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Tuning the Helicity of (2,2′-Bidipyrrinato)-nickel(II) Complexes

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Summary. The influence of the terminal substituents of 2,2′-bidipyrrin ligands on the geometrical and spectroscopic properties of the respective nickel(II) complexes was investigated. Helicity was found to be an intrinsic structural feature of all 2,2′-bidipyrrins studied to date, including a species with minimum helical overlap. Surprisingly, no changes became apparent upon increasing the size of the terminal substituent from methyl to 1,4-butadiyl. *t*-Butyl groups at the termini, however, were found to be sterically too demanding to allow the formation of stable nickel(II) complexes.

Keywords. Helical structures; Ligands; Nickel; Open-chain tetrapyrroles; X-Ray structure determination.

Introduction

Helicity is now a well-recognized phenomenon displayed by an increasing number of coordination compounds [1]. Since metallohelicates are chiral, their potential use as stereoselective catalysts seems obvious. However, despite the many reports and reviews on this peculiarity, only a very limited number of enantiomerically pure helical chiral metal complexes has been reported so far [2], and only one example of a catalytically active complex is known from literature [3].

Metal complexes of open-chain tetrapyrroles like bilenes [4] are among the best studied subgroups of helical coordination compounds [5]. In a recent contribution, we have described the first successful enantioresolution of a nickel(II) complex of 2,2′-bidipyrrinate (**1**; [6]). Interestingly, the helical conformation of the methyl-terminated **1** is extremely stable: no racemization occurred even after prolonged heating to >200°C. As part of our ongoing project to prepare helical chiral tetrapyrrole chelates for asymmetric catalysis, our interest in a deeper understanding towards the factors influencing the degree and stability of the helical twist led us to prepare and study analogous nickel(II) complexes of 2,2′-bidipyrrins bearing terminal substituents of different size. Here, we report a comparison of the structural features of a series of complexes displaying a steady increase in substituent size at the ligand termini (**2**, **3**, and **4**; Scheme 1) and discuss the impact of sterics on the UV/Vis spectra of the species.

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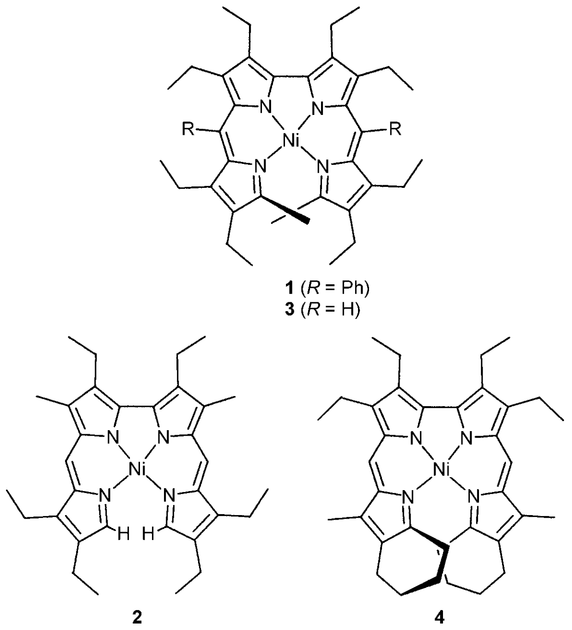


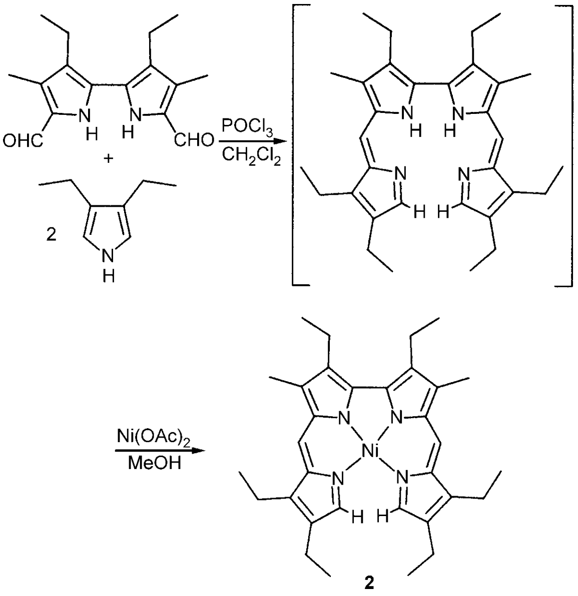
Scheme 1

Results and Discussion

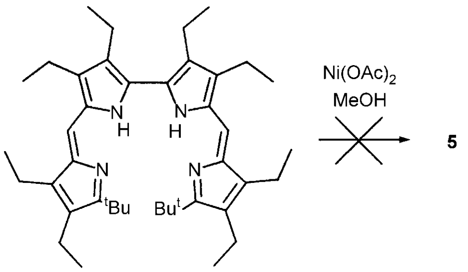
Preparation and characterization

The nickel(II) complex **4** was obtained from 2,2′-bidipyrrin [7] by treatment with nickel acetate hydrate as described earlier [6]. After crystallization from dichloromethane/*n*-hexane, **4** gave dark violet plates in 78% yield. First attempts to prepare the ligand of **2** from the respective pyrrole and bipyrrole precursors by a simple acid induced condensation failed, as did the alternative treatment with hot phosphoryl chloride [8]. In the cold, however, a dilute solution of phosphoryl chloride in dry dichloromethane was found to be the reagent of choice, and after 30 min the desired 2,2′-bidipyrrin could be detected as the major, deep blue product by TLC (Scheme 2). Since a chromatographic purification appeared difficult we decided to prepare the nickel(II) complex **2** from this mixture *in situ* by successive treatment with excess triethylamine and a methanolic solution of nickel(II) acetate hydrate. After extractive work-up, chromatographic filtration over silica with CH_2Cl_2:*n*-hexane = 1:2 and recrystallization from *n*-hexane gave the desired compound as violet blocks in 51% yield. **2** and **4** were fully characterized by proton and carbon NMR, mass, and UV/Vis spectra and by combustion analyses.

The NiN_4 geometry of 2,2′-bidipyrrin complexes with enhanced helical twist deviates strongly from planarity. Therefore, a spin change of the nickel(II) ion can be anticipated above a certain degree of distortion. Our attempts to prepare a high-spin nickel(II) 2,2′-bidipyrrin using terminal *t*-butyl groups as in **5**, however, failed (Scheme 3). Obviously, the steric repulsion of the *t*-butyl groups is too large to be overcome by four Ni–N bonds, so that no stable coordination compound with this ligand could be detected.



Scheme 2



Scheme 3

Structural investigations

Single crystals suitable for X-ray crystallographic studies were obtained from both **2** and **4** by slow concentration from dichloromethane/*n*-hexane solutions. Complex **2** crystallizes as violet rhombohedra in the space group $P2_1/c$ with $a = 14.4640(8)$, $b = 22.2896(12)$, $c = 9.0159(5)$ Å, $\beta = 107.7340(10)°$, and $Z = 4$. Compound **4** was found to crystallize as violet plates in the tetragonal system, space group $P4_32_12$, $a = 9.3193(6)$, $b = 9.3193(6)$, $c = 35.095(3)$ Å, $Z = 4$. The molecular structure of **2** is shown in Fig. 1, that of **4** in Fig. 2. Selected bond length and angles of **2** and **4** are given in Table 1, together with those found earlier for **3** [6].

In general, the molecular structures of **2**, **3**, and **4** show the expected similarities, as manifested in the C–C bond lengths of the C_{18} perimeter of the 2,2′-bidipyrrin ligand. As a typical porphyrinoid feature, the bond lengths within the heterocyclic C_4N units of **2**, **3**, and **4** show the relation C_β–$C_\beta < C_\alpha$–C_β [9]. The C–N bonds, on the other hand, are not symmetric for the terminal pyrrole rings, indicating imine-like substructures with the double bonds being C(1)–N(1) and C(18)–N(4), respectively, in all cases.

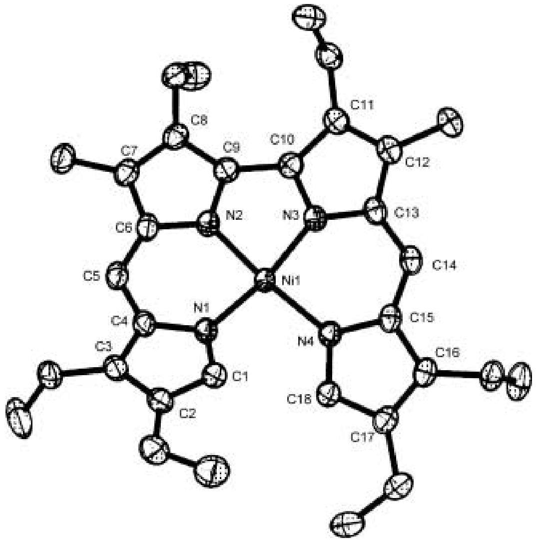


Fig. 1. ORTEP plot of compound **2**; the ellipsoids are drawn at a 50% probability level

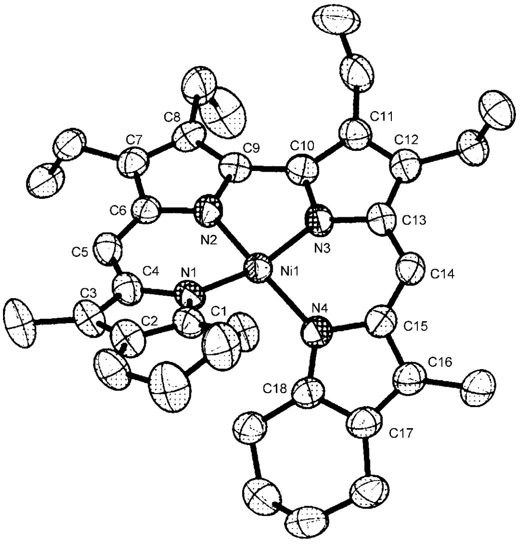


Fig. 2. ORTEP plot of compound **4**; the ellipsoids are drawn at a 50% probability level

The chelation geometry of the central nickel(II) ion is, as expected, characteristically influenced by the size of the different terminal substituents. As the molecular structures of **2**, **3**, and **4** reveal, the ligand twist largely increases on going from **2** to **3**, but is the same for **3** and **4**. A good molecular descriptor for this effect is the angle between the planes N(1)–Ni–N(4) and N(2)–Ni–N(3), which amounts to 13.0, 19.9, and 18.5° for **2**, **3**, and **4**, respectively. The mean deviation of the four nitrogen atoms from the NiN_4 plane of 0.132, 0.203, and 0.190 Å for **2**, **3**, and **4** is also indicative for this trend. The Ni–N bond lengths remain almost the same through this set of compounds. The observed deviations are best interpreted

Table 1. Selected bond lengths (Å) and angles (°) for **2**, **3**, and **4**

	2	**3**	**4**
Ni–N(1)	1.8947(13)	1.9088(15)	1.913(3)
Ni–N(2)	1.8442(13)	1.8451(15)	1.853(4)
Ni–N(3)	1.8487(13)	1.8498(14)	1.853(4)
Ni–N(4)	1.8861(13)	1.9068(15)	1.913(3)
N(1)–C(1)	1.340(2)	1.341(2)	1.335(6)
N(1)–C(4)	1.400(2)	1.409(2)	1.415(5)
N(2)–C(6)	1.373(2)	1.371(2)	1.367(5)
N(2)–C(9)	1.351(2)	1.349(2)	1.353(5)
N(3)–C(10)	1.351(2)	1.353(2)	1.353(5)
N(3)–C(13)	1.372(2)	1.373(2)	1.367(5)
N(4)–C(15)	1.403(2)	1.409(2)	1.415(5)
N(4)–C(18)	1.340(2)	1.340(2)	1.335(6)
C(1)–C(2)	1.413(2)	1.432(3)	1.419(6)
C(2)–C(3)	1.381(2)	1.372(3)	1.364(7)
C(3)–C(4)	1.437(2)	1.432(3)	1.433(6)
C(4)–C(5)	1.392(2)	1.380(3)	1.382(6)
C(5)–C(6)	1.388(2)	1.391(3)	1.402(6)
C(6)–C(7)	1.439(2)	1.426(3)	1.421(6)
C(7)–C(8)	1.385(2)	1.386(3)	1.392(6)
C(8)–C(9)	1.434(2)	1.428(3)	1.422(6)
C(9)–C(10)	1.450(2)	1.457(3)	1.464(8)
C(10)–C(11)	1.433(2)	1.425(3)	1.422(6)
C(11)–C(12)	1.390(2)	1.382(3)	1.392(6)
C(12)–C(13)	1.431(2)	1.430(3)	1.421(6)
C(13)–C(14)	1.395(2)	1.386(3)	1.402(6)
C(14)–C(15)	1.388(2)	1.383(3)	1.382(6)
C(15)–C(16)	1.434(2)	1.435(3)	1.433(6)
C(16)–C(17)	1.384(2)	1.365(3)	1.364(7)
C(17)–C(18)	1.413(2)	1.427(3)	1.419(6)
N(1)–Ni–N(2)	91.16(6)	90.39(7)	90.58(15)
N(1)–Ni–N(3)	167.21(6)	161.72(7)	163.80(15)
N(1)–Ni–N(4)	98.38(6)	101.76(7)	100.5(2)
N(2)–Ni–N(3)	81.23(6)	80.72(7)	81.3(2)
N(2)–Ni–N(4)	167.68(6)	163.08(7)	163.80(15)
N(3)–Ni–N(4)	90.68(6)	90.55(6)	90.58(15)
N(2)–C(9)–C(10)	110.28(14)	109.57(15)	110.3(2)
N(3)–C(10)–C(9)	110.73(14)	109.99(15)	110.3(2)
C(4)–C(5)–C(6)	124.53(15)	125.45(18)	125.2(4)
C(13)–C(14)–C(15)	124.51(15)	125.33(17)	125.2(4)

as simple sterical consequences from the differing degree of nonplanarity rather than by the assumption of an electronic contribution from low-lying excited states of the nickel centre. The finding that **3** and **4** display almost the same molecular structure (within deviations caused by packing effects) and that the helical twists of these two match each other quite well is a bit surprising at the first glance, but obviously stems from the fact that only the sterical interaction of atoms located directly at the terminal positions of the 2,2′-bidipyrrin ligands (C(1) and C(18)) is important for the distortion of the complexes.

With 3.05 Å, the distance between C(1) and C(18) of **2** appears suitable for helix inversion, and an attempt was undertaken to observe the dynamic of this process. Unfortunately, low temperature NMR spectroscopy did not reveal a diastereotopic splitting of the signals for the ethyl–CH_2 groups of **2** until the rotation of the ethyl substituents starts to freeze at 190 K, and no separation of the enantiomeric helices of **2** by chiral MPLC could be achieved. Although these results seem clear and could easily be taken as indicators for a rapid inversion in solution, this interpretation might be misleading. Earlier studies on the methyl-substituted **3** gave the same results, *i.e.* no diastereotopic splitting of CH_2 groups in the proton NMR spectra and no resolution on a chiral column. The structurally similar **1**, however, could unambigously be proven not to invert below 218°C. Whether or not an inversion process on **2** exists must therefore remain open.

Whereas in the NMR spectra of the (2,2′-bidipyrrinato)-nickel(II) complexes **2**–**4** no hint appears about the structural differences of **2** and **3**/**4**, the desired correlation can be found in the optical spectra. The UV/Vis absorption bands of **2** are significantly sharpened and shifted to smaller wavelength compared with those of **3** and **4** which are almost identical to each other (see Experimental). The spectra can best be compared by the major *Soret*-like bands at 413 (**2**), 432 (**3**), and 437 (**4**) nm and by the longest wavelength absorptions at 798 (**2**), 861 (**3**), and 871 (**4**) nm. This correlation of UV/Vis data and structural distortion, which provides a simple spectroscopic method for the determination of the degree of helicity in metallo-2,2′-bidipyrrins, is not a rare observation in oligopyrrole chemistry. Similar effects are usually found for non-planar porphyrins and their metal complexes, and have been well studied and explained for these cases [10].

Conclusions

Of the structural variations generally conceivable for nickel(II)-2,2′-bidipyrrins, spanning from square-planar low-spin complexes to high-spin Ni(II) chelates with strong tetrahedral distortions, only a small section is preparatively available. The limitation towards planar complex structures is given by the fact that the smallest possible substituent, the proton, already induces sufficient steric repulsion to create helicity. The upper limit, however, is reached with the methyl substituent already. Larger substituents do either not induce a significantly larger helical overlap or completely inhibit the coordination of metal centres to the tetrapyrrole ligand. For further studies on metallo-2,2′-bidipyrrins and their potential use as chiral catalysts, these results will set the limitations for ligand design.

Experimental

All reagents and solvents were purchased from commercial sources and used as received. NMR spectra were obtained on a Bruker AC 200 spectrometer. Chemical shifts (δ) are given in ppm relative to *TMS* according to the residual solvent resonances (^1H) or to CD_2Cl_2 (^{13}C). Mass spectra were recorded on a Finnigan 90 MAT instrument; m/z-values are given for the most abundant isotopes only. Melting points were measured by DTA on a Thermoanalyzer DuPont 9000. Elemental analyses (C, H, N) were performed at the microanalytical laboratory of the *Institut für Anorganische Chemie*, *Universität Würzburg*; the results agreed with the calculated values within experimental error. UV/Vis spectra were obtained in CH_2Cl_2 solution ($c \sim 10^{-4}\,mol \cdot dm^{-3}$) on a Hitachi U-3200 spectrophotometer.

(3,3′,8,8′,9,9′-Hexaethyl-4,4′-dimethyl-2,2′-bidipyrrinato)-nickel(II) (**2**; $C_{32}H_{40}N_4Ni$)

3,3′-Diethyl-4,4′-dimethyl-5,5′-diformyl-2,2′-bipyrrole [11] (0.2 mmol, 54.4 mg) and 3,4-diethylpyrrole [12] (0.4 mmol, 48.4 mg) were dissolved in 20 cm^3 dry CH_2Cl_2 and treated with $POCl_3$ (0.1 cm^3) at room temperature for 30 min. The reaction was quenched by the addition of triethylamine (1 cm^3), and a solution of nickel(II)acetate tetrahydrate (2 mmol, 566 mg) in MeOH (30 cm^3) was added. After 15 min, H_2O (100 cm^3) was added, the layers were separated, and the organic layer was dried over Na_2SO_4. After evaporation of all volatiles, the dark residue was subjected to chromatographic filtration with CH_2Cl_2:*n*-hexane = 1:2 on silica, and the dark green major band was collected. Recrystallization from *n*-hexane gave violet blocks.

Yield: 51%; m.p.: 189°C; ^1H NMR (CD_2Cl_2, 200 MHz): $\delta = 7.01$ (s, 2H), 5.31 (s, 2H), 2.67 (q, 4H), 2.66 (q, 4H), 2.46 (q, 4H), 2.24 (s, 6H), 1.22 (t, 6H), 1.21 (t, 6H), 1.16 (t, 6H) ppm; ^{13}C NMR (CD_2Cl_2, 50 MHz): $\delta = 162.07$, 151.87, 146.56, 137.31, 136.43, 134.61, 131.73, 131.29, 119.52, 19.35, 18.82, 18.49, 17.32, 16.44, 15.46, 9.78 ppm; EIMS (70 eV): $m/z = 534(M^+)$; UV/Vis (CH_2Cl_2): $\lambda = 296$, 367sh, 413, 551sh, 589, 798 nm.

Crystallographic data: Single crystals of **2** were grown by slow concentration from CH_2Cl_2/n-hexane; crystal size: $0.40 \times 0.30 \times 0.30$ mm; monoclinic, space group $P2_1/c$ (No. 14); $a = 14.4640(8)$, $b = 22.2896(12)$, $c = 9.0159(5)$ Å, $\beta = 107.7340(10)°$, $U = 2768.6(3)$ Å^3, $Z = 4$, $d_{calc} = 1.294\,g \cdot cm^{-3}$; max. $2\Theta = 50°$ (MoK_α, $\lambda = 0.71073$ Å, graphite monochromator, ω-scan, $T = 173(2)$ K); 32752 reflections scanned, 4875 unique ($R(\text{int}) = 0.0199$), 4654 observed ($I > 2\sigma(I)$); direct methods, 342 parameters, reflect/parameter ratio = 14.25; $R_1 = 0.0303$, $wR_2 = 0.0832$; residual electron density $0.275/-0.194\,e \cdot Å^{-3}$. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-173633. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223 336-033; e-mail: deposit@ccdc.cam.ac.uk).

(3,3′,4,4′-Tetraethyl-8,8′-dimethyl-9,9′,10,10′-di-(1,4-butadiyl)-2,2′-bidipyrrinato)-nickel(II) (**4**; $C_{36}H_{44}N_4Ni$)

3,3′,4,4′-Tetraethyl-8,8′-dimethyl-9,9′,10,10′-di-(1,4-butadiyl)-2,2′-bidipyrrin [7] (0.1 mmol, 55.5 mg) and nickel(II)acetate tetrahydrate (2 mmol, 566 mg) were stirred in a mixture of 30 cm^3 MeOH and 30 cm^3 CH_2Cl_2 for 30 min (colour change from deep blue to brownish-green). The reaction mixture was extracted twice with 100 cm^3 H_2O, dried over Na_2SO_4, and the solvent was removed *in vacuo*. Recrystallization of the dark residue from CH_2Cl_2/MeOH afforded the title compounds as violet crystals.

Yield: 78%; m.p.: 221°C; ^1H NMR (CD_2Cl_2, 200 MHz): $\delta = 5.93$ (s, 2H), 3.88 (m, 2H), 2.60 (m, 2H), 2.18 (q, 4H), 2.16 (q, 4H), 2.33–1.89 (m, 4H), 1.79 (s, 6H), 1.66–1.27 (m, 8H), 1.04 (t, 6H), 0.97 (t, 6H) ppm; ^{13}C NMR (CD_2Cl_2, 50 MHz): $\delta = 170.37$, 152.15, 141.82, 141.15, 139.15, 133.76, 128.16, 127.58, 120.81, 29.34, 24.23, 23.53, 22.11, 18.54, 17.89, 17.35, 16.93, 9.62 ppm; EIMS (70 eV): $m/z = 590$ (M^+); UV/Vis (CH_2Cl_2): $\lambda = 291$sh, 354, 437, 546, 632sh, 871 nm.

Crystallographic data: Single crystals of **4** were grown by slow concentration from CH_2Cl_2/n-hexane; crystal size: $0.10 \times 0.10 \times 0.10$ mm; tetragonal, space group $P4_32_12$ (No. 96); $a = 9.3193(6)$, $b = 9.3193(6)$, $c = 35.095(3)$ Å, $U = 3048.0(4)$ Å^3, $Z = 4$, $d_{calc} = 1.289\,g \cdot cm^{-3}$; max. $2\Theta = 50°$ (MoK_α, $\lambda = 0.71073$ Å, graphite monochromator, ω-scan, $T = 173(2)$ K); 21613 reflections scanned, 2687 unique ($R(\text{int}) = 0.0365$), 2639 observed ($I > 2\sigma(I)$); direct methods, 189 parameters, reflect/parameter ratio = 14.22; $R_1 = 0.0564$, $wR_2 = 0.1394$; residual electron density $0.555/-0.322\,\mathrm{e} \cdot \mathrm{Å}^{-3}$. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-173632. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223 336-033; e-mail: deposit@ccdc.cam.ac.uk).

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