Chemistry of Pyrrocorphins: Structure of Nickel(II) *ccccc*-Octaethyl-pyrrocorphinate in the Solid State and in Solution. Observation of the Inversion Barrier between Enantiomorphically Ruffled Conformers

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An inversion barrier between enantiomorphic saddle conformers of nickel(II) *ccccc*-octaethyl-pyrrocorphinate in solution is observed by ^{1}H n.m.r. spectroscopy.

When a metal ion such as Mg^{II} or Ni^{II} is imposed upon a porphyrinogen, it tautomerizes and forms the metal complex of a pyrrocorphin.[1] This porphyrinogen → pyrrocorphin tautomerization provides preparative access to corphinoid ligand systems directly from porphyrinogens. While investigating the reaction in the octaethyl model series,[1] we obtained hexa- and tetra-hydroporphinoid nickel(II) complexes whose crystal structures[2—4] uniformly displayed the phenomenon of co-ordination hole contraction[5] that manifests itself in a saddle-shaped distortion (ruffling) of the ligand system (see also the recent work of Ibers *et al.*[6]). This conformational deformation is important for the stereochemistry of the ligand periphery[1e,3,7] as well as for the reactivity of the central metal ion.[3,8] We report here the preparation and structure of the nickel(II) pyrrocorphinate (**4**) which, among nickel(II) hydroporphinates,[3] shows the steepest ligand ruffling observed so far.

Treatment of (**1**) with a (3:1) mixture of the bicyclic guanidine derivative (**7**) and its iodomagnesium salt in xylene under strict exclusion of oxygen (conditions i, Scheme 1) gives a reaction mixture of diastereoisomeric (blue) magnesium(II) pyrrocorphinates (**2**). Work-up with acetic acid (conditions ii) demetallates these complexes under kinetic control to produce a mixture of diastereoisomeric (red) pyrrocorphins (**3**) in yields of up to 95%.[1a,b] The most polar fraction (approx. 10—15%) in the h.p.l.c. of such a mixture (see h.p.l.c. reproduced in ref. 1b) is the *ccccc*-diastereoisomer.† On treatment of this crystalline isomer with an excess of nickel(II) acetate (conditions iii), the nickel(II) pyrrocorphinate (**4**) is obtained without noticeable epimerization at the ligand periphery. When exposed to air in dilute benzene–hexane solution, (**4**) cleanly autoxidizes to a mixture of approximately equal amounts of the nickel(II) *ccc*-isobacteriochlorinate (**5**) and the *ccc*-bacteriochlorinate (**6**).

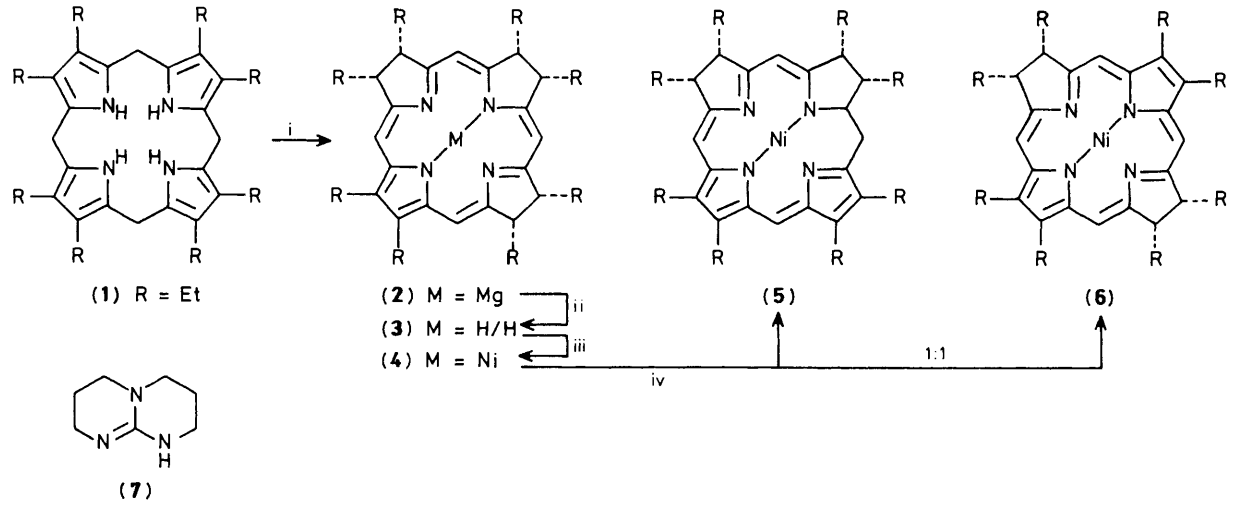
The crystal structure analysis of (**4**) (Figure 1) shows that the ligand system exists in a saddle conformation of approximate S_4 symmetry with the four *meso* carbon atoms lying alternately above and below the co-ordination plane by 0.74 Å. The latter is approximated by a least-squares plane through the four nitrogen centres; the nickel ion deviates from this plane by less than 0.01 Å. The three hydropyrrolic rings are in half-chair conformations whose puckering alternates in such a way that it parallels the wave form of the ligand saddle (W-conformation of the ensemble of hydropyrrolic rings[3]).‡

† For the configurational assignments of some of the other fractions and for a tautomerization procedure which gives a pyrrocorphin mixture containing only the three most stable diastereoisomers (*tctct*, *tttct*, and *tttt*) see refs. 1b,e.

‡ *Crystal Data* (**4**): $C_{36}H_{50}N_4Ni$, monoclinic, space group $P2_1/n$, a = 13.207(4), b = 9.522(2), c = 25.626(14) Å, β = 92.70(1)°, U = 3219 Å^3, Z = 4. Data collected with Mo-K_α radiation (λ = 0.7107 Å, graphite monochromator), Stoe 4-circle diffractometer, 5674 independent reflections recorded ($0 \leq 2\theta \leq 50°$), 2991 significant [$I > 2\sigma(I)$] intensity values, recording temperature T = 113(1) K, R = 0.076, R_w = 0.073 [$w_i = 1/(\sigma^2(F) + 0.0018F^2)$] for 571 parameters and 3041 observations.

(**6**): $C_{36}H_{48}N_4Ni \cdot C_6H_6$, triclinic, space group $P\bar{1}$, a = 11.997(2), b = 12.347(2), c = 13.803(3) Å, α = 86.93(1), β = 89.71(1), γ = 63.18°, Z = 2, Mo-K_α radiation (λ = 0.7107 Å, graphite monochromator), 10577 independent reflections, 6203 significant [$I > 2\sigma(I)$], T = 86(1) K, R = 0.045, R_w = 0.040.

The atomic co-ordinates for the crystal structures of (**4**) and (**6**) are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. For a complete description of the crystal structures of (**4**) and (**6**) see ref. 4.



Scheme 1. || *Reagents and conditions:* i (tautomerization and complexation): 1,5,7-triazabicyclo[4.4.0]dec-5-ene (1.8 mmol) in xylene (10 ml) + EtMgI (0.6 mmol in diethyl ether) + 0.12 mmol (**1**) in 5 ml xylene, 85 °C, 14 h, followed directly by ii; ii (decomplexation): 1 ml of $MeCO_2H$ added to reaction mixture, work-up with water–hexane, h.p.l.c. (*cf.* ref 1b, e); column chromatography (Silica G, benzene–hexane 2:1), deep red pyrrocorphin fraction; isolation of *ccccc*-isomer (**3**): column chromatography (silica for t.l.c., benzene–hexane gradient), crystallised from benzene–methanol m.p. 219 °C; *cf.* ref. 1e, p. 145; iii (complexation): 22 equiv. of $Ni(OAc)_2 \cdot 4H_2O$ in CH_2Cl_2–EtOH (1:5), reflux, crystallised from CH_2Cl_2–methanol, 90%, *cf.* ref. 1e, pp. 208, 197; iv (autoxidation): in benzene–hexane (1:9) (*ca.* 10^{-3}M), air in daylight, 30 h; >90% (**5** + **6**) (h.p.l.c., u.v.-visible), crystallized 38% (**5**), m.p. 240 °C from benzene–methanol and 30% (**6**), m.p. 204 °C from benzene–methanol after h.p.l.c. (Partisil 5, pentane +1% Et_3N); *cf.* ref. 1e, p. 210. All operations except iv carried out under strict exclusion of oxygen; glove box, $[O_2] \leq 5$ p.p.m.

Information so far available on ligand ruffling refers exclusively to complexes in the solid state; with the pyrrocorphinate (**4**), the phenomenon is now observed in solution. Within each of the two pairs of *meso* protons indicated in Figure 2, two protons are constitutionally homotopic but conformationally heterotopic when the molecule is in the saddle conformation. Correspondingly, there are four *meso* proton signals in the ^{1}H n.m.r. spectrum of a solution of (**4**) in carbon disulphide–benzene (9:1) at −71.7 °C. The pair of singlets at lower field belongs to the pair of *meso* protons adjacent to the pyrrole ring (circled H); the broader of them at higher field§ (δ 6.67) is assigned to the proton adjacent to a (shielding) quasi-equatorial ethyl group of the neighbouring half-chair and the sharp§ singlet at δ 6.89 to the proton adjacent to a quasi-axial ethyl group. The singlet pair at higher field (δ 6.04 and 6.31) likewise correlates§ with the pair of uncircled *meso* protons. Conformational inversion of the saddle (Figure 2) with concomitant local inversions of the three half-chairs leads to a conformer which, as a consequence of the specific constitutional and configurational symmetry of the molecule, is enantiomorphic to the original conformer and has interchanged local environments of the protons. Thus, the ^{1}H n.m.r. spectrum taken at room temperature shows only two singlets for the two pairs of *meso* protons (coalescence temperature approx. −35 °C). From ^{1}H n.m.r. data taken at nine temperatures between −61.7 and −15.3 °C, the specific rates of inversion and the activation parameters of the inversion barrier were determined using the program NMREX[10] for the iterative line shape fitting of calculated and observed spectra (for results see Figure 2).¶

Nickel(II) octaethyl-pyrrocorphinates are paramagnetic in nucleophilic solvents such as methanol or acetonitrile,[1e,3] but not in for example benzene, CH_2Cl_2, or CS_2. In nucleophilic solvents, the nickel ion is presumably hexa-co-ordinated and, therefore, its impetus to induce ligand contraction is reduced or absent.[7] Since in a saddle-inversion transition state the nickel ion should be more electrophilic than in the saddle conformer, barrier heights of saddle inversions may, therefore, depend on solvent nucleophilicity.

Barrier heights are also expected to depend on the configuration of the substituents at the ligand periphery.

|| Selected spectral data [for complete data and reaction conditions see ref. 1(e)]:

(**3**): m.p. 219 °C; $\lambda_{max.}$ (benzene) 326 (log ε 4.69, sh.), 341 (4.80, sh.), 347 (4.81), 361 (4.73), 379 (4.64), 443 (3.66, sh.), 470 (3.93, sh.), 503 (4.10), 546 (4.11), and 592 nm (4.17); ^{1}H n.m.r. δ (CS_2–CD_2Cl_2 9:1, 300 MHz) 0.93, 1.04, 1.06 (6 CH_3), 1.27 (2 CH_3), 1.71—1.86 (6 CH_2), 2.85 (2 CH_2), 3.25 (4 CH), 3.36 (2 CH), 5.74 (2 NH), 6.02 (s, C-5-H and C-10-H), 6.60 (s, C-15-H and C-20-H); *m/z* 540 (M^+, 100%).

(**4**): m.p. 232 °C; $\lambda_{max.}$ (hexane) 320—340 (plateau, log ε 4.32), 403 (5.26), 489 (3.45, sh.), 527 (3.61), 603 (3.86), and 661 nm (4.34); ^{1}H n.m.r. δ (CS_2–C_6D_6 9:1, room temp., 300 MHz) 0.961, 0.963, 0.98 (6 CH_3), 1.25 (2 CH_3), 1.44—1.82 (6 CH_2), 2.86 (2 CH_2), 3.17—3.38 (6 CH), 6.20 (sharp s, C-5-H and C-10-H), and 6.83 (broad s, C-15-H and C-20-H); *m/z* 596 (M^+ ^{58}Ni, 100%);

(**6**): m.p. 204 °C, $\lambda_{max.}$ (benzene) 331 (4.60), 389 (4.77), 467 (3.36), 508 (3.68), 694 (3.72, sh.), 772 (4.04, sh.), and 761 nm (4.81); δ (CS_2–$CD_2Cl_2Cl_2$ 2:1) 4.06 (m, 4 CH), and 7.91 (s, 4 *meso* protons); *m/z* 594 (M^+ ^{58}Ni, 100%).

§ Quasi-axial hydrogens show higher allylic–vinylic coupling constants than quasi-equatorial hydrogens (ref. 9).

¶ Theoretical spectra calculated for four isolated spins exchanging in pairs (A,B,C,D; A ⇄ B, C ⇄ D) least-square fitted to the signals of the *meso* protons in the experimental 300 MHz ^{1}H n.m.r. spectra taken at nine different temperatures. For details of the type of calculation and error analysis see ref. 10. Rate constants $k = 5.4\ s^{-1}$ (T = −61.7 °C; *R*-factor[10] = 0.082), 14.4 (−56.5; 0.076), 25.2 (−51.5; 0.071), 46.6 (−46.7; 0.100), 83.4 (−41.6; 0.036), 144.0 (−36.5; 0.037), 278.0 (−31.0; 0.046), 342.0 (−26.6; 0.068), and 1119 (−15.3; 0.081). Error limits deduced from estimated errors for T of ±1.0 °C and relative errors of ±18% for the highest and lowest rate constant.

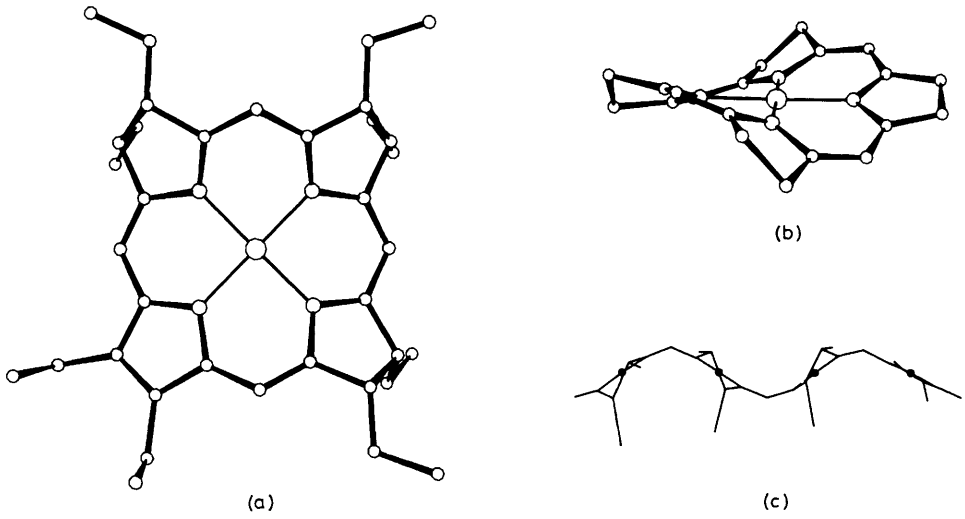


Figure 1. Crystal structure of nickel(II) *ccccc*-octaethyl-pyrrocorphinate (**4**).‡ (a) Projection into the co-ordination plane (H atoms omitted), (b) sideview of the hydroporphinoid ligand showing the saddle deformation (H atoms and ethyl substituents omitted), (c) cylinder projection (H atoms and terminal C atoms of ethyl groups omitted).

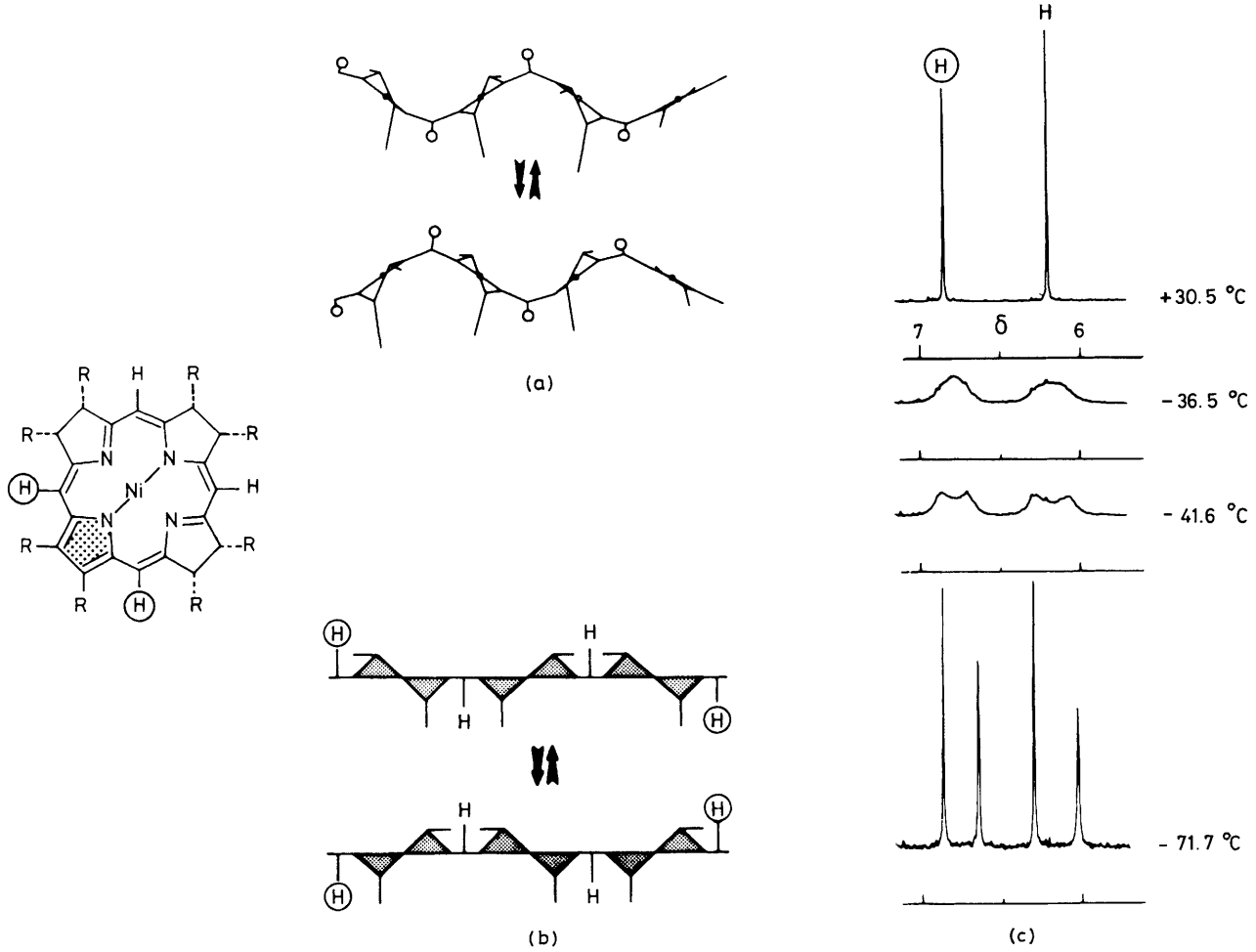


Figure 2. Conformational inversion of (**4**). (a) Cylinder projections, (b) abstraction of cylinder projections (ref. 3), (c) temperature dependence of the *meso* proton region of the ^1H n.m.r. spectrum of (**4**) in CS_2–benzene (9 : 1). Calculated activation parameters of inversion barrier:¶ E_a = 12.1 ± 0.7 kcal/mol^{-1}, log A_o = 13.3 ± 0.7; $\Delta H^{\ddagger}$ = 11.6 ± 0.7 kcal mol^{-1}, $\Delta S^{\ddagger}$ = 1.0 ± 1.4 cal mol^{-1} K^{-1}, $\Delta G^{\ddagger}$ = 11.3 ± 0.1 kcal mol^{-1}; k[25 °C] = 2.9 × 10^4 s^{-1}, 1 kcal = 4.184 kJ.

cis-Vicinal substituents should tend to increase the amplitude of the half-chair of a hydropyrrolic ring and, thereby, of the ligand saddle. In contrast to *trans*-vicinal substituents, *cis*-vicinal substituents must pass each other through an eclipsed conformation when saddle and half-chairs invert. Therefore, *cis*-vicinal substituents should increase the height of the saddle inversion barrier. In accord with this are the observations that, in the crystal, *ccccc*-(**4**) shows a more pronounced saddle than the corresponding *tctcc*- and *tcttc*-diastereoisomers[3] and, out of eight crystal structures of nickel(II) octaethylhydroporphinates,[3] the average half-chair amplitude of 12 hydropyrrolic rings with *trans*-ethyl groups is 0.25 Å, whereas the corresponding value of seven rings with *cis*-configuration is 0.35 Å.[3,4]

The general features of the crystal structure[3]‡ of the nickel(II) *ccc*-bacteriochlorinate (**6**) are similar to those of (**4**), with the exception of a significantly flatter ligand saddle. Accordingly, (**6**) is paramagnetic in MeOH but diamagnetic in MeCN, according to ^{1}H n.m.r. spectroscopy,[3] and the coalescence temperature for the *meso*-proton signals in the ^{1}H n.m.r. spectrum of (**6**) in CS_2–CD_2Cl_2 (2:1) is much lower (around −100 °C).[1e]

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