Molecular and Electronic Structure of (2,2′-Bidipyrrinato)nickel(II) Complexes

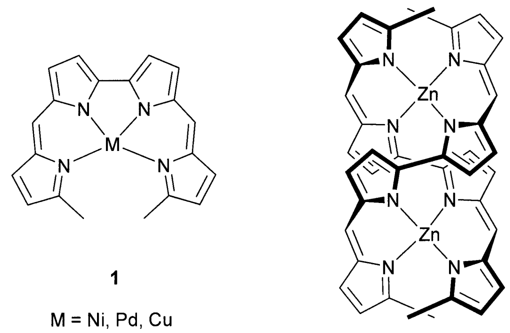
Martin Bröring,*[a] Carsten D. Brandt,[a] Johann Lex,[b] Hans-Ulrich Humpf,[c]
Jordi Bley-Escrich,[d] and Jean-Paul Gisselbrecht[d]

Keywords: Porphyrinoids / Nitrogen ligands / Nickel / Helical structures / Electrochemistry

Nickel complexes of eight differently substituted 2,2′-bidipyrrins have been prepared and fully characterized. The X-ray analyses of three of these complexes revealed helical chiral molecules. Despite the tetrahedral deviation from the square-planar coordination geometry at the metal centres, all compounds were found to be diamagnetic in nature. For (3,3′,4,4′,8,8′,9,9′-octaethyl-10,10′-dimethyl-6,6′-diphenyl-2,2′-bidipyrrinato)nickel, a separation into the enantiomers by chiral MPLC could be achieved, and the first CD spectra of enantiomerically pure tetrapyrrole helicates are reported. An electrochemical study of the new complexes allowed a first insight into the electronic structure of (2,2′-bidipyrrinato)nickel(II), disclosing a rather high energy HOMO and metal–ligand interaction similar to that observed in metalloporphyrins.

Introduction

2,2′-Bidipyrrins constitute fully conjugated, open-chain tetrapyrroles, which serve as dianionic ligands in coordination compounds. Although known for 40 years, little work was performed towards an understanding of the coordinating properties of 2,2′-bidipyrrins, and their use as ligands has been very limited so far. The first 2,2′-bidipyrrins were obtained by Johnson et al. as the respective palladium(II) complexes by a coupling reaction of α,ω-dibromodipyrrins, using 3% palladium oxide on strontium carbonate as the reagent.[1] Only little later did the first free-base ligands as well as some nickel(II) and copper(II) chelates become accessible through a simple demetalation/remetalation protocol.[2,3] The tendency of the employed metal ions Ni^{II}, Pd^{II}, and Cu^{II} to bind to dianionic tetrapyrrole ligands in a square-planar fashion, and the UV/Vis-spectroscopic features observed led to the assignment of these compounds to the metalloporphyrin-like structure **1**. The first X-ray analysis of a metallobidipyrrin was reported in late 1998 by Dolphin et al.[4] Their study of a zinc complex revealed the M_2L_2 complex **2** and proved that 2,2′-bidipyrrin ligands are well suited for adopting different conformations in coordination compounds (Scheme 1). This behaviour, however, has been found earlier in a small number of other bile-pigment analogue complexes.[5,6] We recently showed, that 2,2′-bidipyrrins are in fact sufficiently flexible to stabilise even cluster fragments.[7]



1

M = Ni, Pd, Cu

2

Scheme 1. Known coordination modes of 2,2′-bidipyrrin ligands

Our interest in these ligands arose from the fact, that 2,2′-bidipyrrins contain a dianionic N_4 coordination site, rather than the trianionic one found in most other bile-pigment analogues.[8] In addition to this favourable similarity with the porphyrin ligand, 2,2′-bidipyrrins are easily prepared in substantial amounts,[9] and metal complexes like **1** can be expected to display helical chiral geometries like those of other metalated bilenes.[10−18] As part of our ongoing efforts to establish helical metallo-2,2′-bidipyrrins as chiral analogues of catalytically active metalloporphyrins,[19] the determination of chirality in these complexes and investigations towards the stability of the anticipated, but never proven helical arrangement are of vital importance. This paper reports molecular and electronic features of a set of eight (2,2′-bidipyrrinato)nickel complexes **11−18** with different substituents in the *meso* positions.

Results and Discussion

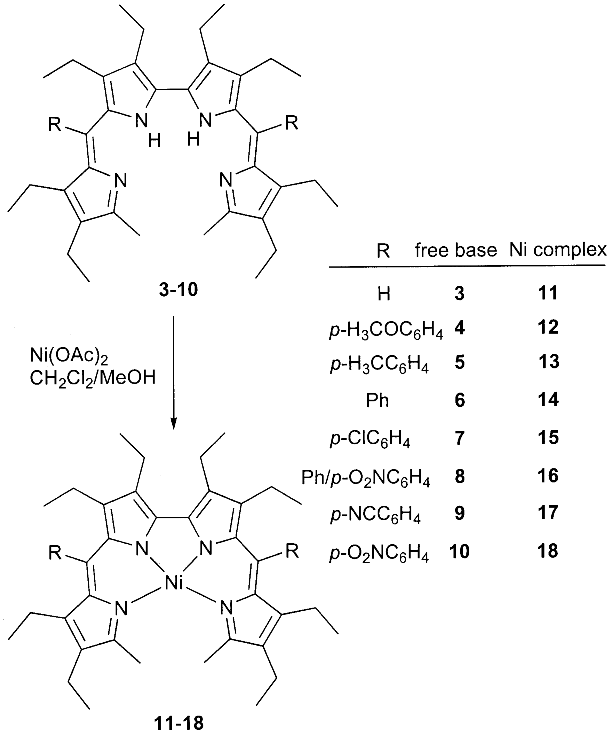
Synthesis and Characterization

The syntheses of (2,2′-bidipyrrinato)nickel complexes was achieved by stirring a solution of the respective ligands

---

[a] Institut für Anorganische Chemie, Universität Würzburg,
Am Hubland, 97074 Würzburg, Germany
E-mail: martin.broering@mail.uni-wuerzburg.de
[b] Institut für Organische Chemie, Universität Köln,
Greinstraße 4, 50939 Köln, Germany
[c] Institut für Pharmazie und Lebensmittelchemie, Universität Würzburg,
Am Hubland, 97074 Würzburg, Germany
[d] UMR 7512 C.N.R.S., Université Louis Pasteur,
4 rue Blaise Pascal, 67000 Strasbourg, France

3−10 [9] and excess nickel(II) acetate tetrahydrate in a 1:1 mixture of dichloromethane and methanol at ambient temperature for 30 min (Scheme 2). Following extractive workup and recrystallization from dichloromethane/methanol, the pure chelates **11−18** are obtained in good to excellent yields (86−94%).



R	free base	Ni complex
H	3	11
p-H$_3$COC$_6$H$_4$	4	12
p-H$_3$CC$_6$H$_4$	5	13
Ph	6	14
p-ClC$_6$H$_4$	7	15
Ph/p-O$_2$NC$_6$H$_4$	8	16
p-NCC$_6$H$_4$	9	17
p-O$_2$NC$_6$H$_4$	10	18

Scheme 2. Synthesis of (2,2′-bidipyrrinato)nickel(II) complexes **11**−**18**

All compounds gave satisfactory elemental analyses and were further characterized by mass spectra (see Exp. Sect.). The ^{1}H-NMR-spectroscopic investigation of **12−18** revealed unsymmetric aryl groups as shown for the dinitro derivative **18** (Figure 1), in that the AA′BB′ system of the respective protons of the free-base ligand is split into four distinct groups of signals for the nickel complex. This observation can be interpreted in terms of a helical conformation of the new complexes. An accompanying diastereotopic splitting of the ethyl CH$_2$ groups, however, could not be detected, since the steric overcrowding of substituents in the periphery leads to hindered rotation with concomitant line broadening. This line broadening is so severe in the ^{13}C NMR spectra, that only incomplete sets of signals could be detected for **12−18**. Despite a tetrahedral distortion from the square-planar environment of the nickel(II) centre, all the complexes **11−18** are found to be low-spin and therefore are diamagnetic in nature. This finding is further supported by the result of variable-temperature NMR-spectroscopic studies conducted on **13**, showing sharp signals for all alkyl groups above 80 °C.

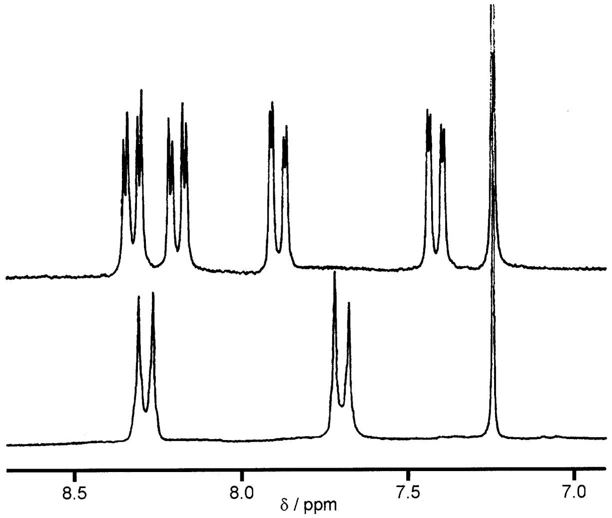


Figure 1. Aromatic regions of the ^{1}H NMR spectra of **10** (bottom) and **18** (top; 200 MHz, CDCl$_3$)

The fact, that the signal of the *meso* protons in **11** is detected $\Delta\delta = 0.62$ upfield with respect to the free base **3**, parallels the observations made in the porphyrin series ($\Delta\delta = 0.41$ for octaethylporphyrin and the respective nickel complex)[20] and gives a first indication, that the metal−ligand interactions are of a similar type in both cases. In agreement with this, the UV/Vis spectra of **11−18** and (porphyrinato)nickel complexes[21] show a somewhat related pattern with strong absorptions at 430 nm and several small ones between 500 and 900 nm (see Exp. Sect.). The red shift observed for **11−18** with respect to (porphyrinato)nickel complexes might be explained either in terms of a strained, nonplanar structure like in dodecasubstituted porphyrins,[22] and/or in a loss of symmetry, a scenario precedented by the absorption patterns of chlorins and bacteriochlorins.[23,24]

X-ray Analyses

The complexes **11**, **14**, and **16** were analysed by X-ray diffraction (Table 1). Crystals were grown in all cases by slow concentration of dichloromethane/*n*-hexane solutions. The pronounced helical structure of (2,2′-bidipyrrinato)-nickel complexes, which was already concluded from the NMR spectra, is the most striking feature of these complexes (**11**: Figure 2; **14**: Figure 3; **16**: Figure 4). The overlapping terminal methyl groups are located as close as 3.34 Å (**11**), 3.15 Å (**14**), and 3.66 Å (**16**) above each other, accounting for a certain degree of strain in these subunits. This strain has to be overcome by strong metal−nitrogen bonds. If the metal−nitrogen bonds are weak, the ligand will rather bind in an open, nonstrained fashion, as was demonstrated recently by Dolphin et al. on zinc complex **2**.[4]

The Ni−N bond lengths are also indicative of this strain, in that the nitrogen donors from the bipyrrolic units are bound more tightly [**11**: 1.8451(15) and 1.8498(14) Å; **14**:

Table 1. Selected bond lengths, distances [Å] and angles [°] for **11**, **14**, and **16**

	11	**14**	**16**
Ni−N(1)	1.9088(15)	1.889(2)	1.865(3)
Ni−N(2)	1.8451(15)	1.834(2)	1.840(3)
Ni−N(3)	1.8498(14)	1.834(2)	1.835(3)
Ni−N(4)	1.9068(15)	1.885(2)	1.893(3)
N(1)−C(1)	1.341(2)	1.342(3)	1.344(4)
N(1)−C(4)	1.409(2)	1.421(3)	1.431(5)
N(2)−C(6)	1.371(2)	1.374(3)	1.365(5)
N(2)−C(9)	1.349(2)	1.361(3)	1.362(4)
N(3)−C(10)	1.353(2)	1.356(3)	1.365(4)
N(3)−C(13)	1.373(2)	1.375(3)	1.362(5)
N(4)−C(15)	1.409(2)	1.418(3)	1.391(5)
N(4)−C(18)	1.340(2)	1.340(3)	1.350(4)
C(1)−C(2)	1.432(3)	1.424(4)	1.423(5)
C(2)−C(3)	1.372(3)	1.370(4)	1.399(5)
C(3)−C(4)	1.432(3)	1.461(4)	1.446(5)
C(4)−C(5)	1.380(3)	1.393(4)	1.413(5)
C(5)−C(6)	1.391(3)	1.419(4)	1.417(5)
C(6)−C(7)	1.426(3)	1.434(4)	1.433(4)
C(7)−C(8)	1.386(3)	1.393(4)	1.387(5)
C(8)−C(9)	1.428(3)	1.416(4)	1.423(5)
C(9)−C(10)	1.457(3)	1.456(4)	1.455(5)
C(10)−C(11)	1.425(3)	1.415(4)	1.412(5)
C(11)−C(12)	1.382(3)	1.395(4)	1.398(5)
C(12)−C(13)	1.430(3)	1.445(4)	1.444(4)
C(13)−C(14)	1.386(3)	1.417(4)	1.436(4)
C(14)−C(15)	1.383(3)	1.391(4)	1.410(5)
C(15)−C(16)	1.435(3)	1.454(4)	1.463(4)
C(16)−C(17)	1.365(3)	1.381(4)	1.360(5)
C(17)−C(18)	1.427(3)	1.426(4)	1.437(5)
$C_{term}\cdots C_{term}$	3.34	3.15	3.66
N(1)−Ni−N(2)	90.39(7)	90.03(10)	90.68(13)
N(1)−Ni−N(3)	161.72(7)	163.81(10)	164.77(13)
N(1)−Ni−N(4)	101.76(7)	100.67(10)	100.11(12)
N(2)−Ni−N(3)	80.72(7)	83.03(10)	83.03(13)
N(2)−Ni−N(4)	163.08(7)	164.10(10)	162.37(13)
N(3)−Ni−N(4)	90.55(6)	89.37(10)	89.53(12)
N(2)−C(9)−C(10)	109.57(15)	110.8(2)	111.2(3)
N(3)−C(10)−C(9)	109.99(15)	111.0(2)	110.6(3)
C(4)−C(5)−C(6)	125.45(18)	124.3(2)	124.5(4)
C(13)−C(14)−C(15)	125.33(17)	124.0(3)	123.2(3)

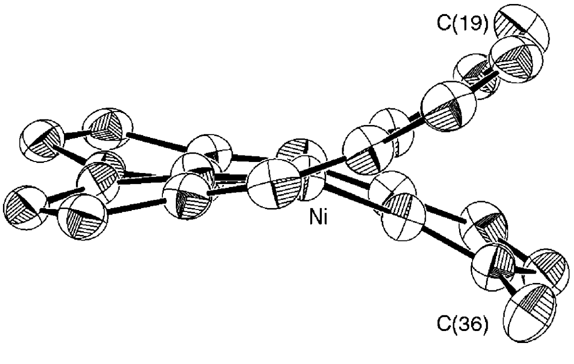


Figure 2. ORTEP plot of the molecular structure of **11** (side view)

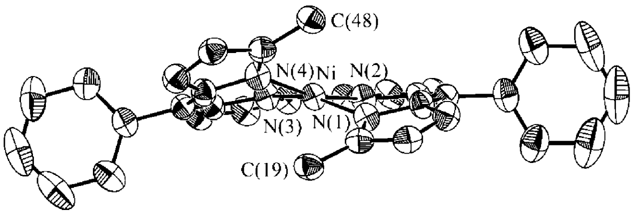


Figure 3. ORTEP plot of the molecular structure of **14** (front view)

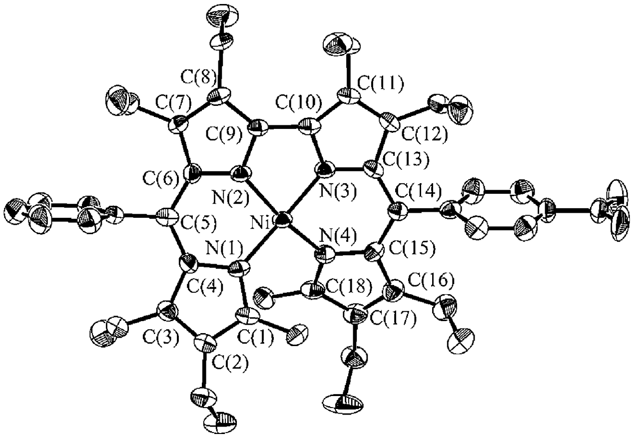


Figure 4. ORTEP plot of the molecular structure of **16** (top view)

1.834(2) and 1.834(2) Å; **16**: 1.835(3) and 1.840(3) Å] than those of the terminal C_4N rings [**11**: 1.9068(15) and 1.9088(15) Å; **14**: 1.885(2) and 1.889(2) Å; **16**: 1.865(3) and 1.893(3) Å]. All these bond lengths are shorter than those found for (porphyrinato)nickel complexes (1.90−1.96 Å), but still normal for low-spin $Ni^{II}-N$ bonds. As a consequence of the helical ligand geometry the nickel coordination spheres show a tetrahedral distortion from planarity [angle between the planes {N(2),N(3),Ni} and {N(1),N(4),Ni} for **11**: 19.9°; for **14**: 18.8°; for **16**: 19.7°].

The steric influence of the additional peripheral aryl substituents in **14** and **16** results in reduced $C_\alpha-C_{meso}-C_\alpha$ angles [for **11**: 125.45(18)° and 125.33(17)°; for **14**: 124.3(2)° and 124.0(3)°; for **16**: 124.5(4)° and 123.2(3)°], and therefore induces a more pronounced overlap of the terminal methyl groups. Due to the open-chain character of 2,2′-bidipyrrins, the ligand framework appears to be sufficiently flexible to overcome steric encumbrance by *in-plane* distortions, and does not parallel the *out-of-plane* twisting modes, which are characteristic for dodecasubstituted porphyrins and their metal chelates.[22] The perpendicular arrangement of the aryl groups in **14** and **16** inhibits a strong electronic communication between the π-systems of the aryl rings and the tetrapyrrole moiety, so that only a small influence of the different substituents of **12−18** on the metal centre may be expected. Therefore, the rather distorted framework of the unsymmetrically substituted complex **16** should be addressed to crystal packing effects rather than to the electronic influence of the additional NO_2 functionality.

It is a typical bond-length characteristic of metalloporphyrins, that the $C_\beta-C_\beta$ bonds within the five-membered rings are shorter than the respective $C_\alpha-C_\beta$ bonds.[25,26] This very same characteristic can be claimed for the (bidipyrrinato)nickel complexes **11**, **14**, and **16**, accounting for a large degree of π-electron delocalization within these compounds. In contrast to this similarity, the $C_\alpha-N-C_\alpha$ moieties of the terminal C_4N rings are found to be non-symmetric (**11**: 1.34 Å/1.41 Å; **14**: 1.34 Å/1.42 Å; **16**: 1.34 and 1.35

Å/1.39 and 1.43 Å) and indicate a partial azafulvene character in these substructures.

Enantioseparation of 14

Although the helical chirality of bile-pigment analogue complexes was recognized early in the history of this branch of porphyrin chemistry, no enantiomerically pure compound has hitherto been published. In one instance, Smith and co-workers conducted an NMR-spectroscopic study on a (*meso*-oxobiladienato)nickel(II) complex bearing diastereotopic side chains, and reported a high racemisation barrier of at least 80 kJ mol^{-1}.[27,28] In a different approach, Mizutani et al. attempted to use the helicity of a zinc complex of a biliverdin derivative for the diastereoselective binding of amino acids and found, that upon addition of enantiomerically pure amines one of the helicates builds up, which is in accordance with a rather low helix inversion barrier.[29−31] Since the literature was not conclusive about the stability of the helical coordination geometry of open-chain metallotetrapyrroles we decided to separate (2,2′-bidipyrrinato)nickel complexes into the enantiomers and study them independently.

Our initial attempts to separate the isomers of **11−18** on an analytical Pirkle column disclosed that this is in fact possible for all aryl-substituted derivatives **12−18**, but not for **11**. Obviously, the interaction of the aryl moieties with the chiral stationary phase is the key to separation. Compound **14** showed the most promising solubility properties of the compounds studied and was therefore chosen for a preparative separation. Using a Pirkle column and 2% acetone in *n*-hexane as the mobile phase, an 85% enrichment was achieved; due to the rather low solubility, however, only 1.3 mg of material could be resolved at a time. Enantiopure complexes were obtained by fractionated crystallisation of the enriched material collected from several runs with dichloromethane/*n*-hexane, from which the racemate crystallises more readily. The optical purity of the helicates was proven by analytical chiral MPLC to be > 97%.

The CD spectra of **14′** and **14′′**, recorded in dichloromethane ($c \approx 10^{-5}$ M), show a pattern similar to that known for biliverdin and its derivatives (Figure 5).[32,33] From the sign of the Cotton effect of the major band at 432 nm, the first eluted enantiomer **14′** can be assigned the *M* helical, and the other, **14′′**, the *P* helical isomer. This assignment is further supported by the recent findings by Vogel et al., who reported the same relationship between the sign of the Cotton effect and the helicity of the ligand for a (cyclooctaphyrinato)dipalladium.[34] The fact, that the maxima of the major CD and UV/Vis absorptions are found at the same wavelength (432 nm), is indicative of a strong electronic coupling, i.e. π-conjugation of both dipyrrin units in **14**, and is also found for biliverdin and other one-chromophore systems. For bilirubin-like tetrapyrroles, on the other hand, in which the dipyrrolic subunits are separated electronically by a CH_2 bridge, the two-chromophore arrangement leads to a bisignate CD signal within the major UV/Vis absorption, caused by exiton coupling of the independent subchromophores.[35,36]

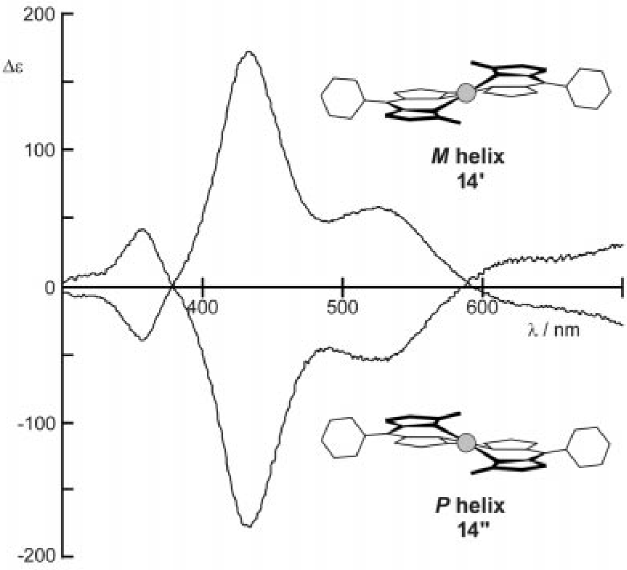


Figure 5. CD spectra of **14′** and **14′′** (CH_2Cl_2, $c \approx 10^{-5}$ M, 1 cm cell)

The stability of **14′** towards helix inversion was studied by prolonged heating of the complex in different solvents and determining the degree of racemisation by analytical chiral MPLC. Astonishingly, racemization was not ob-

Table 2. Electrochemical data for **3** and nickel complexes **11−18**

Compound (R)[a]	Red.2	Red.1	*p*-$O_2NC_6H_4$[b]	Ox.1	Ox.2	HLG[c]	2σ≅[d]
3	n.d.[e]	−1.82		−0.02	0.37	1.80	
11	−2.35	−1.71		−0.18	0.31	1.53	
12 (*p*-$MeOC_6H_4$)	−2.40	−1.77		−0.16	0.33	1.61	−0.536
13 (*p*-MeC_6H_4)	−2.40	−1.76		−0.15	0.35	1.61	−0.340
14 (Ph)	−2.36	−1.75		−0.13	0.36	1.62	0
15 (*p*-ClC_6H_4)	−2.30	−1.69		−0.10	0.38	1.59	0.454
16 (Ph/*p*-$O_2NC_6H_4$)	n.d.	−1.71	−1.44	−0.08	0.40	1.63	0.778
17 (*p*-NCC_6H_4)	−2.14[f]	−1.63		−0.07	0.41	1.56	1.32
18 (*p*-$O_2NC_6H_4$)	n.d.	−1.63	−1.46	−0.05	0.44	1.58	1.556

[a] Measured on a platinum electrode in PhCN solution with 0.1 M $n\text{Bu}_4\text{NPF}_6$. Values are given in V relative to the Fc/Fc^+ couple. − [b] Reversible two-electron reduction of the nitrophenyl substituents. − [c] HOMO−LUMO gap (= $E_{\text{Ox.1}} - E_{\text{Red.1}}$). − [d] σ values taken from ref.[37] − [e] n.d. = not determined. − [f] Quasi-reversible electron transfer.

served in any instance, and even after 14 h in molten naphthalene at 218 °C only the starting enantiomer could be detected. This result is in accordance with the one reported earlier by Smith and co-workers.[27,28] Despite the fact, that the small size of the low-spin d^8-nickel(II) ion and its strong binding to the ligand certainly supports the helix to a large extent, this extreme resistance against inversion processes suggests, that other metallo-2,2′-bidipyrrins will behave in a similar fashion.

Electrochemistry

In order to gain insight into the electronic structure of (bidipyrrinato)nickel complexes an electrochemical investigation was undertaken on the complexes **11−18**. Table 2 summarises the conditions and observed redox potentials for these as well as for the free-base ligand **3**.

All metallated compounds gave well-defined CVs, in which they undergo two reversible one-electron oxidations at rather low potentials. In reduction, the first step is reversible and well resolved (with exception of the nitrophenyl-substituted derivatives **16** and **18**), whereas the second step occurs close to the electrolytic discharge. The nitrophenyl derivatives **16** and **18** display a specific redox behaviour. The waves at −1.44 V (**16**) and −1.46 V (**18**) vs. Fc/Fc$^+$ involve one and two electrons, respectively, and correspond to the reduction of the nitrophenyl units, which act as independent redox centres. As no data on the redox behaviour of porphyrins bearing nitrophenyl substituents on the *meso* positions could be found in the literature, 4,4′-dinitrobiphenyl was used as a reference. This compound showed a similar two-electron wave at −1.49 V. The redox characteristics of the free-base ligand **3** obviously deviate severely from those of the metallated species (Table 2). This behaviour is most probably due to the open conformation of **3**.

When plotting the redox potentials of **12−18** versus the Hammett constants of the phenyl substituents σ, straight lines were obtained in agreement with the previously reported potential evolution for different tetraarylporphyrins (Figure 6). In our case, the observed slopes were equal to 52 and 47 mV for the first and second oxidation, respectively, whereas the slope for the first reduction equals 71 mV. These values also parallel the above-mentioned findings in the porphyrin series.[37] This linear evolution of the redox potentials with the substituents is a good indication of ligand-centred electron transfers as metal-centred electron transfers are less sensitive to substituent effects. Further spectroelectrochemical and EPR studies towards the electronic structure of one- and two-electron-oxidized (2,2′-bidipyrrinato)nickel(II) complexes are currently under investigation.

Comparing the electrochemical behaviour of **11** (NiOEBDP) and (octaethylporphyrinato)nickel(II) (NiOEP), a striking similarity appears in the LUMO energy levels of both compounds, while the HOMO of **11** is raised by 0.58 V with respect to NiOEP. The difference thus occurring in the HOMO−LUMO gaps of these complexes (Figure 7) corresponds qualitatively with the UV/Vis-spectroscopic observation, that the maximum of the longest-wavelength band is detected to be red-shifted from 551 nm in NiOEP to 863 nm in **11**.

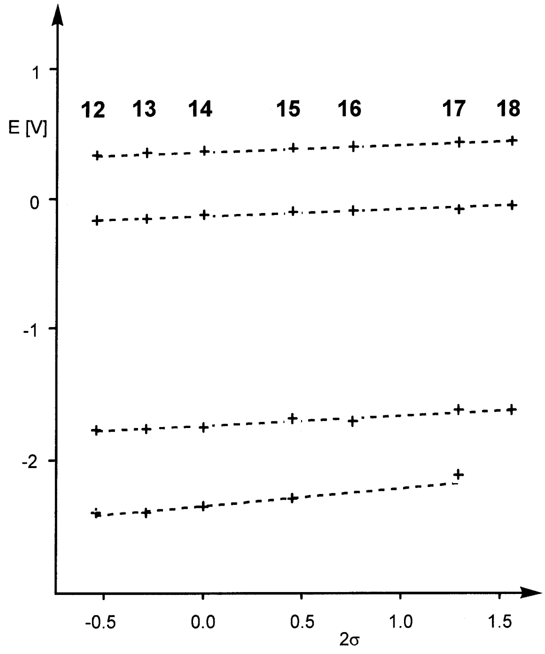


Figure 6. Evolution of redox potentials of **12−18** with Hammett constants σ

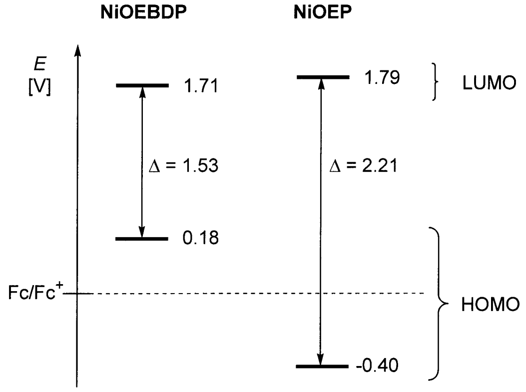


Figure 7. HOMO and LUMO energy levels of (2,2′-bidipyrrinato)nickel(II) (**9**) (NiOEBDP) and (octaethylporphyrinato)nickel(II) (NiOEP) as derived from electrochemical data

Conclusion

Our studies on the (2,2′-bidipyrrinato)nickel complexes **11−18** revealed complexes related to (porphyrinato)nickel complexes with respect to both, structural and electronic properties. Both ligands serve as dianionic N_4 chelates when interacting with the divalent nickel ion and produce low-spin, (distorted) square-planar coordination compounds. However, 2,2′-bidipyrrinato complexes show some special features due to their build-up as open-chain tetrapyrroles, of which the pronounced and stable helical conformation and the high-energy HOMO are the most obvious.

An interpretation of the differences found mainly in the electronic structures of (2,2′-bidipyrrinato)nickel(II) complexes and (porphyrinato)nickel(II) complexes is not trivial at all, since the latter contain an aromatic 22π system, while the open-chain analogues constitute non-aromatic 20π-electron compounds without aromatic stabilisation. From the point of view of ligand electronics, any comparison of these differing classes must therefore fail, and it is quite surprising, that the spectral and structural features of (2,2′-bidipyrrinato)nickel complexes match so well with those obtained on aromatic (porphyrinato)nickel variants like chlorins, bacteriochlorins,[23,24] or overcrowded porphyrins.[22] Well-established interpretation schemes like energetic contributions through a strained, nonplanar structure and/or loss of symmetry do, when applied to these open-chain nickel(II) complexes, in fact, result in a useful description of the observed properties. While electronically the differences between the 2,2′-bidipyrrin and the porphyrin ligand are obvious, the influence on the central nickel(II) ion is too small to be detected by the applied methods. Two dipyrrin units arranged in a way as to form a (distorted) square-planar, dianionic N_4 chelate ligand thus appear sufficient to mimic at least some of the coordination chemistry of aromatic, porphyrinoid ligands.

The data presented here for a group of model complexes suggests, that helical chiral metallo-2,2′-bidipyrrins might well have the potential to serve as valuable porphyrinoid catalysts in enantioselective transformations. We are currently exploring this possibility.

Experimental Section

Solvents for chromatography were HPLC grade. All reagents and solvents were purchased from commercial sources and used as received. − NMR spectra were obtained in $CDCl_3$ solutions with a Bruker AC 200 spectrometer. Chemical shifts (δ) are given in ppm relative to residual protio solvent resonances (^1H spectra) or to chloroform (^{13}C). − Mass spectra (EI, 70 eV or FAB) were recorded with a Finnigan 90 MAT instrument; *m/z* alues are given for the most abundant isotopes only. − Melting points were measured by DTA with a Thermoanalyzer DuPont 9000. − Elemental analyses (C, H N) were performed at the microanalytical laboratory of the Institut für Anorganische Chemie, Universität Würzburg. − UV/Vis spectra were obtained in dichloromethane solution ($c \approx 10^{-4}$ mol l^{-1}) with a Hitachi U-3200 spectrophotometer. − Chiral MPLC was performed on Pirkle-type columns (D-phenylglycine on spherical silica gel; analytical: 25 cm × 4.6 mm, particle size 5 μ; preparative: 50 cm × 21.1 mm, particle size 10 μ), using a Latek P402 chromatographic system, and the fractions were detected by single-point UV absorption at 400 nm. − CD spectra were recorded as dichloromethane solutions in a 1-cm cell with a Jasco J 600 CD spectrometer. − Cyclic voltammetry was carried out in benzonitrile containing nBu_4NPF_6 as supporting electrolyte (0.1 M). Benzonitrile (Aldrich) was dried with anhydrous $CaCl_2$ for 2 d, and further distilled from P_2O_5 under reduced pressure of argon. nBu_4NPF_6 (Fluka, electrochemical grade) was dried under vacuum at 65 °C. Before use, the 0.1 M solution of nBu_4NPF_6 in benzonitrile was purified in a glove box on activated neutral alumina (Merck). The measurements were carried out in the glove box using a classical three-electrode cell. The working electrode was a platinum disk (diameter 2 mm), the pseudo reference electrode and the counter electrode being platinum wires. All potentials are given against the ferrocene/ferrocenium couple used as internal standard. The cell was connected to an EG&G PAR potentiostat (Model 273) interfaced with a PC.

Preparation of the Nickel Complexes

(2,2′-Bidipyrrinato)nickel Complexes 11−18. − General Procedure: 0.1 mmol of 2,2′-bidipyrrin **3−10** and 566 mg (2 mmol) nickel(II) acetate tetrahydrate were stirred in a mixture of 30 mL of methanol and 30 mL of dichloromethane for 30 min (colour change from deep blue to brownish green). The reaction mixture was extracted twice with 100 mL of water, dried with sodium sulfate, and the solvent was removed in vacuo. Recrystallization from dichloromethane/methanol yielded the title compounds as violet crystals.

[3,3′,4,4′,8,8′,9,9′-Octaethyl-10,10′-dimethyl-2,2′-bi(dipyrrinato)]nickel (11): Yield 548 mg (92%); m.p. 257 °C. − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.81 (t, 6 H, ^3J = 7.5 Hz, 2 × CH_3), 0.99 (t, 6 H, ^3J = 7.5 Hz, 2 × CH_3), 1.01 (t, 6 H, ^3J = 7.5 Hz, 2 × CH_3), 1.05 (t, 6 H, ^3J = 7.5 Hz, 2 × CH_3), 1.99 (q, ^3J = 7.5 Hz, 4 H, 2 × CH_2CH_3), 2.31−2.16 (m, 12 H, 6 × CH_2CH_3), 2.32 (s, 6 H, terminal CH_3), 6.04 (s, 2 H, H_{meso}). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.1, 16.7, 17.1, 17.2, 17.4, 17.5, 17.6, 17.8, 18.2, 119.5, 127.8, 130.9, 132.9, 136.9, 140.4, 148.2, 151.5, 168.8. − UV/Vis (dichloromethane): λ_{max} (ε) = 306 (21200), 353 (21100), 432 (80700), 535 (17800), 609 sh (13300), 864 nm (5600 mol^{-1} dm^3 cm^{-1}). − MS (70 eV, EI): *m/z* = 594 [M^+], 297 [M^{2+}]. − $C_{36}H_{48}N_4Ni$ (595.49): calcd. C 72.61, H 8.12, N 9.41; found C 72.50, H 7.84, N 9.28.

Crystallographic Data for 11: $C_{36}H_{48}N_4Ni$, violet cubes obtained by slow concentration of a CH_2Cl_2/*n*-hexane solution, crystal size: 0.25 × 0.20 × 0.20 mm, monoclinic, space group $P2_1/c$, a = 12.867(1), b = 20.140(1), c = 13.270(1) Å, β = 110.42(1)°, V = 3222.7(4) $Å^3$, $\rho_{calcd.}$ = 1.227 g cm^{-3}, Z = 4, $2\theta_{max}$ = 54°, Mo-K_α radiation, λ = 0.71073 Å, scan mode: φ/ω-scans, T = 293(2) K, 24167 measured, 6701 independent reflections, 5457 reflections observed for $I > 2\sigma(I)$, μ = 0.632 mm^{-1}, solved with direct methods (MolEN, Enraf−Nonius), refined with full-matrix least squares on F^2 (SHELXL-97, G. Sheldrick, University of Göttingen), 563 parameters, H atoms refined with isotropic temperature factors. R = 0.0361, wR = 0.0906, residual electron density ρ = 0.338/−0.198 e $Å^{-3}$. Crystallographic data (excluding structure factors) for the structure reported have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-153981. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

[6,6′-Bis(*p*-anisyl)-3,3′,4,4′,8,8′,9,9′-octaethyl-10,10′-dimethyl-2,2′-bidipyrrinato]nickel (12): Yield 759 mg (94%); m.p. 263 °C. − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.60 (t, 6 H, ^3J = 7.5 Hz, 2 × CH_3), 0.62 (t, 6 H, ^3J = 7.5 Hz, 2 × CH_3), 0.80 (t, 6 H, ^3J = 7.5 Hz, 2 × CH_3), 0.97 (t, 6 H, ^3J = 7.5 Hz, 2 × CH_3), 1.13 (m, 4 H, 2 × CH_2CH_3), 1.49 (br.s, 4 H, 2 × CH_2CH_3), 2.1, 2.27 (2 × br.s, 14 H, terminal CH_3 and 4 × CH_2CH_3), 3.85 (s, 6 H, OCH_3), 6.82 (d, ^3J = 8.4 Hz, 2 H, H_{aryl}), 6.92 (d, ^3J = 8.4 Hz, 2 H, H_{aryl}), 7.07 (d, ^3J = 8.4 Hz, 2 H, H_{aryl}), 7.53 (d, H ^3J = 8.4 Hz, H_{aryl}). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.3, 16.8, 17.4, 18.0, 18.5, 19.3, 55.3, 112.7, 113.0, 129.5, 129.8, 130.6, 130.7, 132.7, 142.6, 151.1, 159.4. − UV/Vis (dichloromethane): λ_{max} (ε) = 308 (26700), 354 (21200), 432 (79800), 532 (18100), 613 sh (13700), 859 nm (5900 mol^{-1} dm^3 cm^{-1}). − MS (FAB): *m/z* = 806 [M^+]. − $C_{50}H_{60}N_4NiO_2$ (807.73): calcd. C 74.35, H 7.49, N 6.94; found C 73.99, H 7.38, N 6.70.

[3,3′,4,4′,8,8′,9,9′-Octaethyl-10,10′-dimethyl-6,6′-bis(*p*-tolyl)-2,2′-bidipyrrinato]nickel (13): Yield 683 mg (88%); m.p. > 300 °C. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.59 (t, 6 H, ^3J = 7.5 Hz, 2 × CH_3), 0.60 (t, 6 H, ^3J = 7.5 Hz, 2 × CH_3), 0.80 (t, 6 H, ^3J = 7.5 Hz, 2 × CH_3), 0.97 (t, 6 H, ^3J = 7.5 Hz, 2 × CH_3), 1.11 (m, 4 H, 2 × CH_2CH_3), 1.45 (br.s, 4 H, 2 × CH_2CH_3), 2.2 (m, 14 H, terminal CH_3 and 4 × CH_2CH_3), 2.40 (s, 6 H, $ArCH_3$), 7.06 (m, 4 H, H_{aryl}), 7.19 (d, ^3J = 7.6 Hz, 2 H, H_{aryl}), 7.51 (d, ^3J = 7.6 Hz, 2 H, H_{aryl}). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.4, 16.7, 16.9, 17.4, 17.7, 18.0, 18.5, 19.3, 21.4, 128.1, 129.5, 132.6, 134.4, 137.6, 142.5, 151.0, 168.1. − UV/Vis (dichloromethane): λ_{max} (ε) = 307 (26100), 353 (20800), 434 (78200), 534 (17700), 613 sh (13500), 863 nm (5700 mol^{-1} dm^3 cm^{-1}). − MS (FAB): *m*/*z* = 774 [M$^+$]. − $C_{50}H_{60}N_4Ni$ (775.73): calcd. C 77.42, H 7.80, N 7.22; found C 77.11, H 7.91, N 7.02.

[3,3′,4,4′,8,8′,9,9′-Octaethyl-10,10′-dimethyl-6,6′-diphenyl-2,2′-bidipyrrinato]nickel (14): Yield 658 mg (88%); m.p. 292 °C. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.58 (t, 6 H, ^3J = 7.5 Hz, 2 × CH_3), 0.59 (t, 6 H, ^3J = 7.5 Hz, 2 × CH_3), 0.80 (t, 6 H, ^3J = 7.5 Hz, 2 × CH_3), 0.98 (t, 6 H, ^3J = 7.5 Hz, 2 × CH_3), 0.94−1.54 (m, 8 H, 4 × CH_2CH_3), 1.96, 2.26 (2 × br.s, 14 H, terminal CH_3 and 4 × CH_2CH_3), 7.16−7.66 (m, 10 H, H_{phenyl}). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.4, 16.6, 16.8, 17.3, 17.4, 17.8, 18.0, 18.4, 19.2, 127.3, 127.4, 128.0, 129.6, 129.7, 132.8, 137.5, 142.5. − UV/Vis (dichloromethane): λ_{max} (ε) = 308 (26400), 354 (21000), 433 (79000), 535 (17900), 611 sh (13600), 863 nm (5800 mol^{-1} dm^3 cm^{-1}). − MS (70 eV, EI): *m*/*z* = 746 [M$^+$], 373 (M^{2+}). − $C_{48}H_{56}N_4Ni$ (747.68): calcd. C 77.11, H 7.55, N 7.49; found C 76.88, H 7.29, N 7.39. − Enantioseparation was effected at 10 bar (flow rate 800 mL h^{-1}); elution times: 72.4 min (F1) and 77.0 min (F2). − CD (dichloromethane): λ_{max} (Δε) (**14′**) = 357 (−39.68), 432 (172.97), 527 nm (58.06 l mol^{-1} cm^{-1}); (**14′′**) = 357 (42.02), 432 (−175.71), 527 nm (−54.16 l mol^{-1} cm^{-1}).

Crystallographic Data for 14: $C_{48}H_{56}N_4Ni$, blue-violet needles obtained by slow concentration of a CH_2Cl_2/*n*-hexane solution, crystal size: 0.25 × 0.15 × 0.10 mm, monoclinic, space group $P2_1/n$, *a* = 14.272(1), *b* = 11.529(1), *c* = 25.195(1) Å, β = 93.41(1)°, *V* = 4138.3(5) Å^3, $\rho_{calcd.}$ = 1.200 g cm^{-3}, *Z* = 4, $2\theta_{max}$ = 54°, Mo-K_α radiation, λ = 0.71073 Å, scan mode: φ/ω-scans, *T* = 293(2) K, 28093 measured, 8845 independent reflections, 5818 reflections observed for $I > 2\sigma(I)$, μ = 0.506 mm^{-1}, solved with direct methods (MolEN, Enraf−Nonius), refined with full-matrix least squares on F^2 (SHELXL-97, G. Sheldrick, University of Göttingen), 703 parameters, H atoms refined with isotropic temperature factors. *R* = 0.0577, *wR* = 0.0972, residual electron density ρ = 0.278/−0.232 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-153982. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

[6,6′-Bis(*p*-chlorophenyl)-3,3′,4,4′,8,8′,9,9′-octaethyl-10,10′-dimethyl-2,2′-bidipyrrinato]nickel (15): Yield 759 mg (93%); m.p. > 300 °C. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.60 (t, 6 H, ^3J = 7.5 Hz, 2 × CH_3), 0.61 (t, 6 H, ^3J = 7.5 Hz, 2 × CH_3), 0.80 (t, 6 H, ^3J = 7.5 Hz, 2 × CH_3), 0.97 (t, 6 H, ^3J = 7.5 Hz, 2 × CH_3), 1.11 (m, 4 H, 2 × CH_2CH_3), 1.48 (m, 4 H, 2 × CH_2CH_3), 2.0, 2.25 (2 × br.s, 14 H, terminal CH_3 and 4 × CH_2CH_3), 7.13 (dd, 2 H, ^3J = 8.0 Hz, H_{aryl}), 7.28 (dd, 2 H, ^3J = 8.0 Hz, H_{aryl}), 7.40 (dd, 2 H, ^3J = 8.0 Hz, H_{aryl}), 7.60 (dd, 2 H, ^3J = 8.0 Hz, H_{aryl}). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.3, 16.6, 16.9, 17.3, 17.5, 17.8, 18.0, 18.5, 19.3, 127.8, 129.9, 131.0, 132.5, 133.1, 134.0, 134.9, 135.9, 138.7, 142.5, 150.9, 168.8. − UV/Vis (dichloromethane): λ_{max} (ε) = 310 (26900), 352 (21400), 433 (81100), 535 (18300), 610 sh (13900), 863 nm (6000 mol^{-1} dm^3 cm^{-1}). − MS (FAB): *m*/*z* = 814 [M$^+$]. − $C_{48}H_{54}Cl_2N_4Ni$ (816.58): calcd. C 70.60, H 6.67, N 6.86; found C 70.29, H 6.65, N 6.68.

[3,3′,4,4′,8,8′,9,9′-Octaethyl-10,10′-dimethyl-6-(*p*-nitrophenyl)-6′-phenyl-2,2′-bidipyrrinato]nickel (16): Yield 680 mg (86%); m.p. 241 °C (decomp.). − ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 0.61 (t, 6 H, ^3J = 7.5 Hz, 2 × CH_3), 0.63 (t, 6 H, ^3J = 7.5 Hz, 2 × CH_3), 0.83 (t, 6 H, ^3J = 7.5 Hz, 2 × CH_3), 0.99 (t, 6 H, ^3J = 7.5 Hz, 2 × CH_3), 1.0−1.6 (m, 8 H, 4 × CH_2CH_3), 2.0, 2.31 (2 × br.s, 14 H, terminal CH_3 and 4 × CH_2CH_3), 7.17−8.38 (m, 9 H, H_{aryl}). − ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ = 14.5, 16.8, 17.0, 17.1, 17.4, 17.5, 17.8, 18.3, 18.4, 18.8, 19.0, 19.7, 19.8, 123.2, 123.4, 128.0, 128.1, 128.6, 130.0, 130.1, 130.3, 130.5, 131.7, 132.1, 133.2, 134.0, 134.2, 134.8, 136.0, 137.6, 137.7, 141.0, 142.5, 142.8, 145.2, 148.3, 150.8, 151.0, 152.3, 152.4, 170.1. − UV/Vis (dichloromethane): λ_{max} (ε) = 311 (27700), 357 (20200), 434 (77100), 533 (16600), 619 sh (14600), 860 nm (4900 mol^{-1} dm^3 cm^{-1}). − MS (FAB): *m*/*z* = 791 [M$^+$]. − $C_{48}H_{55}N_5NiO_2$ (792.68): calcd. C 72.73, H 6.99, N 8.84; found C 72.70, H 6.93, N 8.57.

Crystallographic Data for 16: $C_{48}H_{55}N_5NiO_2$, dark violet cubes obtained by slow concentration of a CH_2Cl_2/*n*-hexane solution, crystal size: 0.10 × 0.10 × 0.10 mm, triclinic, space group $P\bar{1}$ *a* = 12.911(3), *b* = 13.442(3), *c* = 14.264(3) Å, α = 108.85(3), β = 105.43(3), γ = 106.38°, *V* = 2103.8(7) Å^3, $\rho_{calcd.}$ = 1.251 g cm^{-3}, *Z* = 2, $2\theta_{max}$ = 50°, Mo-K_α radiation, λ = 0.71073 Å, scan mode: φ-scans, *T* = 173(2) K, 22070 measured, 6950 independent reflections, 3924 reflections observed for $I > 2\sigma(I)$, μ = 0.506 mm^{-1}, solved with direct methods (SHELXS-97, G. Sheldrick, University of Göttingen), refined with full-matrix least squares on F^2 (SHELXL-97, G. Sheldrick, University of Göttingen), 542 parameters, H atoms refined with isotropic temperature factors. *R* = 0.0487, *wR* = 0.0920, residual electron density ρ = 0.371/−0.355 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-161005. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

[6,6′-Bis(*p*-cyanophenyl)-3,3′,4,4′,8,8′,9,9′-octaethyl-10,10′-dimethyl-2,2′-bidipyrrinato]nickel (17): Yield 724 mg (91%); m.p. 224 °C (decomp.). − ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 0.60 (t, 6 H, ^3J = 7.5 Hz, 2 × CH_3), 0.62 (t, 6 H, ^3J = 7.5 Hz, 2 × CH_3), 0.83 (t, 6 H, ^3J = 7.5 Hz, 2 × CH_3), 1.02 (t, 6 H, ^3J = 7.5 Hz, 2 × CH_3), 1.0−1.5 (m, 8 H, 4 × CH_2CH_3), 2.0, 2.28 (2 × br.s, 14 H, terminal CH_3 and 4 × CH_2CH_3), 7.38 (d, ^3J = 8.1 Hz, 2 H, H_{aryl}), 7.66 (d, ^3J = 8.1 Hz, 2 H, H_{aryl}), 7.79 (d, ^3J = 8.1 Hz, 2 H, H_{aryl}), 7.87 (d, ^3J = 8.1 Hz, 2 H, H_{aryl}); δ = ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ = 14.5, 16.9, 17.1, 17.4, 17.8, 18.3, 18.4, 18.9, 19.8, 112.7, 119.2, 130.6, 131.1, 131.4, 131.9, 132.1, 132.3, 134.4, 135.2, 138.3, 142.8, 151.6, 151.7, 170.6. − UV/Vis (dichloromethane): λ_{max} (ε) = 312 (28900), 353 (21000), 435 (79900), 534 (17700), 613 sh (14500), 861 nm (5700 mol^{-1} dm^3 cm^{-1}). − MS (FAB): *m*/*z* = 796 [M$^+$]. − $C_{50}H_{54}N_6Ni$ (797.70): calcd. C 75.29, H 6.82, N 10.54; found C 74.95, H 6.63, N 10.26.

[3,3′,4,4′,8,8′,9,9′-Octaethyl-10,10′-dimethyl-6,6′-bis(*p*-nitrophenyl)-2,2′-bidipyrrinato]nickel (18): Yield 729 mg (87%); m.p. > 300 °C. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.58 (t, 6 H, ^3J =

7.5 Hz, 2 × CH_3), 0.59 (t, 6 H, ^3J = 7.5 Hz, 2 × CH_3), 0.80 (t, 6 H, ^3J = 7.5 Hz, 2 × CH_3), 0.97 (t, 6 H, ^3J = 7.5 Hz, 2 × CH_3), 1.0−1.5 (m, 8 H, 4 × CH_2CH_3), 2.0, 2.26 (2 × br.s, 14 H, terminal CH_3 and 4 × CH_2CH_3), 7.41 (d, ^3J = 8.2 Hz, 2 H, H_{aryl}), 7.88 (d, ^3J = 8.2 Hz, 2 H, H_{aryl}), 8.19 (d, ^3J = 8.2 Hz, 2 H, H_{aryl}), 8.32 (d, ^3J = 8.2 Hz, 2 H, H_{aryl}). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.2, 16.5, 16.9, 17.2, 17.4, 17.9, 18.0, 18.6, 19.4, 122.7, 130.5, 130.9, 131.2, 133.6, 134.3, 137.2, 142.3, 144.7, 147.8, 150.7, 152.2, 169.7. − UV/Vis (dichloromethane): λ_{max} (ε) = 314 (29900), 354 (21100), 434 (79200), 534 (17900), 615 sh (13500), 862 nm (5800 mol^{-1} dm^3 cm^{-1}). − MS (FAB): m/z = 836 [M^+]. − $C_{48}H_{54}N_6NiO_4$ (837.68): calcd. C 68.82, H 6.50, N 10.03; found C 68.45, H 6.33, N 9.69.

Acknowledgments

This work was funded by the Deutsche Forschungsgemeinschaft (Emmy−Noether-Programm) and by the Centre National de la Recherche Scientifique (C.N.R.S). We thank Professor H. Werner (Würzburg) and Professor A. Berkessel (Köln) for their support.

---

[1] A. W. Johnson, R. Price, *J. Chem. Soc.* **1960**, 1649−1653.
[2] A. W. Johnson, I. T. Kay, R. Rodrigo, *J. Chem. Soc.* **1963**, 2336−2342.
[3] D. Dolphin, R. L. N. Harris, J. L. Huppatz, A. W. Johnson, I. T. Kay, J. Leng, *J. Chem. Soc. C* **1966**, 98−106.
[4] Y. Zhang, A. Thompson, S. J. Rettig, D. Dolphin, *J. Am. Chem. Soc.* **1998**, *120*, 13537−13538.
[5] G. Struckmeier, U. Thewalt, J.-H. Fuhrhop, *J. Am. Chem. Soc.* **1976**, *98*, 278−279.
[6] W. S. Sheldrick, J. Engel, *J. Chem. Soc., Chem. Commun.* **1980**, 5−6.
[7] M. Bröring, A. Pfister, K. Ilg, *Chem. Commun.* **2000**, 1407−1408.
[8] H. Falk, *The Chemistry of Linear Oligopyrrols and Bile Pigments*, Springer, Wien, **1989**.
[9] M. Bröring, *Synthesis* **2000**, 1291−1294.
[10] M. Dobler, J. D. Dunitz, *Helv. Chim. Acta* **1971**, *54*, 90−98.
[11] M. Currie, J. D. Dunitz, *Helv. Chim. Acta* **1971**, *54*, 98−112.
[12] J. V. Bonfiglio, R. Bonnett, M. B. Hursthouse, K. M. Abdul Malik, *J. Chem. Soc., Chem. Commun.* **1977**, 83−84.
[13] J. V. Bonfiglio, R. Bonnett, D. G. Buckley, D. Hamzetash, M. B. Hursthouse, K. M. Abdul Malik, A. F. McDonagh, J. Trotter, *Tetrahedron* **1983**, *39*, 1865−1874.
[14] A. L. Balch, M. Mazzanti, B. C. Noll, M. M. Olmstead, *J. Am. Chem. Soc.* **1993**, *115*, 12206−12207.
[15] A. L. Balch, M. Mazzanti, B. C. Noll, M. M. Olmstead, *J. Am. Chem. Soc.* **1994**, *116*, 9114−9122.
[16] S. Attar, A. L. Balch, P. M. Van Calcar, K. Winkler, *J. Am. Chem. Soc.* **1997**, *119*, 3317−3323.
[17] R. Koerner, M. M. Olmstead, A. Ozarowski, S. L. Phillips, R. M. Van Calcar, K. Winkler, A. L. Balch, *J. Am. Chem. Soc.* **1998**, *120*, 1274−1284.
[18] P. A. Lord, M. M. Olmstead, A. L. Balch, *Inorg. Chem.* **2000**, *39*, 1128−1134.
[19] *The Porphyrin Handbook*, vol. 4 (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic, San Diego, CA, **2000**.
[20] C. J. Medforth in *The Porphyrin Handbook*, vol. 5 (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic, San Diego, CA, **2000**, chapter 35, pp. 1−80.
[21] D. L. Cullen, E. F. Meyer, *J. Am. Chem. Soc.* **1974**, *96*, 2095−2102.
[22] M. O. Senge in *The Porphyrin Handbook*, vol. 1 (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic, San Diego, CA, **2000**, chapter 6, pp. 239−347.
[23] G. Peychal-Heiling, G. S. Wilson, *Anal. Chem.* **1971**, *43*, 550−556.
[24] D. Chang, T. Malinski, A. Ulman, K.M. Kadish, *Inorg. Chem.* **1984**, *23*, 817−824.
[25] C. W. Bird, G. W. H. Cheeseman in *Comprehensive Heterocyclic Chemistry*, vol. 4 (Eds.: A. R. Katritzky, C. W. Rees), Pergamon Press, Oxford, **1984**, p. 4.
[26] K. M. Smith in *Comprehensive Heterocyclic Chemistry*, vol. 4 (Eds.: A. R. Katritzky, C. W. Rees), Pergamon Press, Oxford, **1984**, p. 386.
[27] R. G. Khoury, L. Jaquinod, K. M. Smith, *Tetrahedron* **1998**, *54*, 2339−2346.
[28] R. G. Khoury, M. O. Senge, J. E. Colchester, K. M. Smith, *J. Chem. Soc., Dalton Trans.* **1996**, 3937−3950.
[29] T. Mizutani, S. Yagi, A. Honmaru, H. Ogoshi, *J. Am. Chem. Soc.* **1996**, *118*, 5318−5319.
[30] T. Mizutani, S. Yagi, T. Morinaga, T. Nomura, T. Takagishi, S. Kitagawa, H. Ogoshi, *J. Am. Chem. Soc.* **1999**, *121*, 754−759.
[31] T. Mizutani, N. Sakai, S. Yagi, T. Takagishi, S. Kitagawa, H. Ogoshi, *J. Am. Chem. Soc.* **2000**, *122*, 748−749.
[32] G. Blauer, G. Wagnière, *J. Am. Chem. Soc.* **1975**, *97*, 1949−1954.
[33] G. Wagnière, G. Blauer, *J. Am. Chem. Soc.* **1976**, *98*, 7806−7810.
[34] A. Werner, M. Michels, L. Zander, J. Lex, E. Vogel, *Angew. Chem. Int. Ed.* **1999**, *38*, 3650−3653.
[35] N. Harada, K. Nakanishi, *Circular Dichroic Spectroscopy − Exiton Coupling in Organic Stereochemistry*, University Science Books, Mill Valley, CA, **1983**.
[36] K. Nakanishi, N. Berova in *Circular Dichroism − Principles and Applications* (Eds.: K. Nakanishi, N. Berova, R. W. Woody) ,VCH Publishers, Inc., New York, **1994**, p. 361.
[37] K. M. Kadish, M. M. Morrison, *J. Am. Chem. Soc.* **1976**, *98*, 3326−3328.

Received April 5, 2001
[I01120]