DALTON
FULL PAPER

The first (tripyrrinato)nickel(II) complexes, TrpyNiX with X = Cl, Br, I: synthesis, structures and solvent coordination†

Martin Bröring,* Serguei Prikhodovski and Carsten D. Brandt

Institut für Anorganische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany. E-mail: Martin.Broering@mail.uni-wuerzburg.de

Received 13th September 2002, Accepted 24th September 2002
First published as an Advance Article on the web 24th October 2002

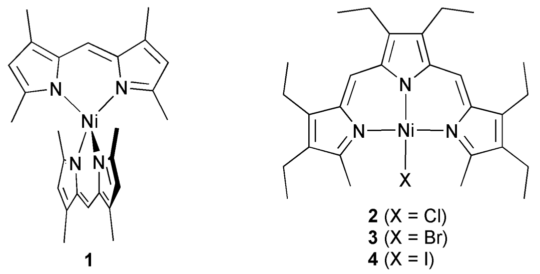
A first series of nickel(II)complexes TrpyNi(II)X of the new tripyrrolic ligand 2,15-dimethyl-3,4,8,9,13,14-hexaethyltripyrrin with X = Cl, Br and I was prepared and characterized by spectroscopic and structural means. The coordination geometry found for the four-coordinate, paramagnetic bromo- and iodo-derivatives in the solid state can best be described as distorted trigonal-bipyramidal with one ligand missing in the trigonal plane. For the chloro derivative, this empty site is occupied in the crystal by a water ligand. As proton NMR studies on the paramagnetic TrpyNiCl reveal, an equilibrium exists between the four- and five-, but not a six-coordinate form, and for pyridine-*N*-oxide as the fifth ligand thermodynamic data of the ligand association could be obtained by a temperature dependent NMR titration study.

Introduction

An interesting contrast can be found between the enormous structural diversity of the coordination chemistry of divalent nickel and the low number of different coordination modes established in nickel(II) porphyrins. In fact, the rigid, macrocyclic and tetradentate nature of the porphyrins and related macrocycles almost exclusively leads to the formation of square-planar low-spin d^8 complexes, with only two general exceptions known so far. In nickel(II) porphyrins with electron-withdrawing substituents on the ligand, coordination of two axial ligands is possible with low affinity, yielding distorted octahedral, six-coordinate species.[1] Nickel(II) complexes of monoanionic porphyrin variants like N-confused porphyrins,[2] oxaporphyrins,[3,4] or thiaporphyrins[5] as the other example, usually form five-coordinate high-spin species, often with a chloro ligand occupying the axial position. This pronounced tendency towards square-planar tetracoordination is also found in a number of more distant relatives of the porphyrins, like the corroles[6] or open-chain bilendions,[7] which are both best described as low-spin nickel(II) complexes of π-radical ligands.

Very recently we reported the first palladium(II) complexes of the tripyrrolic ligand tripyrrin.[8] As we found, (tripyrrinato)-palladium(II) complexes TrpyPdX exhibit two different geometries, one with a planar N_3X coordination sphere but a distorted tripyrrin ligand, and the other with an almost planar $C_{14}N_3$ perimeter and distorted coordination geometry, which are most probably in a rapid equilibrium at room temperature in solution. The dilemma of TrpyPdX complexes, that either the metal centre or the tripyrrolic ligand has to reside in a strained high-energy conformation, is caused by the presence of the terminal methyl substituents of the tripyrrin ligand, which simply render an entirely planar molecule sterically impossible.

In four-coordinate nickel(II) chelates like the dipyrrin complex **1**, a similar steric hindrance leads to a distortion of the complex geometry towards a more or less tetrahedral arrangement at the metal centre, which can conveniently be measured by the angle between the two N–Ni–N′ planes (76.3° for **1**).[9] (Tripyrrinato)nickel(II) complexes like **2**–**4** (Scheme 1), on the other hand, are characterized by three sterically fixed N donors, which should—in general—impose a square-planar (or octahedral) coordination geometry at the nickel centre.[10,11] Due to the presence of the terminal methyl substituents, however, the question may be raised, whether the tripyrrolic ligand remains planar in four coordinate nickel(II) complexes, and if so, to what degree the fourth ligand will deviate from the N_3 plane. We report here on the syntheses, structures and first reactivity study of (tripyrrinato)nickel(II)X complexes with X = Cl, Br and I.



Scheme 1

Results and discussion

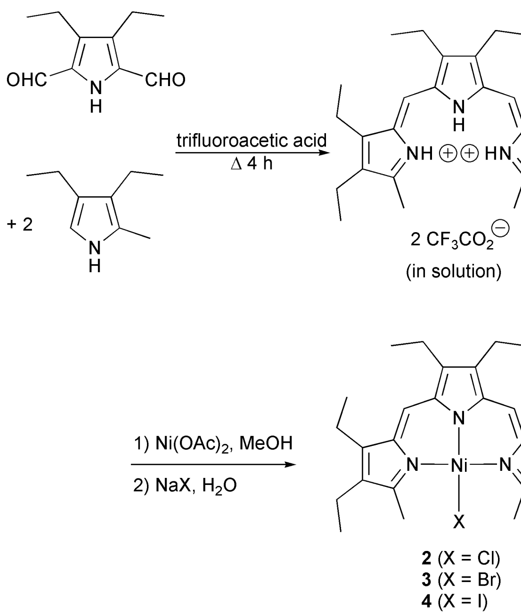
Syntheses of TrpyNiX 2–4

Due to the lability of the tripyrrin ligand,[8] an efficient preparation protocol for the desired nickel complexes **2**–**4** has to circumvent isolation of the tripyrrole and was found in the *in situ* metalation of freshly prepared diprotonated tripyrrin as its trifluoroacetate with a solution of nickel(II)acetate hydrate in methanol (Scheme 2). From the resulting mixture an intense green and highly polar band can be separated by column chromatography on silica, using diethyl ether–methanol 4 : 1 as the eluent. The colouring matter from this solution, which we believe is the bis(methanol) complex as trifluoroacetate [TrpyNi(MeOH)$_2$]OAc$_f$, decays quantitatively upon removal of the solvent. If the purified product solution is directly shaken with a concentrated aqueous NaX solution (X = Cl, Br, I), however, ligand exchange to more stable halide complexes takes place. After evaporation of all volatiles the title compounds **2**, **3** and **4** can be crystallized from a small amount of diethyl ether as violet, microcrystalline solids in 30, 19 and 41% yields, respectively.

---

† Dedicated to Prof. Waldemar Adam on the occasion of his 65th birthday.

DOI: 10.1039/b209212n



Scheme 2 Synthesis of (tripyrrinato)nickel(II) complexes TrpyNiX **2**–**4**.

All three complexes gave correct combustion analyses (**2** as its monohydrate) and were further characterized by MS and UV/Vis spectra (see the Experimental section). Since the proton NMR spectra of **2**, **3** and **4** (see below) indicated paramagnetic substances, the solution magnetic moments μ_{eff} were determined and found to be 3.0 ± 0.1, 2.7 ± 0.1 and 3.3 ± 0.1 μ_{B} at 298 K, respectively, using the Evans method.[12] In CD_2Cl_2 solution, **2** showed normal Curie dependence between 203 and 298 K with a Curie constant of C = 1.25 ml K mol^{-1}, and no EPR signal could be detected at the X-band (CH_2Cl_2, 298 K) as expected for four-coordinate high-spin nickel(II) species.

Structure determination of 2·H_2O, 3 and 4

Slow evaporation from benzene (**3**) or diethyl ether/n-hexane solutions (**4**) gave suitable crystals for X-ray structural investigations of the bromo- and the iodo-derivative. TrpyNiBr **3** yields violet plates and crystallizes in the monoclinic system, space group $P2_1/n$ (no. 14), with four molecules per unit cell [a = 11.4039(6), b = 20.7216(11), c = 11.5191(6) Å, β = 92.4160(10)°]. TrpyNiI **4** grows violet blocks and crystallizes in the triclinic system, space group $P\bar{1}$ (no. 2), with two molecules per unit cell [a = 10.4639(2), b = 11.5821(2), c = 12.4548(2) Å, α = 110.2630(10), β = 95.8150(10), γ = 102.2130(10)°]. The molecular structures of **3** and **4** are shown in Fig. 1 and 2, respectively. Table 1 summarizes selected molecular parameters.

As the figures show, the tripyrrole serves as a planar, meridonal-tridentate ligand in both cases (mean deviation from the $C_{14}N_3$ perimeter plane for **3**: 0.022; for **4**: 0.093 Å). Due to the planarity of the ligand, the interatomic distances of the terminal methyl groups C(1) and C(16) are as close as 4.190 (**3**) and 4.131 Å (**4**). This leaves insufficient space for the bulky bromide and iodide ligands of the TrpyNi complexes, and the respective halide ligand is therefore arranged on top of the tripyrrin plane, distorting the coordination spheres of the nickel(II) centres in **3** and **4** severely towards a pseudotetrahedral arrangement. The bent N_3X geometries can best be characterized by the angles N(1)–Ni–N(3) of 158.15(7)° for **3** and 153.71(7)° for **4**, and N(2)–Ni–X of 115.50(5)° for **3** and 115.57(5)° for **4**. Apparently, the bending of the coordination environment is accompanied by an out-of-plane movement of

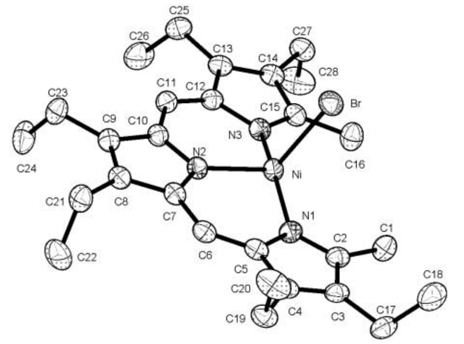


Fig. 1 ORTEP[16] plot of the molecular structure of **3** with numbering scheme (50% probability ellipsoids).

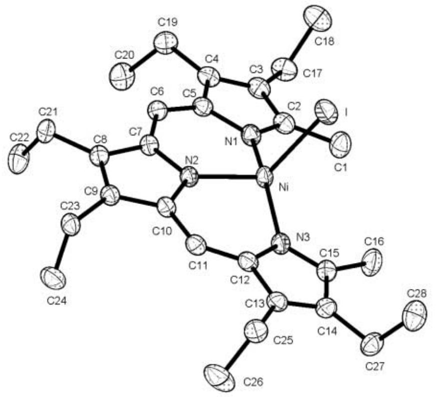


Fig. 2 ORTEP plot of the molecular structure of **4** with numbering scheme (50% probability ellipsoids).

Table 1 Selected bond lengths, distances (Å) and angles (°) for **2**·H_2O, **3** and **4**

	2 [X = Cl]	**3** [X = Br]	**4** [X = I]
Ni–N(1)	2.013(2)	1.9746(16)	1.9732(17)
Ni–N(2)	1.977(2)	1.9456(16)	1.9397(16)
Ni–N(3)	2.014(2)	1.9765(15)	1.9664(17)
Ni–X	2.3567(8)	2.4034(3)	2.5854(3)
Ni–O	2.133(2)		
N(1)–C(2)	1.327(4)	1.325(3)	1.329(3)
N(1)–C(5)	1.401(3)	1.410(2)	1.405(3)
N(2)–C(7)	1.366(3)	1.368(2)	1.368(3)
N(2)–C(10)	1.362(3)	1.362(2)	1.365(3)
N(3)–C(12)	1.401(4)	1.408(2)	1.412(3)
N(3)–C(15)	1.318(4)	1.325(2)	1.328(3)
C(2)–C(3)	1.445(4)	1.443(3)	1.437(3)
C(3)–C(4)	1.360(4)	1.359(3)	1.372(3)
C(4)–C(5)	1.440(4)	1.455(4)	1.447(3)
C(5)–C(6)	1.368(4)	1.362(3)	1.370(3)
C(6)–C(7)	1.410(4)	1.423(3)	1.411(3)
C(7)–C(8)	1.431(4)	1.423(3)	1.429(3)
C(8)–C(9)	1.372(4)	1.392(3)	1.382(3)
C(9)–C(10)	1.427(4)	1.427(3)	1.432(3)
C(10)–C(11)	1.425(4)	1.427(3)	1.418(3)
C(11)–C(12)	1.356(4)	1.365(3)	1.366(3)
C(12)–C(13)	1.457(4)	1.459(3)	1.444(3)
C(13)–C(14)	1.352(4)	1.363(3)	1.366(3)
C(14)–C(15)	1.441(4)	1.449(3)	1.440(3)
C(1) ··· C(16)	4.488	4.190	4.137
C(1) ··· X	3.742	3.860	4.076
C(16) ··· X	3.711	3.819	4.113
N(1)–Ni–N(2)	92.34(9)	93.47(7)	93.69(7)
N(1)–Ni–N(3)	172.54(9)	158.15(7)	153.71(7)
N(1)–Ni–X	90.60(7)	98.42(5)	98.21(5)
N(2)–Ni–N(3)	92.27(9)	93.64(6)	93.33(7)
N(2)–Ni–X	110.39(7)	115.50(5)	115.57(5)
N(3)–Ni–X	93.29(7)	97.08(4)	101.49(5)
N(1)–Ni–O	84.68(9)		
N(2)–Ni–O	108.17(9)		
N(3)–Ni–O	88.31(9)		
Cl–Ni–O	141.30(7)		
C(5)–C(6)–C(7)	128.6(3)	127.97(18)	127.73(19)
C(10)–C(11)–C(12)	128.0(3)	127.41(18)	127.28(19)

the nickel(II) ion of 0.3280 (**3**) and 0.3975 Å (**4**), respectively, towards the halide, which increases with increasing radius of the fourth ligand.

The Ni–N bond lengths of **3** and **4** of 1.9397(16)–1.9765(15) Å are slightly longer than those found for low-spin nickel(II) complexes of several porphyrins[13] and of four-coordinate low-spin complexes of other meridonal tridentate 3N ligands.[10,11] When compared to high-spin Ni(II) complexes of porphyrinoid ligands, however, these bonds are among the shortest ever found[1–5] and strongly reminescent of the Ni–N bonds [1.948(7)–1.957(8) Å] in the high-spin bis(dipyrrin) complex **1**.[9]

Crystals of the chloro derivative $\mathbf{2}\cdot H_2O$ were obtained by slow evaporation from a diethyl ether–acetone solution in air. TrpyNiCl(OH_2) yields violet blocks and crystallizes in the monoclinic system, space group $P2_1/c$ (no. 14), with four molecules per unit cell [a = 13.5240(8), b = 18.8187(11), c = 11.6553(7) Å, β = 106.2280(10)°]. The molecular structure of $\mathbf{2}\cdot H_2O$ is shown in Fig. 3. Selected molecular parameters are given in Table 1.

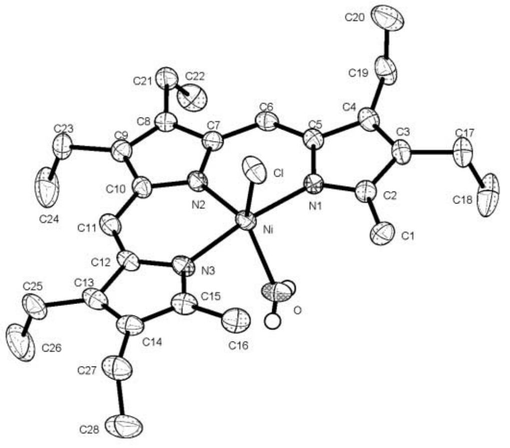


Fig. 3 ORTEP plot of the molecular structure of $\mathbf{2}\cdot H_2O$ with numbering scheme (50% probability ellipsoids).

As the most obvious difference to the above structures of TrpyNiBr **3** and TrpyNiI **4**, the chloro derivative **2** was found to carry a water molecule as a fifth ligand in the solid state. With this additional ligand, the nickel(II) centre is surrounded in a distorted trigonal bipyramidal fashion, with the nitrogen donors of the tripyrrin ligand occupying one equatorial and both apical positions. One consequence of the extra ligation is that the Ni–N bond lengths are widened with respect to those of **3** and **4** by approximately 0.04 Å, and are now in the expected range for a high-spin Ni(II) ion. The angles within the coordination sphere, on the other hand, show relatively small changes. N(1)–Ni–N(3) is enlarged to 172.54(9)° due to a diminuished out-of-plane arrangement of the nickel(II) centre in **2** of 0.0988 Å, and N(2)–Ni–X decreases by only *ca.* 5° to 110.39(7)° (Table 1).

Paramagnetic proton NMR and binding of neutral ligands

As mentioned above, the proton NMR spectroscopic investigation of TrpyNiX complexes **2**, **3** and **4** revealed paramagnetic compounds (S = 1), which display distinct and comparable isotropic shifts. This is true also for the chloro derivative **2**, which is obviously four-coordinate with a dissociated water molecule under the conditions of the measurement (compare with spectra of five-coordinate species, Fig. 5, later).

The NMR spectroscopic data of TrpyNiX complexes **2**–**4** has been analyzed by consideration of their effective symmetry in solution, which is C_s with the plane passing through the nickel, the halide and the central nitrogen N(2). Since the nonplanar geometry of the nickel(II) coordination sphere should give rise to a diastereotopic splitting of the protons of the three symmetry inequivalent methylene groups, eleven signals with relative intensities of 3 : 3 : 3 : 3 : 1 : 1 : 1 : 1 : 1 : 1 : 1 are expected. For the chloro derivative **2**, however, only eight of these are found at 293 K with intensities of 3 : 3 : 3 : 3 : 2 : 2 : 2 : 1, indicating an effectively planar, C_{2v} symmetric molecule (Fig. 4).

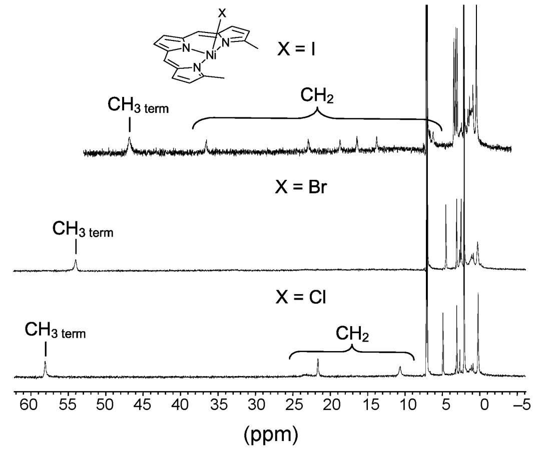


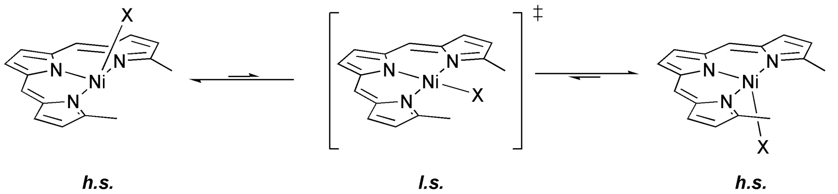
Fig. 4 Room temperature proton NMR spectra of TrpyNiX complexes **2**–**4** in [D_8]toluene.

Temperature dependent NMR spectra of **2** show that below 250 K the expected diastereotopic splitting becomes visible. Due to the intense temperature dependence of the proton NMR shifts of all signals, however, no reliable thermodynamic data could be estimated for this process. The process is obviously dependent on the size of the halide. For X = Br, complex **3** displays coalescence at room temperature, whereas for the large iodide ligand in **4** diastereotopic splitting of all methylene groups is observed (Fig. 4). This size dependence points to an inversion at the nickel centre as the dynamic process, probably *via* a low-spin intermediate as depicted in Scheme 3. In addition to this, conductivity measurements in nitromethane proved **2** to be effectively nonionic in solution, and a third argument for an intramolecular inversion process with a planar, diamagnetic intermediate can be concluded from the fact that the solution magnetic moments of **2**, **3** and **4** are in the range of 2.7–3.3 μ_B and therefore slightly below those expected for a (pseudo)tetrahedral Ni(II) complex (≥3.26 μ_B).

A different habitus in the ^1H spectra of **2**–**4** is observed in [D_6]acetone, [D_3]acetonitrile and [D_4]methanol solutions (Fig. 5). Dramatic shifts of more than 40 ppm were found for some of the proton resonances with respect to the spectra in [D_8]toluene, which can not be assigned to polarity effects only, but indicate the coordinative binding of the solvent at a free fifth coordination site.[14] Comparing the NMR data for the three complexes **2**, **3** and **4** it becomes apparent that in acetone and acetonitrile complexes of the type TrpyNiXL (L = solvent) are formed, while in methanol ionisation takes place to yield the cationic $[\mathrm{TrpyNi(MeOH)_2}]^+$ in all cases. This behaviour has very recently been described for Zn(II) complexes of the related texaphyrin ligand.[15]

In order to examine whether thermodynamic data may be obtained through paramagnetic NMR measurements, the strongly binding, but nonionising 3,5-dimethylpyridine-*N*-oxide ligand (3,5-Me_2PNO) was employed in binding studies on **2**, which were performed in [D_8]toluene at five different temperatures (Fig. 6; for NMR data of TrpyNiCl(3,5-Me_2PNO) see Experimental). For each temperature a ΔG^0 value of the ligand association could be calculated from the equation

$$\Delta G^0 = -RT\ln K_T,$$



Scheme 3

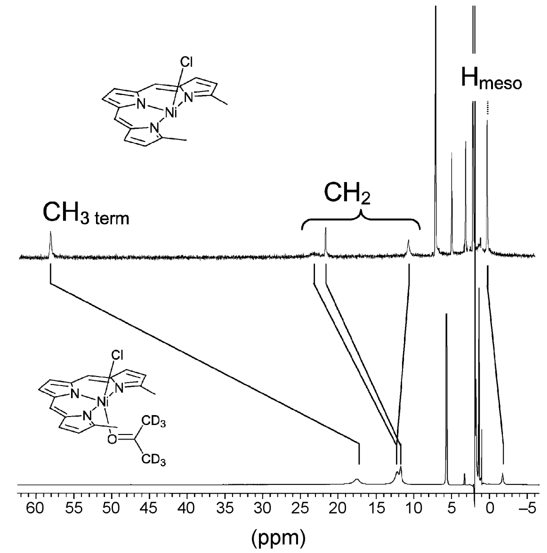


Fig. 5 ^{1}H NMR spectra of TrpyNiCl **2** in [D$_8$]toluene (top) and in [D$_6$]acetone (bottom).

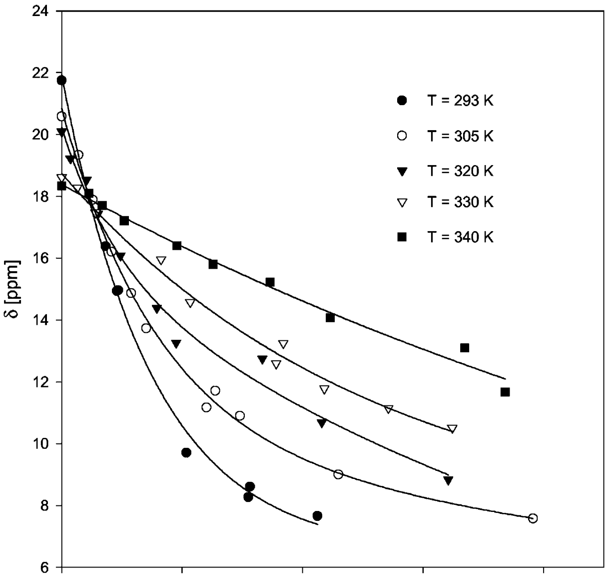


Fig. 6 VT-NMR titration experiment for TrpyNiCl **2** with 3,5-Me$_2$PNO in [D$_8$]toluene (proton resonances of one CH$_2$ group used for the plot).

Table 2 K_T and ΔG^0 values for the NMR titration of **2** with 3,5-Me$_2$PNO

T/K	K_T/l mol^{-1}	ΔG^0/kJ mol^{-1}
293	700	−15.9
305	360	−14.9
320	130	−12.9
330	90	−12.4
340	35	−10.0

in which K_T relates to the measured chemical shift of one of the methylene units of the complex and the relative amounts of complex and 3,5-Me$_2$PNO, determined by integration of NMR signals, as

$$K_T = \Delta_1/[(\Delta_2 - \Delta_1)c(I_{PNO}/I_C - \Delta_1/\Delta_2)]$$

with $\Delta_1 = \delta_{tetra} - \delta_c$, $\Delta_2 = \delta_c - \delta_{penta}$, δ_{tetra} = the chemical shift of the tetracoordinate form, δ_{penta} = the chemical shift of the pentacoordinate form, δ_c = measured chemical shift, c = starting molar concentration of TrpyNiCl, I_C = integration value of a complex methyl group and I_{PNO} = integration value of 3,5-Me$_2$PNO methyl groups (Table 2). The linear relationship between the ΔG^0 values and the temperature then yields the thermodynamic parameters $\Delta H^0 = -51.1 \pm 5$ kJ mol^{-1} and $\Delta S^0 = -119 \pm 15$ J K^{-1} mol^{-1} from the Helmholtz equation.

Conclusion

Other than the large majority of nickel(II) porphyrins and porphyrinoids, Ni(II) complexes of the α,ω-dimethyltripyrrin ligand form paramagnetic species. This particular behaviour is mainly associated with the fact that the terminal methyl groups of the tripyrrolic ligand shield the fourth corner of the square around the nickel centre and therefore force the anionic ligand to bind in a different location, *i.e.* above or below the NiN$_3$ plane. The new coordination compounds can easily accept one, but not two, additional neutral ligands to yield five-coordinate trigonal-bipyramidal complexes. Paramagnetic NMR was shown to be a sensitive tool well suited for the investigation of ligand association processes, by which even thermodynamic data may be obtained if the line-broadening of the spectra does not become too severe. With the structurally characterized **2**, **3** and **4** a new type of nickel(II) complex with a sterically induced *high-spin* ground state could be discussed, which will serve as valuable starting materials for the future development of this topic.

Experimental

All reagents and solvents were purchased from commercial sources and used as received. NMR spectra were obtained on a Bruker AMX 400 spectrometer (Bruker AC 200 for **2**) and measured at room temperature unless stated otherwise. Mass spectra were recorded on a Finnigan 90 MAT instrument. *m*/*z* values are given for the most abundant isotopes only. UV/Vis spectra were obtained in dichloromethane solution (c ~ 10^{-4} mol l^{-1}) on a Hitachi U-3200 spectrophotometer. 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. Single crystal X-ray diffraction studies were undertaken on a Bruker Smart-Apex diffractometer with D8-goniometer and cooling device at 173 K.

Chloro(2,15-dimethyl-3,4,8,9,13,14-hexaethyltripyrrinato)nickel(II)·H$_2$O 2, bromo(2,15-dimethyl-3,4,8,9,13,14-hexaethyltripyrrinato)nickel(II) 3 and iodo(2,15-dimethyl-3,4,8,9,13,14-hexaethyltripyrrinato)nickel(II) 4—general procedure

3,4-Diethyl-2,5-diformylpyrrole (175 mg, 1.4 mmol) and 3,4-diethyl-2-methylpyrrole (384 mg, 2.8 mmol) were dissolved in trifluoroacetic acid (10 ml) and heated to reflux for 4 h. After cooling to room temperature all volatiles were removed *in vacuo*, and the resulting dark residue was treated with a solution of nickel(II)acetate tetrahydrate (374 mg, 1.5 mmol) and sodium acetate (369 mg, 4.5 mmol) in dry methanol (50 ml). After stirring at room temperature for 5 min the solvent was reduced to 10 ml and the mixture subjected to column chromatography on silica (diethyl ether–methanol 4 : 1). The last, green–blue fraction was collected, diluted with diethyl ether (500 ml) and washed twice with water (500 ml). The organic phase was then stirred for 5 min with a saturated solution of the respective sodium salt (NaCl, NaBr or NaI, 100 ml), the layers separated, dried with sodium sulfate and evaporated to dryness. Crystallization of the dark residue from diethyl ether–pentane yielded the title compounds as air-stable violet microcrystals.

Spectroscopic data for 2·H₂O. (221 mg, 30%), mp 219°C (decomp.) (Found: C, 63.11; H, 7.13; N, 7.77. $C_{28}H_{40}ClN_3NiO$ requires: C, 63.60; H, 7.62; N, 7.95%). ^{1}H NMR ([D$_8$]toluene): δ 58.2 (br s, 6H, term. CH_3), 23.2 (br s, 4H, CH_2), 21.8 (br s, 4H, CH_2), 10.9 (br s, 4H, CH_2), 5.00 (br s, 6H, CH_3), 3.2 (br s, 6H, CH_3), 2.0 (br s, 6H, CH_3), 0.0 (br s, 2H, H_{meso}). ^{1}H NMR ([D$_8$]toluene, 4 equiv. 3,5-Me$_2$PNO): δ 18.5 (br.s, 4H, CH_2), 11.0 (br.s, 4H, CH_2), 7.6 (br.s, 4H, CH_2), 5.8 (br.s, 12H, 2 × CH_3), 0.2 (br.s, 6H, CH_3), −5.7 (br.s, 2H, H_{meso}), −12.1 (br.s, 6H, term. CH_3). ^{1}H NMR ([D$_6$]acetone): δ 17.5 (br.s, 6H, term. CH_3), 12.2 (br.s, 8H, 2 × CH_2), 11.7 (br.s, 4H, CH_2), 5.6 (2 × br.s, 12H, CH_3), 1.4 (br.s, 6H, CH_3), −1.3 (br.s, 2H, H_{meso}). ^{1}H NMR ([D$_3$]acetonitrile): δ 19.2 (br.s, 4H, CH_2), 12.0 (v.br.s, 4H, CH_2), 9.3 (br.s, 4H, CH_2), 5.9 (br.s, 6H, CH_3), 5.7 (br.s, 6H, CH_3), 0.7 (br.s, 6H, CH_3), −2.2 (br.s, 6H, term. CH_3), −5.5 (br.s, 2H, H_{meso}). ^{1}H NMR ([D$_4$]methanol): δ 19.0 (br.s, 4H, CH_2), 7.8 (v.br.s, 4H, CH_2), 7.2 (br.s, 4H, CH_2), 4.9 (br.s, 6H, CH_3), 4.7 (br.s, 6H, CH_3), 0.2 (br.s, 6H, CH_3), −9.1 (br.s, 2H, H_{meso}), −12.2 (br.s, 6H, term. CH_3). MS (EI, 70 eV): *m/z* 474, [M − Cl]$^+$. UV: λ_{max}/nm (CH$_2$Cl$_2$) 292 (ε/dm^3 mol^{-1} cm^{-1} 6200), 356 (26900), 406 (4100), 488 (2300), 637 sh (10100) and 685 (14300).

Crystal data for 2·H₂O. $C_{28}H_{40}ClN_3NiO$, M = 528.79, monoclinic, a = 13.5240(8), b = 18.8187(11), c = 11.6553(7) Å, β = 106.2280(10)°, U = 2848.1(3) Å^3, T = 173 K, space group $P2_1/c$, Z = 4, μ(Mo-Kα) = 0.799 mm^{-1}, 39984 reflections measured, 5014 unique (R_{int} = 0.0454), which were used in all calculations. The final $wR(F^2)$ was 0.1083 (all data).

CCDC reference number 180751.

Spectroscopic data for 3. (147 mg, 19%), mp 213°C (decomp.) (Found: C, 60.31; H, 6.79; N, 7.43. $C_{28}H_{38}BrN_3Ni$ requires: C, 60.57; H, 6.90; N, 7.57%). ^{1}H NMR ([D$_8$]toluene): δ 54.0 (br.s, 6H, term. CH_3), 40.0–8.0 (v.br.s, 12H, CH_2), 4.60 (br.s, 6H, CH_3), 3.0 (br.s, 6H, CH_3), 2.5 (br.s, 6H, CH_3), 0.1 (br.s, 2H, H_{meso}). ^{1}H NMR ([D$_6$]acetone): δ 17.5 (br.s, 6H, term. CH_3), 11.2 (br.s, 8H, 2 × CH_2), 7.9 (br.s, 4H, CH_2), 5.6 (br.s, 6H, CH_3), 5.4 (br.s, 6H, CH_3), 1.3 (br.s, 6H, CH_3), −3.0 (br.s, 2H, H_{meso}). ^{1}H NMR ([D$_3$]acetonitrile): δ 19.1 (br.s, 4H, CH_2), 11.1 (v.br.s, 4H, CH_2), 9.0 (br.s, 4H, CH_2), 5.6 (br.s, 6H, CH_3), 5.4 (br.s, 6H, CH_3), 0.6 (br.s, 6H, CH_3), −5.7 (br.s, 6H, term. CH_3), −6.9 (br.s, 2H, H_{meso}). ^{1}H NMR ([D$_4$]methanol): δ 19.0 (br.s, 4H, CH_2), 7.8 (v.br.s, 4H, CH_2), 7.2 (br.s, 4H, CH_2), 4.9 (br.s, 6H, CH_3), 4.7 (br.s, 6H, CH_3), 0.2 (br.s, 6H, CH_3), −9.1 (br.s, 2H, H_{meso}), −12.2 (br.s, 6H, term. CH_3). MS (EI, 70 eV): *m/z* 474, [M − Br]$^+$. UV: λ_{max}/nm (CH$_2$Cl$_2$) 284 (ε/dm^3 mol^{-1} cm^{-1} 7400), 354 (21700), 406 (4700), 492 (3600), 638 sh (8700) and 684 (12900).

Crystal data for 3. $C_{28}H_{38}BrN_3Ni$, M = 555.23, monoclinic, a = 11.4039(6), b = 20.7216(11), c = 11.5191(6) Å, β = 92.4160(10)°, U = 2719.6(2) Å^3, T = 173 K, space group $P2_1/n$, Z = 4, μ(Mo-Kα) = 2.202 mm^{-1}, 32189 reflections measured, 4773 unique (R_{int} = 0.0251), which were used in all calculations. The final $wR(F^2)$ was 0.0711 (all data).

CCDC reference number 180752.

Spectroscopic data for 4. (350 mg, 41%), mp 240°C (decomp.) (Found: C, 55.51; H, 6.10; N, 7.10. $C_{28}H_{38}IN_3Ni$ requires: C, 55.84; H, 6.36; N, 6.98%). ^{1}H NMR ([D$_8$]toluene): δ 46.8 (br.s, 6H, term. CH_3), 36.5, 23.0, 18.8, 16.4, 13.7, 6.2 (6×br.s, 12H, CH_2), 3.3 (br.s, 6H, CH_3), 3.1 (br.s, 6H, CH_3), 2.9 (br.s, 6H, CH_3), 0.1 (br.s, 2H, H_{meso}). ^{1}H NMR ([D$_6$]acetone): δ 17.3 (br.s, 6H, CH_3), 14.0 (br.s, 8H, 2 × CH_2), 10.5 (br.s, 4H, CH_2), 5.2 (br.s, 6H, CH_3), 4.9 (br.s, 6H, CH_3), 0.8 (br.s, 6H, CH_3), −5.2 (br.s, 2H, H_{meso}). ^{1}H NMR ([D$_3$]acetonitrile): δ 19.3 (br.s, 4H, CH_2), 9.6 (v.br.s, 4H, CH_2), 9.0 (br.s, 4H, CH_2), 5.0 (br.s, 6H, CH_3), 4.9 (br.s, 6H, CH_3), 0.4 (br.s, 6H, CH_3), −8.0 (br.s, 6H, term. CH_3), −8.8 (br.s, 2H, H_{meso}). ^{1}H NMR ([D$_4$]methanol): δ 19.0 (br.s, 4H, CH_2), 7.8 (v.br.s, 4H, CH_2), 7.2 (br.s, 4H, CH_2), 4.9 (br.s, 6H, CH_3), 4.7 (br.s, 6H, CH_3), 0.2 (br.s, 6H, CH_3), −9.1 (br.s, 2H, H_{meso}), −12.2 (br.s, 6H, term. CH_3). MS (EI, 70 eV): *m/z* 474, [M − I]$^+$. UV: λ_{max}/nm (CH$_2$Cl$_2$) 286 (ε/dm^3 mol^{-1} cm^{-1} 6700), 354 (19800), 402 (3700), 534 (2300), 639 sh (6100) and 694 (9200).

Crystal data for 4. $C_{28}H_{38}IN_3Ni$, M = 602.22, triclinic, a = 10.4639(2), b = 11.5821(2), c = 12.4548(2) Å, α = 110.2630(10), β = 95.8150(10), γ = 102.2130(10)°, U = 1358.66(4) Å^3, T = 173 K, space group $P\bar{1}$, Z = 2, μ(Mo-Kα) = 1.870 mm^{-1}, 22548 reflections measured, 4792 unique (R_{int} = 0.0221), which were used in all calculations. The final $wR(F^2)$ was 0.0583 (all data).

CCDC reference number 180753.

See http://www.rsc.org/suppdata/dt/b2/b209212n/ for crystallographic data in CIF or other electronic format.

Acknowledgements

Funding was kindly provided by the Deutsche Forschungsgesellschaft and the Fonds der Chemischen Industrie. The continued support from Prof. Dr. Helmut Werner (Würzburg) is gratefully acknowledged.

References and notes

1 J. F. Kirner, J. Garofalo Jr. and W. R. Scheidt, *Inorg. Nucl. Chem. Lett.*, 1975, **11**, 107–112; A. L. Balch, M. M. Olmstead and S. L. Phillips, *Inorg. Chem.*, 1993, **32**, 3931–3936; M. W. Renner, K. M. Barkigia, D. Melamed, K. M. Smith and J. Fajer, *Inorg. Chem.*, 1996, **35**, 5120–5121; K. Ozette, P. Leduc, M. Palacio, J.-F. Bartolic, K. M. Barkigia, J. Fajer, P. Battioni and D. Mansuy, *J. Am. Chem. Soc.*, 1997, **119**, 6442–6443; H. Duval, V. Bulach, J. Fisher and R. Weiss, *Acta Crystallogr., Sect. C*, 1997, **53**, 1027–1029; S.-L. Jia, W. Jentzen, M. Shang, X.-Z. Song, J.-G. Ma, W. R. Scheidt and J. A. Shelnutt, *Inorg. Chem.*, 1998, **37**, 4402–4412.

2 P. J. Chmielewski, L. Latos-Grażyński and T. Glowiak, *J. Am. Chem. Soc.*, 1996, **118**, 5690–5701.

3 P. J. Chmielewski, L. Latos-Grażyński, M. M. Olmstead and A. L. Balch, *Chem. Eur. J.*, 1997, **3**, 268–278.

4 B. Sridevi, S. J. Narayanan, A. Srinivasan, T. K. Chandrashekar and J. Subramanian, *J. Chem. Soc., Dalton Trans.*, 1998, 1979–1984; E. Pacholska, P. J. Chmielewski and L. Latos-Grażyński, *Inorg. Chim. Acta*, 1998, **273**, 184–190.

5 L. Latos-Grażyński, J. Lisowski, M. M. Olmstead and A. L. Balch, *Inorg. Chem.*, 1989, **28**, 1183–1188; P. J. Chmielewski, M. Grzeszczuk, L. Latos-Grażyński and J. Lisowski, *Inorg. Chem.*, 1989, **28**, 3546–3552; L. Latos-Grażyński, M. M. Olmstead and A. L. Balch, *Inorg. Chem.*, 1989, **28**, 4065–4066; J. Lisowski, L. Latos-Grażyński and L. Szterenberg, *Inorg. Chem.*, 1992, **31**, 1933–1940; R. J. Chmielewski and L. Latos-Grażyński, *Inorg. Chem.*, 1992, **31**, 5231–5235; R. P. Pandian and T. K. Chandrashekar, *J. Chem. Soc., Dalton Trans.*, 1993, 119–125; R. P. Pandian and T. K. Chandrashekar, *Inorg. Chem.*, 1994, **33**, 3317–3324; P. Chmielewski, L. Latos-Grażyński and E. Pacholska, *Inorg. Chem.*, 1994, **33**, 1992–1999.

6 S. Will, J. Lex, E. Vogel, H. Schmickler, J.-P. Gisselbrecht, C. Haubtmann, M. Bernard and M. Gross, *Angew. Chem., Int. Ed.*

Engl., 1997, **36**, 357–361; A. Ghosh, T. Wondimagegn and A. B. J. Parusel, *J. Am. Chem. Soc.*, 2000, **122**, 5100–5104.

7 J. V. Bonfiglio, R. Bonnett, M. B. Hursthouse and K. M. Abdul Malik, *J. Chem. Soc., Chem. Commun.*, 1977, 83–84; J. V. Bonfiglio, R. Bonnett, D. G. Buckley, D. Hamzetash, M. B. Hursthouse, K. M. Abdul Malik, A. F. McDonagh and J. Trotter, *Tetrahedron*, 1983, **39**, 1865–1874; P. A. Lord, M. M. Olmstead and A. L. Balch, *Inorg. Chem.*, 2000, **39**, 1128–1134.

8 M. Bröring and C. D. Brandt, *Chem. Commun.*, 2001, 499–500; M. Bröring and C. D. Brandt, *J. Chem. Soc., Dalton Trans.*, 2002, 1391–1395.

9 F. A. Cotton, B. G. DeBoer and J. R. Pipal, *Inorg. Chem.*, 1970, **9**, 783–788; compare also R. J. Butcher, C. J. O'Connor and E. Sinn, *Inorg. Chem.*, 1979, **18**, 492–497.

10 R. J. Letcher, W. Zhang, C. Bensimon and R. J. Crutchley, *Inorg. Chim. Acta*, 1993, **210**, 183–191; aggregates have also been observed, see T. I. Benzer, L. Dann, C. R. Schwitzgebel, M. D. Tamburro and E. P. Dudek, *Inorg. Chem.*, 1971, **10**, 2204–2209.

11 J. L. Sessler, A. Gebauer, V. Král and V. Lynch, *Inorg. Chem.*, 1996, **35**, 6636; R. G. Khoury, M. O. Senge, J. E. Colchester and K. M. Smith, *J. Chem. Soc., Dalton Trans.*, 1996, 3937–3950.

12 D. F. Evans, *J. Chem. Soc.*, 1955, 2003–2005; D. F. Evans and T. A. James, *J. Chem. Soc., Dalton Trans.*, 1979, 723–726.

13 W. R. Scheidt, in *The Porphyrin Handbook*, eds. K. M. Kadish, K. M. Smith and R. Guilard, Academic, San Diego, CA, 2000, vol. 3, ch. 16, p. 67, and references given therein.

14 Solvent coordination is frequently observed for tetracoordinate Ni(II) complexes with N ligands. For examples, see: R. H. Holm and K. Swaminathan, *Inorg. Chem.*, 1962, **1**, 599–607; L. Rusnak and R. B. Jordan, *Inorg. Chem.*, 1971, **10**, 2199–2204; A. Anichini, L. Fabbrizzi and P. Paoletti, *Inorg. Chim. Acta*, 1977, **24**, L21–L23; N. Herron and P. Moore, *Inorg. Chim. Acta*, 1979, **36**, 89–96; L. Sabatini and L. Fabbrizzi, *Inorg. Chem.*, 1979, **18**, 438–444; E. H. Curzon, N. Herron and P. Moore, *J. Chem. Soc., Dalton Trans.*, 1980, 574–578; L. Helm, P. Meier, A. E. Merbach and P. A. Tregloan, *Inorg. Chim. Acta*, 1983, **73**, 1–9; P. Moore, J. Sachinidis and G. R. Willey, *J. Chem. Soc., Chem. Commun.*, 1983, 522–523; P. Moore, J. Sachinidis and R. Willey, *J. Chem. Soc., Dalton Trans.*, 1984, 1323–1327.

15 S. Hannah, V. Lynch, D. M. Guldi, N. Gerasimchuk, C. L. B. MacDonald, D. Magda and J. L. Sessler, *J. Am. Chem. Soc.*, 2002, **124**, 8416–8427.

16 M. N. Burnett and C. K. Johnson, ORTEP, Report ORNL-6895, Oak Ridge National Laboratory, Oak Ridge, TN, 1996.