Resolution of Seven-Coordinate Complexes

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Abstract: The crystal structures of [Pr(dbm)$_3$H$_2$O] (**1**), [Sm(dbm)$_3$H$_2$O] (**2**), and [Er(dbm)$_3$H$_2$O] (**3**) have been determined (dbm = dibenzoylmethane). They display seven-coordinate propeller-shaped molecules, which are chiral and crystallize as conglomerates in space group *R*3. Analysis of the crystal structures reveals supramolecular interactions, including formation of a quadruple helix, which explain how stereochemical information can be transferred between stacks of molecules. A method to quantify the *ee* in bulk samples of stereochemically labile compounds by using solid-state CD spectroscopy is described. Using this method, it has been shown that compounds **1**–**3** undergo total spontaneous resolution directly after synthesis, forming a microcrystalline reaction product that is essentially enantiopure. The resolution of bulk quantities of seven-coordinate complexes (without chiral or polydentate ligands) is thus reported for the first time. Because the crystallization starts without seeding, the overall preparation may be regarded as absolute asymmetric synthesis.

Keywords: asymmetric synthesis · chiral resolution · chirality · circular dichroism · lanthanides

Introduction

In 1848, Pasteur resolved four-coordinate enantiomers by hand-sorting the enantiomorphic crystals in a conglomerate of ammonium sodium tartrate, and in 1911, Werner reported the first resolution of a six-coordinate complex.[1] Instrumental to Werner's success was the fact that many octahedral complexes (like tetrahedral carbon compounds) are substitutionally inert. Seven-coordinate chiral complexes (with exclusively achiral mono- or bidentate ligands) frequently enantiomerize in solution, and the resolution of such racemates has remained an unconquered challenge.[2] Indeed, simply determining the enantiomeric excess (*ee*) in a labile reaction product (i.e., a resolution attempt) is problematic, as rapid racemization in solution means that only solid-state methods can be used. We recently reported the synthesis and spontaneous resolution of eight-coordinate enantiomers of [SmI$_2$(dme)$_3$] (dme = 1,2-dimethoxyethane).[3] In this work, we have attempted to isolate enantiopure bulk quantities[4] of seven-coordinate enantiomers of [Ln(dbm)$_3$H$_2$O] (dbm = dibenzoylmethane). As can be seen from Figure 1, such seven-coordinate complexes are the missing link in a simple sequence; the first member is a six-coordinate Werner complex with three bidentate ligands, and the last member is eight-coordinate [SmI$_2$(dme)$_3$]. (Analogous to six-coordinate Werner complexes with three bidentate ligands, see Figure 1, we named the seven- and eight-coordinate enantiomers Δ and Λ, respectively.) We also investigated the potential of solid-state CD spectroscopy for the quantitative determination of the *ee* in bulk samples of stereochemically labile molecules.

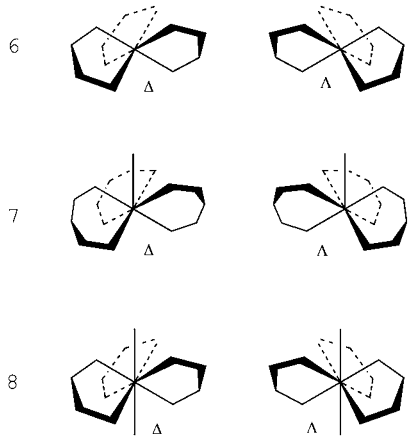

Figure 1. Together with the classical six-coordinate complexes, seven- and eight-coordinate enantiomers (with three bidentate ligands) form a series of chiral propeller molecules (with monodentate ligands on the threefold axis).

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Results and Discussion

The synthesis of [Ln(dbm)$_3$H$_2$O] complexes is a straightforward process:[5,6] reaction of LnCl$_3$ and dibenzoylmethane in a basic solution leads to the formation of microcrystalline products in high yield. The crystal structures of [Pr(dbm)$_3$H$_2$O] (**1**), [Sm(dbm)$_3$H$_2$O] (**2**), and [Er(dbm)$_3$H$_2$O] (**3**) all display chiral, propeller-like molecules, in which the aqua ligand is situated on the crystallographic threefold axis (Figure 2); therefore, these compounds are isostructural with the previously characterized [Nd(dbm)$_3$H$_2$O][7] and [Ho(dbm)$_3$H$_2$O].[8]

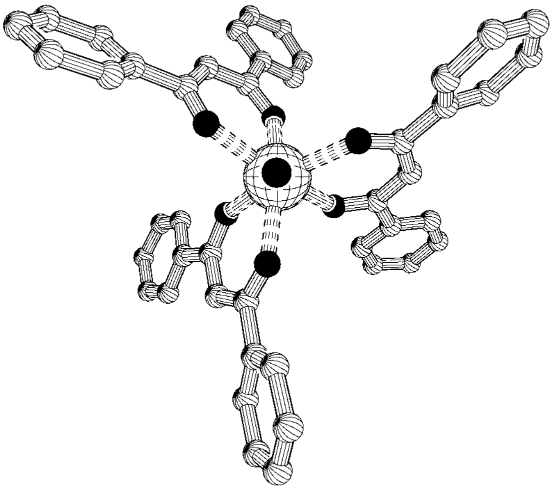

Figure 2. View of Δ-[Ln(dbm)$_3$H$_2$O] along the threefold propeller axis.

Resolution: Complexes **1**–**3** crystallize in space group *R*3 and are conglomerates; that is, the Δ- and Λ-enantiomers crystallize separately. The coordination geometry around the Ln atoms is best described as a capped octahedron, in which the six dbm oxygen atoms are at the corners of the octahedron, and the aqua ligand caps one of its surfaces. The pentagonal bipyramid and the capped trigonal prism are other common seven-coordinate geometries that exhibit similar stability.[9] Low transformational barriers between the different coordination arrangements can be assumed, which means that **1**–**3** should racemize rapidly in solution. We found that this is indeed the case, because acetone solutions of enantiopure (prior to dissolution) Δ-[Sm(dbm)$_3$H$_2$O] show no optical activity. Such "labile conglomerates" can undergo crystallization-induced asymmetric transformation (also known as total spontaneous resolution),[10] as depicted in Figure 3. If primary nucleation is slow relative to secondary nucleation, preferential crystallization (e.g., single-colony crystallization) can give a product with 100% yield and *ee*. A necessary condition is, of course, that enantiomerization in solution is fast compared to crystal growth. If the crystallization starts without seeding, the overall preparation may be regarded as absolute asymmetric synthesis,[11–13] that is, the creation of optical activity from achiral (or racemic) precursors without the participation of molecular optical activity. Absolute asymmetric synthesis is relevant to speculation concerning the origin of biomolecular homochirality.[14–23]

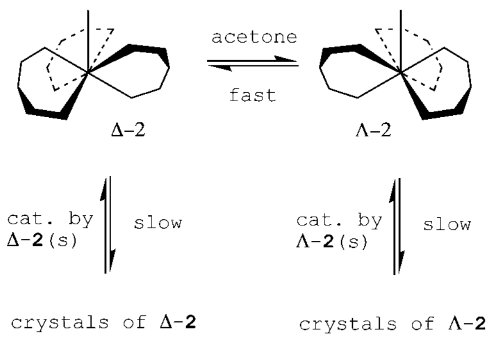

Figure 3. Crystallization-induced asymmetric transformation of **2**.

We concentrated our studies on [Sm(dbm)$_3$H$_2$O] (**2**), because it is easy to recrystallize the yellow bulk product obtained after the mother liquor yielded by the synthesis of **2** is allowed to reach ambient temperature. By layering an acetone/water solution of this microcrystalline product onto a water surface, large needle-shaped crystals of good quality can be obtained. In a first attempt to determine the *ee* from such a recrystallization, we collected X-ray data from fragments of ten large, single crystals, which represented approximately 10% of the total batch mass. As shown by anomalous dispersion,[24–25] all ten crystals had the Δ-configuration, which indicates a high *ee* in the product. It is likely that the Δ-enantiomer content is higher than 93%, because $0.93^{10} = 0.48$; however, a method that uses a sample representative of the whole bulk product would clearly be more informative, especially as collecting repeated diffraction data sets is very time consuming. Furthermore, a general method would be useful, because syntheses of new substances often result in microcrystalline products that are unsuitable for single crystal analysis by using X-rays, polarized light, or crystal shape.

Determination of *ee* in bulk samples of Δ-2: Qualitative characterization of microcrystalline samples by using solid-state CD spectroscopy has recently been discussed.[26] However, use of the CD signal from stereochemically labile solid samples for the quantitative determination of the enantiomeric excess has not yet been reported. The spectra shown in Figure 4 were obtained for selected single crystals of Δ-**2** and Λ-**2** (see Experimental Section), which had been very carefully ground (to minimize dispersion effects and concentration variations) together with KBr, and then pressed into thin, translucent disks. The spectra of Δ-**2** and Λ-**2** were mirror images and independent of disk rotation in the beam. Because solutions of **2** are CD-silent, spectral artefacts due to partial dissolution can be excluded, which is beneficial in the recording of solid-state CD spectra of stereochemically labile samples. A plot of the magnitude of the strong CD signal at 292 nm versus the mass of enantiopure (and homochiral) single crystals in the disk resulted in a straight line

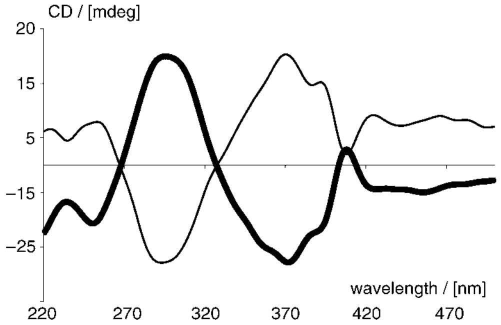

Figure 4. Solid-state CD spectra of Δ-**2** (bold) and Λ-**2**.

for 0.05–0.20 mg of Δ-**2** crystals (Figure 5). This was a welcome outcome, as we had suspected that variations in particle size and disk quality may have resulted in low reproducibility. Consequently, we mixed Δ-and Λ-crystals in specific proportions and prepared a KBr disk in the same manner as for the enantiopure samples. The point representing the difference in mass between Δ-and Λ-crystals and the corresponding CD signal fitted nicely to the line in Figure 5. This means that for weighed samples of **2** of unknown optical purity, the *ee* can be determined immediately after a calibration line, such as that in Figure 5, has been recorded. In other words, the CD signal can be used as a quantitative measure of the *ee* in a microcrystalline (powder) sample. A subjective error estimate, considering crystal weighing errors and CD signal variations for different disk orientations, suggests a maximum error of ±3%. The maximum deviation of the calibration points from the calibration line is <2%.

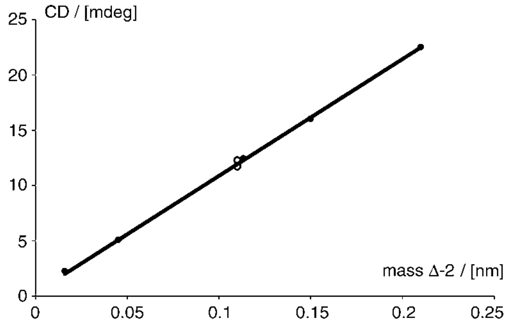

Figure 5. The enantiopure crystal mass of Δ-**2** in each KBr disk is directly proportional to the magnitude of the CD signal at 292 nm. Open circles show *ee* determination of the microcrystalline bulk product.

After mixing and grinding all of the crystals in one batch, followed by the removal of a sample (which represents the whole batch), we could determine that recrystallized batches of Δ-**2** were essentially enantiopure, as the X-ray data from ten different crystals had indicated. Remarkably, even the bulk reaction product displayed *ee*'s of between 97 and 100%, as indicated by the open circles in Figure 5. Apparently, slow recrystallization is not neccessary to obtain an enantiopure product, which means that preferential crystallization, and thus total spontaneous resolution, is indeed spontaneous in this system. In fact, it is harder to obtain a racemic product of **2** than an enantiopure product. If this is a common behavior among labile conglomerates, it suggests that a mechanism that couples crystallization-induced asymmetric transformation with transfer of the chirality to stereochemically inert molecules may have been instrumental in the creation of a homochiral pool of molecules on prebiotic Earth.

Crystal structure: The molecular structure of Δ-**2** is shown in Figure 6. Although Δ-**1** and Δ-**3** are isostructural, there are variations in Ln−O lengths, according to the diminishing ionic radius in going from Pr to Er, as demonstrated in Table 1. Selected lengths and angles in Δ-**2** are given in Table 2. The coordination model that best describes these propeller-shaped molecules is a capped octahedron. The capping causes considerable flattening of the corresponding tripod along the crystallographic threefold axis, which is re-

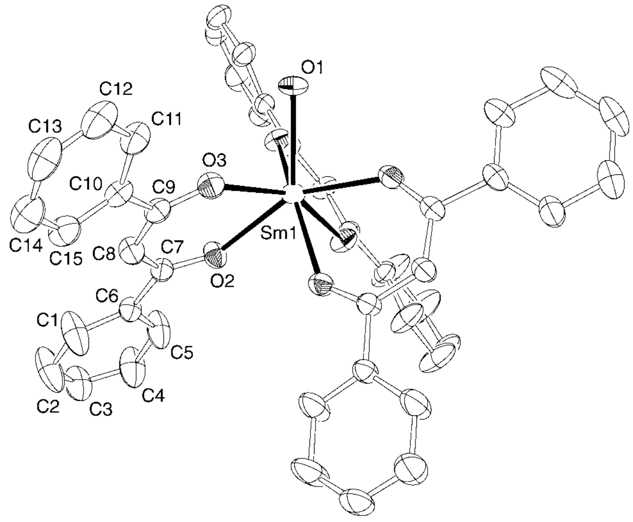

Figure 6. ORTEP drawing of Δ-**2**, showing the crystallographic numbering. Thermal ellipsoids enclose 50% probability.

Table 1. Ln−O bond lengths [Å] in Δ-**1**, Δ-**2**, and Δ-**3**.

Pr1−O1	2.452(6)	Sm1−O1	2.447(5)	Er1−O1	2.398(8)
Pr1−O2	2.356(3)	Sm1−O2	2.354(3)	Er1−O2	2.284(4)
Pr1−O3	2.335(3)	Sm1−O3	2.342(3)	Er1−O3	2.259(4)

Table 2. Selected bond lengths [Å] and angles [°] in Δ-**2**[a].

C5−C6	1.345(6)	O1-Sm1-O2	130.70(8)
C6−C7	1.493(5)	O1-Sm1-O3	74.82(7)
C9−C10	1.497(5)	O2-Sm1-O3	72.24(10)
O2−C7	1.270(5)	O2-Sm1-O2*	82.08(12)
O3−C9	1.260(5)	O2-Sm1-O3*	152.88(10)
C7−C8	1.384(5)	O3-Sm1-O2*	85.83(12)
C8−C9	1.395(6)	O3-Sm1-O3*	113.40(6)

[a] Symmetry code *: *y*–*x*, 1–*x*, *z*.

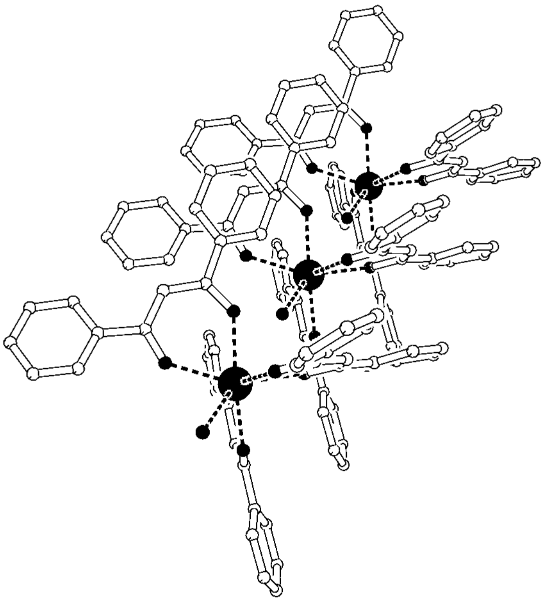

Figure 7. Homochiral rows along *c* are formed in **2**. The disordered aqua hydrogen atoms (not shown) contribute to the homochiral stacking facilitated by intermolecular hydrogen bonds.

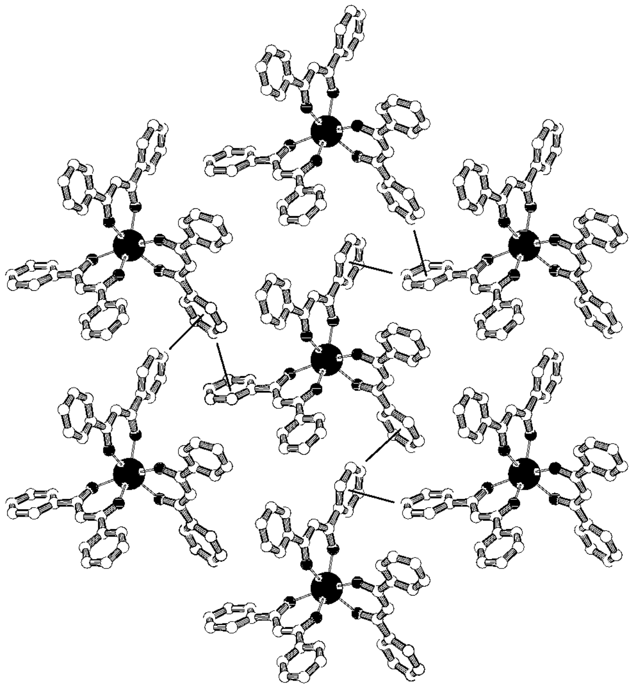

Figure 8. Short CH–π distances (2.79 Å) in Δ-**2** (indicated by solid lines) mediate the transfer of stereochemical information between different stacks.

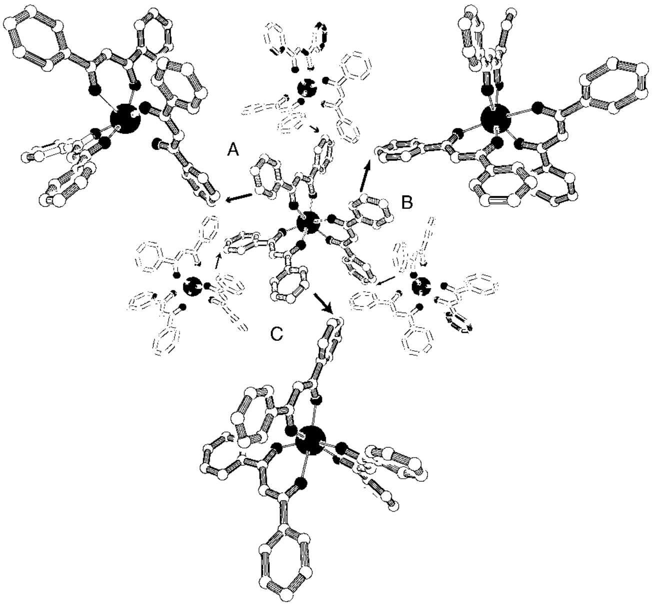

Figure 9. Formation of three (A–C) quadruple helices (along *c*) in Δ-**2**. Only one quarter of each quadruple helix is shown.

flected by the fact that the O3-Sm1-O3* angles exceed 113°, whereas the O2-Sm1-O2* angles are approximately 82°. Opposite the capped side of the octahedron, as can be seen in Figure 7, the three O2 atoms are involved in hydrogen bonding with the aqua hydrogen atoms of a neighboring molecule. Because the aqua oxygen atom sits on a threefold axis, the corresponding hydrogen atoms must be disordered, which means that a detailed description of hydrogen bonding can be only speculative, at best. The closest C_{aryl}–C_{aryl} contact within each stack is 3.69 Å, which is indicative of attraction; however, it is reasonable to assume that the hydrogen bonds also contribute significantly to the tendency of these lanthanide complexes to form homochiral stacks. The stacking may be described as resulting in polymers comprising $(\text{-Ln-O-Ln-O-})_8$ chains, which resemble the eight-coordinate complexes in Figure 1. The resolution of **1–3** relies on the crystals to form a conglomerate, and the ability to design molecules that crystallize as conglomerates is desirable. Molecules that fit into rows or stacks, such as $[Ln(dbm)_3H_2O]$, can form phases in which heterochirality is eliminated in at least one dimension. Regarding the other two dimensions, along *a* and *b*, Figure 8 shows how stereochemical information in **2** is transferred between stacks of $[Sm(dbm)_3H_2O]$ complexes by the interaction of aryl "propeller wings" through short CH/π contacts. All six CH–π distances indicated in Figure 8 are related by symmetry; the distances are 2.79 Å and the C-H-π angles are 163.5°. Although such vertex-to-face interactions are weak, they are known to play a significant role in the assembly of crystalline compounds.[27] Figure 9 illustrates another set of CH/π interactions in **2**, in this case between molecules at different heights (along *c*), in which CH–C distances of 2.88 Å result in left-handed helices (contrary to the right-handed Δ-helicity of the molecule itself) along *c*. These helices, which involve three stacks, are actually quadruple helices with a pitch height of 25.54 Å (the Sm–Sm distance within a stack is 6.384 Å).

Conclusion

The resolution of bulk quantities of seven-coordinate complexes (without chiral or polydentate ligands) has been demonstrated for the first time, and illustrates how crystallization-induced asymmetric transformation can be a powerful tool for resolving stereochemically labile isomers. Analysis of the crystal structure of these [Ln(dbm)$_3$H$_2$O] complexes reveals supramolecular CH/π interactions (including formation of a quadruple helix). These interactions demonstrate how stereochemical information is transferred between stacks of molecules, enabling [Ln(dbm)$_3$H$_2$O] to crystallize as a conglomerate. The solid-state CD-spectroscopic method described can be used to quantify the *ee* in bulk samples of stereochemically labile compounds. Therefore, it is now possible to investigate whether labile conglomerates in general are as willing as [Ln(dbm)$_3$H$_2$O] to undergo total spontaneous resolution.

Experimental Section

General: None of the complexes were air-sensitive; however, recrystallizations were performed in sealed tubes to minimize contamination from optically active trace impurities. Commercial dibenzoylmethane (Aldrich) and lanthanide halides (Apollo Scientific) were used as received. Acetone was purchased from Riedel de Haen (PA) or Scharlau (extra pure), and the water was doubly distilled.

Preparation of Δ-[Pr(dbm)$_3$H$_2$O] (Δ-1): Dibenzoylmethane (1.30 g, 6.00 mmol) was dissolved in acetone (50 mL), and an aqueous solution of KOH (12 mL, 0.5 M) was added. The mixture was heated to reflux, and a solution of PrCl$_3$·7H$_2$O (0.76 g, 2.00 mmol) in 10 mL water was added drop-wise. The hot solution was filtered by suction, and green-yellow needles started to form in the filtrate, which was cooled on an ice/salt bath to complete crystallization. The crystals were collected by filtration and then washed with water and cold diethyl ether. Yield: 1.51 g (91 %), *ee*: > 97 %.

Preparation of Δ-[Sm(dbm)$_3$H$_2$O] (Δ-2): Synthesis of the samarium complex (Δ-2) was identical to the preparation of the praseodymium complex (Δ-1) described above; however, the fact that commercially available samarium(III) chloride can vary in hydrate content should be considered. Small, yellow needles of Δ-2, obtained directly from the mother liquor, were collected by filtration and washed with water and cold diethyl ether. Yield: 1.52 g (94 %), *ee*: > 97 %. Large crystals could be obtained by layering a solution (0.034 M) of **2** in acetone onto a water surface in a test tube.

Preparation of Λ-[Sm(dbm)$_3$H$_2$O] (Λ-2): Numerous attempts to spontaneously crystallize Λ-2 from acetone/water solutions of **2** failed, because only Δ-2 crystals could be obtained. An optically active trace impurity was probably present in the laboratory, which influenced the crystallization process. Although extensive precautions were taken to exclude contamination by Δ-2 seeds, their presence cannot be excluded. Only after spiking the acetone/water solution of **2** with Δ-[Co(acac)$_3$], as done by Addadi and Lahav,[28–29] were crystals of Λ-2 obtained. Once the first Λ-2 crystals were obtained, seeding resulted in a crystalline bulk product with *ee* > 97 %.

Preparation of Δ-[Er(dbm)$_3$H$_2$O] (Δ-3): Yellow-orange microcrystals of this compound were obtained in the same way as for the praseodymium and samarium complexes, but the yield was lower. Yield: 1.02 g (60 %), *ee*: > 97 %. Recrystallization from acetone/water gave crystals of a quality suitable for X-ray crystallographic analysis.

Solid-state CD spectroscopy: Solid-state CD spectra were recorded by using a Jasco J-175 spectropolarimeter, together with thin (100 mg) KBr disks of 13 mm diameter. For *ee* determinations, the CD signal at 292 nm was averaged over 15 different positions for each disk. To avoid problems with different background levels, the difference between the signals at 292 and 500 nm was recorded. The calibration line was obtained by preparing disks containing various amounts of enantiopure (and homochiral) crystals. The disks were prepared by weighing a crystal sample (approximately 1 mg) and then manually mixing and grinding it with a weighed amount of KBr (approximately 1 g). The best result was obtained by adding KBr in four small portions, with each addition being followed by careful manual grinding, until a homogeneous mixture was obtained. Approximately 100 mg of the mixture was collected and weighed before pressing it for 2 min at 8 ton into a disk. This resulted in a disk containing approximately 0.1 mg crystal mass. A similar procedure was used for all of the disks represented in Figure 5, in which the crystal mass and/or the KBr-mediated dilution was varied.

Solution CD spectroscopy: Solutions were prepared by dissolving enantiopure (and homochiral) single crystals of Δ-2 in acetone and CD spectra were recorded immediately. No CD signal from the complex could be detected, indicating rapid racemization.

X-ray crystallography: Diffracted intensities were recorded by using a Rigaku R-AXIS IIc image plate system with graphite-monochromated Mo$_{K\alpha}$ (λ = 0.710 73 Å) radiation from a Rigaku RU200 rotating anode operated at 50 kV and 90 mA. Cell constants were obtained by applying least-squares refinement of all reflections. Diffraction data from 90 oscillation photos with a rotation angle of 2° were processed by using the

Table 3. Crystallographic data for Δ-1, Δ-2, and Δ-3.

Compound	Δ-1	Δ-2	Δ-3
empirical formula	$C_{45}H_{35}O_7Pr$	$C_{45}H_{35}O_7Sm$	$C_{45}H_{35}O_7Er$
formula weight	828.64	838.08	854.99
T [K]	293(2)	293(2)	293(2)
λ [Å]	0.71073	0.71073	0.71073
crystal system	trigonal	trigonal	trigonal
space group	*R*3	*R*3	*R*3
a [Å]	22.547(5)	22.563(4)	22.692(5)
b [Å]	22.547(5)	22.563(4)	22.692(5)
c [Å]	6.3807(18)	6.3837(14)	6.3019(19)
V [Å^3]	2809.2(11)	2814.6(10)	2810.3(12)
Z	3	3	3
δ_{calcd} [g cm^{-3}]	1.469	1.483	1.516
μ [mm^{-1}]	1.353	1.617	2.292
size [mm^3]	0.1 × 0.1 × 0.1	0.1 × 0.1 × 0.1	0.1 × 0.1 × 0.1
color	yellow/green	yellow	yellow/orange
θ range [°]	3.1–26.0	3.1–26.0	3.1–26.0
reflns collected	6582	6613	6579
independent reflns	2248	2365	2241
observed reflns	2247	2365	2218
parameters	164	164	164
$R1$ (all data)	0.0283	0.0276	0.0338
$wR2$ (all data)	0.0662	0.0655	0.0763
Flack parameter	0.078(16)	0.018(12)	0.019(17)
max peak [e Å^{-3}]	0.31	0.28	0.50
max hole [e Å^{-3}]	−0.59	−0.61	−0.49

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CrystalClear software package. A multiscan absorption correction was applied by using the REQAB program from CrystalClear. Crystal and refinement data for compounds **1**–**3** are summarized in Table 3. All structures were solved by using SHELXS-97[30] and refined by using SHELXL-97[30] (full-matrix least-squares calculations on F^2) operating in the WinGX program package.[31] Anisotropic thermal displacement parameters were refined for all the non-hydrogen atoms. All hydrogen atoms were included in calculated positions and refined by using a riding model, except the two water hydrogen atoms, which were disordered over three positions. Structural illustrations were drawn by using ORTEP-3 for Windows[32] and PLUTON[33] from WinGX. CCDC 222388 (Δ-**1**), 222391 (Δ-**2**), 222389 (Λ-**2**), and 222390 (Δ-**3**) contain the supplementary crystallographic data (excluding structure factors) for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

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[1] A. Werner, *Ber.* **1911**, *44*, 1887.
[2] A. von Zelewsky, *Stereochemistry of Coordination Compounds*, Wiley, **1996**, p. 101.
[3] M. Hakansson, M. Vestergren, B. Gustafsson, G. Hilmersson, *Angew. Chem.* **1999**, *111*, 2336; M. Hakansson, M. Vestergren, B. Gustafsson, G. Hilmersson, *Angew. Chem. Int. Ed.* **1999**, *38*, 2199.
[4] Spontaneous resolution is essentially a phenomenon at the single crystal level, and does not necessarily yield an enantiopure bulk product.
[5] A. Perrotto, R. G. Charles, *J. Inorg. Nucl. Chem.* **1964**, *26*, 373.
[6] L. Sacconi, R. Ercoli, *Gazz. Chim. Ital.* **1949**, *79*, 731.
[7] A. F. Kirby, R. A. Palmer, *Inorg. Chem.* **1981**, *20*, 1030.
[8] A. Zalkin, D. H. Templeton, D. G. Karraker, *Inorg. Chem.* **1969**, *8*, 2680.
[9] D. L. Kepert in *Comprehensive Coordination Chemistry, Vol. 1* (Eds.: G. Wilkinson, R. D. Gillard, J. A. McCleverty), Pergamon, Oxford, **1987**, p. 31.
[10] E. L. Eliel, S. H. Wilen, L. N. Mander, *Stereochemistry of Organic Compounds*, Wiley, **1994**, p. 1267.
[11] B. L. Feringa, R. A. Van Delden, *Angew. Chem.* **1999**, *111*, 3624; B. L. Feringa, R. A. Van Delden, *Angew. Chem. Int. Ed.* **1999**, *38*, 3419.
[12] M. Vestergren, J. Eriksson, M. Hakansson, *Chem. Eur. J.* **2003**, *9*, 4678.
[13] M. Vestergren, B. Gustafsson, O. Davidsson, M. Hakansson, *Angew. Chem.* **2000**, *112*, 3577; M. Vestergren, B. Gustafsson, O. Davidsson, M. Hakansson, *Angew. Chem. Int. Ed.* **2000**, *39*, 3435.
[14] J. S. Siegel, *Chirality* **1998**, *10*, 24.
[15] A. Saghatelian, Y. Yokobayashi, K. Soltani, M. R. Ghadiri, *Nature* **2001**, *409*, 797.
[16] W. A. Bonner, *Chirality* **2000**, *12*, 114.
[17] J. L. Bada, *Nature* **1995**, *374*, 594.
[18] A. J. MacDermott, *Enantiomer* **2000**, *5*, 153.
[19] M. Avalos, R. Babiano, P. Cintas, J. L. Jimenez, J. C. Palacios, *Chem. Commun.* **2000**, 887.
[20] a) D. A. Singleton, L. K. Vo, *J. Am. Chem. Soc.* **2002**, *124*, 10010; b) D. A. Singleton, L. K. Vo, *Org. Lett.* **2003**, *5*, 4337.
[21] G. L. J. A. Rikken, E. Raupach, *Nature* **2000**, *405*, 932.
[22] M. Avalos, R. Babiano, P. Cintas, J. L. Jimenez, J. C. Palacios, L. D. Barron, *Chem. Rev.* **1998**, *98*, 2391.
[23] J. S. Siegel, *Nature* **2002**, *419*, 346.
[24] H. D. Flack, G. Bernardinelli, *J. Appl. Crystallogr.* **2000**, *33*, 1143.
[25] H. D. Flack, G. Bernardinelli, *Acta Crystallogr.* **1999**, *A55*, 908.
[26] R. Kuroda, T. Honma, *Chirality* **2000**, *12*, 269.
[27] M. Nishio, *CrystEngComm* **2004**, *6*, 130.
[28] L. Addadi, S. Weinstein, E. Gati, I. Weissbuch, M. Lahav, *J. Am. Chem. Soc.* **1982**, *104*, 4610.
[29] L. Addadi, Z. Berkovitch-Yellin, N. Domb, E. Gati, M. Lahav, L. Leiserowitz, *Nature* **1982**, *296*, 21.
[30] G. M. Sheldrick, SHELX97: Programs for Crystal Structure Analysis (Release 97–2), Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen (Germany), **1998**.
[31] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837.
[32] L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565.
[33] A. L. Spek, PLATON: A Multipurpose Crystallographic Tool, Utrecht University (The Netherlands), **2002**.

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