not fully operational in the *N*-type sugar conformation, the charge density at the O3′ lone pair ($^1n_{sp^2(p\text{-}type)}$, O3′) is fully available to act as a donor and interact through the anomeric effect with the antibonding $\sigma^*_{P3'-O(ester)}$ orbital (AE(O3′-P3′-OCH_2CH_3)[3a, 11]), when C3′–O3′ is in ε^t, O3′–P3′ in ζ^-, and P3′-O5′ in α^- conformations. The Newman projection (Figure 3c) shows that the overlap between the O3′ lone pair orbitals and the $\sigma^*_{P3'-O(ester)}$ orbital ($n_{O3'} \rightarrow \sigma^*_{P3'-O(ester)}$ orbital mixing) stabilizes ε^t over ε^-. This is not only due to an antiperiplanar orientation of $^1n_{sp^2(p\text{-}type)}$ with respect to the P3′–O(ester) bond, as $\Phi(^1n_{sp^2(p\text{-}type)}$-O3′-P3′-$OCH_2CH_3)$ is nearly the same for the two cases, but largely owing to the greater electron density availible at $n_{O3'}$, arising from the absence of 3′-GE in the *N*-type sugar. The conformational parameters used to build up the model structure of *N*, ε^t, ζ^-, α^-, and *S*, ε^-, ζ^-, α^- conformations of **1** to draw the Newman projections are provided in Table S6 in the Supporting Information.

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"Figure Eight" Cyclooctapyrroles: Enantiomeric Separation and Determination of the Absolute Configuration of a Binuclear Metal Complex**

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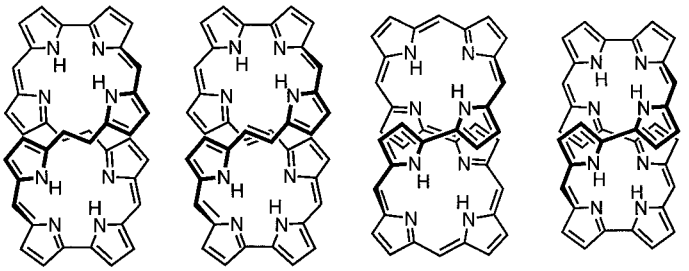
Dedicated to Professor Karl Schlögl on the occasion of his 75th birthday

Cyclooctapyrroles (octaphyrins), of which compounds **1**–**4** (in each case as the hexadecaethyl derivative, Scheme 1) are representatives, have developed as an unexpected sideline of our research into porphyrin and corrole isomers.[1] It was during studies on the synthesis of the still hypothetical *trans*-corrphycene that a versatile route to such polypyrrole macrocycles and potential ligands unfolded. We found that cyclooctapyrroles are formed as—in many cases dominating—competing products to cyclotetrapyrroles (porphyrin isomers, corroles, porphyrins-(1.0.1.0), and others) when two suitably functionalized dipyrrole components, of which at least one must be a bipyrrole derivative, are subject to an acid-catalyzed MacDonald condensation.[2]

Although **1**, **3**, and **4** (**2** is derived from **1** by dehydrogenation) were originally formed in only minor quantities, these



1 **2** **3** **4**

5: Pd–Pd complex **6**: Pd–Pd complex **7**: Cu–Cu complex

several homo- and heterobinuclear complexes have already been prepared[3]

Scheme 1. The figure eight ligands **1**–**4**.

macrocycles are now obtainable in yields of 40, 42, and 25%, respectively (i.e., on a preparative scale), when acid catalysis is replaced by BF_3 catalysis[4] (cyclotetrapyrrole formation is completely suppressed with **1**, **3**, and **4**).

A geometric feature of all previously known cyclooctapyrroles is that—in analogy to Sessler's cyclodecapyrrole turcasarin[5]—both in solution and (where structural analysis is available) in the crystal they exist in a chiral, figure eight conformation of two equidirectional helices (*P*,*P* or *M*,*M*),[6] which, assuming sufficiently restricted mobility, is expected to allow enantiomeric separation. Both **2** and its (according to molecular models) less rigid tetrahydro derivative **1** as well as **3** are highly promising candidates for enantiomeric separation: Based on the observation that the diastereotopicity of the ethyl CH_2 protons remains intact, also in ^{1}H NMR spectra measured at elevated temperature, the inversion barrier of the figure eight loop is expected to be at least 85 kJ mol^{-1}.[1a] In contrast, the NMR study and theoretical calculations[7] show **4** to be a dynamic molecule, even at room temperature, so there is not much chance that stable enantiomers can be obtained.

The cyclooctapyrroles **1**–**4** appear predestined to form binuclear metal complexes since the loop-shaped conformation of these macrocycles exhibits two structurally identical, helical N_4 cavities. Enantiomers of such complexes, which are presumably generally very stable towards racemization owing to the rigidity of the molecule imposed by the incorporation of the metal, are of interest as possible models for binuclear metalloenzymes[8] and as potential catalysts in asymmetric synthesis.[9] In this study, therefore, compounds **1** and **2** as well as their recently obtained palladium and copper complexes **5**–**7** were investigated as examples to effect enantiomeric separation. The success of these efforts is reported here. However, before the separations as such are described in detail, the hitherto still outstanding X-ray structural analyses[10] of **1** and **2** are included and the aforementioned metal complexes of these ligands are described.

According to the analysis, the molecular frameworks of the cyclooctapyrroles **1** and **2** show the figure eight conformation previously derived from the NMR studies (Figure 1a and 1b). As can be seen from the side view of **2** (Figure 1c), the four dipyrrin units are in each case almost planar, so that the helical conformation of the two tetrapyrrole substructures is

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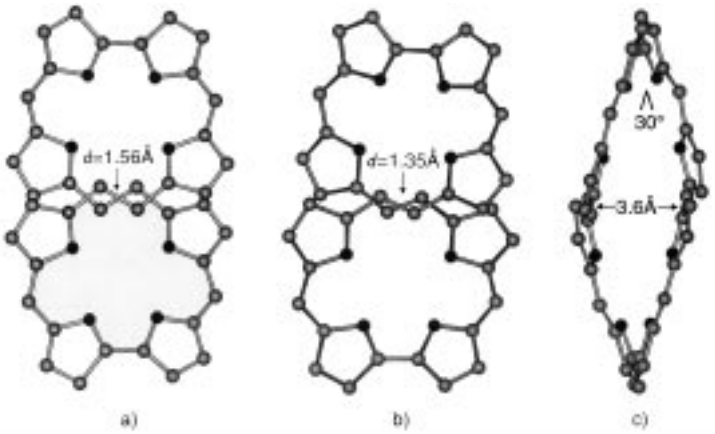

Figure 1. Structures **1** und **2** in the crystal of the racemate: a) plan view of **1**; b) plan view and c) side view of **2**. The ethyl groups are omitted for clarity.

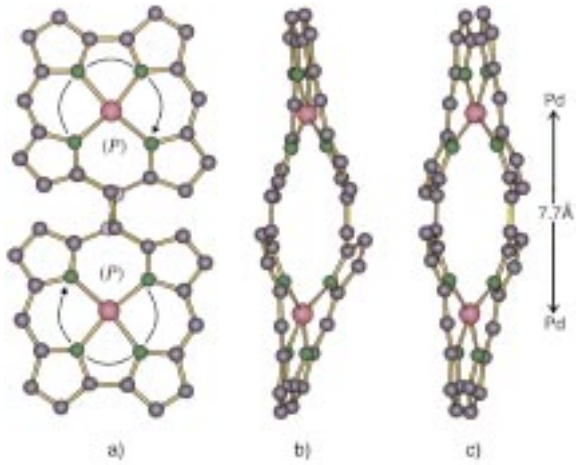

Figure 2. Structure of the (*P*,*P*)-configured enantiomer of the palladium complex **6** (first eluate) in the crystal of the enantiomer: a) plan view and b) side view. Structure of the (*P*,*P*)-configured enantiomer of **6** in the crystal of the racemate: c) side view. The ethyl groups are omitted for clarity.

mainly attributable to the torsions of the bipyrrole C–C single bonds (N-C-C′-N′ torsion angle: $\Phi = 30^\circ$).

The ability of the cyclooctapyrroles **1** and **2** to form binuclear chelates was confirmed by the preparation of the homobinuclear palladium(II) complexes **5** and **6** as well as the copper(II) complex **7**[11] (see the Experimental Section and Table 1). X-ray structure analysis[10] of complexes **6** and **7** show that on incorporation of two Pd^{II} or Cu^{II} ions into the two N_4 cavities of **2** the molecular symmetry remains unaffected, but there are marked conformational changes in the ligand framework (Figure 2 for the palladium complex **6**; the same applies for **7**). The intramolecular separations of the metal centers of **6** (7.70 Å) and **7** (7.48 Å) are not conducive to significant intermetal interactions. Accordingly, a temperature-independent effective magnetic moment, the value of which can be accommodated by a model in which the two copper(II) centers are practically uncoupled, can be derived from the magnetic susceptibility of **7**.[12]

Table 1. Selected physical data of the metal complexes **5**–**7**. ^{1}H NMR: 300 MHz; ^{13}C NMR: 75.5 MHz; IR: CsI; UV/Vis: CH_2Cl_2.

5: ^{1}H NMR ($CDCl_3$, 298 K): $\delta = 6.24$ (s, 4H, H-9,20,29,40), 3.83/3.72 (AA′BB′ system, 8H, H-14,15,34,35), ABX_3 systems: 2.43/2.36/1.09 (20H, H-2a,b,7a,b,22a,b,27a,b), 2.41/2.39/1.03 (20H, H-3a,b,6a,b,23a,b,26a,b), 2.35/2.26/1.01 (20H, H-11a,b,18a,b,31a,b,38a,b), 2.16/2.01/0.96 (20H, H-12a,b,17a,b,32a,b,37a,b); ^{13}C NMR ($CDCl_3$, 298 K): $\delta = 165.86$, 149.95, 149.19, 138.61, 135.36, 131.52, 131.25, 128.25, 120.05, 29.30, 18.39, 17.90, 17.68, 17.39, 17.39, 17.21, 16.74, 15.21; IR: $\tilde{\nu} = 2963$, 2929, 2869, 1587, 1302, 1196, 1107, 1012, 997, 952, 871 cm^{-1}; UV/Vis: λ_{max} (ε) = 441 (72200), 543 (57400), 652 (19100); MS (FAB): *m/z* (%): 1282 (100) [M^+]

6: ^{1}H NMR ($CDCl_3$/thiophenol, 298 K): $\delta = 6.99$ (s, 4H, H-9,20,29,40), 6.88 (s, 4H, H-14,15,34,35), ABX_3 systems: 2.70/1.22 (20H, H-2a,b,7a,b,22a,-b,27a,b), 2.70/1.28 (20H, H-11a,b,18a,b,31a,b,38a,b), 2.66/1.18 (20H, H-3a,b,6a,b,23a,b,26a,b), 2.38/0.91 (20H, H-12a,b, 17a,b,32a,b,37a,b); ^{13}C NMR ($CDCl_3$/thiophenol, 298 K): $\delta = 162.06$, 150.30, 145.11, 140.10, 139.65, 135.27, 134.18, 130.80, 130.00, 118.97, 11.84, 11.68, 17.98, 17.91, 17.63, 17.35, 17.00, 14.28; IR: $\tilde{\nu} = 2961$, 2929, 2868, 1587, 1279, 1195, 1012, 955, 876, cm^{-1}; UV/Vis: λ_{max} (ε) = 281 (27000), 355 (37700), 396 (32500), 559 (60000), 654 (166000); MS (FAB): *m/z* (%): 1278 (100) [M^+]

7: IR: $\tilde{\nu} = 2962$, 2928, 2868, 1587, 1387, 1287, 1188, 1012, 955, 876 cm^{-1}; UV/Vis: λ_{max} (ε) = 359 (47000), 594 (70000), 638 (246000); MS (FAB): *m/z* (%): 1192 (100) [M^+]

Correct C, H, N analytical data are available for **5**–**7**.

The enantiomeric separation of cyclooctapyrrole ligand **2** tried first was carried out on an analytical HPLC column (4.6 × 250 mm) with commercially available Chiralcel OD (silica gel coated with cellulose tris(3,5-dimethylphenyl carbamate) (CDMPC)) from the company DAICEL.[13] The samples used for the measurement of the circular dichroism (CD) spectra of the enantiomers of **2** were separated by applying 200-μL volumes of a saturated solution of the racemate in eluent to the analytical column (separation factor $\alpha = 2.28$; Table 2). The mirror-image CD spectra show that the racemate separation had been successful (Figure 3). Owing to the intense color of the solution it was not possible to measure the optical rotation with any reliability (this applies to all the compounds investigated here). The enantiomers of **2** are optically stable, as their solutions in *n*-hexane can be warmed at 60 °C for several hours without measurable racemization occurring.

Table 2. Chromatographic data of the analytical and preparative enantiomeric separation of the cyclooctapyrroles **1** and **2** and the metal complexes **5**–**7**.[a]

Compd.	Analytical (HPLC, Chiralcel OD)				Preparative (CDMPC-C_8)			
	k_1	k_2	α	R_S	k_1	k_2	α	R_S
1	0.15	0.35	2.37	2.87	–	–	–	–
2	0.18	0.41	2.28	3.10	0.1	0.21	2.16	1.33
5	0.25	0.32	1.28	0.96	0.19	1.2	6.3	4.9
6	0.55	1.05	1.91	3.43	0.15	8.51	56.7	27
7	0.36	0.36	1	0	0.15	1.53	10	8.1

[a] Eluent: *n*-Hexane with addition of 2-propanol (0.25%) and diethylamine (0.1–0.2%); room temperature (at 15 °C for **1** because of the tendency to racemize); equilibration time: 3 h; k_1, k_2: capacity factors of the enantiomers; α: separation factor; R_S: resolution.

The tetrahydro derivative **1** of **2** can also be separated into the enantiomers on the above HPLC column. Since the enantiomers of **1** racemize even at room temperature, the

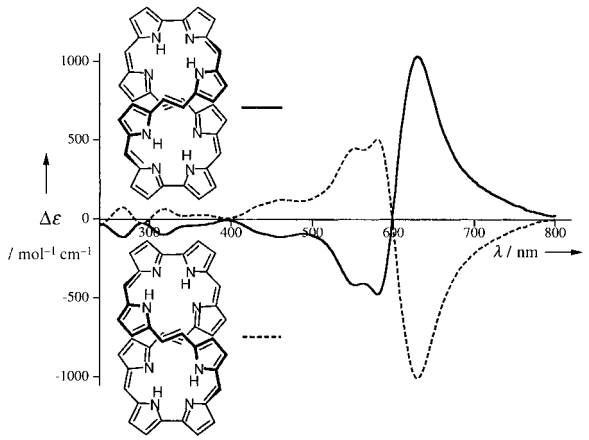

Figure 3. CD spectra (CH_2Cl_2) of the enantiomers of **2**; first eluate: (*M*,*M*) enantiomer (——); second eluate: (*P*,*P*) enantiomer (- - - -).[17]

separation was carried out at 15 °C ($\alpha = 2.37$; Table 2) under otherwise identical conditions as with **2**. The two enantiomer fractions were kept in an ice bath and then freed of solvent under high vacuum (ice cooling), and the enantiomers remaining were dried at 0.001 Torr. This separation procedure was repeated with the already highly enriched samples (70–80 % *ee*), with the effect that the enantiomeric purity was increased to over 95 % *ee*.

The kinetics of racemization in *n*-hexane of the enantiomers of **1** thus obtained were determined by CD spectroscopy on the basis of the changes in circular dichroism with time. The measurements were carried out at three temperatures (299 K: $k = 7.2 \times 10^{-5}\,s^{-1}$; 312 K: $k = 2.3 \times 10^{-4}\,s^{-1}$, and 321 K: $k = 4.7 \times 10^{-4}\,s^{-1}$) and at $\lambda = 396$ nm, the most intense band in the UV/Vis spectrum of **1**. The rate constants k of the racemization were determined from a logarithmic plot of the change in extinction against time t. A value of 96.5 ($\pm$0.5) kJ mol^{-1} was thus derived for the free activation enthalpy $\Delta G^{\neq}_{298}$ of racemization. The prognosis, based upon NMR results,[1a] that the inversion barrier, not only for **2** but also for the less rigid **1**, is greater than 85 kJ mol^{-1} is thus confirmed.

The enantiomeric separation of **2** on a preparative scale, which is of interest for the synthesis of enantiomeric metal complexes, required the preparation of an appropriate chiral stationary phase. Based upon the investigations of Matlin et al.[14] spherical silica gel with a pore diameter of 120 Å and a particle size of 30 μm (Hyperprep) was used; after successive treatment with dimethyloctylchlorosilane and trimethylchlorosilane[15] (formation of "octyl silica gel") the gel was coated with 10 wt% of the chiral selector CDMPC. This stationary phase (CDMPC-C_8), packed in a thermostated glass column (25 × 300 mm), enabled 15 mg of racemic **2** to be separated into the enantiomers by cyclic medium pressure chromatography (closed loop technique) with the eluent proven from the analytical method (separation factor $\alpha = 2.16$, Table 2). The fractions thus obtained with an enantiomeric excess of over 97 % *ee* were brought to a purity of greater than 99.8 % *ee* by repeated chromatography on this phase.

Most notably, the metal complexes **5**–**7** could be separated into the enantiomers particularly efficiently on the preparative phase CDMPC-C_8, whereas on the analytical HPLC column a base-line separation was obtained only with **6** (Table 2). In accord with the increase in the rigidity of the ring framework associated with the metallation of **1** and **2**, not only did the enantiomers of **6** and **7** prove to be optically fully stable, but so did those of **5**, which were derived from the readily racemizable tetrahydrooctaphyrin **1**.[17]

The remarkably high enantioselectivity of the chiral cellulose phase CDMPC-C_8 towards the palladium complex **6** (separation factor $\alpha = 56.7$!, Table 2) allowed racemate separation on a 100-mg scale without undue effort. This made possible the growth of single crystals of the two enantiomers of **6** for the determination of their absolute configuration—and consequently that of the enantiomers of **2**—by X-ray structural analysis.[10] The analysis, which was carried out with use of the anomalous scatter contribution of the two heavy atoms, showed that in the case of the first eluted enantiomer of **6** the four pyrrole units of a coordination sphere are each arranged equidirectionally in a right-handed (*P*)-helix around the palladium atom (Figure 2a).[6] A comparison of the side views of the structures of the (*P*,*P*)-configured enantiomer and the racemate of **6** (Figures 2b and c) shows that the structure of the single enantiomer exhibits a distinctive curvature as a result of different packing effects in the crystal lattice. Whereas the crystals of the enantiomers of **6** belong to the noncentrosymmetric, monoclinic $P2_1$ space group, the crystals of the racemate form a lattice of the triclinic $P\bar{1}$ space group with an inversion center.

This study confirms the expectation that figure eight cyclooctapyrroles and—presumably in general—their binuclear metal complexes are amenable to preparative enantiomeric separation by chromatography on suitable phases (here a CDMCP coated silica gel proved suitable). With a view to potential applications, particularly in asymmetric catalysis, it is intended to subject a selection of the fairly large number of homo- and heterobinuclear metal complexes of ligands **3** and **4** already synthesized to racemate separation.[18,19]

Experimental Section

Cyclooctapyrrole **1**: Bis(5-benzyloxycarbonyl-3,4-diethyl-2-pyrrolyl)ethane[1a] (540 mg, 1 mmol) and 3,3′,4,4′-tetraethyl-5,5′-diformyl-2,2′-bipyrrole (300 mg, 1 mmol) are dissolved in tetrahydrofuran/methanol (3/2, 300 mL). Boron trifluoride ethyl etherate (15 mL) is added with vigorous stirring to this solution over 30 min at −10 °C, and the mixture is allowed to stand at room temperature for 15 h. The reaction mixture is then neutralized with 2 M sodium hydroxide and extracted with toluene (3 × 250 mL). The organic phase is washed several times with water, dried over sodium sulfate, and evaporated to dryness under reduced pressure. On chromatography of the residue on basic aluminum oxide (activity II–III, Merck AG, Darmstadt; column 50 × 300 mm) with *n*-hexane/toluene (2/1) **1** elutes as the first, red-brown fraction. Compound **1** is obtained as violet needles (decomp. 250 °C) by crystallization from *n*-hexane/dichloromethane (4/1); yield: 215 mg (40 %).

Standard synthetic method for the metal complexes **5**–**7**: The hexadecaethylcyclooctapyrroles **1** or **2** (53 mg, 0.05 mmol) are dissolved in chloroform (40 mL) and triethylamine (2 mL), and after the addition of a solution of the respective metal diacetate (0.25 mmol) in methanol (20 mL) the solution is allowed to stand at room temperature under an inert atmosphere (**5** and **6**: $Pd(OAc)_2$, 16 h; **7**: $Cu(OAc)_2$, 1 h). The reaction mixture is then treated with more chloroform (50 mL). The organic phase is washed several times with water, dried over sodium sulfate, and evaporated to dryness under reduced pressure. On chromatography of the residue on

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basic alumina (activity II – III, column: 20 × 120 mm) with *n*-hexane/toluene (1/1) the binuclear metal complexes are eluted first as intensely colored fractions (**5**: blood red: **6**: blue; **7**: blue-green); **5**: violet crystals (from methanol/dichloromethane), decomp. 280 °C, yield: 45 mg (70 %); **6**: golden crystals (from methanol/dichloromethane), decomp. > 310 °C, yield: 50 mg (78 %); **7**: dark green crystals (from acetonitrile/dichloromethane), decomp. > 310 °C, yield: 48 % (80 %).

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[10] Crystal structure data for **1**: $C_{72}H_{96}N_8$; $M = 1073.57$ g mol^{-1}; crystals from methanol, crystal dimensions 0.30 × 0.25 × 0.20 mm; monoclinic, space group $P2_1/c$, $a = 13.055(1)$, $b = 38.565(1)$, $c = 25.878(1)$ Å, $\beta = 90.65(2)^\circ$, $V = 13027.5(12)$ Å^3; $Z = 8$, $\rho_{calcd} = 1.095$ g cm^{-3}; $F(000) = 4672$; $\mu_{Mo} = 0.064$ mm^{-1}; 38374 measured, 21095 independent, 10015 observed reflections ($F_o^2 > 2\sigma F_o^2$); $\Theta_{max} = 25.0^\circ$; $R1 = 0.079$, $wR2 = 0.192$. Crystal structure data for **2**: $C_{72}H_{92}N_8$; $M = 1069.6$ g mol^{-1}; crystals from acetonitrile, crystal dimensions 0.25 × 0.20 × 0.10 mm; monoclinic, space group $P2_1/c$, $a = 13.061(1)$, $b = 38.398(2)$, $c = 25.648(1)$ Å, $\beta = 90.86(1)^\circ$, $V = 12861.4(13)$ Å^3; $Z = 8$, $\rho_{calcd} = 1.105$ g cm^{-3}; $F(000) = 4640$; $\mu_{Mo} = 0.065$ mm^{-1}; 18366 measured, 18121 independent, 10352 observed reflections ($F_o^2 > 2\sigma F_o^2$); $\Theta_{max} = 27^\circ$; $R1 = 0.059$, $wR2 = 0.129$. Crystal structure data of **6** (racemate): $C_{72}H_{88}N_8Pd_2$; $M = 1278.30$ g mol^{-1}; crystals from *n*-hexane, crystal dimensions 0.25 × 0.20 × 0.20 mm; triclinic, space group $P\bar{1}$, $a = 9.449(1)$, $b = 13.801(1)$, $c = 25.793(1)$ Å, $\alpha = 89.78(1)$, $\beta = 96.51(1)$, $\gamma = 108.97(1)^\circ$, $V = 3158.4(4)$ Å^3; $Z = 2$, $\rho_{calcd} = 1.344$ g cm^{-3}; $F(000) = 1336$; $\mu_{Mo} = 0.618$ mm^{-1}; 12403 measured, 12403 independent, 7612 observed reflections ($F_o^2 > 2\sigma F_o^2$); $\Theta_{max} = 26.0^\circ$; $R1 = 0.045$, $wR2 = 0.0942$. Crystal structure data for **6** (*P*,*P* enantiomer): crystals from acetonitrile, crystal dimensions 0.35 × 0.30 × 0.25 mm; monoclinic, space group $P2_1$, $a = 14.131(1)$, $b = 17.714(1)$, $c = 14.226(1)$ Å, $\beta = 115.47(1)^\circ$, $V = 3214.9(4)$ Å^3; $Z = 2$, $\rho_{calcd} = 1.321$ g cm^{-3}; $F(000) = 1336$; $\mu_{Mo} = 0.607$ mm^{-1}; 13234 measured, 13078 independent, 12347 observed reflections ($F_o^2 > 2\sigma F_o^2$); $\Theta_{max} = 26.37^\circ$; $R1 = 0.059$, $wR2 = 0.153$; absolute structure parameters (Flack parameters): −0.044(13). Nonius-Kappa-CCD diffractometer, room temperature, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å); the structures were solved by direct methods and refined with F^2 for all independent reflections (heavy atoms with anisotropic, H atoms with isotropic temperature factors); $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. Programs used: SHELXS-97 for structure determination and SHELXL-97 for refinement (G. M. Sheldrick, Universität Göttingen). Calculations were carried out on the data processing systems of the regional computer center of the Universität Köln. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-120832 (**1**), -120833 (**2**), -121628 (**5**), -120834 (**6**, racemate), -120835 (**6**, (*P*,*P*) enantiomer), -120836 (**6**, (*M*,*M*) enantiomer), and -120837 (**7**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[11] Further examples of metal complexes of **1** and **2**: ref. [3b].

[12] We thank Dr. E. Bill of the Max – Planck – Institut für Strahlenchemie, Mülheim an der Ruhr, for the measurement of the magnetic susceptibility of **7** and the evaluation of the experimental data.

[13] Review: Y. Okamoto, E. Yashima, *Angew. Chem.* **1998**, *110*, 1072; *Angew. Chem. Int. Ed.* **1998**, *37*, 1021.

[14] a) S. A. Matlin, S. J. Grieb, A. M. Belenguer, *J. Chem. Soc. Chem. Commun.* **1995**, 301; b) S. J. Grieb, S. A. Matlin, A. M. Belenguer, H. J. Ritchie, *J. Chromatogr. A* **1995**, *697*, 271.

[15] After derivatization of Hyperprep Si 120 (30 μm) with dimethyloctylchlorosilane the residual SiOH groups were endcapped with trimethylchlorosilane. This ensured that the enantiomeric selectivity of the chiral coating was not impaired by nonspecific retention by the support material (see also Table 2).

[16] a) J. Dingenen, J. N. Kinkel, *J. Chromatogr. A* **1994**, *666*, 627; b) A. Werner, *Kontakte* (Darmstadt) **1989**, *3*, 50. A comprehensive publication on enantiomeric separation of figure eight cyclooctapyrroles and their metal complexes is in preparation.

[17] In the case of the enantiomeric separation of **2** and its Pd^{II} and Cu^{II} complexes **6** and **7** a comparison of the CD spectra of all pure enantiomers showed that the sequence of elution of the optical isomers reversed after complex formation; the second eluted enantiomer of the binuclear complexes **6** and **7** (in each case the (*M*,*M*) form) corresponded to the first eluted enantiomer of **2** and vice versa. This result was also confirmed by the preparation of the enantiomeric complexes from the enantiomers of **2** and the subsequent comparison of the CD spectra and the HPL chromatograms. In these investigations it must be noted that enantiomers of **2** can racemize in solution by the action of acids. If basic conditions are used (an excess of triethylamine) the enantiomeric Pd^{II} and Cu^{II} complexes **6** and **7** can be prepared from the corresponding enantiomers of **2** without the occurrence of racemization.

[18] A recently published simple synthesis of the ligand **4** (with *meso*-phenyl substituents) appears likely to increase the interest in figure eight cyclooctapyrroles and their metal complexes: J. Setsune, Y. Katakami, N. Iizuna, *J. Am. Chem. Soc.* **1999**, *121*, 8957.

[19] Note added in proof (November 9, 1999): The synthesis of an octaphyrin-(1.0.0.0.1.0.0.0) has just been realized. This cyclooctapyrrole containing two C-H spacers less than **4**, possesses a twisted boat rather than a figure eight conformation; J. L. Sessler, D. Seidel, V. Lynch, *J. Am. Chem. Soc.*, in press.

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