Synthesis and X-ray Crystal Structure of the First Mononuclear Nickel(II) Alkane Thiolate Complex with a Mixed (S,N,N,O) Ligand Field☆

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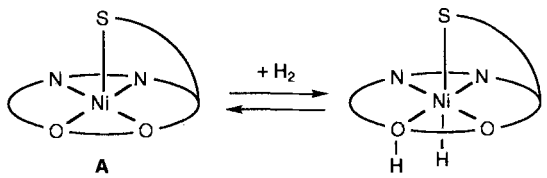
The six-step synthesis of a chiral, pentadentate dihydrosalen ligand, carrying a mercaptomethyl group as additional binding site, is described. When this ligand was treated with nickel(II) salts, a planar tetracoordinated nickel chelate was obtained, and not the expected pentacoordinated species. This complex was fully characterized, including X-ray crystallography. The crystal structure revealed that the nickel ion is coordinated by the thiolate anion, both the amine and the imine nitrogen atoms of the ligand, and by one phenolate anion. The second phenolic oxygen atom of the ligand does not participate in the coordination of the nickel ion. This chelate is the first mononuclear nickel(II) thiolate complex having a mixed (S,N,N,O) ligand field. Cyclic voltammetry did not indicate a reduction up to −2.1 V (vs. Fc/Fc^+). In the anodic range, no reversible but two irreversible oxidation processes were observed.

Transition metal complexes of oligodentate ligands with N, O, and S heteroatoms play an important role as models for the active sites of metallo-enzymes, such as methyl-coenzyme-M-reductase[1,2], nitrogenase[3], and in particular hydrogenases[1,4]. The latter enzymes catalyze the reaction shown in eq. (1). This simple process is of vital importance for all hydrogen-metabolizing and -producing microorganisms. One part of our ongoing research in biomimetic catalysis[5] aims at mimicking the catalytic activity of the so-called [Ni,Fe]-hydrogenases with low-molecular weight, mononuclear nickel chelates. In fact, the first X-ray crystal structure[6] of a. [Ni,Fe]-hydrogenase (from *Desulfovibrio gigas*) showed that the active site harbors two transition metal ions (Fe, Ni), the nickel ion being coordinated by four sulfur atoms derived from cysteines. However, biophysical measurements on other [Ni,Fe]-hydrogenases[1,7] point to mononuclear active sites with mixed (N, O, S) coordination spheres. Therefore we believe that nickel complexes with pentadentate ligands of the general structure **A** (Scheme 1) may be suitable candidates for the above purpose: The hydrogen molecule is hoped to be bound and activated at the vacant axial coordination site. Upon heterolysis of the H_2 molecule, a nickel hydride species may form, and the basic heteroatoms of the ligand are expected to support the heterolysis by accepting the proton.

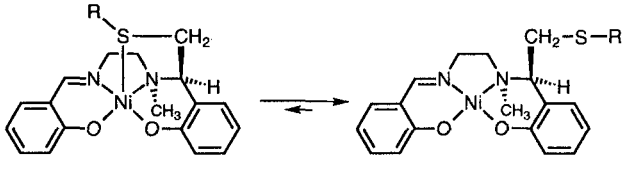
$$H_2 \xrightleftharpoons{\text{Hydrogenase}} 2\,H^+ + 2\,e^- \qquad (1)$$

With this in mind, we synthesized[2,8] the dihydrosalen nickel(II) chelates *rac*-**1a,b**, carrying a thioether moiety as the axial sulfur donor. As it turned out, none of these complexes showed hydrogenase activity. A detailed NMR analysis gave an explanation for this unexpected result[2b]: It revealed that the pentacoordinated conformer is not the major species in solution: Both complexes greatly prefer to adopt a conformation in which the nickel ion is planar and tetracoordinated, and in which the thioether does not participate in the coordination of the nickel ion. We reasoned that an exchange of the benzyl thioether for a thiolate group should reverse this situation: Thiolate anions are well-known to bind nickel(II) ions much more strongly than thioethers[9,10]. For the preparation of such a thiolate complex, a reductive debenzylation of the nickel chelate *rac*-**1b** appeared as the most convenient approach. However,

Scheme 1



A



1a*): R = Ph; **1b***): R = CH_2Ph *)Racemic mixture

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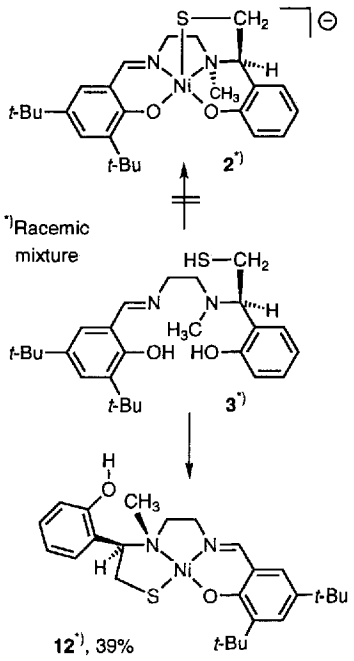
attempts to carry out this deprotection on the complex *rac*-**1b** failed: Treatment with e.g. sodium amalgam resulted in decomposition. Under no circumstances, any indication of debenzylation – e.g. the formation of toluene or bibenzyl – could be observed. We therefore embarqued on an alternative approach, i.e. the synthesis of a preformed thiol ligand, such as *rac*-**3** (Scheme 2). This pentadentate ligand was hoped to yield the desired complex *rac*-**2** upon treatment with nickel(II) salts. In this paper, we describe the synthesis of the ligand *rac*-**3** and its complexation with nickel(II) ions. As it turned out, the novel mononuclear, electrically neutral tetracoordinated thiolate complex *rac*-**12** and *not* the pentacoordinated, anionic chelate *rac*-**2** was obtained from this reaction (Scheme 2)

Scheme 2



Reaction conditions: $Ni(OAc)_2 \cdot 4\,H_2O$, EtOH

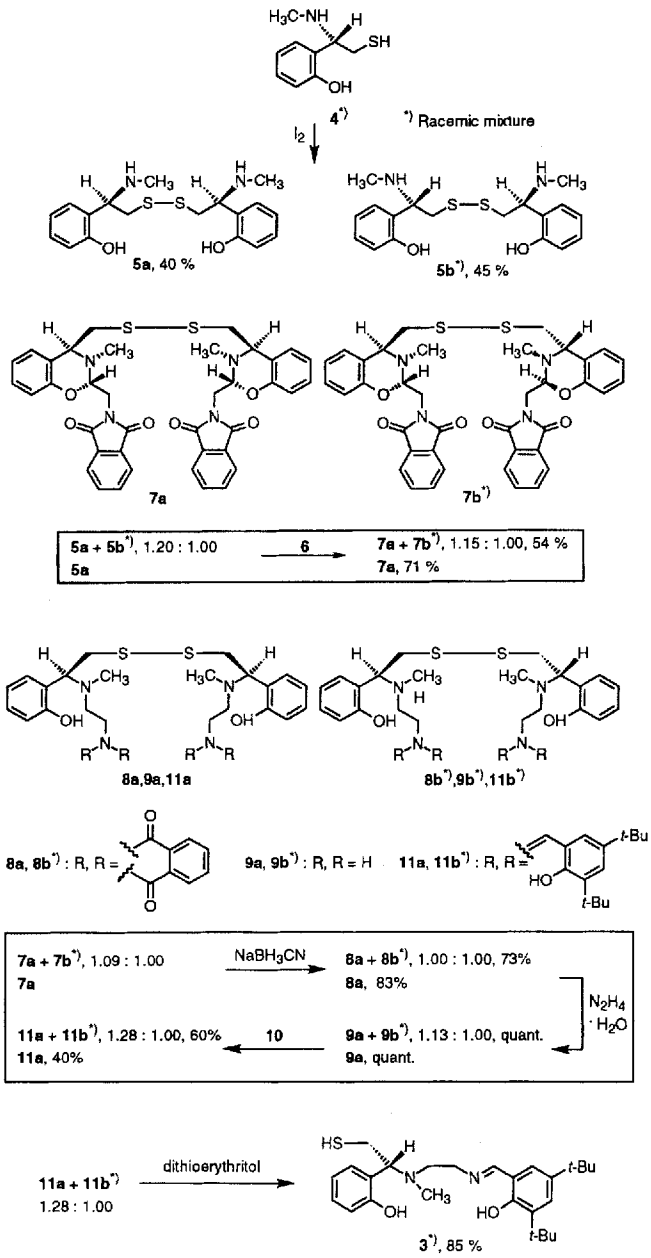
Results

Synthesis of the Ligand rac-3

Our synthetic sequence leading to the pentadentate ligand *rac*-**3** is summarized in Scheme 3. The thiol *rac*-**4** served as the starting material (see ref.[12] for the preparation of *rac*-**4**). In the first step, the mercapto group was protected by oxidation to the disulfide. The diastereomers **5a** and *rac*-**5b** were formed in approximately equal amounts, and they could be separated by extracting the racemate *rac*-**5b** from the mixture with ether. The structural assignment of the diastereomeric disulfides **5a**/*rac*-**5b** is based on the X-ray crystal structure of the *meso* compound **5a** (not shown, see ref.[11]).

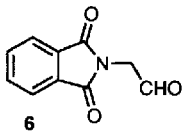
For the further course of the synthesis, separation of the diastereomeric mixture of **5a**/*rac*-**5b** is not required: In the final step, the disulfide bond is cleaved reductively. Consequently, both **5a** and *rac*-**5b** finally afford the racemic ligand *rac*-**3**. Nevertheless, as indicated in Scheme 3, we conducted the synthetic sequence with both the mixture of the diastereomers **5a**/*rac*-**5b** and with the pure *meso* compound **5a**. By doing so, the NMR-spectroscopic data of the racemic mixtures of the intermediates could be obtained by subtracting the spectra of the *meso* intermediates from those of the diastereomeric mixtures.

Scheme 3

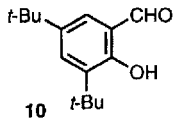


In the second step, the aminophenols **5a** and *rac*-**5b** were condensed with 2-(*N*-phthalimido)acetaldehyde **6**, affording the dihydrobenzoxazines **7a** and *rac*-**7b**. Reductive cleavage of the acetalic C–O bond using sodium cyanoborohydride gave the *N*-phthaloyl-protected ethylene diamines **8a** and *rac*-**8b**. Deprotection by hydrazinolysis proceeded smoothly,

and the primary amines **9a** and *rac*-**9b** were finally condensed with 3,5-di-*tert*-butylsalicylic aldehyde **10**, affording the double Schiff bases **11a** and *rac*-**11b**.



6



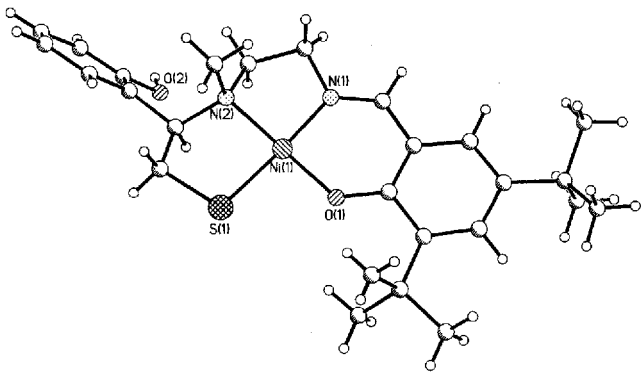
10

To complete the synthesis of the ligand *rac*-**3**, the disulfide bond needed to be reductively cleaved without reducing or hydrolyzing the C=N bonds. From the variety of reducing agents and conditions tried, only one combination of reagents proved suitable: When the disulfides **11a** and *rac*-**11b** were treated with dithioerythritol and triethylamine in dichloromethane at room temperature, the desired thiol *rac*-**3** was obtained in 85% yield.

Complexation of Nickel(II) Ions with the Ligand rac-3

With the ligand *rac*-**3** in hand, we studied its complexation behavior. Treatment with nickel(II) acetate tetrahydrate with exclusion of oxygen afforded a dark, red-brown solution. By careful crystallization, the nickel complex *rac*-**12** could be isolated in 39% yield in analytically pure form. Slow cooling of saturated solutions in absol. ethanol yielded single crystals suitable for X-ray structural analysis. The results are shown in Figures 1 and 2.

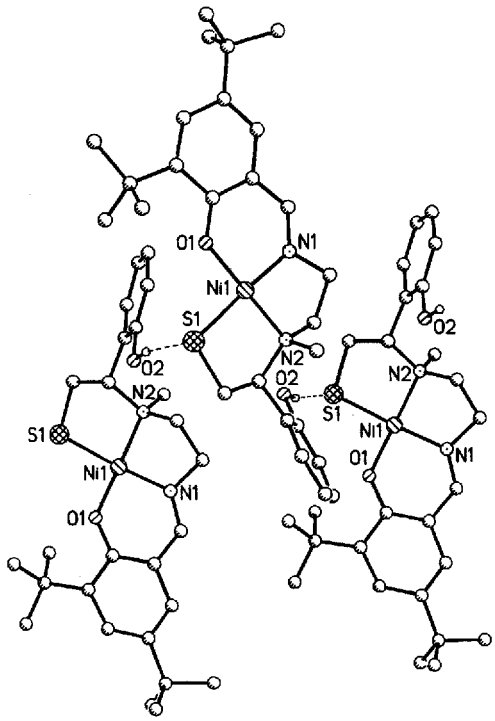
Figure 1. X-ray crystal structure of the nickel complex *rac*-**12** (only the *R* enantiomer is shown); selected bond lengths [Å]: Ni(1)–S(1) 2.192(1), Ni(1)–N(1) 1.859(3), Ni(1)–N(2) 1.931(3), Ni(1)–O(1) 1.833(2)



In the mononuclear complex *rac*-**12**, the thiol *rac*-**3** does not act as a pentadentate ligand. Instead, the nickel ion is planar, tetracoordinated. The four coordination sites are occupied by the thiolate sulfur atom, the imine and amine nitrogen atoms, and by the oxygen atom derived form the "right", di-*tert*-butylated phenolic substructure of the ligand. The oxygen atom of the "left", unsubstituted phenolic moiety does not participate in the coordination of the nickel ion.

To the best of our knowledge, *rac*-**12** is the first mononuclear nickel(II) thiolate complex with a mixed (S,N,N,O) ligand field. Most likely, the square-planar coordination mode of the nickel chelate *rac*-**12** is conserved in solution: The low-spin, diamagnetic character of the complex is nicely reflected by the well-resolved ^{1}H- and ^{13}C-NMR

Figure 2. Crystal packing diagram of the nickel complex *rac*-**12**; the intermolecular packing is stabilized by a hydrogen bond; H(2)···S(1) 2.37(1) Å, O(2)···S(1) 3.178(3) Å, O(2)–H(2)···S(1) 167(4)°



spectra. In fact, all resonances (except for aryl-H and -C) could be assigned on the basis of H,C-COSY and NOE spectra (see Experimental for the assignments). Attempts to induce additional binding of the phenol moiety by deprotonation failed: The addition of non-nucleophilic bases such as ethyldiisopropylamine (Hünig's base) did not induce any spectral changes (UV/Vis, NMR).

The cyclic voltammetry of the complex is characterized by the lack of a reduction wave up to a potential of −2.1 V [(vs. Fc/Fc^+), cyclic voltammogram not shown]. In the anodic range, two irreversible oxidation processes occur [E_{pa1} = 310 mV, E_{pa2} = 560 mV (vs. Fc/Fc^+) at a scan rate of 100 mV/s]. According to the peak currents measured, both processes most likely are one-electron oxidations. The irreversible anodic peaks may be interpreted by oxidative transformations of the thiolate group (e.g., formation of a dimeric disulfide) or by the oxidation of the noncomplexing phenolic moiety.

Conclusion

(1) We have described the synthesis of a novel pentadentate dihydrosalen ligand, carrying a mercaptomethyl group as the fifth binding site (*rac*-**3**). Our synthetic approach is a modular one and allows the construction of a great variety of related new ligands. (2) The reaction of the ligand *rac*-**3** with nickel(II) acetate afforded a new structural motif in nickel thiolate coordination chemistry: The first mononuclear nickel thiolate complex with a mixed (S,N,N,O) ligand field was synthesized and fully characterized, including X-ray structural analysis. (3) Apparently, the tendency

of the d^8-nickel(II) ion to form tetracoordinated, planar low-spin complexes overrides the potential of the ligand *rac*-**3** to bind in a pentadentate fashion. (4) It is expected that transition metals other than nickel(II), e.g. copper(II), may well form pentacoordinated chelates with the ligand *rac*-**3**. (5) As a consequence, for the generation of nickel(II) complexes of type **A** discussed initially (Scheme 1), a rigid, conformationally locked ligand system may be more suitable.

This work was supported by the *Deutsche Forschungsgemeinschaft* (grant no. Be 998/2) and by the *Fonds der Chemischen Industrie*. We gratefully acknowledge the careful electrochemical measurements performed by Dr. *Dennis H. Evans* and *Stephen E. Treimer*, Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, USA.

Experimental

General Methods: ^{1}H-NMR spectra were recorded with a Bruker AC-200, a Bruker AM 250 or a Bruker AM-300 instrument. The spectra were calibrated relative to the solvent signals or to tetramethylsilane as internal standard. – FT-IR spectra were measured with a Perkin-Elmer 1600 Series spectrometer. – UV/Vis spectra were recorded with a Beckman DU 640 instrument. – Mass spectrometry was performed with a Finigan MAT Mass Spectrometer 8200 and a Bruker Biflex. – Cyclic voltammetry was carried out by using 1 mM solutions of the complex *rac*-**12** in acetonitrile at 25 °C, containing 0.1 M tetrabutylammonium hexafluorophosphate. Potentials were measured with a platinum disk working electrode and a $Ag/AgNO_3$ reference electrode. – Melting points were determined in capillary tubes and are corrected. – Elemental analyses were carried out with a Heraeus CHN-O-Rapid or an Element vario EL instrument. – For column chromatography silica gel 60 (40–63 mesh) from Merck or neutral aluminia (grade I) from Macherey-Nagel was used.

Substances: The thiol *rac*-**4** was prepared as described by us earlier[12]. 2-(*N*-Phthalimido)acetaldehyde **6**) was obtained in two steps from 2-bromo-1,1-dimethoxyethane[13]. 3,5-Di-*tert*-butylsalicylic aldehyde (**10**) was prepared from 2,4-di-*tert*-butylphenol[14].

(R,S*)-2,2'-{Dithiobis[1-(methylamino)-2,1-ethanediyl]}-bis(phenol)* (**5a**) *and (R*,R*)-2,2'-{Dithiobis[1-(methylamino)-2,1-ethanediyl]}bis(phenol)* (*rac*-**5b**): A 50-ml round-bottomed flask, equipped with a dropping funnel, was charged with a solution of 1.00 g (5.50 mmol) of the amine *rac*-**4** in 3 ml of absol. dichloromethane and 3 ml of saturated aqueous sodium bicarbonate. With vigorous stirring, a solution of 0.70 g (2.75 mmol, 0.50 eq.) of iodine in dichloromethane was added dropwise from the dropping funnel until the brown color of the reaction mixture persisted. The solution was then decolorized by adding sodium sulfite. The aqueous layer was extracted several times with dichloromethane and the combined organic layers were dried with anhydrous potassium carbonate. The solvent was evaporated and a semisolid crude product was obtained. By comparison of the intensity of the ^{13}C-NMR signals at δ = 44.23/42.47 and at δ = 63.74/62.84, a ratio of diastereomers **5a**/*rac*-**5b** of 1.00:0.92 was determined. Trituration with ether (3 × 20 ml) at room temperature allowed the separation of the crude *meso* compound **5a** as a colorless solid. The filtrate was concentrated to afford crude *rac*-**5b** as a colorless oil.

5a: Recrystallization of the crude material from ether afforded colorless crystals, 0.40 g (40%); m.p. 146–147 °C. – TLC: R_f = 0.51 (ethyl acetate/methanol, 3:1). – IR (KBr): $\tilde{\nu}$ = 3288 cm^{-1}, 3048, 2952, 2903, 2849, 1610, 1588, 1493, 1480, 1390, 1259, 758, 747. – UV ($CHCl_3$): λ_{max} (log ε) = 280 nm (3.818). – ^{1}H NMR ($CDCl_3$): δ = 2.45 (s, 6H, CH_3), 3.01 (m, 4H, CH_2), 3.89 (Ψt, *J* = 7.4 Hz, *J* = 6.9 Hz, 2H, CH), 6.77–7.26 (m, 8H, aryl-H). – ^{13}C NMR ($CDCl_3$): δ = 34.14 (q, CH_3), 44.23 (t, CH_2), 63.74 (d, CH), 117.02 (d, aryl-CH), 119.43 (d, aryl-CH), 122.86 (s, aryl-C), 128.78 (d, aryl-CH), 129.17 (d, aryl-CH), 157.65 (s, aryl-C). – $C_{18}H_{24}N_2O_2S_2$ (364.34): calcd. C 59.31, H 6.64, N 7.68; found C 59.28, H 6.40, N 7.68. – See ref.[11] for the X-ray crystal structure of **5a**.

rac-**5b**: The oily crude product was purified by flash chromatography (adsorbent/substrate ratio: 60:1, elution with ethyl acetate/*n*-hexane, 1:2). Drying at 80 °C and 10^{-5} Torr afforded 0.45 g (45%) of a colorless powder. Analytically pure material was obtained by recrystallization from diethyl ether. Colorless crystals, m.p. 113 °C. – TLC: R_f = 0.51 (ethyl acetate/methanol, 3:1). – IR (KBr): $\tilde{\nu}$ = 3312 cm^{-1}, 3046, 2956, 2907, 2854, 1609, 1588, 1490, 1425, 1398, 1259, 755, 732. – ^{1}H NMR ($CDCl_3$): δ = 2.46 (s, 6H, CH_3), 2.94 (dd, *J* = 10.4 Hz, *J* = 14.1 Hz, 2H, C*H*HS), 3.03 (dd, *J* = 3.7 Hz, *J* = 14.1 Hz, 2H, CH*H*S), 3.94 (dd, *J* = 10.4 Hz, *J* = 3.7 Hz, 2H, CH), 6.77–7.19 (m, 8H, aryl-H). – ^{13}C NMR ($CDCl_3$): δ = 34.18 (q, CH_3), 42.47 (t, CH_2), 62.84 (d, CH), 116.97 (d, aryl-CH), 119.42 (d, aryl-CH), 122.93 (s, aryl-C), 128.78 (d, aryl-CH), 129.10 (d, aryl-CH), 157.69 (s, aryl-C). – $C_{18}H_{24}N_2O_2S_2$ (364.34): calcd. C 59.31, H 6.64, N 7.68; found C 59.34, H 6.66, N 7.71.

[2α,4β(2R,4R*,2'S*,4'S*)]-2,2'-{Dithiobis[methylene-(3,4-dihydro-3-methyl-2H-1,3-benzoxazine-4,2-diyl)methylene]}bis-[1H-isoindole-1,3(2H)-dione]* (**7a**) *and [2α,4β(2R*,4R*,2'R*,4'R*)]-2,2'-{Dithiobis[methylene-(3,4-dihydro-3-methyl-2H-1,3-benzoxazine-4,2-diyl)methylene]}bis[1H-isoindole-1,3(2H)-dione]* (*rac*-**7b**): A 50-ml Schlenk flask was charged under nitrogen with a solution of 588 mg (1.61 mmol) of a mixture of **5a** and *rac*-**5b** (diastereomeric ratio *meso*/*rac* = 1.20:1.00) in 8 ml of absol. tetrahydrofuran, and 626 mg (3.31 mmol, 2.05 eq.) of the aldehyde **6** was added. The mixture was stirred at room temp. for 20 h, and the solvent was evaporated. Column chromatography of the crude product on neutral alumina (grade I; adsorbent/substrate, 35:1, eluent ethyl acetate/*n*-hexane, 1:5) afforded 613 mg (54%) of a mixture of **7a** and *rac*-**7b**. By comparison of the CH_3 signals in the ^{1}H-NMR spectrum, the diastereomeric ratio *meso*/*rac* was found to be 1.15:1.00. Colorless foam, m.p. 74–82 °C. – TLC: R_f = 0.65 (ethyl acetate/*n*-hexane, 1:1). – IR (KBr): $\tilde{\nu}$ = 3061 cm^{-1}, 2957, 1774, 1716, 1610, 1581, 1485, 1396, 1079, 756, 719. – ^{1}H NMR ($CDCl_3$): δ = 2.41 [s, 6H, (*rac*-**7b**), CH_3], 2.43 [s, 6H, (**7a**), CH_3], 2.82–2.90 [m, 2H (**7a**), 2H (*rac*-**7b**), C*H*HS], 2.98–3.08 [m, 2H (**7a**), 2H (*rac*-**7b**), CH*H*S], 3.69 [dd, *J* = 10.2 Hz, *J* = 4.9 Hz, 2H, (**7a**), 2H (*rac*-**7b**), C*H*CH_2S], 3.97–4.05 [m, 2H, (**7a**), 2H (*rac*-**7b**), C*H*HN(C=O)$_2$], 4.11–4.19 [m, 2H (**7a**), 2H (*rac*-**7b**), CH*H*N(C=O)$_2$], 5.14 [dd, *J* = 7.9 Hz, *J* = 5.7 Hz, 2H (**7a**), C*H*CH_2N(C=O)$_2$], 5.16 [dd, *J* = 7.9 Hz, *J* = 5.7 Hz, 2H (*rac*-**7b**), C*H*CH_2N(C=O)$_2$], 6.80–7.26 [m, 8H (**7a**), 8H (*rac*-**7b**), aryl H], 7.65–7.88 [m, 8H (**7a**), 8H (*rac*-**7b**), phthaloyl-H]. – ^{13}C NMR ($CDCl_3$): δ = 34.72 (q, CH_3), 34.82 (q, CH_3), 38.21 (t, CH_2), 38.29 (t, CH_2), 46.23 (t, CH_2), 46.37 (t, CH_2), 61.48 (d, CH), 61.51 (d, CH), 81.67 (d, CH), 81.72 (d, CH), 116.79, 121.08 (both d, aryl-CH), 121.98 (s, aryl-C), 123.37, 128.21, 128.66 (all d, aryl-CH), 132.04 (s, aryl-C), 134.01 (d, aryl-CH), 134.05 (d, aryl-CH), 153.63, 153.71, 168.02, 168.05 (all s, aryl-C). – MS (EI): *m/z* (%) = 353 (26) [$M^+ - C_{19}H_{17}N_2O_3S$], 307 (100) [$M^+ - C_{20}H_{19}N_2O_3S_2$]. – $C_{38}H_{34}N_4O_6S_2$ (706.83): calcd. C 64.57, H 4.85, N 7.93; found C 64.32, H 4.88, N 7.94.

[2α,4β(2R,4R*,2'S*,4'S*)]-2,2'-{Dithiobis[methylene(3,4-dihydro-3-methyl-2H-1,3-benzoxazine-4,2-diyl)methylene]}bis-[1H-isoindole-1,3(2H)-dione]* (**7a**): The *meso* compound **7a** (3.70

g, 71%) was obtained by condensation of 2.67 g (7.32 mmol) of the pure diastereomer **5a** with 2.78 g (14.7 mmol, 2.01 eq.) of the aldehyde **6** as described above. Recrystallization from dichloromethane/methanol afforded a colorless powder, m.p. 115–118°C. – TLC: R_f = 0.56 (ethyl acetate/*n*-hexane, 1:1). – IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}, 2956, 1774, 1716, 1609, 1581, 1484, 1395, 1078, 756, 719. – ^1H NMR ($CDCl_3$): δ = 2.43 (s, 6H, CH_3), 2.86 (dd, *J* = 13.6 Hz, *J* = 4.9 Hz, 2H, C*H*HS), 3.04 (dd, *J* = 13.6 Hz, *J* = 10.2 Hz, 2H, CH*H*S), 3.69 (dd, *J* = 10.2 Hz, *J* = 4.9 Hz, 2H, C*H*CH_2S), 4.00 [dd, *J* = 14.0 Hz, *J* = 5.7 Hz, 2H, C*H*HN(C=O)$_2$], 4.15 [dd, *J* = 14.0 Hz, *J* = 7.9 Hz, 2H, CH*H*N(C=O)$_2$], 5.14 [dd, *J* = 7.9 Hz, *J* = 5.7 Hz, 2H, C*H*CH_2N(C=O)$_2$], 6.80–7.26 (m, 8H, aryl-H), 7.65–7.85 (m, 8H, phthaloyl H). – ^{13}C NMR ($CDCl_3$): δ = 34.69 (q, CH_3), 38.18 (t, CH_2), 46.35 (t, CH_2), 61.48 (d, CH), 81.64 (d, CH), 116.74, 121.04 (both d, aryl-CH), 121.94 (s, aryl-C), 123.35, 128.19, 128.64 (all d, aryl-CH), 132.02 (s, aryl-C), 134.01 (d, aryl-CH), 153.60, 168.04 (both s, aryl-C).

[2α,4β-(2R,4R*,2'R*,4'R*)]-2,2'-{Dithiobis[methylene(3,4-dihydro-3-methyl-2H-1,3-benzoxazine-4,2-diyl)methylene]}bis[1H-isoindole-1,3(2H)-dione]* (*rac*-**7b**): The ^1H-NMR spectrum of *rac*-**7b** was obtained by substracting the ^1H-NMR spectrum of **7a** from the spectrum of the mixture of both diastereomers. – ^1H NMR ($CDCl_3$): δ = 2.41 (s, 6H, CH_3), 2.85 (dd, *J* = 13.6 Hz, *J* = 4.8 Hz, 2H, C*H*HS), 3.03 (dd, *J* = 13.6 Hz, *J* = 10.2 Hz, 2H, CH*H*S), 3.69 (dd, *J* = 10.2 Hz, *J* = 4.8 Hz, 2H, C*H*CH_2S), 4.01 [dd, *J* = 14.0 Hz, *J* = 5.9 Hz, 2H, C*H*HN(C=O)$_2$], 4.14 [dd, *J* = 14.0 Hz, *J* = 7.7 Hz, 2H, CH*H*N(C=O)$_2$], 5.16 [dd, *J* = 7.7 Hz, *J* = 5.9 Hz, 2H, C*H*CH_2N(C=O)$_2$], 6.80–7.26 (m, 8H, aryl-H), 7.65–7.85 (m, 8H, phthaloyl-H).

(R,S*)-2,2'-[4,9-Bis(2-hydroxyphenyl)-3,10-dimethyl-6,7-dithia-3,10-diazadodecane-1,12-diyl]bis[1H-isoindole-1,3(2H)-dione]* (**8a**) *and (R*,R*)-2,2'-[4,9-Bis(2-hydroxyphenyl)-3,10-dimethyl-6,7-dithia-3,10-diazadodecane-1,12-diyl]bis[1H-isoindole-1,3(2H)-dione]* (*rac*-**8b**): A 500-ml Schlenk flask was charged with a solution of 7.08 g (10.0 mmol) of a mixture of **7a** and *rac*-**7b** (diastereomeric ratio *meso*/*rac* = 1.09:1.00) in a mixture of 50 ml of absol. dichloromethane and 50 ml of absol. acetonitrile. Sodium cyanoborohydride (1.60 g, 25.5 mmol, 2.55 eq.) was added and the mixture was acidified with methanolic hydrochloric acid to pH of ca. 2. After 6 h, the mixture was acidified with conc. hydrochloric acid to pH ca. 1. After 1 h of stirring, the solvent was removed. The residue was dried in vacuo and extracted with a 9:1 mixture of dichloromethane/methanol (saturated with ammonia). The solvent was evaporated and the residue again vacuum-dried. Recrystallization of the crude product from absol. methanol at −40°C afforded 5.17 g (73%) of a mixture of *rac*-**8b** and **8a**. By comparison of the intensity of the CH_3 signals in the ^1H-NMR spectrum, the diastereomeric ratio *rac*/*meso* was determined as 1.0:1.0. Colorless solid, m.p. 78–88°C. – TLC: R_f = 0.53 (ether/ethyl acetate, 95:5). – IR (KBr): $\tilde{\nu}$ = 3041 cm^{-1}, 2942, 2853, 1772, 1712, 1612, 1587, 1489, 1396, 1253, 1083, 756, 719. – ^1H NMR ($CDCl_3$): δ = 2.41 [s, 6H (**8a**), CH_3], 2.48 [s, 6H (*rac*-**8b**), CH_3], 2.70–2.79 [m, 4H (**8a**), 4H (*rac*-**8b**), N(CH_3)CH_2], 2.97–3.20 [m, 4H, (**8a**), 4H (*rac*-**8b**), CH_2S], 3.67–3.87 [m, 6H (**8a**), 6H (*rac*-**8b**), CH, CH_2N(C=O)$_2$], 6.21–7.05 [m, 8H, (**8a**), 8H (*rac*-**8b**), aryl-H], 7.70–7.82 [m, 8H (**8a**), 8H (*rac*-**8b**), phthaloyl-H], 9.80 [br. s, 1H (**8a**), 1H (*rac*-**8b**), OH]. – ^{13}C NMR: ($CDCl_3$): δ = 34.99 (t, CH_2), 35.05 (t, CH_2), 37.60 (q, CH_3), 37.86 (q, CH_3), 38.25 (t, CH_2), 38.56 (t, CH_2), 51.21 (t, CH_2), 51.39 (t, CH_2), 67.08 (d, CH), 67.42 (d, CH), 116.72, 119.23, 119.29, 123.19 (all d, aryl-CH), 123.46, 123.56 (both s, ary-C), 128.27, 128.52, 129.13, 129.16 (all d, aryl-CH), 132.19 (s, aryl-C), 133.83 (d, aryl-CH), 156.61, 156.75 (both s, aryl-C), 168.24 (s, C=O). – $C_{38}H_{38}N_4O_6S_2$ (710.87): calcd. C 64.21, H 5.39, N 7.88; found C 64.11, H 5.44, N 7.78.

(R,S*)-2,2'-[4,9-Bis(2-hydroxyphenyl)-3,10-dimethyl-6,7-dithia-3,10-diazadodecane-1,12-diyl]bis[1H-isoindole-1,3(2H)-dione]* (**8a**): The tertiary amine **8a** was prepared by reaction of 2.18 g (3.08 mmol) of **7a** with 485 mg (7.71 mmol, 2.50 eq.) of sodium cyanoborohydride in a mixture of 25 ml of absol. dichloromethane and 25 ml of absol. acetonitrile. Flash chromatography of the crude product (adsorbent/substrate, 40:1; eluent ethyl acetate/*n*-hexane, 1:1) afforded 1.82 g (83%) of **7a** as a colorless foam, m.p. 77–79°C. – TLC: R_f = 0.53 (ether/ethyl acetate, 95:5). – IR (KBr): $\tilde{\nu}$ = 3041 cm^{-1}, 2941, 2853, 1772, 1710, 1612, 1586, 1489, 1467, 1396, 1252, 1082, 755, 719. – ^1H NMR ($CDCl_3$): δ = 2.41 (s, 6H, CH_3), 2.68–2.78 [m, 4H, N(CH_3)CH_2], 3.01 (dd, *J* = 13.2 Hz, *J* = 9.5 Hz, 2H, C*H*HS), 3.12 (dd, *J* = 13.2 Hz, *J* = 3.4 Hz, 2H, CH*H*S), 3.68–3.81 [m, 4H, CH_2N(C=O)$_2$], 3.85 (dd, *J* = 9.5 Hz, *J* = 3.4 Hz, 2H, CH), 6.21–7.04 (m, 8H, aryl-H), 7.71–7.82 (m, 8H, phthaloyl-H), 9.78 (br. s, 1H, OH). – ^{13}C NMR ($CDCl_3$): δ = 35.05 (t, CH_2), 37.58 (q, CH_3), 38.25 (t, CH_2), 51.21 (t, CH_2), 67.07 (d, CH), 116.74, 119.29, 123.19, (all d, aryl-CH), 123.45 (s, aryl-C), 128.27, 129.14 (both d, aryl-CH), 132.20 (s, aryl-C), 133.83 (d, aryl-CH), 156.75 (s, aryl-C), 168.24 (s, C=O).

(R,R*)-2,2'-[4,9-Bis(2-hydroxyphenyl)-3,10-dimethyl-6,7-dithia-3,10-diazadodecane-1,12-diyl]bis[1H-isoindole-1,3(2H)-dione]* (*rac*-**8b**): The ^{13}C-NMR signals of the aliphatic C atoms of *rac*-**8b** were assigned by substracting the ^{13}C-NMR spectrum of **8a** from that of the mixture of both diastereomers. – ^{13}C NMR ($CDCl_3$): δ = 34.99 (t, CH_2), 37.86 (q, CH_3), 38.56 (t, CH_2), 51.39 (t, CH_2), 67.42 (d, CH).

(R,S*)-2,2'-{Dithiobis[1-[(2-aminoethyl)methylamino]-2,1-ethanediyl]}bis[phenol]* (**9a**) *and (R*,R*)-2,2'-{Dithiobis[1-[(2-aminoethyl)methylamino]-2,1-ethanediyl]}bis[phenol]* (*rac*-**9b**): Under nitrogen, a 100-ml round-bottomed flask was charged with a solution of 2.50 g (3.52 mmol) of a mixture of **8a** and *rac*-**8b** (diastereomeric ratio *meso*/*rac* = 1.00:1.00) in 5 ml of absol. tetrahydrofuran and 5 ml of absol. ethanol. Hydrazine hydrate (99%, 0.85 ml, 17.6 mmol, 5.00 eq.) was added. After stirring at room temp. for 20 h, the reaction mixture was acidified with conc. hydrochloric acid to pH of ca. 1 and stirred for another 10 min. The solvent was evaporated, and the residue was extracted with water (3 × 20 ml). The combined aqueous phases were adjusted to pH 11 by addition of aqueous potassium hydroxide and extracted with dichloromethane (3 × 30 ml). The combined organic phases were dried with anhydrous potassium carbonate, and the solvent was evaporated. The semisolid residue was dried in vacuo, affording 1.60 g (quant.) of a white foam, m.p. 55–60°C. By comparison of the intensities of the CH_3 signals in the ^1H-NMR spectrum, the diastereomeric ratio of **9a** and *rac*-**9b** was determined to be *meso*/*rac* = 1.13:1.00. – IR (KBr): $\tilde{\nu}$ = 3350 cm^{-1}, 3055, 2932, 2855, 2794, 1589, 1454, 1290, 1254, 754. – ^1H NMR ($CDCl_3$): δ = 2.17 [s, 6H (**9a**), CH_3], 2.21 [s, 6H (*rac*-**9b**), CH_3], 2.48–2.52 [m, 4H (**9a**), C$H_2$$NH_2$], 2.53–2.58 [m, 4H (*rac*-**9b**), C$H_2$$NH_2$], 2.74–2.89 [m, 4H (**9a**), 4H (*rac*-**9b**), N(CH_3)CH_2], 3.03–3.21 [m, 4H (**9a**), 4H (*rac*-**9b**), CH_2S], 3.96–4.03 [m, 2H (**9a**), 2H (*rac*-**9b**), CH], 4.42 [br. s, 4H (**9a**), 4H (*rac*-**9b**), NH], 6.79–7.19 [m, 8H (**9a**), 8H (*rac*-**9b**), aryl-H]. – ^{13}C NMR ($CDCl_3$): δ = 37.24 (q, CH_3), 37.33 (t, CH_2), 37.41 (q, CH_3), 37.64 (t, CH_2), 39.25 (t, CH_2), 56.21 (t, CH_2), 56.38 (t, CH_2), 65.13 (d, CH), 65.61 (d, CH), 116.99, 118.93 (both d, aryl-CH), 123.86, 123.93 (both s, aryl-C), 128.10, 129.07, 129.09 (d, aryl-CH), 157.44, 157.46 (both s, aryl-C). – MS (FAB, nibeol): *m*/*z* (%) = 451 (98) [M^+ + H], 377 (83) [M^+ − $C_3H_9N_2$], 258 (100) [M^+ + H − $C_{11}H_{17}N_2O$], 225 (55) [M^+ − $C_{11}H_{17}N_2OS$].

(R,S*)-2,2'-{Dithiobis[1-[(2-aminoethyl)methylamino]-2,1-ethanediyl]}bis[phenol]* (**9a**): The primary amine **9a** was obtained as a white foam (1.05 g, quant.) by treatment of 1.67 g (2.34 mmol) of **8a** with 683 µl (14.1 mmol, 6.00 eq.) of 99% hydrazine hydrate in a mixture of 20 ml of absol. tetrahydrofuran and 20 ml of absol. ethanol for 9 h, m.p. 55–57°C. – IR (KBr): $\tilde{\nu}$ = 3415 cm^{-1}, 3054, 2946, 2855, 2796, 1590, 1454, 1293, 1254, 755. – ^1H NMR ($CDCl_3$): δ = 2.17 (s, 6H, CH_3), 2.48–2.52 (m, 4H, CH_2NH_2), 2.79–2.88 (m, 4H, $N(CH_3)CH_2$), 3.07 (dd, *J* = 13.3 Hz, *J* = 4.1 Hz, 2H, CHHS), 3.12 (dd, *J* = 13.3 Hz, *J* = 9.2 Hz, 2H, CHHS), 4.02 (dd, *J* = 9.2 Hz, *J* = 4.0 Hz, 2H, CH), 4.39 (br. s, 2H, NH) 6.82–7.26 (m, 8H, aryl-H). – ^{13}C NMR ($CDCl_3$): δ = 37.21 (t, CH_2), 37.26 (q, CH_3), 39.31 (t, CH_2), 56.31 (t, CH_2), 65.18 (d, CH), 117.04, 118.94 (both d, aryl-CH), 123.81 (s, aryl-C), 128.06, 129.09 (both d, aryl-CH), 157.52 (s, aryl-C).

(R,R*)-2,2'-{Dithiobis[1-[(2-aminoethyl)methylamino]-2,1-ethanediyl]}bis[phenol]* (*rac*-**9b**): The ^1H-NMR spectrum of *rac*-**9b** was obtained by substracting that of **9a** from the ^1H-NMR spectrum of the mixture of both diastereomers. – ^1H NMR ($CDCl_3$): δ = 2.21 (s, 6H, CH_3), 2.53–2.58 (m, 4H, CH_2NH_2), 2.74–2.89 [m, 4H, $N(CH_3)CH_2$], 3.06 (dd, *J* = 13.2 Hz, *J* = 4.1 Hz, 2H, CHHS), 3.15 (dd, *J* = 13.2 Hz, *J* = 8.8 Hz, 2H, CHHS), 3.98 (dd, *J* = 8.7 Hz, *J* = 4.1 Hz, 2H, CH), 6.79–7.19 (m, 8H, aryl-H).

(R,S*)-2,2'-[Dithiobis(1-{[2-({[3,5-bis(1,1-dimethylethyl)-2-hydroxyphenyl]methylene}amino)ethyl]methylamino}-2,1-ethanediyl)]bis[phenol]* (**11a**) *and (R*,R*)-2,2'-[Dithiobis(1-{[2-({3,5-bis(1,1-dimethylethyl)-2-hydroxyphenyl]methylene}amino)-ethyl]methylamino}-2,1-ethanediyl)]bis[phenol]* (*rac*-**11b**): Under nitrogen, a 50-ml round-bottomed flask was charged with a solution of 950 mg (2.11 mmol) of a mixture of **9a** and *rac*-**9b** (diastereomeric ratio *meso*/*rac* = 1.13:1.00) in 20 ml absol. tetrahydrofuran, and 990 mg (4.22 mmol, 2.00 eq.) of the aldehyde **10** was added. The solution turned yellow instantaneously. After stirring for 4 h at room temp., the solvent was removed. Flash chromatography (adsorbent/substrate, 50:1; eluent *n*-hexane/ethyl acetate, 6:1) of the resulting oil afforded 1.20 g (60%) of a mixture of **11a** and *rac*-**11b** as a yellow foam, m.p. 59–65°C. The diastereomeric ratio was determined by comparing the intensities of the CH_3 signals at δ = 2.35 (**11a**) and δ = 2.40 (*rac*-**11b**) in the ^1H-NMR spectrum, *meso*/*rac* = 1.28:1.00. – TLC: R_f = 0.36 (*n*-hexane/ethyl acetate, 2:1). – IR (KBr): $\tilde{\nu}$ = 2958 cm^{-1}, 2908, 2866, 1631, 1588, 1468, 1441, 1252, 754. – ^1H NMR ($CDCl_3$): δ = 1.31 [s, 18H (**11a**), 18H (*rac*-**11b**), $C(CH_3)_3$], 1.44 [s, 18H (**11a**), 18H (*rac*-**11b**), $C(CH_3)_3$], 2.35 [s, 6H (**11a**), CH_3], 2.40 [s, 6H (*rac*-**11b**), CH_3], 2.81–2.89 [m, 4H (**11a**), 4H (*rac*-**11b**), $N(CH_3)CH_2$], 3.11–3.18 [m, 4H (**11a**), 4H (*rac*-**11b**), CH_2S], 3.66–3.74 [m, 4H (**11a**), 4H (*rac*-**11b**), $=NCH_2$], 3.89–3.96 [m, 2H (**11a**), 2H, (*rac*-**11b**), CH], 6.80–7.48 [m, 12H (**11a**), 12H (*rac*-**11b**), aryl-H], 8.34 [s, 2H (**11a**), 2H (*rac*-**11b**), N=CH]. – ^{13}C NMR ($CDCl_3$): δ = 29.45 [q, $C(CH_3)_3$], 31.52 [q, $C(CH_3)_3$], 34.15 [s, $C(CH_3)_3$], 35.04 [s, $C(CH_3)_3$], 38.42 (t, CH_2), 38.61 (t, CH_2), 38.84 (q, CH_3), 39.08 (q, CH_3), 54.32 (t, CH_2), 54.41 (t, CH_2), 57.45 (t, CH_2), 57.54 (t, CH_2), 67.36 (d, CH), 67.56 (d, CH), 117.03 (d, aryl-CH), 117.76 (s, aryl-C), 119.18 (d, aryl-CH), 123.44 (s, aryl-C), 123.50 (s, aryl-C), 126.07, 127.17, 128.42, 128.54, 129.31 (all d, aryl-CH), 136.69, 140.18, 157.27, 157.38, 157.91 (all s, aryl-C), 167.44 (d, N=CH). – MS (FAB, nibeol): *m*/*z* (%) = 883 (5) [M^+], 474 (12) [M^+ – $C_{26}H_{37}N_2O_2$], 441 (17) [M^+ – $C_{26}H_{37}N_2O_2S$], 409 (21) [M^+ – $C_{26}H_{37}N_2O_2S_2$], 395 (100) [M^+ – $C_{27}H_{39}N_2O_2S_2$]. – $C_{52}H_{74}N_4O_4S_2$ (883.31): calcd. C 70.71, H 8.44, N 6.34; found C 70.99, H 8.44, N 5.88.

(R,S*)-2,2'-[Dithiobis(1-{[2-({[3,5-bis(1,1-dimethylethyl)-2-hydroxyphenyl]methylene}amino)ethyl]methylamino}-2,1-ethanediyl)]bis[phenol]* (**11a**): The Schiff's base **11a** was obtained as a yellow solid (600 mg, 40%) by reaction of 767 mg (1.70 mmol) of **9a** with 837 mg (3.57 mmol, 2.10 eq.) of the aldehyde **10** in 20 ml of absol. tetrahydrofuran for 24 h, m.p. 68–70°C. – TLC: R_f = 0.36 (*n*-hexane/ethyl acetate, 2:1). – IR (KBr): $\tilde{\nu}$ = 3042 cm^{-1}, 2958, 2909, 2867, 1632, 1589, 1467, 1441, 1252, 1031, 754. – ^1H NMR ($CDCl_3$): δ = 1.30 [s, 18H, $C(CH_3)_3$], 1.44 [s, 18H, $C(CH_3)_3$], 2.35 (s, 6H, CH_3), 2.80–2.87 [m, 4H, $N(CH_3)CH_2$], 3.09 (dd, *J* = 13.2 Hz, *J* = 8.8 Hz, 2H, CHHS), 3.16 (dd, *J* = 13.2 Hz, *J* = 4.0 Hz, 2H, CHHS), 3.66–3.74 (m, 4H, $=NCH_2$), 3.96 (dd, *J* = 8.5 Hz, *J* = 4.0 Hz, 2H, CH), 6.79–7.38 (m, 12H, aryl-H), 8.34 (s, 2H, N=CH). – ^{13}C NMR ($CDCl_3$): δ = 29.45 [q, $C(CH_3)_3$], 31.51 [q, $C(CH_3)_3$], 34.15 [s, $C(CH_3)_3$], 35.03 [s, $C(CH_3)_3$], 38.44 (t, CH_2), 38.84 (q, CH_3), 54.33 (t, CH_2), 57.54 (t, CH_2), 67.36 (d, CH), 117.03 (d, aryl-CH), 117.76 (s, aryl-C), 119.17 (d, aryl-CH), 123.45 (s, aryl-C), 126.07, 127.17, 128.42, 129.30 (all d, aryl-CH), 136.69, 140.18, 157.38, 157.92 (all s, aryl-C), 167.44 (d, N=CH).

(R,R*)-2,2'-[Dithiobis(1-{[2-({[3,5-bis(1,1-dimethylethyl)-2-hyroxyphenyl]methylene}amino)ethyl]methylamino}-2,1-ethanediyl)]bis[phenol]* (*rac*-**11b**): The ^{13}C-NMR signals of the aliphatic C atoms of *rac*-**11b** were assigned by substracting of the ^{13}C-NMR spectrum of **11a** from that of the mixture of both diastereomers. – ^{13}C NMR ($CDCl_3$): δ = 29.45 [q, $C(CH_3)_3$], 31.52 [q, $C(CH_3)_3$], 34.15 [s, $C(CH_3)_3$], 35.04 [s, $C(CH_3)_3$], 38.61 (t, CH_2), 39.08 (q, CH_3), 54.41 (t, CH_2), 57.45 (t, CH_2), 67.56 (d, CH).

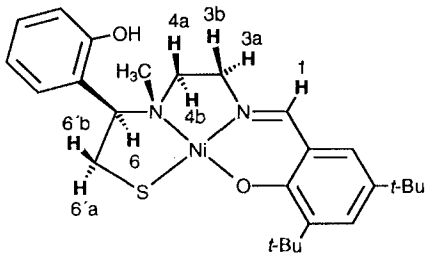
(±)-2,4-Bis(1,1-dimethylethyl)-6-{[(2{[1-(2-hydroxyphenyl)-2-mercaptoethyl]methylamino}ethyl)imino]methyl}phenol (*rac*-**3**): Under nitrogen, a 20-ml Schlenk flask was charged with a solution of 150 mg (0.17 mmol) of a mixture of the disulfides **11a** and *rac*-**11b** (diastereomeric ratio *meso*/*rac*: 1.28:1.00) in 15 ml of deoxygenated absol. dichloromethane. To the yellow solution 0.25 ml (1.80 mmol, 10.6 eq.) of triethylamine and 78.6 mg (0.51 mmol, 3.00 eq.) of dithioerythritol were added. The solution was stirred at room temp. for 5 h, and the solvent was evaporated. Flash chromatography of the residue on deoxygenated silica gel (adsorbent/substrate, 80:1; eluent *n*-hexane/ethyl acetate, 4:1) afforded 128 mg (85%) of *rac*-**3** as a viscous yellow oil. – TLC: R_f= 0.22 (*n*-hexane/ethyl acetate, 2:1). – IR (film): $\tilde{\nu}$ = 2959 cm^{-1}, 2908, 2867, 1630, 1589, 1468, 1444, 1248, 755. – ^1H NMR ($CDCl_3$): δ = 1.30 [s, 9H, $C(CH_3)_3$], 1.44 [s, 9H, $C(CH_3)_3$], 2.48 (s, 3H, CH_3), 2.86–3.04 [m, 4H, $N(CH_3)CH_2$, SCH_2], 3.66–3.77 (m, 3H, $=NCH_2$, CH), 6.80–7.60 (m, 6H, aryl-H), 8.36 (s, 1H, N=CH). – ^{13}C NMR ($CDCl_3$): δ = 24.93 (t, CH_2), 29.48 [q, $C(CH_3)_3$], 31.55 [q, $C(CH_3)_3$], 34.29 [s, $C(CH_3)_3$], 35.06 [s, $C(CH_3)_3$], 39.49 (q, CH_3), 54.91 (t, CH_2), 57.29 (t, CH_2), 71.65 (d, CH), 117.09 (d, aryl-CH), 117.80 (s, aryl-C), 118.99 (d, aryl-CH), 123.27 (s, aryl-C), 126.08, 127.20, 129.27, 129.53 (all d, aryl-CH), 136.73, 140.21, 157.12, 157.94 (all s, aryl-C), 167.44 (d, N=CH). – MS (MALDI-TOF, nitroanthracene): *m*/*z* (%) = 443 (29) [M^+ + H], 441 (28) [M^+ – H], 409 (34) [M^+ – SH], 395 (100) [M^+ – $HSCH_2$], 291 (62) [M^+ – C_8H_8OS]. – $C_{26}H_{38}N_2O_2S$ (442.66): calcd. C 70.55, H 8.65, N 6.33; found C 70.31, H 8.73, N 5.94.

Synthesis of (±)-(SP-4-3)-{[2,4-Bis(1,1-dimethylethyl)-6-{[(2-{[1-(2-hydroxyphenyl)-2-mercaptoethyl]methylamino}ethyl)-imino]methyl}phenolato](2–)-N,N',O,S}nickel (*rac*-**12**): Under nitrogen, a 30-ml Schlenk flask was charged with a solution of 610 mg (1.38 mmol) of the thiol *rac*-**3** and 343 mg (1.38 mmol, 1.00 eq.) of nickel acetate tetrahydrate in 19 ml of deoxygenated absol. ethanol. The solution was refluxed for 3 h, and the precipitate was filtered off under nitrogen. The red-brown crystals were washed with 1 ml of deoxygenated absol. ethanol and dried in vacuo (95

mg, 14%). Concentration of the filtrate to about 1 ml afforded a second crop of *rac*-**12**. Overall, 264 mg (39%) of the complex *rac*-**12** was obtained as red-brown crystals, m.p. >265°C. – IR (KBr): $\tilde{\nu}$ = 2953 cm^{-1}, 2906, 2867, 1615, 1529, 1456, 1255, 1172, 752. – UV (EtOH): λ_{max} (log ε) = 358 nm (3.591), 426 (3.422). – ^1H NMR ([D$_6$]DMSO): δ = 1.10 [s, 9H, C(CH$_3$)$_3$], 1.19 [s, 9H, C(CH$_3$)$_3$], 1.43 (dd, *J* = 11.8 Hz, *J* = 4.3 Hz, 1H, 4-Ha), 1.83 (dd, *J* = 12.8 Hz, *J* = 5.2 Hz, 1H, 6′-Ha), 2.69 (s, 3H, CH$_3$), 3.07 (ψt, *J* = 13.7 Hz, *J* = 12.5 Hz, 1H, 6′-Hb), 3.23 (m, 1H, 4-Hb), 3.59 (dd, *J* = 14.7 Hz, *J* = 6.1 Hz, 1H, 3-Ha), 3.85 (m, 1H, 3-Hb), 4.93 (dd, *J* = 12.3 Hz, *J* = 5.0 Hz, 1H, 6-H), 6.70–7.21 (m, 6H, aryl-H), 7.92 (s, 1H, 1-H), 9.90 (s, 1H, OH). Peak assignment was based on H,C-COSY and NOE spectra. – ^{13}C NMR ([D$_6$]DMSO): δ = 28.55 (t, CH$_2$), 29.20 [q, C(*C*H$_3$)$_3$], 31.22 [q, C(*C*H$_3$)$_3$], 33.31 [s, *C*(CH$_3$)$_3$], 34.65 [s, *C*(CH$_3$)$_3$], 36.48 (q, CH$_3$), 57.39 (t, CH$_2$), 58.00 (t, CH$_2$), 71.50 (d, CH), 115.73, 118.31 (both d, aryl-CH), 118.90, 119.04 (both s, aryl-C), 126.12, 126.58, 129.44, 129.95 (all d, aryl-CH), 134.39, 139.54, 155.49, 160.03 (all s, aryl-C), 160.97 (d, N=CH). – $C_{26}H_{36}N_2NiO_2S$ (499.34): calcd. C 62.54, H 7.27, N 5.61, S 6.42, Ni 11.75; found C 62.27, H 7.16, N 5.52, S 6.13, Ni 11.81.

The indication Ha and Hb in the ^1H-NMR spectral data denotes resonances of diastereotopic methylene hydrogen atoms at higher and lower field, respectively. An assignment of the resonances to the diastereotopic hydrogen atoms was performed on the basis of H,C-COSY and NOE spectra and is shown in Figure 3.

Figure 3. Assignment of ^1H-NMR resonances to the protons of the nickel chelate *rac*-**12**



12

X-ray Crystal-Structure Determination of rac-**12**: Crystals suitable for X-ray structural analysis could be obtained by slow cooling of a hot saturated solution of *rac*-**12** in absol. ethanol. A brown-red crystal of the dimensions 0.3 × 0.1 × 0.1 mm was measured on an Enraf Nonius CAD4 diffractometer. $C_{26}H_{36}N_2NiO_2S$, monoclinic, space group *C*2/*c*, *a* = 38.23(1), *b* = 8.783(1), *c* = 15.445(4) Å, β = 92.38(1)°, *V* = 5182(2) Å^3, $\rho_{calcd.}$ = 1.280 Mg/m^3, *Z* = 8; Cu-K_α radiation, Θ = 2.31–54.94°, a total of 5595 reflections was measured with 3253 symmetry-independent reflections. *R* = 0.0512 [R_w (based on F^2) = 0.1336]; data-to-parameter ratio: 11.2:1; maximal residual density = 0.285 e/Å^3. Further details of the crystal structure investigation of *rac*-**12** may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information GmbH, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-59261, the names of the authors and the journal citation.

☆ Dedicated to Professor *Rolf Gleiter* on the occasion of his 60th birthday.

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