub>] (Figure 1).<sup>[2]</sup>

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meso-(1)<sub>n</sub>: meso-[({Csc[( $\Delta,\Delta$ )-Ni<sub>2</sub>(L<sup>1</sup>)<sub>3</sub>]}Cs)({Csc[( $\Lambda,\Lambda$ )-Ni<sub>2</sub>(L<sup>1</sup>)<sub>3</sub>]}Cs)]<sub>n</sub>



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).



<sup>[‡]</sup> Chelate Complexes, Part 37. Part 36: Ref.<sup>[1]</sup>

#### **Results and Discussion**

In the course of our ongoing studies on supramolecular coordination chemistry with nickel(II)<sup>[2]</sup> and copper(II),<sup>[2-4]</sup> we focused on the development of new oligonuclear complexes by self-assembly<sup>[5]</sup> 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)<sub>n</sub> (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  $\Delta/\Lambda$ -(2)<sub>n</sub> crystallizes in the triclinic space group  $P\overline{1}$  (Table 1).<sup>[6]</sup> In  $\Delta/\Lambda$ -(2)<sub>n</sub>, the {2}metallacryptand [Mg<sub>2</sub>(L<sup>1</sup>)<sub>3</sub>]<sup>2-</sup> core is composed of two magnesium centres linked through three hexadentate catecholate-spacered bis(1,3-diketo) dianions (L1)2-. Therefore, each magnesium ion is coordinated octahedrally by six diketo oxygen donors. The resulting {2}-metallacryptands are homochiral with either  $(\Delta, \Delta)$ -fac or  $(\Lambda, \Lambda)$ -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  $\{C_{s} \subset [(\Delta, \Delta)/(\Lambda, \Lambda) - Mg_{2} - Mg_{2}$  $(L^{1})_{3}$ ]<sup>-</sup> is achieved through extra external cesium ions to give the neutral self-complementary building blocks  $[{Cs \subset [(\Delta, \Delta)/(\Lambda, \Lambda)-Mg_2(L^1)_3]}Cs]$ . However, contrary to *meso-* $(1)_n$ , these building blocks aggregate in the solid state end-on across the external cesium ions to give the homo*chiral* strings  $[{Cs \subset [(\Delta, \Delta) - Mg_2(L^1)_3]}Cs]_n [\Delta - (2)_n]$  and  $[{Cs \subset [(\Lambda,\Lambda)-Mg_2(L^1)_3]}Cs]_n [\Lambda-(2)_n]^{[6]}$  which are packed in the crystal in alternating homochiral layers (Figure 2). In  $\Delta/\Lambda$ -(2)<sub>n</sub>, 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  $\Delta/\Lambda$ - $(2\cdot 3 MeCN)_n$ . Therefore, the stereogenic metal centres are controlled, simply by varying hexacoordinate Ni<sup>II</sup> in meso- $(1)_n$  to Mg<sup>II</sup> in  $\Delta/\Lambda$ - $(2)_n$ .

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



Scheme 1. Synthesis and schematic presentation of the repeating units of the homochiral strings  $\Delta$ -(2)<sub>n</sub> and  $\Lambda$ -(2)<sub>n</sub> [= *rac*-(2)<sub>n</sub>].



Figure 2. Stereo presentation (POVRAY) of a layer of  $\Lambda$ -(2)<sub>n</sub> in the crystal together with the coordinating acetonitrile solvent molecules. Mg grey, Cs light grey.

In meso-(3e)<sub>n</sub>, two enantiomers {Cs $\subset$ [( $\Delta,\Delta/\Lambda,\Lambda$ )-Co<sub>2</sub>- $(L^2)_3$ ]<sup>-</sup> 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-{[( $\{Cs \subset [(\Delta, \Delta)-Co_2(L^2)_3]\}Cs_{end}$ )- $({Cs \subset [(\Lambda,\Lambda)-Co_2(L^2)_3]}Cs_{side})][({Cs \subset [(\Lambda,\Lambda)-Co_2(L^2)_3]} Cs_{end}$  ({ $Cs \subset [(\Delta, \Delta) - Co_2(L^2)_3]$ } Cs<sub>side</sub>)]}<sub>n</sub> [meso-(**3e**)<sub>n</sub>]. Therefore, the Cs<sub>end</sub> links two enantiomers  $\{Cs \subset [(\Delta, \Delta/\Lambda, \Lambda) Co_2(L^2)_3]$ , whereas the  $Cs_{side}$  links the *meso-*[({ $Cs \subset [(\Delta, \Delta) Co_2(L^2)_3$   $Cs_{end}$   $(Cs \subset [(\Lambda, \Lambda) - Co_2(L^2)_3] Cs_{side})$  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  $\mathrm{Cs}_{\mathrm{end}}.$  The  $\mathrm{Cs}_{\mathrm{side}}$ 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*- $(3\mathbf{b}, \mathbf{e})_n$  are packed in the crystal in parallel. The repetitive unit of the structure in the crystal is therefore



 $meso-(\mathbf{3})_{n}: meso-\{[(\{M^{1} \subset [(\Delta, \Delta) - M^{2}_{2}(L^{2})_{3}]\}M^{1}_{end})(\{M^{1} \subset [(\Lambda, \Lambda) - M^{2}_{2}(L^{2})_{3}]\}M^{1}_{side})][(\{M^{1} \subset [(\Lambda, \Lambda) - M^{2}_{2}(L^{2})_{3}]\}M^{1}_{end})(\{M^{1} \subset [(\Delta, \Delta) - M^{2}_{2}(L^{2})_{3}]\}M^{1}_{side})]]_{n} = (A, A) =$ 

meso-( <b>3</b> ) <sub>n</sub>	а	b	c	d	е
$\bigcirc \equiv (M^1)^+$	Cs <sup>+</sup>	Rb⁺	Cs <sup>+</sup>	Rb <sup>+</sup>	Cs <sup>+</sup>
$\bigcirc \equiv (M^2)^{2+}$	Mg <sup>2+</sup>	Mg <sup>2+</sup>	Zn <sup>2+</sup>	Zn <sup>2+</sup>	Co <sup>2+</sup>

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)<sub>n</sub> in the crystal without solvent molecules. Co grey, Cs light grey.



Figure 4. Simplified stereo presentation (POVRAY) of meander *meso*-(3e)<sub>*n*</sub>. The Cs $\subset$ , Cs<sub>end</sub> and Co centres are connected by lines and are arranged in angles, linked by the Cs<sub>side</sub> 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 {Cs  $\subset$  [Zn<sub>2</sub>(L<sup>2</sup>)<sub>2</sub>OAc]} 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  $C_{2\nu}$  molecule symmetry (Table 1).<sup>[6]</sup> Two hexadentate bis(1,3-diketo) dianions  $(L^2)^{2-}$  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  $\mu_1$ -donor to one zinc ion and the other as a  $\mu_2$ -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  $-\pi$  interaction of neighboring phenyl groups (Figure 5 bottom).<sup>[7]</sup>



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**)<sub>n</sub> and *meso*-(**3**)<sub>n</sub> also in solution, we carried out <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic studies of diamagnetic *rac*-(**2**)<sub>n</sub> and *meso*-(**3a**-**d**)<sub>n</sub>. It turned out that the spectra of all five compounds were not very significant [5 <sup>1</sup>H and 8 <sup>13</sup>C NMR signals for *rac*-(**2**)<sub>n</sub> and 7 <sup>1</sup>H and 11 <sup>13</sup>C NMR signals for *meso*-(**3a**-**d**)<sub>n</sub>]. We were unable to detect an AB pattern for the diastereotopic OCH<sub>2</sub> protons, even by using variable temperature techniques.<sup>[8]</sup> The compounds *meso*-(**3a**)<sub>n</sub> and *meso*-(**3c**)<sub>n</sub> 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 <sup>13</sup>C 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 [D<sub>6</sub>]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 <sup>13</sup>C NMR signals for cryptates  $meso-(3a)_n$  and  $meso-(3c)_n$  and their 1:1 mixture in [D<sub>6</sub>]acetone (Figure 6).



Figure 6. <sup>13</sup>C NMR signals for the carbonyl atoms of *meso*-(**3a**)<sub>*n*</sub> and *meso*-(**3c**)<sub>*n*</sub> and their 1:1 mixture in  $[D_6]$ acetone at ca. 25 °C.

The number of <sup>13</sup>C NMR signals found for *meso*-(**3a**)<sub>n</sub> and *meso*-(**3c**)<sub>n</sub> 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 <sup>13</sup>C NMR spectroscopic data would also match a heterochiral ( $\Delta,\Lambda$ ) 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 <sup>13</sup>C 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 <sup>13</sup>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 onedimensional polymers [{Cs $\subset$ [( $\Delta,\Delta$ )-Mg<sub>2</sub>(L<sup>1</sup>)<sub>3</sub>]}Cs]<sub>n</sub> [ $\Delta$ -(2)<sub>n</sub>] and [{Cs $\subset$ [( $\Lambda,\Lambda$ )-Mg<sub>2</sub>(L<sup>1</sup>)<sub>3</sub>]}Cs]<sub>n</sub> [ $\Lambda$ -(2)<sub>n</sub>] and the one dimensional meander polymers *meso*-{[({M<sup>1</sup> $\subset$ [( $\Delta,\Delta$ )-M<sup>2</sup><sub>2</sub>-(L<sup>2</sup>)<sub>3</sub>]}M<sup>1</sup><sub>end</sub>)({M<sup>1</sup> $\subset$ [( $\Lambda,\Lambda$ )-M<sup>2</sup><sub>2</sub>(L<sup>2</sup>)<sub>3</sub>]}M<sup>1</sup><sub>side</sub>)][({M<sup>1</sup> $\subset$ [( $\Lambda,\Lambda$ )-M<sup>2</sup><sub>2</sub>(L<sup>2</sup>)<sub>3</sub>]}M<sup>1</sup><sub>end</sub>)({M<sup>1</sup> $\subset$ [( $\Lambda,\Delta$ )-M<sup>2</sup><sub>2</sub>(L<sup>2</sup>)<sub>3</sub>]}M<sup>1</sup><sub>side</sub>)]]<sub>n</sub> [*meso*-(3)<sub>n</sub>] (M<sup>1</sup> = Cs<sup>+</sup>, Rb<sup>+</sup>; M<sup>2</sup> = Mg<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup>). The structures of complexes 1–4 were solved by the combination of mass spectroscopy, single-crystal X-ray analyses and <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. Most importantly, the <sup>13</sup>C NMR spectrum of a mixture of *meso*-(3a,c) unequivocally proved the existence of the intact cryptates {Cs $\subset$ [Mg<sub>2</sub>-(L<sup>2</sup>)<sub>3</sub>]<sup>2-</sup> of *meso*-(3a)<sub>n</sub> and {Cs $\subset$ [Zn<sub>2</sub>(L<sup>2</sup>)<sub>3</sub>]<sup>2-</sup> of *meso*-(3c)<sub>n</sub> 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<sub>3</sub>, 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<sub>3</sub> (<sup>1</sup>H 7.27 ppm, <sup>13</sup>C 77.0 ppm); [D<sub>6</sub>]acetone (<sup>1</sup>H 2.05 ppm; <sup>13</sup>C 29.85 ppm).<sup>[9]</sup> The resonance multiplicity is indicated as s (singlet), d (doublet) and m (multiplet). MS (FAB) spectra were recorded with a Micromass ZAB-Spec (Cs<sup>+</sup>) 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 H<sub>2</sub>L<sup>1,2</sup>:**<sup>[2,10]</sup> 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<sup>[11]</sup> (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 H<sub>2</sub>L<sup>1,2</sup> are present as a tautomeric mixture of the diketo, monoenol and bisenol species. Below, only signals of the dominating bisenol form are listed.

H<sub>2</sub>L<sup>1</sup>: Acetone (7.34 mL). Yield: 5.5 g (36%), bright-beige crystals (methanol). M.p. 92 °C. <sup>1</sup>H NMR (300.1 MHz):  $\delta$  = 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<sub>2</sub>), 2.10 (s, 6 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75.5 MHz):  $\delta$  = 191.88 (2 C-OH), 190.50 (2 C=O), 148.04 (2 Ar-C-O), 122.57 (2 Ar-C-H, m-C<sub>6</sub>H<sub>4</sub>), 114.69 (2 Ar-C-H, o-C<sub>6</sub>H<sub>4</sub>), 97.44 (2 CH), 70.24 (2 CH<sub>2</sub>), 24.47 (2 CH<sub>3</sub>) ppm. IR:  $\tilde{v}$  = 2922, 1609, 1589, 1509, 1225, 1124 cm<sup>-1</sup>. MS: *m*/*z* (%) = 307 (100) [M + H]<sup>+</sup>, 222 (9) [M – COCH<sub>2</sub>COMe]<sup>+</sup>. C<sub>16</sub>H<sub>18</sub>O<sub>6</sub> (306.32): calcd. C 62.74, H 5.92; found C 62.85, H 6.04.

**H**<sub>2</sub>**L**<sup>2</sup>: Acetophenone (11.67 mL). Yield: 10.3 g (48%), colorless cotton-like crystals (methanol). M.p. 117 °C. <sup>1</sup>H NMR (300.1 MHz):  $\delta$  = 15.87 (br. s, 2 H, OH), 7.78–7.76 (m, 4 H, Ar-H, o-C<sub>6</sub>H<sub>5</sub>), 7.41–7.36 (m, 2 H, Ar-H, p-C<sub>6</sub>H<sub>5</sub>), 7.30–7.25 (m, 4 H, Ar-H, m-C<sub>6</sub>H<sub>5</sub>), 6.93–6.86 (m, 4 H, Ar-H, C<sub>6</sub>H<sub>4</sub>), 6.66 (s, 2 H, CH), 4.72 (s, 4 H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR (75.5 MHz):  $\delta$  = 193.70 (2 C-OH), 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<sub>6</sub>H<sub>5</sub>), 128.62 (4 Ar-C-H, C<sub>6</sub>H<sub>5</sub>), 127.11 (4 Ar-C-H, C<sub>6</sub>H<sub>5</sub>), 122.54 (2 Ar-C-H, m-C<sub>6</sub>H<sub>4</sub>), 114.68 (2 Ar-C-H, o-C<sub>6</sub>H<sub>4</sub>), 93.44 (2 CH), 70.73 (2 CH<sub>2</sub>) ppm. IR:  $\tilde{v}$  = 3050, 2890, 2830, 1610, 1575, 1509, 1262, 1227, 1127 cm<sup>-1</sup>. MS: m/z (%) = 431 (100) [M]<sup>+</sup>. C<sub>26</sub>H<sub>22</sub>O<sub>6</sub> (430.46): calcd. C 72.55, H 5.15; found C 72.19, H 5.13.

 $\Delta/\Lambda$ -(2)<sub>n</sub>: 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 Mg(OAc)<sub>2</sub>·4H<sub>2</sub>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  $\Delta/\Lambda$ -(2·3CH<sub>3</sub>-CN), suitable for X-ray structure determination. Yield: 25 mg (47%) of  $\Delta/\Lambda$ -(2)<sub>n</sub> after drying for 8 h under reduced pressure  $(10^{-3} \text{ mbar})$ . M.p. >260 °C (decomp). <sup>1</sup>H NMR (300.1 MHz, XXXX):  $\delta = 6.76$  (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<sub>2</sub>), 1.78 (br. s, 18 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (100.5 MHz, XXXX):  $\delta$  = 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<sub>2</sub>), 28.21 (6 CH<sub>3</sub>) ppm. IR:  $\tilde{v} = 3065$ , 2910, 1613, 1521, 1235, 1127, 1054 cm<sup>-1</sup>. MS: m/z (%) = 1359 (15)  $[Cs \subset Mg_2L_3 + 2Cs]^+$ , 1227 (22)  $[Cs \subset Mg_2L_3 + Cs]^+$ , 789 (100)  $[Mg_2L_2 \ + \ Cs]^+, \ 691 \ (16) \ [Mg_2L_2 \ + \ Cs \ - \ CH_2COCHCOCH_3]^+.$ C48H48Cs2Mg2O18 (1227.40): calcd. C 46.97, H 3.95; found C 46.47, H 4.13.

**General Procedure for** *meso-*(**3a,b,e**)<sub>*n*</sub>: 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 M<sup>2</sup>(OAc)<sub>2</sub>·xH<sub>2</sub>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)<sub>n</sub>: CsOAc (15 mg) and Mg(OAc)<sub>2</sub>·4H<sub>2</sub>O (17 mg). Yield: 38 mg (62%), colorless crystals after drying for 8 h under reduced pressure (10<sup>-3</sup> mbar). M.p. >220 °C (decomp). <sup>1</sup>H NMR (300.1 MHz, [D<sub>6</sub>]acetone):  $\delta$  = 7.88–7.85 (m, 12 H, Ar-*H*, *o*-C<sub>6</sub>H<sub>5</sub>), 7.41–7.31 (m, 18 H, Ar-*H*, *m*- and *p*-C<sub>6</sub>H<sub>5</sub>), 6.61–6.58 (m, 6 H, Ar-*H*, C<sub>6</sub>H<sub>4</sub>), 6.33–6.30 (m, 6 H, Ar-*H*, C<sub>6</sub>H<sub>4</sub>), 5.63 (br. s, 6 H, C*H*), 4.33 (br. s, 12 H, C*H*<sub>2</sub>) ppm. <sup>13</sup>C NMR (75.5 MHz, [D<sub>6</sub>]acetone):  $\delta$  = 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<sub>6</sub>H<sub>5</sub>), 128.64 (12 Ar-C-H, C<sub>6</sub>H<sub>5</sub>), 128.16 (12 Ar-C-H, C<sub>6</sub>H<sub>5</sub>), 121.41 (6 Ar-C-H, *m*-C<sub>6</sub>H<sub>4</sub>), 112.57 (6 Ar-C-H, *o*-C<sub>6</sub>H<sub>4</sub>), 92.30 (6 CH), 69.60 (6 CH<sub>2</sub>) ppm. IR:

$$\begin{split} \tilde{v} &= 3065,\,2918,\,1610,\,1575,\,1502,\,1247,\,1127,\,1042\,\,cm^{-1}.\,\,MS:\,m/z \\ (\%) &= 1732\,\,(83)\,\,[Cs \subset Mg_2L_3\,+\,2Cs]^+,\,\,1601\,\,(23)\,\,[Cs \subset Mg_2L_3\,+\,\\Cs]^+,\,\,1038\,\,(100)\,\,[Mg_2L_2\,+\,Cs]^+,\,\,877\,\,(32)\,\,[Mg_2L_2\,+\,Cs\,-\,\\CH_2COCHCOC_6H_5]^+,\,\,718\,\,(21)\,\,[Mg_2L_2\,+\,Cs\,-\,2CH_2COCH-COC_6H_5]^+.\,\,C_{78}H_{60}O_{18}Cs_2Mg_2\,\,(1599.82):\,calcd.\,\,C\,\,58.56,\,H\,\,3.79; \\ found C\,\,57.71,\,H\,\,3.93. \end{split}$$

meso-(3b)n: RbOAc (11 mg) and Mg(OAc)2·4H2O (17 mg), colorless crystals of meso-(3b·2CH<sub>3</sub>CN)<sub>n</sub> suitable for X-ray structure determination. Yield: 21 mg (36%) of meso-(**3b**)<sub>n</sub> after drying for 8 h under reduced pressure (10<sup>-3</sup> mbar). M.p. >190 °C (decomp). <sup>1</sup>H NMR (300.1 MHz,  $[D_6]$ acetone):  $\delta = 7.88-7.85$  (br. s, 12 H, Ar-H,  $o-C_6H_5$ ), 7.40–7.30 (m, 18 H, Ar-H, m- and  $p-C_6H_5$ ), 6.57 (br. s, 6 H, Ar-H, C<sub>6</sub>H<sub>4</sub>), 6.26 (br. s, 6 H, Ar-H, C<sub>6</sub>H<sub>4</sub>), 5.60 (br. s, 6 H, CH), 4.28 (br. s, 12 H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR (75.5 MHz, [D<sub>6</sub>]acetone):  $\delta = 185.79$  (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-C<sub>6</sub>H<sub>5</sub>), 128.03 (12 Ar-C-H, C<sub>6</sub>H<sub>5</sub>), 127.63 (12 Ar-C-H, C<sub>6</sub>H<sub>5</sub>), 120.85 (6 Ar-C-H, m-C<sub>6</sub>H<sub>4</sub>), 112.07 (6 Ar-C-H, o-C<sub>6</sub>H<sub>4</sub>), 92.12 (6 CH), 69.24 (6 CH<sub>2</sub>) ppm. IR:  $\tilde{v} = 3065, 2922, 1606, 1575, 1502, 1247, 1127, 1038 \text{ cm}^{-1}$ . MS: m/z (%) = 1590 (27) [Rb $\subset$ Mg<sub>2</sub>L<sub>3</sub> + 2 Rb]<sup>+</sup>, 1505 (28)  $[Rb \subset Mg_2L_3 + Rb]^+$ , 991 (100)  $[Mg_2L_2 + Rb]^+$ , 831 (25)  $[Mg_2L_2 + Rb]^+$  $Rb - CH_2COCHCOC_6H_5]^+$ .  $C_{78}H_{60}Mg_2O_{18}Rb_2$  (1504.94): calcd. C 62.26, H 4.02; found C 63.00, H 3.89.

*meso*-(**3e**)<sub>*n*</sub>: CsOAc (15 mg) and Co(OAc)<sub>2</sub>·4H<sub>2</sub>O (19 mg), red crystals of *meso*-(**3e**·10CH<sub>3</sub>CN·18CH<sub>3</sub>OH)<sub>*n*</sub> suitable for X-ray structure determination. Yield: 45 mg (70%) of *meso*-(**3e**)<sub>*n*</sub> after drying for 8 h under reduced pressure (10<sup>-3</sup> mbar). M.p. >220 °C (decomp). IR:  $\tilde{v} = 3061$ , 2918, 1598, 1571, 1502, 1243, 1127, 1038 cm<sup>-1</sup>. MS: *m/z* (%) = 1799 (42) [Cs⊂Co<sub>2</sub>L<sub>3</sub> + 2Cs]<sup>+</sup>, 1669 (74) [Cs⊂Co<sub>2</sub>L<sub>3</sub> + Cs]<sup>+</sup>, 1536 (31) [Cs⊂Co<sub>2</sub>L<sub>3</sub><sup>+</sup>, 1107 (100) [Co<sub>2</sub>L<sub>2</sub> + Cs]<sup>+</sup>, 947 (27) [Co<sub>2</sub>L<sub>2</sub> + Cs - CH<sub>2</sub>COCHCOC<sub>6</sub>H<sub>5</sub>]<sup>+</sup>. C<sub>78</sub>H<sub>60</sub>O<sub>18</sub>Co<sub>2</sub>Cs<sub>2</sub> (1669.06): calcd. C 56.13, H 3.63; found C 56.68, H 3.81.

**General Procedure for** *meso-*(**3c**,**d**),*i*: A solution of cesium or rubidium acetate (116  $\mu$ mol) in MeOH (1 mL) was added to a solution of ligand H<sub>2</sub>L<sup>2</sup> (75 mg, 174  $\mu$ mol) in acetonitrile (5 mL). The mixture was heated to boiling. Then a solution of Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (13 mg, 58  $\mu$ mol) 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*-(**3**c)<sub>*n*</sub>: CsOAc (22 mg). Yield: 32 mg (66%), colorless crystals of *meso*-(**3**c)<sub>*n*</sub> after drying for 8 h under reduced pressure (10<sup>-3</sup> mbar). M.p. >190 °C (decomp). <sup>1</sup>H NMR (300.1 MHz, [D<sub>6</sub>]-acetone):  $\delta$  = 7.85–7.83 (m, 12 H, Ar-*H*, *o*-C<sub>6</sub>H<sub>5</sub>), 7.31–7.41 (m, 18 H, Ar-*H*, *m*- and *p*-C<sub>6</sub>H<sub>5</sub>), 6.57 (br. s, 6 H, Ar-*H*, C<sub>6</sub>H<sub>4</sub>), 6.35 (br. s, 6 H, Ar-*H*, C<sub>6</sub>H<sub>4</sub>), 5.56 (br. s, 6 H, Ar-*H*, C<sub>6</sub>H<sub>4</sub>), 6.35 (br. s, 6 H, Ar-*H*, C<sub>6</sub>H<sub>4</sub>), 6.35 (br. 1<sup>3</sup>C NMR (100.5 MHz, [D<sub>6</sub>]acetone):  $\delta$  = 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*-C<sub>6</sub>H<sub>5</sub>), 128.68 (12 Ar-*C*-H, C<sub>6</sub>H<sub>5</sub>), 128.10 (12 Ar-*C*-H, C<sub>6</sub>H<sub>5</sub>), 121.43 (6 Ar-*C*-H, *m*-C<sub>6</sub>H<sub>4</sub>), 112.57 (6 Ar-*C*-H, *o*-C<sub>6</sub>H<sub>4</sub>), 92.11 (6 *C*H), 69.58 (6 *C*H<sub>2</sub>) ppm. IR:  $\hat{\nu}$  = 3065, 2918, 1598, 1571, 1502, 1243, 1127, 1038 cm<sup>-1</sup>. MS: *m*/*z* (%) = 1813 (33) [Cs⊂Zn<sub>2</sub>L<sub>3</sub> + 2Cs]<sup>+</sup>, 1683 (11) [Cs⊂Zn<sub>2</sub>L<sub>3</sub> + Cs]<sup>+</sup>, 1121 (100) [Zn<sub>2</sub>L<sub>2</sub> + Cs]<sup>+</sup>, 961 (16) [Zn<sub>2</sub>L<sub>2</sub> + Cs - CH<sub>2</sub>COCHCOC<sub>6</sub>H<sub>5</sub>]<sup>+</sup>. C<sub>78</sub>H<sub>60</sub>O<sub>18</sub>Cs<sub>2</sub>Zn<sub>2</sub> (1681.98); calcd. C 55.70, H 3.60; found C 55.56, H 3.69.

*meso*-(3d)<sub>*n*</sub>: RbOAc (17 mg). Yield: 14 mg (45%), colorless crystals of *meso*-(3d)<sub>*n*</sub> after drying for 8 h under reduced pressure (10<sup>-3</sup> mbar). M.p. >180 °C (decomp). <sup>1</sup>H NMR (300.1 MHz, [D<sub>6</sub>]-acetone):  $\delta$  = 7.81 (br. s, 12 H, Ar-*H*, *o*-C<sub>6</sub>H<sub>5</sub>), 7.38–7.32 (m, 18 H, Ar-*H*, *m*- and *p*-C<sub>6</sub>H<sub>5</sub>), 6.56 (br. s, 6 H, Ar-*H*, C<sub>6</sub>H<sub>4</sub>), 6.30 (br. s, 6 H, Ar-*H*, C<sub>6</sub>H<sub>4</sub>), 5.52 (br. s, 6 H, C*H*), 4.24 (br. s, 12 H, C*H*<sub>2</sub>) ppm. <sup>13</sup>C NMR (75.5 MHz, [D<sub>6</sub>]acetone):  $\delta$  = 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,  $p-C_6H_5$ ), 128.11 (12 Ar-C-H,  $C_6H_5$ ), 127.60 (12 Ar-C-H,  $C_6H_5$ ), 120.87 (6 Ar-C-H,  $m-C_6H_4$ ), 112.15 (6 Ar-C-H,  $o-C_6H_4$ ), 92.02 (6 CH), 69.22 (6 CH<sub>2</sub>) ppm. IR:  $\tilde{v} = 3065$ , 2918, 1598, 1571, 1513, 1247, 1127, 1038 cm<sup>-1</sup>. MS: m/z (%) = 1671 (32) [Rb $\subset$ Zn<sub>2</sub>L<sub>3</sub> + 2Rb]<sup>+</sup>, 1587 (17) [Rb $\subset$ Zn<sub>2</sub>L<sub>3</sub> + Rb]<sup>+</sup>, 1073 (100) [Zn<sub>2</sub>L<sub>2</sub> + Rb]<sup>+</sup>, 913 (27) [Zn<sub>2</sub>L<sub>2</sub> + Rb - CH<sub>2</sub>COCHCOC<sub>6</sub>H<sub>5</sub>]<sup>+</sup>. C<sub>78</sub>H<sub>60</sub>O<sub>18</sub>Rb<sub>2</sub>Zn<sub>2</sub> (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  $\mu$ mol) in MeOH (1 mL) was added to a solution of ligand H<sub>2</sub>L<sup>2</sup> (25 mg, 58  $\mu$ mol) in acetonitrile (3 mL). The mixture was heated to boiling. Then a solution of Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (25 mg, 116  $\mu$ mol) 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·3CH<sub>3</sub>CN 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). <sup>1</sup>H NMR (300.1 MHz):  $\delta$  = 7.93–7.91 (m, 8 H, Ar-H, o-C<sub>6</sub>H<sub>5</sub>), 7.42-7.31 (m, 12 H, Ar-H, m- and p-C<sub>6</sub>H<sub>5</sub>), 6.95 (*ps*-s, 8 H, Ar-*H*, C<sub>6</sub>H<sub>4</sub>), 5.97 (s, 4 H, C*H*), 4.71 (d,  ${}^{2}J$  = 12.0 Hz, 4 H, CH<sub>2</sub>), 4.36 (d,  ${}^{2}J$  = 12.0 Hz, 4 H, CH<sub>2</sub>), 2.20 (s, 3 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75.5 MHz):  $\delta$  = 188.30 (4 C=O), 186.51 (4 C=O), 180.38 (H<sub>3</sub>C-CO<sub>2</sub>), 148.46 (4 Ar-C-O), 139.72 (4 Ar-C-C=O), 131.05 (2 Ar-C-H, p-C<sub>6</sub>H<sub>5</sub>), 128.03 (4 Ar-C-H, C<sub>6</sub>H<sub>5</sub>), 127.57 (8 Ar-C-H, C<sub>6</sub>H<sub>5</sub>), 122.82 (4 Ar-C-H, m-C<sub>6</sub>H<sub>4</sub>), 115.95 (4 Ar-C-H, o-C<sub>6</sub>H<sub>4</sub>), 93.79 (4 CH), 73.90 (4 CH<sub>2</sub>), 24.56 (CH<sub>3</sub>-CO<sub>2</sub>) ppm. IR: v = 3065, 2903, 2849, 1598, 1567, 1521, 1254, 1119, 1034 cm<sup>-1</sup>. MS: m/z (%) = 1121 (84) [Cs $\subset$ Zn<sub>2</sub>L<sub>2</sub>]<sup>+</sup>, 959 (11) [Cs $\subset$ Zn<sub>2</sub>L<sub>2</sub> -CH<sub>2</sub>COCHCOC<sub>6</sub>H<sub>5</sub>]<sup>+</sup>, 625 (17) [ZnL + Cs]<sup>+</sup>. C<sub>54</sub>H<sub>43</sub>O<sub>14</sub>CsZn<sub>2</sub> (1179.66): calcd. C 54.98, H 3.68; found C 54.81, H 3.69.

4b: RbOAc (4 mg). Colorless crystals of 4b·2CH<sub>3</sub>CN·CH<sub>3</sub>OH 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  $(10^{-3} \text{ mbar})$ . M.p. >210 °C (decomp). <sup>1</sup>H NMR (300.1 MHz):  $\delta$  = 7.94-7.91 (m, 8 H, Ar-H, o-C<sub>6</sub>H<sub>5</sub>), 7.43-7.32 (m, 12 H, Ar-H, mand p-C<sub>6</sub>H<sub>5</sub>), 6.99 (ps-s, 8 H, Ar-H, C<sub>6</sub>H<sub>4</sub>), 5.94 (s, 4 H, CH), 4.71  $(d, {}^{2}J = 12.6 \text{ Hz}, 4 \text{ H}, CH_{2}), 4.37 (d, {}^{2}J = 12.6 \text{ Hz}, 4 \text{ H}, CH_{2}), 2.25$ (s, 3 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75.5 MHz):  $\delta$  = 188.10 (4 C=O), 186.79 (4 C=O), 180.67 (H<sub>3</sub>C-CO<sub>2</sub>), 148.76 (4 Ar-C-O), 139.69 (4 Ar-C-C=O), 131.05 (2 Ar-C-H, p-C<sub>6</sub>H<sub>5</sub>), 128.04 (4 Ar-C-H, C<sub>6</sub>H<sub>5</sub>), 127.53 (8 Ar-C-H, C<sub>6</sub>H<sub>5</sub>), 123.07 (4 Ar-C-H, m-C<sub>6</sub>H<sub>4</sub>), 116.71 (4 Ar-C-H, o-C<sub>6</sub>H<sub>4</sub>), 93.31 (4 CH), 73.78 (4 CH<sub>2</sub>), 24.74 (CH<sub>3</sub>-CO<sub>2</sub>) ppm. IR:  $\tilde{v} = 3065, 2903, 2845, 1594, 1563, 1521, 1254, 1119,$ 1034 cm<sup>-1</sup>. MS: *m*/*z* (%) = 1073 (100) [Rb⊂Zn<sub>2</sub>L<sub>2</sub>]<sup>+</sup>, 913 (23)  $[Rb \subset Zn_2L_2 - CH_2COCHCOC_6H_5]^+$ , 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  $\Delta/\Lambda$ -(2)<sub>n</sub>, meso-(3e)<sub>n</sub>, 4a and 4b were collected with a Nonius Kappa CCD area detector by using Mo- $K_{\alpha}$  radiation ( $\lambda = 0.71073$  Å). The structures were solved by direct methods with SHELXS-97<sup>[12]</sup> and refined with full-matrix least-squares against  $F^2$  using the SHELXL-97 program system.<sup>[13]</sup> All non-hydrogen atoms were fixed in ideal positions (riding model) and were included without refinement and with fixed isotropic U. Data for meso-(3b)<sub>n</sub> were collected with a Bruker-Nonius KappaCCD dif-



#### Table 1. Crystal and structure refinement data for complexes $\Delta/\Lambda$ -(2)<sub>n</sub>, meso-(3b)<sub>n</sub>, meso-(3e)<sub>n</sub>, 4a and 4b.

	$\Delta/\Lambda$ -(2) <sub>n</sub>	$meso-(\mathbf{3b})_n$	$meso-(3e)_n$
Empirical formula	C <sub>48</sub> H <sub>48</sub> Cs <sub>2</sub> Mg <sub>2</sub> O <sub>18</sub> ·3CH <sub>3</sub> CN	C <sub>156</sub> H <sub>120</sub> Mg <sub>4</sub> O <sub>36</sub> Rb <sub>4</sub> ·2CH <sub>3</sub> CN	C312H240C08C88O72·10CH3CN·18CH3OH
Mr [g mol <sup>-1</sup> ]	1350.47	3091.84	7663.06
Crystal size [mm]	$0.35 \times 0.20 \times 0.15$	$0.18 \times 0.16 \times 0.13$	$0.25 \times 0.20 \times 0.20$
Crystal system	triclinic	monoclinic	monoclinic
Space group	PI	P2 / n	P2 / m
	11 0122(2)	25 642(2)	25.0740(2)
	11.9122(3) 16.1044(2)	25.045(2)	23.9749(3)
	10.1944(2)	21.033(2)	21.0337(2)
c [A]	1/./46/(3)	29./56(2)	30.2700(3)
	114.852(1)		
β [°]	96.960(1)	90.502(6)	90.077(3)
γ [°]	95.055(1)		
V [Å <sup>3</sup> ]	3046.65(10)	16523(2)	17011.3(3)
Ζ	2	4	2
$\rho_{\rm calcd}$ [Mgm <sup>-3</sup> ]	1.472	1.243	1.496
T[K]	173(2)	100(2)	173(2)
Absorption coeff [mm <sup>-1</sup> ]	1 286	1 263	1 308
F(000)	1360	6336	7776
$\theta$ range [9]	$1.74 \pm 27.50$	2 28 to 27 00	$1.02 \pm 26.01$
	$1.74 \ 10 \ 27.50$	3.38  to  27.00	$21 \pm 1 \pm 22$
Index ranges	$-15 \le h \le 15$	$-32 \le h \le 32$	$-31 \le h \le 32$
	$-21 \le k \le 21$	$-2/\leq k\leq 2/$	$-24 \le k \le 26$
	$-23 \le l \le 23$	$-37 \le l \le 37$	$-37 \le l \le 37$
Reflections collected	26391	166961	88290
Independent reflections	13968	35804	31901
Refl. observed $[I \ge 2\sigma(I)]$	10176	22949	19074
Absorption correction	Scalepack	SADABS	Scalepack
Refinement method	full-matrix least-squares on $F^2$	full-matrix least-squares on $F^2$	full-matrix least-squares on $F^2$
Max /Min_transm	0.8305/0.6617	0.850/0.783	0 7799/0 7357
	0.0226	0.0699	0.0705
[Aint]	12068/722	25804/1022	21001/2002
Data/parameters	13906/732	1.007	31901/2093
Goodness-of-fit on $F^2$	0.983	1.067	0.929
Final $R_1 [I \ge 2\sigma(I)]$	0.0430	0.0537	0.0484
$wR_2$ (all data)	0.1470	0.1425	0.1520
Largest residuals [e A <sup>-3</sup> ]	2.019/-1.330	2.913/-1.162	1.263/-1.252
	4a	4b	
Empirical formula	C.H.C.O. 7n.·3CH.CN	C.H.O. RhZn.·2CH.CN·CH.C	рН
Mr [amol <sup>-1</sup> ]	1202 70	1246 24	011
MI [gilloi ]	1302.70	1240.24	
Converted along [maged]		11 /11 × 11 /11 × 11 /11	
Crystal size [mm]	$0.30 \times 0.30 \times 0.30$	0.20 × 0.20 × 0.20	
Crystal size [mm] Crystal system	monoclinic	monoclinic	
Crystal size [mm] Crystal system Space group	$\begin{array}{c} 0.30 \times 0.30 \times 0.30 \\ \text{monoclinic} \\ P2_1/c \end{array}$	monoclinic $P2_1/c$	
Crystal size [mm] Crystal system Space group <i>a</i> [Å]	0.30 × 0.30 × 0.30 monoclinic $P2_1/c$ 19.0036(3)	monoclinic $P2_1/c$ 18.7116(4)	
Crystal size [mm] Crystal system Space group <i>a</i> [Å] <i>b</i> [Å]	$\begin{array}{c} 0.30 \times 0.30 \times 0.30 \\ \text{monoclinic} \\ P2_1/c \\ 19.0036(3) \\ 14.4150(2) \end{array}$	$\begin{array}{c} \text{monoclinic} \\ P2_1/c \\ 18.7116(4) \\ 14.6150(3) \end{array}$	
Crystal size [mm] Crystal system Space group <i>a</i> [Å] <i>b</i> [Å] <i>c</i> [Å]	$\begin{array}{c} 0.30 \times 0.30 \times 0.30 \\ \text{monoclinic} \\ P2_1/c \\ 19.0036(3) \\ 14.4150(2) \\ 20.5309(3) \end{array}$	$\begin{array}{c} 0.20 \times 0.20 \times 0.20 \\ monoclinic \\ P2_1/c \\ 18.7116(4) \\ 14.6150(3) \\ 20.3408(4) \end{array}$	
Crystal size [mm] Crystal system Space group $a [\mathring{A}]$ $b [\mathring{A}]$ $c [\mathring{A}]$ a [°]	$\begin{array}{l} 0.50 \times 0.30 \times 0.30 \\ \text{monoclinic} \\ P2_1/c \\ 19.0036(3) \\ 14.4150(2) \\ 20.5309(3) \end{array}$	$\begin{array}{c} 0.20 \times 0.20 \times 0.20 \\ \text{monoclinic} \\ P2_1/c \\ 18.7116(4) \\ 14.6150(3) \\ 20.3408(4) \end{array}$	
Crystal size [mm] Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta [°]$	$\begin{array}{c} 0.30 \times 0.30 \times 0.30 \\ \text{monoclinic} \\ P2_1/c \\ 19.0036(3) \\ 14.4150(2) \\ 20.5309(3) \\ 103.511(1) \end{array}$	$\begin{array}{c} 0.20 \times 0.20 \times 0.20 \\ monoclinic \\ P2_1/c \\ 14.6150(3) \\ 20.3408(4) \\ 103.419(1) \end{array}$	
Crystal size [mm] Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta [°]$ $\gamma [°]$	$\begin{array}{l} 0.30 \times 0.30 \times 0.30 \\ \text{monoclinic} \\ P2_1/c \\ 19.0036(3) \\ 14.4150(2) \\ 20.5309(3) \\ 103.511(1) \end{array}$	$\begin{array}{c} 0.20 \times 0.20 \times 0.20 \\ \text{monoclinic} \\ P2_1/c \\ 18.7116(4) \\ 14.6150(3) \\ 20.3408(4) \\ 103.419(1) \end{array}$	
Crystal size [mm] Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta$ [°] $\gamma$ [°] $\gamma$ [°] $\gamma$ [ $\lambda$ ]	$\begin{array}{l} 0.30 \times 0.30 \times 0.30 \\ \text{monoclinic} \\ P2_1/c \\ 19.0036(3) \\ 14.4150(2) \\ 20.5309(3) \\ 103.511(1) \\ 5468 52(14) \end{array}$	$\begin{array}{c} 0.20 \times 0.20 \times 0.20 \\ \text{monoclinic} \\ P2_1/c \\ 14.6150(3) \\ 20.3408(4) \\ 103.419(1) \\ 5410.73(19) \end{array}$	
Crystal size [mm] Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta$ [°] $\gamma$ [°] $\gamma$ [°] Z	$\begin{array}{c} 0.30 \times 0.30 \times 0.30 \\ \text{monoclinic} \\ P2_1/c \\ 19.0036(3) \\ 14.4150(2) \\ 20.5309(3) \\ 103.511(1) \\ 5468.52(14) \\ 4 \end{array}$	$\begin{array}{c} 0.20 \times 0.20 \\ \text{monoclinic} \\ P2_1/c \\ 18.7116(4) \\ 14.6150(3) \\ 20.3408(4) \\ 103.419(1) \\ 5410.73(19) \\ 4 \end{array}$	
Crystal size [mm] Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta$ [°] $\gamma$ [°] V [Å <sup>3</sup> ] Z $\sum \beta = 2 \sum \beta =$	$\begin{array}{c} 0.30 \times 0.30 \times 0.30 \\ \text{monoclinic} \\ P_{2_{1}/c} \\ 19.0036(3) \\ 14.4150(2) \\ 20.5309(3) \\ 103.511(1) \\ 5468.52(14) \\ 4 \\ 1.582 \end{array}$	$\begin{array}{c} 0.20 \times 0.20 \\ \text{monoclinic} \\ P2_1/c \\ 18.7116(4) \\ 14.6150(3) \\ 20.3408(4) \\ 103.419(1) \\ 5410.73(19) \\ 4 \\ 1.520 \end{array}$	
Crystal size [mm] Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta [°]$ $\gamma [°]$ $V [Å^3]$ Z $\rho_{calcd.} [Mgm^{-3}]$	$\begin{array}{c} 0.30 \times 0.30 \times 0.30 \\ \text{monoclinic} \\ P_2_{1/c} \\ 19.0036(3) \\ 14.4150(2) \\ 20.5309(3) \\ 103.511(1) \\ 5468.52(14) \\ 4 \\ 1.582 \\ 172(2) \end{array}$	$\begin{array}{c} 0.20 \times 0.20 \times 0.20 \\ \text{monoclinic} \\ P2_1/c \\ 18.7116(4) \\ 14.6150(3) \\ 20.3408(4) \\ 103.419(1) \\ 5410.73(19) \\ 4 \\ 1.530 \\ 172(2) \end{array}$	
Crystal size [mm] Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta$ [°] $\gamma$ [°] V [Å <sup>3</sup> ] Z $\rho_{\text{calcd.}}$ [Mg m <sup>-3</sup> ] T [K]	$\begin{array}{c} 0.30 \times 0.30 \times 0.30 \\ \text{monoclinic} \\ P2_1/c \\ 19.0036(3) \\ 14.4150(2) \\ 20.5309(3) \\ 103.511(1) \\ 5468.52(14) \\ 4 \\ 1.582 \\ 173(2) \\ 1602 \end{array}$	$\begin{array}{c} 0.20 \times 0.20 \times 0.20 \\ \text{monoclinic} \\ P2_1/c \\ 18.7116(4) \\ 14.6150(3) \\ 20.3408(4) \\ 103.419(1) \\ 5410.73(19) \\ 4 \\ 1.530 \\ 173(2) \\ 102.20 \end{array}$	
Crystal size [mm] Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta$ [°] $\gamma$ [?] $\gamma$ [Å] Z $\rho_{calcd.}$ [Mg m <sup>-3</sup> ] T [K] Absorption coeff. [mm <sup>-1</sup> ]	$\begin{array}{c} 0.30 \times 0.30 \times 0.30 \\ \text{monoclinic} \\ P2_1/c \\ 19.0036(3) \\ 14.4150(2) \\ 20.5309(3) \\ 103.511(1) \\ 5468.52(14) \\ 4 \\ 1.582 \\ 173(2) \\ 1.605 \\ \end{array}$	$\begin{array}{c} 0.20 \times 0.20 \times 0.20 \\ \text{monoclinic} \\ P2_1/c \\ 18.7116(4) \\ 14.6150(3) \\ 20.3408(4) \\ 103.419(1) \\ 5410.73(19) \\ 4 \\ 1.530 \\ 173(2) \\ 1.852 \\ 1.852 \end{array}$	
Crystal size [mm] Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta$ [°] $\gamma$ [°] V [ų] Z $\rho_{calcd.}$ [Mg m <sup>-3</sup> ] T [K] Absorption coeff. [mm <sup>-1</sup> ] F(000)	$\begin{array}{c} 0.30 \times 0.30 \times 0.30 \\ \text{monoclinic} \\ P2_1/c \\ 19.0036(3) \\ 14.4150(2) \\ 20.5309(3) \\ 103.511(1) \\ 5468.52(14) \\ 4 \\ 1.582 \\ 173(2) \\ 1.605 \\ 2640 \end{array}$	$\begin{array}{c} 0.20 \times 0.20 \times 0.20 \\ \text{monoclinic} \\ P2_1/c \\ 18.7116(4) \\ 14.6150(3) \\ 20.3408(4) \\ 103.419(1) \\ 5410.73(19) \\ 4 \\ 1.530 \\ 173(2) \\ 1.852 \\ 2552 \end{array}$	
Crystal size [mm] Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta$ [°] $\gamma$ [°] V [Å3] Z $\rho_{\text{calcd.}}$ [Mg m <sup>-3</sup> ] T [K] Absorption coeff. [mm <sup>-1</sup> ] F(000) $\theta$ range [°]	$\begin{array}{c} 0.30 \times 0.30 \times 0.30 \\ \text{monoclinic} \\ P2_1/c \\ 19.0036(3) \\ 14.4150(2) \\ 20.5309(3) \\ 103.511(1) \\ 5468.52(14) \\ 4 \\ 1.582 \\ 173(2) \\ 1.605 \\ 2640 \\ 1.10 \text{ to } 27.49 \end{array}$	$\begin{array}{c} 0.20 \times 0.20 \times 0.20 \\ \text{monoclinic} \\ P2_1/c \\ 18.7116(4) \\ 14.6150(3) \\ 20.3408(4) \\ 103.419(1) \\ 5410.73(19) \\ 4 \\ 1.530 \\ 173(2) \\ 1.852 \\ 2552 \\ 2.06 \text{ to } 27.48 \end{array}$	
Crystal size [mm] Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta$ [°] $\gamma$ [°] V [Å <sup>3</sup> ] Z $\rho_{calcd.}$ [Mg m <sup>-3</sup> ] T [K] Absorption coeff. [mm <sup>-1</sup> ] F(000) $\theta$ range [°] Index ranges	$\begin{array}{l} 0.30 \times 0.30 \times 0.30 \\ \text{monoclinic} \\ P_{2_{1}/c} \\ 19.0036(3) \\ 14.4150(2) \\ 20.5309(3) \\ 103.511(1) \\ 5468.52(14) \\ 4 \\ 1.582 \\ 173(2) \\ 1.605 \\ 2640 \\ 1.10 \text{ to } 27.49 \\ -24 \leq h \leq 24 \end{array}$	$\begin{array}{l} \text{monoclinic} \\ P2_1/c \\ 18.7116(4) \\ 14.6150(3) \\ 20.3408(4) \\ 103.419(1) \\ 5410.73(19) \\ 4 \\ 1.530 \\ 173(2) \\ 1.852 \\ 2552 \\ 2.06 \text{ to } 27.48 \\ -24 \leq h \leq 24 \end{array}$	
Crystal size [mm] Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta [°]$ $\gamma [°]$ $V [Å^3]$ Z $\rho_{calcd.} [Mgm^{-3}]$ T [K] Absorption coeff. [mm <sup>-1</sup> ] F(000) $\theta$ range [°] Index ranges	$\begin{array}{l} 0.30 \times 0.30 \times 0.30 \\ \text{monoclinic} \\ P_2_{1/c} \\ 19.0036(3) \\ 14.4150(2) \\ 20.5309(3) \\ 103.511(1) \\ 5468.52(14) \\ 4 \\ 1.582 \\ 173(2) \\ 1.605 \\ 2640 \\ 1.10 \text{ to } 27.49 \\ -24 \leq h \leq 24 \\ -18 \leq k \leq 17 \end{array}$	$\begin{array}{l} \text{monoclinic} \\ P2_1/c \\ 18.7116(4) \\ 14.6150(3) \\ 20.3408(4) \\ 103.419(1) \\ 5410.73(19) \\ 4 \\ 1.530 \\ 173(2) \\ 1.852 \\ 2552 \\ 2.06 \text{ to } 27.48 \\ -24 \leq h \leq 24 \\ -18 \leq k \leq 17 \end{array}$	
Crystal size [mm] Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta$ [°] $\gamma$ [°] V [Å <sup>3</sup> ] Z $\rho_{calcd.}$ [Mg m <sup>-3</sup> ] T [K] Absorption coeff. [mm <sup>-1</sup> ] F(000) $\theta$ range [°] Index ranges	$\begin{array}{l} 0.30 \times 0.30 \times 0.30 \\ \text{monoclinic} \\ P_2_{1/c} \\ 19.0036(3) \\ 14.4150(2) \\ 20.5309(3) \\ 103.511(1) \\ 5468.52(14) \\ 4 \\ 1.582 \\ 173(2) \\ 1.605 \\ 2640 \\ 1.10 \text{ to } 27.49 \\ -24 \leq h \leq 24 \\ -18 \leq k \leq 17 \\ -26 \leq l \leq 26 \end{array}$	$\begin{array}{l} \text{monoclinic} \\ P2_1/c \\ 18.7116(4) \\ 14.6150(3) \\ 20.3408(4) \\ 103.419(1) \\ 5410.73(19) \\ 4 \\ 1.530 \\ 173(2) \\ 1.852 \\ 2552 \\ 2.06 \text{ to } 27.48 \\ -24 \leq h \leq 24 \\ -18 \leq k \leq 17 \\ -26 \leq l \leq 26 \end{array}$	
Crystal size [mm] Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta$ [°] $\gamma$ [°] $\gamma$ [°] $\gamma$ [°] $\gamma$ [°] $\gamma$ [Å] Z $\rho_{calcd.}$ [Mg m <sup>-3</sup> ] T [K] Absorption coeff. [mm <sup>-1</sup> ] F(000) $\theta$ range [°] Index ranges Reflections collected	$\begin{array}{l} 0.30 \times 0.30 \times 0.30 \\ \text{monoclinic} \\ P_2_{1/c} \\ 19.0036(3) \\ 14.4150(2) \\ 20.5309(3) \\ 103.511(1) \\ 5468.52(14) \\ 4 \\ 1.582 \\ 173(2) \\ 1.605 \\ 2640 \\ 1.10 \text{ to } 27.49 \\ -24 \leq h \leq 24 \\ -18 \leq k \leq 17 \\ -26 \leq l \leq 26 \\ 23739 \end{array}$	$\begin{array}{l} 0.20 \times 0.20 \times 0.20 \\ \text{monoclinic} \\ P2_1/c \\ 18.7116(4) \\ 14.6150(3) \\ 20.3408(4) \\ 103.419(1) \\ 5410.73(19) \\ 4 \\ 1.530 \\ 173(2) \\ 1.852 \\ 2552 \\ 2.06 \text{ to } 27.48 \\ -24 \leq h \leq 24 \\ -18 \leq k \leq 17 \\ -26 \leq l \leq 26 \\ 22634 \end{array}$	
Crystal size [mm] Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta$ [°] $\gamma$ [?] $\gamma$ [Å] Z $\rho_{calcd.}$ [Mg m <sup>-3</sup> ] T [K] Absorption coeff. [mm <sup>-1</sup> ] F(000) $\theta$ range [°] Index ranges Reflections collected Independent reflections	$\begin{array}{l} 0.30 \times 0.30 \times 0.30 \\ \text{monoclinic} \\ P2_1/c \\ 19.0036(3) \\ 14.4150(2) \\ 20.5309(3) \\ 103.511(1) \\ 5468.52(14) \\ 4 \\ 1.582 \\ 173(2) \\ 1.605 \\ 2640 \\ 1.10 \text{ to } 27.49 \\ -24 \leq h \leq 24 \\ -18 \leq k \leq 17 \\ -26 \leq l \leq 26 \\ 23739 \\ 12546 \end{array}$	$\begin{array}{l} \text{monoclinic} \\ P2_1/c \\ 18.7116(4) \\ 14.6150(3) \\ 20.3408(4) \\ 103.419(1) \\ 5410.73(19) \\ 4 \\ 1.530 \\ 173(2) \\ 1.852 \\ 2552 \\ 2.06 \text{ to } 27.48 \\ -24 \leq h \leq 24 \\ -18 \leq k \leq 17 \\ -26 \leq l \leq 26 \\ 22634 \\ 12355 \end{array}$	
Crystal size [mm] Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta$ [°] $\gamma$ [°] $\gamma$ [Å] Z $\rho_{calcd.}$ [Mg m <sup>-3</sup> ] T [K] Absorption coeff. [mm <sup>-1</sup> ] F(000) $\theta$ range [°] Index ranges Reflections collected Independent reflections Refl. observed [ $L \ge 2\pi/L$ ]	$\begin{array}{l} 0.30 \times 0.30 \times 0.30 \\ \text{monoclinic} \\ P_{2_{1}/c} \\ 19.0036(3) \\ 14.4150(2) \\ 20.5309(3) \\ 103.511(1) \\ 5468.52(14) \\ 4 \\ 1.582 \\ 173(2) \\ 1.605 \\ 2640 \\ 1.10 \text{ to } 27.49 \\ -24 \leq h \leq 24 \\ -18 \leq k \leq 17 \\ -26 \leq l \leq 26 \\ 23739 \\ 12546 \\ 9906 \end{array}$	$\begin{array}{l} \text{monoclinic} \\ P2_1/c \\ 18.7116(4) \\ 14.6150(3) \\ 20.3408(4) \\ 103.419(1) \\ \\ 5410.73(19) \\ 4 \\ 1.530 \\ 173(2) \\ 1.852 \\ 2552 \\ 2.06 \text{ to } 27.48 \\ -24 \leq h \leq 24 \\ -18 \leq k \leq 17 \\ -26 \leq l \leq 26 \\ 22634 \\ 12355 \\ 7781 \end{array}$	
Crystal size [mm] Crystal system Space group $a [\mathring{A}]$ $b [\mathring{A}]$ $c [\mathring{A}]$ $c [\mathring{A}]$ a [°] $\beta [°]$ $\gamma [°]$ $\gamma [°]$ $V [\mathring{A}^3]$ Z $\rho_{calcd.} [Mg m^{-3}]$ T [K] Absorption coeff. [mm <sup>-1</sup> ] F(000) $\theta$ range [°] Index ranges Reflections collected Independent reflections Refl. observed $[I \ge 2\sigma(I)]$ Absorption correction	$\begin{array}{l} 0.30 \times 0.30 \times 0.30 \\ \text{monoclinic} \\ P_{2_{1}/c} \\ 19.0036(3) \\ 14.4150(2) \\ 20.5309(3) \\ 103.511(1) \\ 5468.52(14) \\ 4 \\ 1.582 \\ 173(2) \\ 1.605 \\ 2640 \\ 1.10 \text{ to } 27.49 \\ -24 \leq h \leq 24 \\ -18 \leq k \leq 17 \\ -26 \leq l \leq 26 \\ 23739 \\ 12546 \\ 9906 \\ \text{Scalepack} \end{array}$	$\begin{array}{c} 0.20 \times 0.20 \times 0.20 \\ \text{monoclinic} \\ P2_1/c \\ 18.7116(4) \\ 14.6150(3) \\ 20.3408(4) \\ 103.419(1) \\ 5410.73(19) \\ 4 \\ 1.530 \\ 173(2) \\ 1.852 \\ 2552 \\ 2.06 \text{ to } 27.48 \\ -24 \leq h \leq 24 \\ -18 \leq k \leq 17 \\ -26 \leq l \leq 26 \\ 22634 \\ 12355 \\ 7781 \\ \text{Scalepack} \end{array}$	
Crystal size [mm] Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta [°]$ $\gamma [°]$ $\gamma [°]$ $V [Å^3]$ Z $\rho_{calcd.} [Mgm^{-3}]$ T [K] Absorption coeff. [mm <sup>-1</sup> ] F(000) $\theta$ range [°] Index ranges Reflections collected Independent reflections Refl. observed $[I \ge 2\sigma(I)]$ Absorption correction Refinement method	$\begin{array}{l} 0.30 \times 0.30 \times 0.30 \\ \text{monoclinic} \\ P_{2_{1}/c} \\ 19.0036(3) \\ 14.4150(2) \\ 20.5309(3) \\ 103.511(1) \\ 5468.52(14) \\ 4 \\ 1.582 \\ 173(2) \\ 1.605 \\ 2640 \\ 1.10 \text{ to } 27.49 \\ -24 \leq h \leq 24 \\ -18 \leq k \leq 17 \\ -26 \leq l \leq 26 \\ 23739 \\ 12546 \\ 9906 \\ \text{Scalepack} \\ \text{full matrix loast squares on } P_{2}^{2} \end{array}$	$\begin{array}{l} \text{monoclinic} \\ P2_1/c \\ 18.7116(4) \\ 14.6150(3) \\ 20.3408(4) \\ 103.419(1) \\ 5410.73(19) \\ 4 \\ 1.530 \\ 173(2) \\ 1.852 \\ 2552 \\ 2.06 \text{ to } 27.48 \\ -24 \leq h \leq 24 \\ -18 \leq k \leq 17 \\ -26 \leq l \leq 26 \\ 22634 \\ 12355 \\ 7781 \\ \text{Scalepack} \\ \text{full matrix least squares on } F^2 \end{array}$	
Crystal size [mm] Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta [°]$ $\gamma [°]$ $\gamma [°]$ $V [Å^3]$ Z $\rho_{calcd.} [Mg m^{-3}]$ T [K] Absorption coeff. [mm <sup>-1</sup> ] F(000) $\theta$ range [°] Index ranges Reflections collected Independent reflections Refl. observed $[I \ge 2\sigma(I)]$ Absorption correction Refinement method May (Min. transport	0.50 × 0.30 × 0.30 monoclinic $P_{2_1/c}$ 19.0036(3) 14.4150(2) 20.5309(3) 103.511(1) 5468.52(14) 4 1.582 173(2) 1.605 2640 1.10 to 27.49 $-24 \le h \le 24$ $-18 \le k \le 17$ $-26 \le l \le 26$ 23739 12546 9906 Scalepack full-matrix least-squares on $F^2$	$\begin{array}{l} \text{monoclinic} \\ P2_1/c \\ 18.7116(4) \\ 14.6150(3) \\ 20.3408(4) \\ 103.419(1) \\ 5410.73(19) \\ 4 \\ 1.530 \\ 173(2) \\ 1.852 \\ 2552 \\ 2.06 \text{ to } 27.48 \\ -24 \leq h \leq 24 \\ -18 \leq k \leq 17 \\ -26 \leq l \leq 26 \\ 22634 \\ 12355 \\ 7781 \\ \text{Scalepack} \\ \text{full-matrix least-squares on } F^2 \\ 0.70820(7.792) \\ \end{array}$	
Crystal size [mm] Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta$ [°] $\gamma$ [°] $\gamma$ [°] $\gamma$ [°] $\gamma$ [°] V [Å <sup>3</sup> ] Z $\rho_{calcd.}$ [Mg m <sup>-3</sup> ] T [K] Absorption coeff. [mm <sup>-1</sup> ] F(000) $\theta$ range [°] Index ranges Reflections collected Independent reflections Refl. observed [ $I \ge 2\sigma(I)$ ] Absorption correction Refinement method Max./Min. transm.	$\begin{array}{l} 0.30 \times 0.30 \times 0.30 \\ \text{monoclinic} \\ P_2_{1/c} \\ 19.0036(3) \\ 14.4150(2) \\ 20.5309(3) \\ 103.511(1) \\ 5468.52(14) \\ 4 \\ 1.582 \\ 173(2) \\ 1.605 \\ 2640 \\ 1.10 \text{ to } 27.49 \\ -24 \leq h \leq 24 \\ -18 \leq k \leq 17 \\ -26 \leq l \leq 26 \\ 23739 \\ 12546 \\ 9906 \\ \text{Scalepack} \\ \text{full-matrix least-squares on } F^2 \\ 0.6446/0.6446 \\ 0.0247 \end{array}$	$\begin{array}{c} 0.20 \times 0.20 \times 0.20 \\ \text{monoclinic} \\ P2_1/c \\ 18.7116(4) \\ 14.6150(3) \\ 20.3408(4) \\ 103.419(1) \\ 5410.73(19) \\ 4 \\ 1.530 \\ 173(2) \\ 1.852 \\ 2552 \\ 2.06 \text{ to } 27.48 \\ -24 \leq h \leq 24 \\ -18 \leq k \leq 17 \\ -26 \leq l \leq 26 \\ 22634 \\ 12355 \\ 7781 \\ \text{Scalepack} \\ \text{full-matrix least-squares on } F^2 \\ 0.7083/0.7083 \\ 0.0417 \end{array}$	
Crystal size [mm] Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta$ [°] $\gamma$ [°] $\gamma$ [°] $\gamma$ [°] $\gamma$ [Å] Z $\rho_{calcd.}$ [Mg m <sup>-3</sup> ] T [K] Absorption coeff. [mm <sup>-1</sup> ] F(000) $\theta$ range [°] Index ranges Reflections collected Independent reflections Refl. observed [ $I \ge 2\sigma(I)$ ] Absorption correction Refinement method Max./Min. transm. [ $R_{ind}$ ]	0.50 × 0.30 × 0.30 monoclinic $P_{2_1/c}$ 19.0036(3) 14.4150(2) 20.5309(3) 103.511(1) 5468.52(14) 4 1.582 173(2) 1.605 2640 1.10 to 27.49 $-24 \le h \le 24$ $-18 \le k \le 17$ $-26 \le l \le 26$ 23739 12546 9906 Scalepack full-matrix least-squares on $F^2$ 0.6446/0.6446 0.0247	$\begin{array}{l} \text{monoclinic} \\ P2_1/c \\ 18.7116(4) \\ 14.6150(3) \\ 20.3408(4) \\ \hline 103.419(1) \\ 5410.73(19) \\ 4 \\ 1.530 \\ 173(2) \\ 1.852 \\ 2552 \\ 2.06 \text{ to } 27.48 \\ -24 \leq h \leq 24 \\ -18 \leq k \leq 17 \\ -26 \leq l \leq 26 \\ 22634 \\ 12355 \\ 7781 \\ \text{Scalepack} \\ \text{full-matrix least-squares on } F^2 \\ 0.7083/0.7083 \\ 0.0417 \\ 1205572 \\ \end{array}$	
Crystal size [mm] Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta$ [°] $\gamma$ [?] $\gamma$ [?] $\gamma$ [Å] Z $\rho_{calcd.}$ [Mg m <sup>-3</sup> ] T [K] Absorption coeff. [mm <sup>-1</sup> ] F(000) $\theta$ range [°] Index ranges Reflections collected Independent reflections Refl. observed [ $I \ge 2\sigma(I)$ ] Absorption correction Refinement method Max./Min. transm. [ $R_{int}$ ] Data/parameters	$\begin{array}{l} 0.30 \times 0.30 \times 0.30 \\ \text{monoclinic} \\ P_{2_{1}/c} \\ 19.0036(3) \\ 14.4150(2) \\ 20.5309(3) \\ 103.511(1) \\ 5468.52(14) \\ 4 \\ 1.582 \\ 173(2) \\ 1.605 \\ 2640 \\ 1.10 \text{ to } 27.49 \\ -24 \leq h \leq 24 \\ -18 \leq k \leq 17 \\ -26 \leq l \leq 26 \\ 23739 \\ 12546 \\ 9906 \\ \text{Scalepack} \\ \text{full-matrix least-squares on } F^{2} \\ 0.6446/0.6446 \\ 0.0247 \\ 12546/721 \\ \end{array}$	$\begin{array}{l} \text{monoclinic} \\ P2_1/c \\ 18.7116(4) \\ 14.6150(3) \\ 20.3408(4) \\ 103.419(1) \\ \\ 5410.73(19) \\ 4 \\ 1.530 \\ 173(2) \\ 1.852 \\ 2552 \\ 2.06 \text{ to } 27.48 \\ -24 \leq h \leq 24 \\ -18 \leq k \leq 17 \\ -26 \leq l \leq 26 \\ 22634 \\ 12355 \\ 7781 \\ \text{Scalepack} \\ \text{full-matrix least-squares on } F^2 \\ 0.7083/0.7083 \\ 0.0417 \\ 12355/712 \\ \end{array}$	
Crystal size [mm] Crystal system Space group a [Å] b [Å] c [Å] c [Å] a [°] $\beta [°]$ $\gamma [°]$ $\gamma [°]$ $V [Å^3]$ Z $\rho_{calcd.} [Mg m^{-3}]$ T [K] Absorption coeff. [mm <sup>-1</sup> ] F(000) $\theta$ range [°] Index ranges Reflections collected Independent reflections Refl. observed $[I \ge 2\sigma(I)]$ Absorption correction Refinement method Max./Min. transm. $[R_{int]}$ Data/parameters Goodness-of-fit on $F^2$	$\begin{array}{l} 0.30 \times 0.30 \times 0.30 \\ \text{monoclinic} \\ P_{2_{1}/c} \\ 19.0036(3) \\ 14.4150(2) \\ 20.5309(3) \\ 103.511(1) \\ 5468.52(14) \\ 4 \\ 1.582 \\ 173(2) \\ 1.605 \\ 2640 \\ 1.10 \text{ to } 27.49 \\ -24 \leq h \leq 24 \\ -18 \leq k \leq 17 \\ -26 \leq l \leq 26 \\ 23739 \\ 12546 \\ 9906 \\ \text{Scalepack} \\ \text{full-matrix least-squares on } F^{2} \\ 0.6446/0.6446 \\ 0.0247 \\ 12546/721 \\ 1.022 \\ \end{array}$	$\begin{array}{l} \text{monoclinic} \\ P2_1/c \\ 18.7116(4) \\ 14.6150(3) \\ 20.3408(4) \\ 103.419(1) \\ \\ 5410.73(19) \\ 4 \\ 1.530 \\ 173(2) \\ 1.852 \\ 2552 \\ 2.06 \text{ to } 27.48 \\ -24 \leq h \leq 24 \\ -18 \leq k \leq 17 \\ -26 \leq l \leq 26 \\ 22634 \\ 12355 \\ 7781 \\ \text{Scalepack} \\ \text{full-matrix least-squares on } F^2 \\ 0.7083/0.7083 \\ 0.0417 \\ 12355/712 \\ 1.000 \\ \end{array}$	
Crystal size [mm] Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta [°]$ $\gamma [°]$ $V [Å^3]$ Z $\rho_{calcd.} [Mg m^{-3}]$ T [K] Absorption coeff. [mm <sup>-1</sup> ] F(000) $\theta$ range [°] Index ranges Reflections collected Independent reflections Refl. observed $[I \ge 2\sigma(I)]$ Absorption correction Refinement method Max./Min. transm. $[R_{int}]$ Data/parameters Goodness-of-fit on $F^2$ Final $R_1 [I \ge 2\sigma(I)]$	0.50 × 0.30 × 0.30 monoclinic $P_{2_1/c}$ 19.0036(3) 14.4150(2) 20.5309(3) 103.511(1) 5468.52(14) 4 1.582 173(2) 1.605 2640 1.10 to 27.49 $-24 \le h \le 24$ $-18 \le k \le 17$ $-26 \le l \le 26$ 23739 12546 9906 Scalepack full-matrix least-squares on $F^2$ 0.6446/0.6446 0.0247 12546/721 1.022 0.0328	$\begin{array}{l} \text{monoclinic} \\ P2_1/c \\ 18.7116(4) \\ 14.6150(3) \\ 20.3408(4) \\ 103.419(1) \\ \\ 5410.73(19) \\ 4 \\ 1.530 \\ 173(2) \\ 1.852 \\ 2552 \\ 2.06 \text{ to } 27.48 \\ -24 \leq h \leq 24 \\ -18 \leq k \leq 17 \\ -26 \leq l \leq 26 \\ 22634 \\ 12355 \\ 7781 \\ \text{Scalepack} \\ \text{full-matrix least-squares on } F^2 \\ 0.7083/0.7083 \\ 0.0417 \\ 12355/712 \\ 1.000 \\ 0.0479 \\ \end{array}$	
Crystal size [mm] Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta [°]$ $\gamma [°]$ $V [Å^3]$ Z $\rho_{calcd.} [Mg m^{-3}]$ T [K] Absorption coeff. [mm <sup>-1</sup> ] F(000) $\theta$ range [°] Index ranges Reflections collected Independent reflections Refl. observed $[I \ge 2\sigma(I)]$ Absorption correction Refinement method Max./Min. transm. $[R_{int}]$ Data/parameters Goodness-of-fit on $F^2$ Final $R_1 [I \ge 2\sigma(I)]$ $wR_2$ (all data)	0.50 × 0.30 × 0.30 monoclinic $P_{2_1/c}$ 19.0036(3) 14.4150(2) 20.5309(3) 103.511(1) 5468.52(14) 4 1.582 173(2) 1.605 2640 1.10 to 27.49 $-24 \le h \le 24$ $-18 \le k \le 17$ $-26 \le l \le 26$ 23739 12546 9906 Scalepack full-matrix least-squares on $F^2$ 0.6446/0.6446 0.0247 12546/721 1.022 0.0328 0.1049	$\begin{array}{c} \text{nonoclinic} \\ P2_1/c \\ 18.7116(4) \\ 14.6150(3) \\ 20.3408(4) \\ 103.419(1) \\ \\ 5410.73(19) \\ 4 \\ 1.530 \\ 173(2) \\ 1.852 \\ 2552 \\ 2.06 \text{ to } 27.48 \\ -24 \leq h \leq 24 \\ -18 \leq k \leq 17 \\ -26 \leq l \leq 26 \\ 22634 \\ 12355 \\ 7781 \\ \text{Scalepack} \\ \text{full-matrix least-squares on } F^2 \\ 0.7083/0.7083 \\ 0.0417 \\ 12355/712 \\ 1.000 \\ 0.0479 \\ 0.1321 \\ \end{array}$	

fractometer by using Mo- $K_{\alpha}$  radiation ( $\lambda = 0.71073$  Å), 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.<sup>[14]</sup> A semiempirical absorption correction based on multiple scans (SADABS)<sup>[15]</sup> 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 proceeding 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.<sup>[16]</sup>

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