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Isolation and Spontaneous Resolution of Eight-Coordinate Stereoisomers[**]

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Björn Gustafsson, and Göran Hilmersson

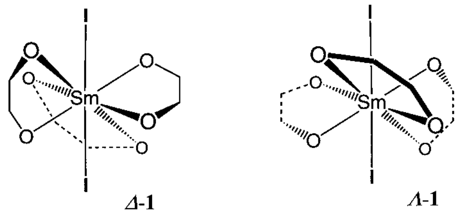
While geometrical and optical isomers are numerous among four- and six-coordinate complexes, the isolation of such stereoisomers with coordination number eight remains a challenge to synthetic chemists. Eight-coordinate complexes are usually labile since the energy differences between the most frequent geometries are small, as is the energy barrier for interconversion between them.[1a] Thus only two pairs of eight-coordinate stereoisomers have been structurally characterized, namely, diastereomeric *cis*- and *trans*-$[SmI_2\{O(CH_2CH_2OCH_3)_2\}_2]$[2] and *cis*- and *trans*-$[ReH_2(mhp)_2(PPh_3)_2]PF_6$ (mhp = monoanion of 2-methyl-6-hydroxypyridine).[3] We now report the spontaneous resolution of configurationally chiral[1b] eight-coordinate complexes Δ-**1** and Λ-**1**[4] (dme = 1,2-dimethoxyethane). A racemic phase (**2**) exhibiting conformational isomers can also be isolated.[5]

Δ-$[SmI_2(dme)_3]$	Δ-**1**
Λ-$[SmI_2(dme)_3]$	Λ-**1**
rac-$[SmI_2(dme)_3]$	**2**

The chemistry of divalent lanthanides—established with Sm, Eu, and Yb and recently expanded into Tm[6]—is currently developing rapidly. In particular, following the pioneering work of Kagan et al.,[7] solutions of SmI_2 in THF have become commercially available and are finding an ever-increasing role as selective one-electron reducing reagents in a variety of reactions.[8] The dominant species in such solutions in THF is probably the seven-coordinate $[SmI_2(thf)_5]$, and similar pentagonal-bipyramidal coordination geometry has also been found in $[SmI_2(dme)(thf)_3]$ and $[SmI_2(dme)_2(thf)]$, which were isolated from mixtures of THF and DME.[9]

Samarium reacts smoothly[10] with 1,2-diiodoethane in DME at 50 °C to yield a dark blue solution of SmI_2. Crystals can be isolated from this solution both at ambient temperature and at -20 °C. X-ray crystallographic data[11] were collected using seven different crystals obtained from solutions at ambient temperature, which resulted in three crystal structures of Δ-**1** and four of Λ-**1** (see Figure 2). Assignment of the chiral space group $P2_1$ was unequivocal, and the absolute configuration determination was conclusive with no indication of racemic twinning. X-ray structure analyses[11] proved that the crystals obtained at −20 °C constitute a different phase—racemic **2** (see Figure 3).[5] It thus seems as if crystallization from the blue solution at −20 °C yields racemic **2**, while crystallization at ambient temperature results in a mixture of chiral crystals comprising either the Δ-**1** or the Λ-**1** enantiomer. The chiral crystals can be separated manually using a microscope with polarized light, but due to their intense color this procedure is not practical for larger quantities. Such hand-picked crystals can, however, be used to seed a supersaturated solution in order to exclusively crystallize one enantiomer from the racemate, a technique which is known as preferential crystallization.[12] We are presently searching for the optimal conditions for this procedure.

The enantiomers of **1** have the shape of a propeller, the shaft being represented by the I-Sm-I axis and the blades by the three Sm–dme rings (Figures 1 and 2). The enantiomers D-**1** and Λ-**1** then correspond to a right- and left-threaded propeller, respectively. There is a distortion in **1** such that the "propeller" axis is bent towards one "blade", which consequently is close to an equatorial conformation. The Sm–I and Sm–O distances are normal, that is, somewhat longer than in the seven-coordinate thf/dme complexes.[9] An analysis of the 28 angles formed by the donor atoms around Sm in **1** suggests that the coordination geometry is best described as a distorted hexagonal bipyramid, or alternatively as a distorted triangular dodecahedron.[13]



Δ-**1** Λ-**1**

Figure 1. Schematic representation of the propeller-shaped enantiomers of **1** (methyl groups are excluded for clarity).

Samarium and the dme ligands in **1** form five-membered rings which exhibit chiral conformations. It is noteworthy that in Δ-**1** all three rings have the λ conformation (i.e., $\Delta\lambda\lambda\lambda$), while in Λ-**1** all three are δ conformers (i.e., $\Lambda\delta\delta\delta$). This can be illustrated by the fact that the C2–C3, C5–C6, and

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[**] This work was supported by the Swedish Natural Science Research Council (NFR).

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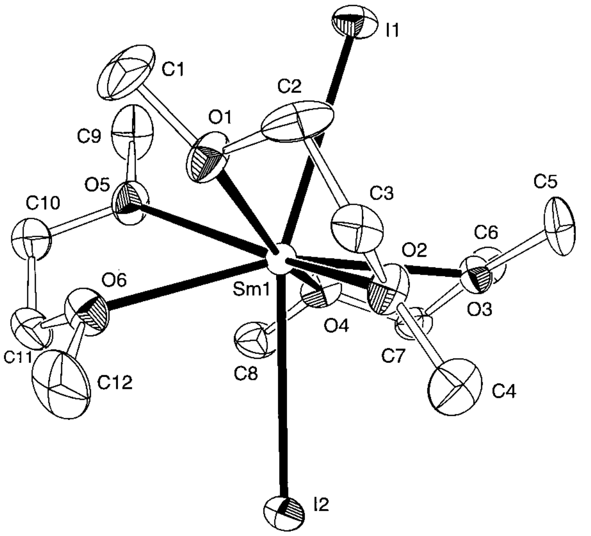

Figure 2. Molecular structure of Λ-**1**. Selected bond lengths [Å] and angles [°]: Sm1–I1 3.3550(8), Sm2–I2 3.3832(8), Sm1–O1 2.666(7), Sm1–O2 2.656(7), Sm1–O3 2.681(6), Sm1–O4 2.678(6), Sm1–O5 2.669(7), Sm1–O6 2.660(6); O2-Sm1-O6 100.4(2), O2-Sm1-O1 60.8(2), O6-Sm1-O1 65.6(2), O2-Sm1-O5 153.9(2), O6-Sm1-O5 60.2(2), O1-Sm1-O5 93.9(3), O2-Sm1-O4 134.7(2), O6-Sm1-O4 114.8(2), O1-Sm1-O4 160.1(2), O5-Sm1-O4 71.4(2), O2-Sm1-O3 73.58(19), O6-Sm1-O3 160.51(19), O1-Sm1-O3 123.1(2), O5-Sm1-O3 130.5(2), O4-Sm1-O3 63.7(2), O2-Sm1-I1 96.65(15), O6-Sm1-I1 123.42(14), O1-Sm1-I1 77.43(18), O5-Sm1-I1 82.55(17), O4-Sm1-I1 87.23(14), O3-Sm1-I1 76.01(12), O2-Sm1-I2 84.97(15), O6-Sm1-I2 77.28(13), O1-Sm1-I2 121.32(18), O5-Sm1-I2 105.39(17), O4-Sm1-I2 76.55(14), O3-Sm1-I2 83.67(12), I1-Sm1-I2 158.18(2).

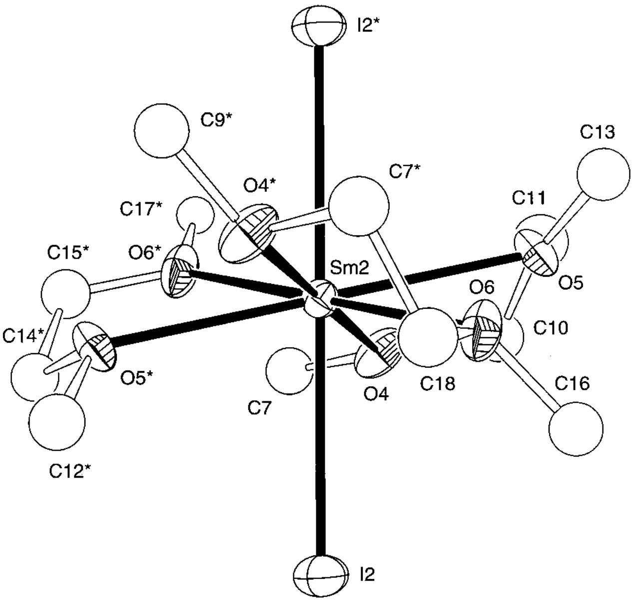

Figure 3. Molecular structure of the disordered geometric isomer in a crystal of **2**. For clarity, only half of the disordered carbon atoms are shown. Selected bond lengths [Å] and angles [°]: Sm2–I2 3.3003(13), Sm2–O4 2.690(10), Sm2–O5 2.746(9), Sm2–O6 2.652(10); O6-Sm2-O4 116.2(3), O6-Sm2-O4* 63.8(3), O6-Sm2-O5 63.3(3), O4-Sm2-O5 64.6(3), O6-Sm2-O5* 116.7(3), O4-Sm2-O5* 115.4(3), O6-Sm2-I2 78.9(2), O6*-Sm2-I2 101.1(2), O4-Sm2-I2 78.8(2), O4*-Sm2-I2 101.2(2), O5-Sm2-I2 102.3(2), O5*-Sm2-I2 77.7(2). Symmetry code: $-x+1/2, -y+1/2, -z$.

C10–C11 bonds prefer a parallel orientation with respect to the approximate C_3 axis along I-Sm-I (Figure 2). For six-coordinate octahedral complexes with three bidentate ligands such lel_3 molecules have been predicted to be more stable than their $\Delta\delta\delta\delta$ and $\Lambda\lambda\lambda\lambda$ diastereomers.[14]

There are two crystallographically unique molecules[15] in the unit cell of **2**;[16] one closely resembles **1**, while the other differs from **1** mainly in that the I-Sm-I angle is 180° (Figure 3). Unfortunately, the carbon atoms in this "linear" isomer are disordered, but a model made from a 50/50 enantiomeric mixture resolves the disorder well. This isomer and *trans*-$[\mathrm{SmI_2\{O(CH_2CH_2OCH_3)_2\}_2}]$[2] are similar in that both have linear I-Sm-I geometry and are eight-coordinate. The crystallographic inversion center at Sm in the latter rules out, however, any possibility of chirality.

Since crystals of **1** can even be handled in air for short periods of time without significant loss of DME or oxidation, such complexes are interesting solid-state alternatives to the solutions of $\mathrm{SmI_2}$ in THF available commercially. Provided rapid racemization in solution can be prohibited, we furthermore suggest that configurationally chiral glyme complexes of $\mathrm{SmI_2}$ have a large potential as reagents in enantioselective syntheses.[17] It is consequently important to determine the energy barrier for conversion between Δ-**1** and Λ-**1** in solution. Although eight-coordinate complexes are notoriously labile, chelated complexes such as $[\mathrm{Ta(S_2CNMe_2)_4}]^+$[18] and $[\mathrm{W(bmpd)}_n\mathrm{(mpic)}_{n-4}]$[19] (bmpd = 5-*tert*-butyl-2-mercaptopyrimidinato, mpic = 5-methylpicolinato) are stereochemically rigid on the NMR time scale, and *cis*- and *trans*-$[\mathrm{ReH_2(mhp)_2(PPh_3)_2}]\mathrm{PF_6}$[3] retain their structural identity in solution even at ambient temperature. As shown in Figure 4, the methyl groups of the dme ligands contribute significantly to the steric crowding in **1**, so that racemization should require bond breaking.

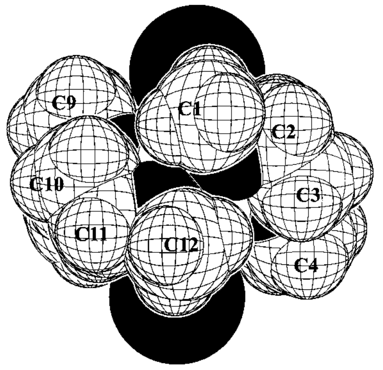

Figure 4. Space-filling model of **1**, showing how the methyl groups (e.g. C1 and C12) prevent easy "oxygen slipping" on samarium.

Experimental Section

All operations were carried out under argon using Schlenk or low-temperature[20] techniques.

Samarium chips (0.080 g, 0.53 mmol) and 1,2-diiodoethane (0.072 g, 0.26 mmol) were sonicated for 3 h at 50 °C in DME (10 mL). The resulting suspension was kept at 50 °C until the solids settled (by centrifugation if necessary), and the clear dark blue solution was then transferred by syringe to another Schlenk vessel. (Higher yields can be accomplished by extraction with more DME.) After 24 h at ambient temperature X-ray quality, purple (almost black) crystals of Δ-**1** and Λ-**1** formed. The still dark blue mother liquor was transferred (see below), and the crystals were washed with DME (2 × 1 mL) and dried briefly under vacuum. Yield:

0.031 g, 18%. IR (Nujol, Fluorolube): $\tilde{\nu} = 2923$ (s), 2853 (m), 1450 (m), 1372 (w), 1242 (w), 1192 (m), 1116 (m), 1060 (s), 1029 (m), 861 cm^{-1} (m).

The dark blue mother liquor from above was stored at $-20\,^{\circ}$C for 24 h to yield a second crop of purple crystals, however this time of **2**. The crystals were washed with DME (2×1 mL) and dried briefly under vacuum. Yield: 0.034 g, 19%. IR (Nujol, Fluorolube): $\tilde{\nu} = 3009$ (w), 2925 (s), 2828 (m), 1455 (s), 1365 (w), 1241 (w), 1191 (m), 1114 (s), 1064 (s), 1027 (s), 860 (m), 722 cm^{-1} (w).

Under argon, crystals of **1** and **2** decompose without melting above 200 °C, but are stable without loss of DME at ambient temperature for extended periods of time. In air, decomposition is remarkably slow; the crystals are covered with a thin layer of yellow Sm$^{\text{III}}$ only after several minutes. Both **1** and **2** are virtually insoluble in diethyl ether and toluene; the solubility in DME is approximately 0.01M.

Received: January 21, 1999 [Z12946IE]
German version: *Angew. Chem.* **1999**, *111*, 2336–2338

Keywords: coordination modes · enantiomeric resolution · isomers · samarium

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[11] Crystal structure data for Λ-**1** ($\text{SmI}_2\text{O}_6\text{C}_{12}\text{H}_{30}$): crystal size $0.1 \times 0.1 \times 0.1$ mm, monoclinic, space group $P2_1$ (no. 4), $a = 8.4797(15)$, $b = 10.601(3)$, $c = 12.3120(15)$ Å, $\beta = 93.743(12)^{\circ}$, $V = 1104.4(4)$ Å^3, $Z = 2$, $\rho_{\text{calcd}} = 2.028$ g cm^{-3}, $2\theta_{\max} = 50.0^{\circ}$, Mo$_{K\alpha}$ radiation, $\omega/2\theta$ scan mode, $T = -130\,^{\circ}$C, psi scans (abs. range 0.915–0995), $\mu = 5.47$ mm^{-1}. Refinement on F^2 for 2060 reflections and 196 parameters gave $R1 = 0.023$ and $wR2 = 0.060$ for $I > 2.0\sigma(I)$. The Sm, I, O, and C atoms were refined with anisotropic thermal displacement parameters, and the H atoms were included in calculated positions and allowed to ride on their respective carbon atom during refinement; max./min. residual electron density 0.56/$-$0.59 e Å^{-3}; Flack parameter $-0.02(3)$. Crystals of Δ-**1** gave similar data. Crystal structure data for **2** ($\text{SmI}_2\text{O}_6\text{C}_{12}\text{H}_{30}$): crystal size $0.2 \times 0.1 \times 0.1$ mm, monoclinic, space group $C2/c$ (no. 15), $a = 25.059(7)$, $b = 13.157(4)$, $c = 14.598(6)$ Å, $\beta = 115.74(2)^{\circ}$, $V = 4335(3)$ Å^3, $Z = 8$, $\rho_{\text{calcd}} = 2.067$ g cm^{-3}, $2\theta_{\max} = 50.0^{\circ}$, Mo$_{K\alpha}$ radiation, $\omega/2\theta$ scan mode, $T = -130\,^{\circ}$C, psi scans (abs. range 0.777–0998), $\mu = 5.575$ mm^{-1}. Refinement on F^2 for 3818 reflections and 186 parameters gave $R1 = 0.041$ and $wR2 = 0.11$ for $I > 2.0\sigma(I)$. The Sm, I, O, and ordered C atom were refined with anisotropic thermal displacement parameters, while the disordered C atoms were refined isotropically with the SOFs fixed to 0.5. The H atoms were refined with the riding model, but the H atoms on the disordered C atoms were not located; max./min. residual electron density 1.48/$-$1.61 e Å^{-3}. Both structures were solved using SHELXS and refined using SHELXL-97. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-114182 (Λ-**1**) and CCDC-114183 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[15] Since the space group is centrosymmetric, the enantiomer of each geometrical isomer is generated in the unit cell, making **2** racemic.

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New Types of Stable Aldehydes: Formylphosphane and Formylphosphane Oxide**

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Very few stable derivatives featuring the formyl group directly bound to a heavy Group 14 or 15 element have previously been prepared. Only two formylsilanes have been isolated.[1] Although β-, γ-, and ω-phosphorylated aldehydes are popular reagents,[2] α-phosphorus-substituted aldehydes have not even been spectroscopically characterized.[3] In contrast, several stable masked derivatives are known,[4] the formylphosphonic acid hydrate even being an antiviral agent.[5] Here we report the synthesis and characterization of the formylphosphanes **2a, b** and formylphosphane oxide **4** (see Scheme 1); the crystal structure of **2b** is also presented.

Treatment of the iminium salts **1a, b**[6] with a suspension of KOH in thf at room temperature affords the desired formylphosphanes **2a, b**, which were isolated as a yellow oil (78% yield) and white crystals (82% yield), respectively (Scheme 1). The ^{31}P NMR signal for the formylphosphane **2a** is a doublet at $\delta = 68.1$ with a remarkably large phosphorus–proton coupling ($^2J(\text{P,H}) = 84$ Hz).[7, 4d] Interestingly, the ^{1}H ($\delta = 11.1$) and ^{13}C NMR signals ($\delta = 220.1$, $^1J(\text{P,C}) = 17$ Hz) for the formyl group appear at rather low field, and the ν(CO) IR stretching frequency at 1668 cm^{-1} is unusually low for an aldehyde.

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[**] Thanks are due to the CNRS for financial support of this work.