Self-Assembly of Nickel(II) Complexes of New Bis-Bidentate Schiff Base Ligands[‡]

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Nickel(II) complexes derived from three new bis-bidentate Schiff bases, H_2L^{1-3}, having two N-n-propyl-salicylaldiminate units linked by an $O–(CH_2)_n–O$ spacer ($n = 4, 8, 12$, respectively) at the 3-position of the salicyl moieties, are described. The pyridine adduct of the complex with the shorter spacer forms a cyclic trinuclear structure, $[Ni_3(L^1)_3(py)_6]$ (**2**), in the solid state, where each Ni^{II} ion is octahedrally coordinated by two N,O-bidentate arms of two different ligands and two pyridine nitrogens. The base with $n = 8$ leads to the double-helical dinuclear complex, $[Ni_2(L^2)_2]\cdot THF$ (**3**), which is the first example of a structurally characterised helicate based on a square-planar N_2O_2 coordination geometry. In CHCl$_3$ solution, **3** undergoes a disassembly process which results in an equilibrium mixture where the mononuclear species is largely predominant.

In recent years there has been increasing interest in the dinuclear and polynuclear coordination complexes of relatively simple ligands which exhibit, in solution and/or in the solid state, unusual, in some cases unexpected, structural complexity.[1] Helicates,[2] grids,[3] boxes and rings[4] are examples of supramolecular structures generated by the complexation of multidentate ligands with metal ions.

Interesting studies have been devoted to the development of synthetic procedures in order to prepare new multidentate ligands exhibiting the potential ability to give bridged polynuclear species. In particular, a number of attractive ligands with bidentate, chelating binding sites with flexible spacers between them have recently been reported.[5]

Here we describe a general procedure for the facile preparation of new tetradentate Schiff base ligands containing two N,O-bidentate chelating moieties linked through flexible polymethylene dioxo spacers, and their coordination behaviour with nickel(II).

The ligands H_2L^1, H_2L^2 and H_2L^3 were prepared in good yields (ca. 50%) by reaction of the dianion of 2,3-dihydroxybenzaldehyde with the appropriate alkyl α,ω-dibromide in dimethyl sulfoxide,[6] followed by the treatment of the resulting dialdehydes with n-propylamine. Reaction of the ligands with Ni(OAc)$_2$·4H$_2$O in a 1:1 molar ratio in ethanol afforded the complexes **1a−c** as light-green solids (Scheme 1).
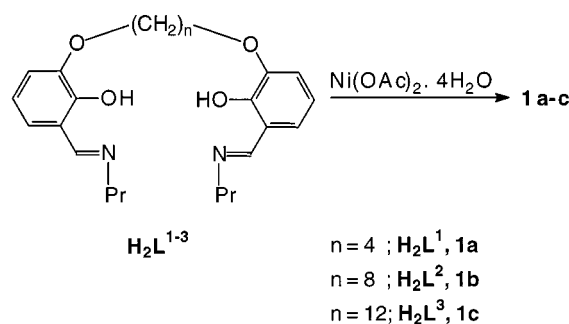
Scheme 1

Elemental analyses suggest the formation of 1:1 complexes for all three systems; however, **1a** exhibits quite different properties from those of both **1b** and **1c**. While the latter complexes have relatively low melting points (190−192 °C and 120−122 °C, respectively) and are moderately (Et$_2$O, dioxane) or very soluble (chloroform, THF, toluene) in organic solvents, **1a** has a melting point >320 °C and is insoluble in most common organic solvents, suggesting a higher structural complexity. However, **1a** is soluble in pyridine (py), and on addition of Et$_2$O to the pyridine solution the crystalline green solid **2**, analysing as **1a·2py**, precipitates; this material is paramagnetic, while **1a** is diamagnetic, similar to **1b** and **1c**. These data suggest that nickel(II) adopts a square-planar (SP) coordination geometry in **1a−c** and a nonplanar geometry in the pyridine adduct **2**, at least in the solid state.

Electrospray ionization mass spectroscopy (ESI-MS) of acetonitrile solutions of **1b**, **1c** and **2** indicates the presence of Ni^{II}/ligand 1:1 complexes, but higher mass peaks, corresponding to 2:2 aggregates or species resulting from their fragmentation, suggest the existence in solution of dinuclear complexes, in substantial amounts for **2**, and in small amounts for **1b** and **1c**. The spectrum of **2** also shows a very weak peak corresponding to a trinuclear species.

The ^1H NMR spectrum of **2** in $CDCl_3$ shows broad signals whose chemical shift depends on the concentration (mainly for the imine and aromatic protons and for the *ortho* protons of the complexed pyridine) suggesting the presence of an equilibrium involving Ni^{II} ions in a nonplanar environment. Single crystals of **2** were grown from pyridine/diethyl ether and studied by X-ray diffraction. The complex is the cyclic trimer $[Ni_3(L^1)_3(py)_6]$ shown in Figure 1. Each
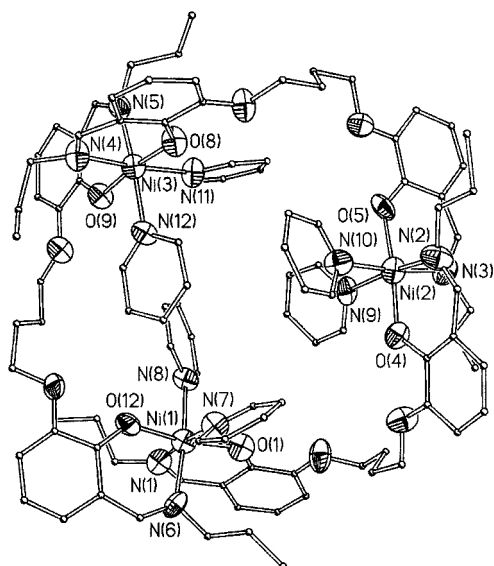
nickel(II) ion is octahedrally coordinated by two pairs of O,N coordination sites of two different ligands and two pyridine nitrogens. The molecule posses a pseudo threefold axis (C_3), that in the Figure points out of the page. As the ligands turn around as a helix fragment, the molecule is chiral, but forms racemic crystals because helices of opposite chirality regularly alternate in the centrosymmetric $P2_1/c$ space group.

Single crystals of the complex $[Ni_2(L^2)_2] \cdot THF$ (**3**) were obtained by slow evaporation of a solution of **1b** in THF/Et_2O. X-ray diffraction analysis shows that dinuclear molecules (Figure 2) result from the coordination of two $(L^2)^{2-}$ ligands to two nickel centres. Each metal atom is linked in a *trans*-square-planar (*trans*-SP) geometry by two N,O-coordination sites of different ligands. The nickel atoms and chelating groups lie approximately on parallel planes (max. deviations 0.31 and 0.22 Å, respectively) spaced by 3.46 Å. The planes are bonded by two octyl chains which are twisted forming a double helix. On going from Ni(1) to Ni(2) the chains twist by a quarter of a turn. The whole molecule possesses a *pseudo* D_2 symmetry, one of the twofold axes passing through the nickel atoms.
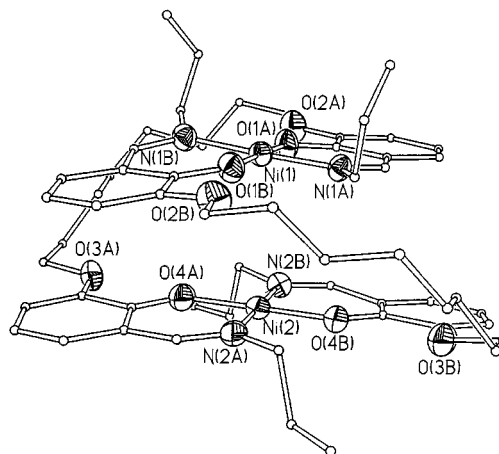

Figure 1. Crystal structure of **$[Ni_3(L^1)_3(py)_6]$** (**2**); Ni, O and N atoms are represented by 30% probability thermal ellipsoids; C atoms are represented by small spheres and H atoms are omitted for clarity; relevant bond lengths (Å) and angles (°): Ni(1)−O(1) 2.007(12), Ni(1)−O(12) 2.02(1), Ni(1)−N(1) 2.11(1), Ni(1)−N(6) 2.11(1), Ni(1)−N(8) 2.15(1), Ni(1)−N(7) 2.16(1), Ni(2)−O(4) 2.00 (1), Ni(2)−O(5) 2.02(1), Ni(2)−N(2) 2.12(1), Ni(2)−N(3) 2.14(2), Ni(2)−N(9) 2.16(1), Ni(2)−N(10) 2.22(1), Ni(3)−O(9) 1.988(9), Ni(3)−O(8) 2.013(9), Ni(3)−N(4) 2.10(1), Ni(3)−N(5) 2.11(1), Ni(3)−N(12) 2.17(1), Ni(3)−N(11) 2.20(1); O(1)−Ni(1)−O(12) 169.6(4), O(1)−Ni(1)−N(1) 89.4(5), O(12)−Ni(1)−N(1) 97.7(5), O(1)−Ni(1)−N(6) 98.5(5), O(12)−Ni(1)−N(6) 89.5(4), N(1)−Ni(1)−N(6) 86.9(5), O(1)−Ni(1)−N(8) 86.3(5), O(12)−Ni(1)−N(8) 86.2(5), N(1)−Ni(1)−N(8) 89.5(5), N(6)−Ni(1)−N(8) 174.0(5), O(1)−Ni(1)−N(7) 86.8(4), O(12)−Ni(1)−N(7) 86.8(5), N(1)−Ni(1)−N(7) 173.3(5), N(6)−Ni(1)−N(7) 88.2(5), N(8)−Ni(1)−N(7) 95.7(5), O(4)−Ni(2)−O(5) 173.9(4), O(4)−Ni(2)−N(2) 89.0(5), O(5)−Ni(2)−N(2) 96.4(5), O(4)−Ni(2)−N(3) 94.4(5), O(5)−Ni(2)−N(3) 88.0(5), N(2)−Ni(2)−N(3) 93.9(6), O(4)−Ni(2)−N(9) 83.2(5), O(5)−Ni(2)−N(9) 91.1(5), N(2)−Ni(2)−N(9) 170.1(5), N(3)−Ni(2)−N(9) 92.8(5), O(4)−Ni(2)−N(10) 90.4(5), O(5)−Ni(2)−N(10) 87.5(5), N(2)−Ni(2)−N(10) 83.4(6), N(3)−Ni(2)−N(10) 174.5(6), N(9)−Ni(2)−N(10) 90.4(5), O(9)−Ni(3)−O(8) 173.0(4), O(9)−Ni(3)−N(4) 95.3(5), O(8)−Ni(3)−N(4) 89.4(5), O(9)−Ni(3)−N(5) 88.4(5), O(8)−Ni(3)−N(5) 96.9(5), N(4)−Ni(3)−N(5) 88.3(5), O(9)−Ni(3)−N(12) 84.1(4), O(8)−Ni(3)−N(12) 90.5(5), N(4)−Ni(3)−N(12) 93.3(5), N(5)−Ni(3)−N(12) 172.5(5), O(9)−Ni(3)−N(11) 90.2(5), O(8)−Ni(3)−N(11) 85.3(4), N(4)−Ni(3)−N(11) 174.2(5), N(5)−Ni(3)−N(11) 89.9(5), N(12)−Ni(3)−N(11) 89.2(5)

Figure 2. Perspective view of the molecular structure of **$[Ni_2(L^2)_2] \cdot THF$ (3)**; Ni, O and N atoms are represented by 30% probability thermal ellipsoids; C atoms are represented by small spheres, and H atoms and clathrated THF are omitted for clarity; only the most populated positions of the disordered propyl groups are shown; relevant bond lengths (Å) and angles (°): Ni(1)−O(1A) 1.844(8), Ni(1)−O(1B) 1.852(8), Ni(1)−N(1A) 1.908(8), Ni(1)−N(1B) 1.925(9), Ni(2)−O(4A) 1.858(7), Ni(2)−O(4B) 1.859(7), Ni(2)−N(2B) 1.892(11), Ni(2)−N(2A) 1.909(10); O(1A)−Ni(1)−O(1B) 177.4(49), O(1A)−Ni(1)−N(1A) 92.9(4), O(1B)−Ni(1)−N(1A) 87.9(4), O(1A)−Ni(1)−N(1B) 86.4(4), O(1B)−Ni(1)−N(1B) 92.9(4), N(1A)−Ni(1)−N(1B) 178.0(4), O(4A)−Ni(2)−O(4B) 179.6(4), O(4A)−Ni(2)−N(2B) 86.6(4), O(4B)−Ni(2)−N(2B) 93.4(4), O(4A)−Ni(2)−N(2A) 92.8(4), O(4B)−Ni(2)−N(2A) 87.2(4), N(2B)−Ni(2)−N(2A) 179.4(4)

The square-planar geometry found for **3** is rather unusual[7] for double-stranded helical complexes, but not surprising in this case. In fact it is known[8] that in bis(*N*-alkylsalicylaldiminato)nickel(II) complexes, in the absence of space-demanding alkyl substituents, the nickel atom exhibits planar geometry.

The ^1H NMR spectra of a $CDCl_3$ solution of microcrystalline **1b** and **1c** show a major set (>90%) of resonances and some signals of very low intensity. The major reson-

ances, corresponding to a largely predominant species, and the minor set of signals can be assigned, according to the ESI-MS data, to the mononuclear and dinuclear complexes, respectively. The mononuclear complexes have been characterized by ROESY analysis (see Experimental Section). As far as the set of minor resonances is concerned, it can be unambiguously assigned, at least in the case of **1b**, to the dinuclear species interconverting with the mononuclear complex in solution. In fact, the ^{1}H NMR spectra of a CDCl$_3$ solution of **3** recorded at different times after dissolution of the solid sample shows a decrease of the intensity of the signals corresponding to the dinuclear species and a concomitant increase of the intensity of the resonances due to the mononuclear complex (Figure 3a and Figure 3b). When equilibrium is reached (>29 h), the spectrum is identical to that of the mononuclear complex **1b** (Figure 3b and Figure 3c).
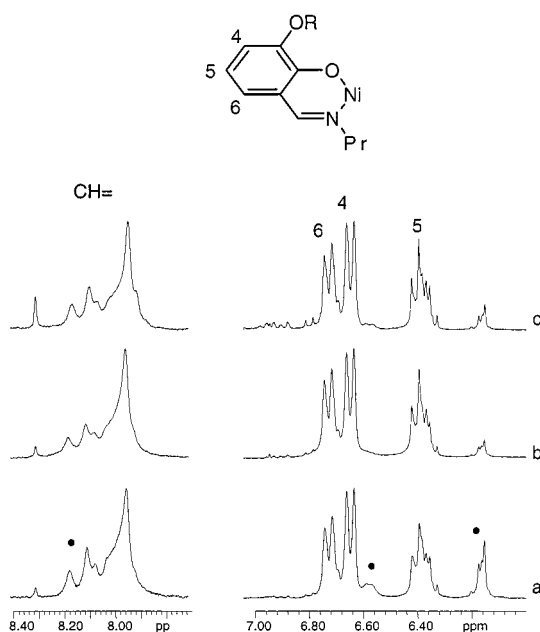

Figure 3. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C) spectral regions corresponding to aromatic and imine protons of: (a) the dinuclear complex **3** after 10 min, (b) the dinuclear complex **3** after 29 h and (c) complex **1b**; a filled circle denotes resonances corresponding to the dinuclear species

The existence of an interconversion equilibrium between dinuclear and mononuclear species is also demonstrated by a ^{1}H NMR saturation transfer experiment. In fact, the selective irradiation of the resonance at δ = 6.16, corresponding to the dinuclear species, produces saturation transfer at δ = 6.38, corresponding to the resonance of the H$_5$ proton of the mononuclear species (Figure 4).

Thus, while in the solid state the ligand (**L^2**)$^{2-}$ is able to coordinate each chelating arm to a different metal centre to give a bridged dinuclear species, in solution it prefers to act as a tetradentate chelate to a single Ni^{II} ion, presumably in a *cis*-SP geometry; in fact, a space filling representation[9] of **1b** indicates that the spacer appears not to be long enough to make accessible to Ni^{II} ion the sterically preferred *trans*-SP coordination geometry. Moreover, molecular mechanics calculations[9] suggest that the system con-
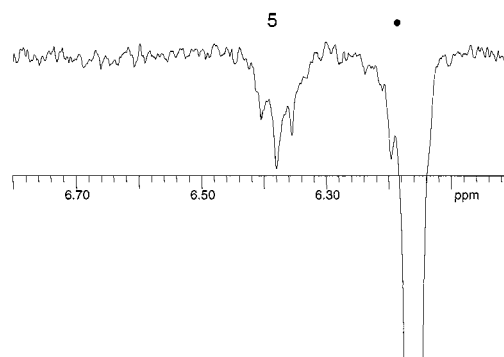

Figure 4. Saturation transfer difference spectrum (300 MHz, CDCl$_3$, 25 °C) of equilibrium mixture **3/1b** corresponding to the irradiation of the resonance at δ = 6.16

sisting of two mononuclear units of **1b** with the Ni^{II} ion adopting a *cis*-SP coordination geometry is more stable (ca. 4 kcal/mol in vacuo, ca. 9 kcal/mol in THF solution) than the calculated minimum-energy dinuclear structure, whose distances and angles are in good agreement with those found by X-ray analysis. These results indicate that the octamethylene bridging unit supplies the ligand (**L^2**)$^{2-}$ with optimal geometric requirements to easily wrap about the Ni^{II} ions to produce both mono- and dinuclear complexes with a small energetic difference, and that the solvation energy and crystal packing forces must play a fundamental role in the stabilisation of either species.

Finally, it can be envisaged that structural modifications of the spacer (length and flexibility) and of the steric hindrance of the substituents on the imine nitrogen atoms, combined with the stereoelectronic preference of the metal ion, could easily modulate the coordination geometry of this new class of bis-bidentate ligands, in order to favour the self-assembly process of high-nuclearity species. Work along these lines is in progress.

Experimental Section

IR spectra were collected on a Perkin−Elmer Paragon 500 FTIR spectrophotometer and electronic absorption spectra with a Perkin−Elmer Lambda 9 spectrophotometer in chloroform; λ$_{max}$ in nm and ε in M^{-1} cm^{-1}. ESI mass spectra were recorded on a PE Sciex API III plus triple quadrupole mass spectrometer equipped with an Atmospheric Pressure Ionization source and an articulated Ionspray interface. The sample was dissolved in chloroform (1 mg/mL) and diluted 1:100 with acetonitrile. Experimental conditions included: IS voltage, 5.5 kV; OR voltage, 90 V.

NMR measurements were performed on a Varian VXR-300 spectrometer in CDCl$_3$ as solvent; the temperature was controlled by the Varian control unit (±0.1 °C). ^{1}H NMR chemical shifts are referenced to TMS as external standard. The 2D NMR spectra were obtained by using standard sequences. The phase-sensitive ROESY spectra were acquired with a spectral width of 3000 Hz in 2 K data points using 8 scans for each of the 256 t$_1$ increments, with a mixing time ranging from 200−600 ms. A Gaussian function was applied for processing in both dimensions.

In the saturation transfer experiments, selective irradiation was applied for up to 2 s immediately prior to the observation pulse (with a 1-ms interval to allow for electronic recovery), and a total pulse interval of 3 s was used. The spectra were acquired in an interleaved fashion, first by saturating the resonance of interest and then by applying the decoupler significantly off-resonance. The difference spectra were obtained by subtracting the transformed off-resonance spectrum from the on-resonance spectrum.

Preparation of the Dialdehydes: To a solution of 2,3-dihydroxybenzaldehyde (6.5 g, 47 mmol) in anhydrous DMSO (100 mL) was added NaH (2.5 g, 104 mmol) under nitrogen. After stirring for 1 h at room temperature, 23 mmol of the appropriate dibromide was added and the resulting solution was allowed to stir for 24 h. The reaction mixture was poured into water (300 mL) and washed with chloroform. The aqueous layer was subsequently acidified with 6 M HCl and extracted with chloroform (3 × 50 mL). The combined chloroform extracts were dried over anhydrous Na_2SO_4, filtered, concentrated under reduced pressure, and methanol (20 mL) added. A colourless solid was obtained, which was filtered off and dried. Yields: from 60% to 65%.

1,4-Bis(3-formyl-2-hydroxy)phenoxybutane: m.p. 153−155 °C. − IR (Nujol): $\tilde{v}$ = 1646 cm^{-1} (C=O). − ^{1}H NMR (CDCl$_3$): δ = 11.07 (s, 2 H, OH), 9.93 (s, 2 H, CHO), 7.18−6.96 (m, 6 H, C$_6$H$_3$), 4.18 (t, 4 H, CH$_2$O), 2.11 [t, 4 H, (CH$_2$)$_2$]. − C$_{18}$H$_{18}$O$_6$ (330.33): calcd. C 65.45, H 5.49; found C 65.19, H 5.63.

1,8-Bis(3-formyl-2-hydroxy)phenoxyoctane: m.p. 116−119 °C. − IR (Nujol): $\tilde{v}$ = 1646 cm^{-1} (C=O). − ^{1}H NMR (CDCl$_3$): δ = 11.02 (s, 2 H, OH), 9.91 (s, 2 H, CHO), 7.18−6.96 (m, 6 H, C$_6$H$_3$), 4.04 (t, 4 H, CH$_2$O), 1.89−1.42 [m, 12 H, (CH$_2$)$_6$]. − C$_{22}$H$_{26}$O$_6$ (386.44): calcd. C 68.38, H 6.78; found C 68.89, H 7.10.

1,12-Bis(3-formyl-2-hydroxy)phenoxydodecane: m.p. 92 °C. − IR (Nujol): $\tilde{v}$ = 1646 cm^{-1} (C=O). − ^{1}H NMR (CDCl$_3$): δ = 11.03 (s, 2 H, OH), 9.94 (s, 2 H, CHO), 6.96−7.18 (m, 6 H, C$_6$H$_3$), 4.07 (t, 4 H, CH$_2$O), 1.89−1.31 [m, 20 H, (CH$_2$)$_{10}$]. − C$_{26}$H$_{34}$O$_6$ (442.55): calcd. C 70.56, H 7.74; found C 70.32, H 7.53.

Preparation of the Ligands H$_2$L$^{1-3}$ and Their Ni^{II} Complexes: The Schiff bases were synthesised following standard procedures. A mixture of dialdehyde (2.2 mmol) and *n*-propylamine (12 mmol) in ethanol (20 mL) was heated to reflux for 2 h. After cooling, a yellow solid precipitated out on addition of water. Recrystallisation from CHCl$_3$/hexane afforded yellow crystalline material. Yields: 80−90%.

H$_2$L^1: m.p. 108−110 °C. − IR (Nujol): $\tilde{v}$ = 1628 cm^{-1} (C=N). − ^{1}H NMR (CDCl$_3$): δ = 14.19 (s, 2 H, OH), 8.33 (s, 2 H, CH=N), 6.99−6.74 (m, 6 H, C$_6$H$_3$), 4.16 (t, 4 H, CH$_2$O), 3.58 (t, 4 H, CH$_2$N), 2.16 [t, 4 H, (CH$_2$)$_2$], 1.74 (m, 4 H, CH$_2$), 1.01 (t, 6 H, CH$_3$). − C$_{24}$H$_{32}$N$_2$O$_4$ (412.52): calcd. C 69.88, H 7.82, N 6.79; found C 69.74, H 7.94, N 6.67. − UV/Vis: λ_{max} (10^{-3} ε) = 243 (sh) (17), 262 (23), 305 (sh) (4.1), 330 (5.4), 425 (0.92).

H$_2$L^2: m.p. 84−86 °C. − IR (Nujol): $\tilde{v}$ = 1627 cm^{-1} (C=N). − ^{1}H NMR (CDCl$_3$): δ = 14.22 (s, 2 H, OH), 8.33 (s, 2 H, CH=N), 6.95−6.74 (m, 6 H, C$_6$H$_3$), 4.04 (t, 4 H, CH$_2$O), 3.57 (t, 4 H, CH$_2$N), 1.92−1.44 (m, 16 H, CH$_2$), 1.00 (t, 6 H, CH$_3$). − C$_{28}$H$_{40}$N$_2$O$_4$ (468.63): calcd. C 71.76, H 8.60, N 5.98; found C 71.24, H 8.88, N 5.60. − UV/Vis: λ_{max} (10^{-3} ε) = 243 (sh) (18), 262 (25), 305 (sh) (4.6), 330 (5.8), 425 (1.0).

H$_2$L^3: m.p. 73−75 °C. − IR (Nujol): $\tilde{v}$ = 1629 cm^{-1} (C=N). − ^{1}H NMR (CDCl$_3$): δ = 14.19 (s, 2 H, OH), 8.32 (s, 2 H, CH=N), 6.95−6.74 (m, 6 H, C$_6$H$_3$), 4.04 (t, 4 H, CH$_2$O), 3.58 (t, 4 H, CH$_2$N), 1.95−1.31 (m, 24 H, CH$_2$), 1.00 (t, 6 H, CH$_3$). − C$_{32}$H$_{48}$N$_2$O$_4$ (524.74): calcd. C 73.25, H 9.22, N 5.34; found C 72.92, H 9.22, N 5.03. − UV/Vis: λ_{max} (10^{-3} ε) = 243 (sh) (19), 262 (26), 305 (sh) (4.8), 330 (6.0), 425 (1.0).

The reaction of H$_2$L$^{1-3}$ with Ni^{II} acetate tetrahydrate in a 1:1 molar ratio in ethanol at room temperature gave light green solids. A solution of H$_2$L$^{1-3}$ (2 mmol) in EtOH (20 mL) was added dropwise to a solution of Ni(CH$_3$COO)$_2$·4H$_2$O (2 mmol) in EtOH (20 mL). After stirring at room temperature for 2 h, green microcrystalline **1a**,**1b** and **1c**, respectively**,** were collected by filtration, washed with diethyl ether and dried in vacuo. Yields: 90%. The adduct **2** was obtained by addition of Et$_2$O to a pyridine solution of **1a**.

[Ni$_x$(L^1)$_x$] (1a): m.p. >320 °C. − IR (Nujol): $\tilde{v}$ = 1612 cm^{-1} (C=N). − C$_{24}$H$_{30}$N$_2$NiO$_4$ (469.20): calcd. C 61.44, H 6.44, N 5.97; found C 61.57, H 6.70, N 5.42.

[Ni$_3$(L^1)$_3$(py)$_6$] (2): m.p. 120−125 °C (dec.). − IR (Nujol): $\tilde{v}$ = 1617 cm^{-1} (C=N). − ESI-MS: *m/z* (%) = 413 (100) [H$_2$L^1 + H]$^+$, 469 (90) [NiL^1 + H]$^+$, 881 (50) [Ni(L^1)$_2$ + 3 H]$^+$, 938 (traces) [(NiL^1)$_2$ + H]$^+$, 1426 (traces) [(NiL^1)$_3$ + Na]$^+$. − ^{1}H NMR (CDCl$_3$): δ = 9.16 (4 H, Py), 7.73 (2 H, Py), 7.45 (4 H, Py), 6.85 (2 H, Ph), 6.69 (2 H, Ph), 6.32 (2 H, Ph), 4.43 (2 H, CH=N), 3.87 (4 H, CH$_2$), 1.87 (8 H, CH$_2$), 1.60 (4 H, CH$_2$), 0.99 (6 H, CH$_3$). − C$_{102}$H$_{120}$N$_{12}$Ni$_3$O$_{12}$ (1872.2): calcd. C 65.09, H 6.43, N 8.93; found C 64.25, H 5.86, N 8.69. − UV/Vis: λ_{max} (10^{-3} ε) = 251 (141), 268 (156), 335 (26.7), 420 (12.6), 625 (0.26).

[NiL^2] (1b): m.p. 190−192 °C (CHCl$_3$/hexanes). − IR (Nujol): $\tilde{v}$ = 1611 cm^{-1} (C=N). − ESI-MS: *m/z* (%) = 469 (25) [H$_2$L^2 + H]$^+$, 525 (100) [NiL^2 + H]$^+$, 1051 (traces) [(NiL^2)$_2$ + H]$^+$. − ^{1}H NMR (CDCl$_3$): δ = 7.96 (s, 2 H, CH=N), 6.71 (dd, 2 H, H$_6$), 6.63 (dd, 2 H, H$_4$), 6.38 (dd, 2 H, H$_5$), 3.82 (t, 4 H, CH$_2$O), 3.53 (t, 4 H, CH$_2$N), 1.95 (m, 4 H, CH$_2$CH$_2$N), 1.74 (m, 4 H, CH$_2$CH$_2$O), 1.42 (m, 4 H, CH$_2$CH$_2$CH$_2$N), 1.35 (m, 4 H, CH$_2$CH$_2$CH$_2$CH$_2$O), 1.00 (t, 6 H, CH$_3$). − C$_{28}$H$_{38}$N$_2$NiO$_4$ (525.31): calcd. C 64.02, H 7.29, N 5.33; found C 64.28, H 7.49, N 5.32. − UV/Vis: λ_{max} (10^{-3} ε) = 251 (43), 268 (51), 335 (8.9), 420 (4.2), 625 (0.12).

[Ni$_2$(L^2)$_2$]·THF (3): m.p. 134−135 °C (THF/Et$_2$O). − IR (Nujol): $\tilde{v}$ = 1611 cm^{-1} (C=N). − ESI-MS identical to that of **1b**. − ^{1}H NMR, see text. − C$_{56}$H$_{76}$N$_4$Ni$_2$O$_8$·C$_4$H$_8$O (1122.7): calcd. C 64.19, H 7.54, N 4.99; found C 64.45, H 7.87, N 4.73. − UV/Vis: λ_{max} and ε (calculated taking into account the concentration of the NiN$_2$O$_2$ unit) are identical to those of **1b**.

[NiL^3] (1c): m.p. 120−122 °C (CHCl$_3$/hexanes). − IR (Nujol): $\tilde{v}$ = 1611 cm^{-1} (C=N). − ESI-MS: *m/z* (%) = 525 (100) [H$_2$L^3 + H]$^+$, 581 (95) [NiL^3 + H]$^+$, 1106 (traces) [Ni(L^3)$_2$ + 3 H]$^+$, 1161 (traces) [(NiL^3)$_2$ + H]$^+$. − ^{1}H NMR (CDCl$_3$): δ = 7.59 (s, 2 H, CH=N), 6.71 (dd, 2 H, H$_6$), 6.62 (dd, 2 H, H$_4$), 6.38 (dd, 2 H, H$_5$), 3.81 (t, 4 H, CH$_2$O), 3.51 (t, 4 H, CH$_2$N), 1.96 (m, 4 H, CH$_2$CH$_2$N), 1.73 (m, 4 H, CH$_2$CH$_2$O), 1.41 (m, 4 H, CH$_2$CH$_2$CH$_2$N), 1.40−1.20 (m, 12 H, CH$_2$), 1.00 (t, 6 H, CH$_3$). − C$_{32}$H$_{46}$N$_2$NiO$_4$ (581.41): calcd. C 66.11, H 7.97, N 4.82; found C 66.16, H 8.25, N 4.66. − UV/Vis: λ_{max} (10^{-3} ε) = 251 (45), 268 (54), 335 (8.4), 420 (4.0), 625 (0.09).

X-ray Crystallographic Study: X-ray diffraction measurements were carried out with a Siemens P4 diffractometer equipped with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Compound **2**, green square-section needle-like crystals, in part hollow as square tubes, C$_{102}$H$_{120}$N$_{12}$Ni$_3$O$_{12}$; M = 1882.23; T = 293(2) K, monoclinic, space group $P2_1/c$ (No. 14); a = 9.078(4), b = 34.150(14), c = 32.815(9) Å, U = 10173(7) Å^3; Z = 4; μ = 0.613 mm^{-1}; crystal size (mm) 0.92 × 0.23 × 0.22. 12353 reflections collected, 9455 independent, R_{int} = 0.1514. The structure was solved by the automatic direct methods of the SIR97 programme.[10] The structure was refined by full-matrix least-squares methods with the SHELX97 program.[11] Owing to the relatively high internal R value, calculated on the equivalent reflections, anisotropic thermal factors were used only for Ni, N and O atoms. The hydrogen atoms were introduced in calculated positions and allowed to ride on the connected heavy atoms. Final reliability factors for 652 parameters,

refined with no restraints: R_1 = 0.1158 calculated for 4893 reflections with $I > 2\sigma$ (I), wR_2 = 0.2201 for all 9455 reflections in the refinement; GOF = 1.187.

Compound **3**, deep olive green prismatic crystals, $C_{60}H_{88}N_4Ni_2O_9$; M = 1126.76; T = 293(2) K, Orthorhombic, space group $Pna2_1$ (No. 33); a = 14.813(2), b = 21.540(2), c = 18.277(2) Å, U = 5831.7(11) Å^3; Z = 4; μ = 0.703 mm^{-1}; crystal size (mm) 0.58 × 0.38 × 0.19. 4911 reflections collected, 4245 independent, R_{int} = 0.0282. The structure was solved by standard automatic direct methods and refined by least-squares methods. Abnormally high values of thermal factors and inconsistent geometry revealed a conformational disorder in two of the terminal propyl groups and in the clathrated THF. The two propyl groups were refined as distributed in two different conformations with a constrained geometry, while the THF molecule was refined with a fixed conformation taken from a well-refined structure in the literature.[11] At the end of the refinement, residual peaks and holes of 0.403 and -0.339 e·Å^{-3} were present around the disordered solvent molecule of the difference Fourier map. The solution and constrained refinement were done by means of the SHELX97 programme.[12] Final reliability factors for 632 parameters, refined with five restraints: R_1 = 0.0583 calculated for 3020 reflections with $I > 2\sigma$ (I), wR_2 = 0.0904 for all 4245 reflections in the refinement; GOF = 1.023.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-147138 (**2**) and -147139 (**3**). 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].

Acknowledgments

[1] J.-M. Lehn, *Supramolecolar Chemistry, Concepts and Perspectives*, VCH, Weinheim, **1995**; F. Vögtle, *Supramolecular Chemistry*, John Wiley & Sons, Chichester, **1991**.

[2] Reviews and very recent references: C. Piguet, G. Bernardinelli, G. Hopfgartner, *Chem. Rev.* **1997**, 97, 2005−2062; E. C. Constable, *Prog. Inorg. Chem.* **1994**, 42, 67−138; P. J. Stang, *Chem. Eur. J.* **1998**, 4, 19−27; A. von Zelewsky, O. Mamula, *J. Chem. Soc., Dalton Trans.* **2000**, 219−231; G. Baum, E. C. Constable, D. Fenske, C. E. Housecroft, T. Kulke, *Chem. Eur. J.* **1999**, 5, 1862−1873; G. Baum, E. C. Constable, D. Fenske, C. E. Housecroft, T. Kulke, M. Neuburger, M. Zehnder, *J. Chem. Soc., Dalton Trans.* **2000**, 945−959; M. J. Hannon, S. Bunce, A. J. Clarke, N. W. Alcock, *Angew. Chem. Int. Ed.* **1999**, 38, 1277−1278; M.-H. Shu, W.-Y. Sun, C.-Y. Duan, Y.-J. Fu, W.-J. Zhang, W.-X. Tang, *J. Chem. Soc., Dalton Trans.* **1999**, 729−734; N. K Solanki, A. E. H. Wheatley, S. Radojevic, M. McPartlin, M. A. Halcrow, *J. Chem. Soc., Dalton Trans.* **1999**, 521−523; M. Greenwald, D. Wessely, E. Katz, I. Willner, Y. Cohen, *J. Org. Chem.* **2000**, 65, 1050−1058; Y. Zhang, L. Jianmin, M. Nishiura, H. Hou, W. Deng, T. Imamoto, *J. Chem. Soc., Dalton Trans.* **2000**, 293−297; R. L. Paul, S. M. Couchman, J. C. Jeffery, J. A. McCleverty, Z. R. Reeves, M. D. Ward, *J. Chem. Soc., Dalton Trans.* **2000**, 845−851.

[3] J. Rojo, J.-M. Lehn, G. Baum, D. Fenske, O. Waldmann, P. Müller, *Eur. J. Inorg. Chem.* **1999**, 517−522; J. Rojo, F. Romero-Salguero, J.-M. Lehn, G. Baum, D. Fenske, *Eur. J. Inorg. Chem.* **1999**, 1421−1428; A. M. Garcia, F. J. Romero-Salguero, D. M. Bassani, J.-M. Lehn, G. Baum, D. Fenske, *Chem. Eur. J.* **1999**, 5, 1803−1808.

[4] N. Matsumoto, Y. Motoda, T. Matsuo, T. Nakashima, N. Re, F. Dahan. J.-P. Tuchagues, *Inorg. Chem.* **1999**, 38, 1165−1173; K. Yamanari, I. Fukuda, Y. Kushi, A. Fuyuhiro, N. Kubota, T. Fukuo, R. Arakawa, *Inorg. Chem.* **1998**, 37, 5611−5618; M. J. Hannon, C. L. Painting, W. Errington, *Chem. Commun.* **1997**, 307−308; C. M. Hartshorn, P. Steel, *Chem. Commun.* **1997**, 541−542; P. L. Jones, K. J. Byrom, J. C. Jeffery, J. A. McCleverty, M. D. Ward, *Chem. Commun.* **1997**, 1361−1362; G. R. Newkome, T. J. Cho, C. N. Moorefield, G. R. Baker. R. Cush, P. S. Russo, *Angew. Chem. Int. Ed.* **1999**, 38, 3717−3721; A. Neels, H. Stoeckli-Evans, *Inorg. Chem.* **1999**, 38, 6164−6170; B.-L. Fei, W.-Y. Sun, K.-B. Yu, W.-X. Tang, *J. Chem. Soc., Dalton Trans.* **2000**, 805−811; X.-H. Bu, H. Morishita, K. Tanaka, K. Biradha, S. Furusho, M. Shiiionoya, *Chem. Commun.* **2000**, 971−972.

[5] N. Yoshida, H. Oshio, T. Ito, *J. Chem. Soc., Perkin Trans. 2* **1999**, 975−983 and references therein; N. Yoshida, K. Ichikawa, M. Shiro, *J. Chem. Soc., Perkin Trans. 2* **2000**, 17−26 and references therein; B. J. McNelis, L. C. Nathan, C. J. Clark, *J. Chem. Soc., Dalton Trans.* **1999**, 1831−1834; K. L. V. Mann, J. C. Jeffery, J. A. McCleverty, M. D. Ward, *J. Chem. Soc., Dalton Trans.* **1998**, 3029−3035 and references therein; A. G. J. Ligtenbarg, E. K. van den Beuken, A. Meetsma, N. Veldman, W. J. J. Smeets, A. L. Spek, B. L. Feringa, *J. Chem. Soc., Dalton Trans.* **1998**, 263−270; C. Provent, P. Chautemps, G. Gellon, J.-L. Pierre, *Bull. Soc. Chim. Fr.* **1997**, 134, 487−493.

[6] V. Kessar, Y. P. Gupta, T. Mohammed, K. Sawal, *J. Chem. Soc., Chem. Commun.* **1983**, 400−401.

[7] Recently, D. Datta and co-workers have described the preparation of a dinuclear diamagnetic Ni^{II}−N4 complex, for which molecular mechanics calculations suggest the existence of a minimum-energy double-stranded helical structure (M. Zimmer, D. A. Tocher, G. K. Patra, J. P. Naskar, D. Datta, *Indian J. Chem.* **1999**, 38A, 1087−1091).

[8] R. Knoch, H. Elias, H. Paulus, *Inorg. Chem.* **1995**, 34, 4032−4040.

[9] All calculations were performed with GAUSSIAN (GAUSSIAN 99, Revision A.10, Gaussian Inc., Pittsburg PA, 1998) using the UFF force field and the PCM model of solvation (J. Tomasi, M. Persico, *Chem. Rev.* **1994**, 94, 2027−2094).

[10] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Molitemi, G. Polidori, R. Spagna, *J. Appl. Crys.* **1999**, 32, 115−119.

[11] A. Klauck, K. Seppelt, *Angew. Chem. Int. Ed. Engl*, **1994**, *33*, 93.

[12] G. M. Sheldrick, SHELXL97, A FORTRAN program for the solution and refinement of X-ray structures, University of Göttingen, **1997**.