A Self-Assembled Dinuclear Double-Stranded Helicate Based on a Square-Planar Coordination Geometry

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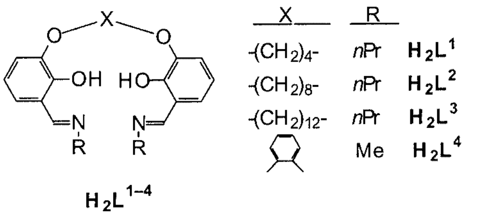
The nickel(II) complex of a new bis-*N,O*-bidentate Schiff base, in which two salicylaldiminate units are connected by an α,α′-dioxo-*ortho*-xylidene spacer via the 3-position of salicyl moieties, was structurally characterised in the solid state and in solution as a dinuclear double helicate based on a square-planar coordination geometry.

In the field of supramolecular chemistry, intense research activities have been focused on the helicates.[1] Almost all supramolecular structures of this type have been prepared by using neutral ligands containing nitrogen donor sets, so that the helical metal moieties have positive charges.[2]

Only in a few cases have anionic ligands been used, thus leading to neutral[3a−3f] or negatively charged helical structures.[3g,3h] Furthermore, in the four-coordinate helicates, the metal ions are invariably tetrahedral, suggesting that such a geometry is a requisite for generating a helicate with tetracoordinated metals.

Recently, we reported a facile preparation of nickel(II) complexes (Scheme 1) derived from a new class of bis-bidentate Schiff-base ligands capable of generating supramolecular architectures.[4] These new ligands contain two *N,O*-bidentate chelating moieties linked through a flexible polymethylene spacer (**H_2L^{1-3}**).



Scheme 1

In particular, by a self-assembly process the base with the octamethylene bridge yields the double-helical dinuclear complex $[Ni_2(L^2)_2]$·THF, where each metal atom is linked in a *trans*-square-planar geometry by two *N,O*-coordination sites of different ligands. As far as we are aware, this is the first example of a structurally characterised helicate based on a square-planar geometry.[5] However, in $CHCl_3$ solution this supramolecular structure undergoes a disassembly process resulting in an equilibrium mixture in which the mononuclear species is largely predominant.

In light of these results, we started an investigation in order to explore the role of the spacers and the substituent on the imine nitrogen in determining the outcome of self-assembly reactions. To favour the formation of stable helicates, an ideal candidate for the replacement of the polymethylene bridging unit was envisaged to be the more rigid *ortho*-xylidene group, in which the flexibility is restricted to the methylene groups and the *ortho*-linkage is suitable for helication. On the basis of this premise, H_2L^4 was prepared following the general procedure previously described.[4] Reaction of H_2L^4 with $[Ni(OAc)_2]$·$4H_2O$ in a 1:1 molar ratio in ethanol at room temperature yielded olive green microcrystals after recrystallization from chloroform that analysed as $[Ni_2(L^4)_2]$·$CHCl_3$.

Single crystals of the compound were obtained by slow evaporation of a chloroform solution. The X-ray structural analysis clearly shows that the compound has a dinuclear helical structure in the solid state. The molecular structure is sketched in the two projections of Figure 1. Each metal atom is linked in a *trans*-square-planar geometry by *N,O*-coordination sites from two different ligands, winding in a helical loop from Ni(1) to Ni(2). The nickel atoms and chelating groups lie approximately(± 0.25 Å) on two parallel planes, with a Ni(1)···Ni(2) distance of 3.554 Å. The two phenylene rings of the bridges are approximately perpendicular to the previous ones. The concurrence of ligand sizes with the distance between the coordination planes makes

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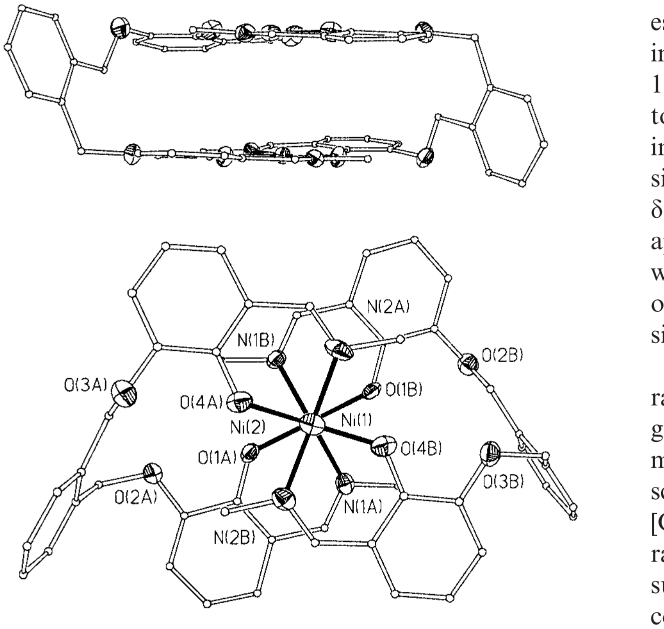


Figure 1. Two projections of the molecular structure of $[Ni_2(L^4)_2]$ along the pseudo-twofold axis (up) and down the coordination planes (down); Ni, O and N atoms are represented by 30% probability thermal ellipsoids; C atoms are represented by small spheres and H atoms are omitted for clarity; relevant bond lengths (Å) and angles (°): Ni(1)−O(1A) 1.82(1), Ni(1)−O(1B) 1.84(1), Ni(1)−N(1A) 1.89(2), Ni(1)−N(1B) 1.92(1), Ni(2)−O(4B) 1.82(1), Ni(2)−O(4A) 1.84(1), Ni(2)−N(2A) 1.90(2), Ni(2)−N(2B) 1.92(1); O(1A)−Ni(1)−O(1B) 177.2(5), O(1A)−Ni(1)−N(1A) 92.8(5), O(1B)−Ni(1)−N(1A) 87.7(5), O(1A)−Ni(1)−N(1B) 86.7(5), O(1B)−Ni(1)−N(1B) 92.8(5), N(1A)−Ni(1)−N(1B) 179.0(6), O(4B)−Ni(2)−O(4A) 176.2(5), O(4B)−Ni(2)−N(2A) 87.5(7), O(4A)−Ni(2)−N(2A) 92.4(7), O(4B)−Ni(2)−N(2B) 93.5(6), O(4A)−Ni(2)−N(2B) 86.8(6), N(2A)−Ni(2)−N(2B) 177.1(7)

the nickel coordination squares almost exactly staggered with an O(1A)−Ni(1)···Ni(2)−O(4A) dihedral angle of 43.7°. The molecule does not possess any crystallographic symmetry, but it shows nearly local symmetry 2(C_2), with the twofold axis parallel to the coordination planes and passing between the two metals. One chloroform molecule, not shown in Figure 1, is also present in the solid, with its hydrogen atom pointing towards a position between O(1B) and O(2B).

A mass spectrometry analysis using electrospray ionization suggests the presence of the dinuclear species as the only molecular species in solution. The main signal observed at m/z = 921 in the ESI-MS spectrum is indeed due to the protonated dinuclear complex, whereas the other important ions present in the spectrum at m/z = 405, 461 and 865 are attributable to the free ligand, to the mononuclear species and to the $[Ni_2(L^4)_2]-Ni^{II}$ species, respectively. MS-MS experiments suggest that these three ions are due to the fragmentation of the main peak at m/z = 921.

The ^1H NMR spectrum of the complex in $CDCl_3$ confirms the presence of a unique molecular species and the persistence in solution of the helical arrangement. In general, all the resonances of the complex are shifted upfield relative to the free ligand, and some resonances undergo significant changes upon coordination, giving important information regarding intramolecular interactions. The largest coordination shifts observed are the upfield shifts of the iminic protons (≈ 1.5 ppm) and of the methyl groups (≈ 1.2 ppm). In the crystal structure of the helicate, these protons lie above the salicyl moiety of the other ligand and are in the shielding region generated by the aromatic ring. The signal of the methylene groups of the bridge is a singlet at δ = 5.33 ppm in the free ligand, but upon complexation appears as doublets at δ = 5.21 and 5.01 ppm. On the whole, these spectral changes, particularly the manifestation of the diastereotropism, provide strong evidence for the persistence of the helical structure in solution.

Reaction of H_2L^4 with $[Cu(OAc)_2]\cdot 4H_2O$ in a 1:1 molar ratio, followed by usual treatment, yielded a light brownish-green compound, whose elemental analysis indicates a 1:1 metal:ligand ratio. Also in this case the ESI mass spectroscopic data are consistent with a dinuclear complex, i.e., $[Cu_2(L^4)_2]$. Despite several attempts, we could not isolate X-ray quality crystals, but the 2:2 metal:ligand stoichiometry suggests that, like the nickel(II) complex, the copper(II) complex is a double helicate. Efforts to elucidate the structure are in progress.

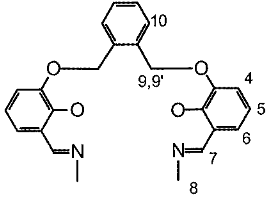
To summarise, we have shown that by careful selection of spacer sub-unit the behaviour of related ligands in the self-assembly process may be controlled. Applying this principle, we have tailored a new ligand to construct a dinuclear double-stranded helical nickel(II) complex, which is the second example of a helicate based on a square-planar geometry, but the first to be stable both in the solid state and in solution.

We are currently exploring the potential of this new class of ligands and investigating alternative linkage strategies for modelling supramolecular structures.

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.

NMR measurements were performed on a Varian VXR-300 spectrometer in $CDCl_3$ as solvent and were referred to TMS as external standard.



Preparation of Precursor Dialdehyde α,α′-Bis(3-formyl-2-hydroxy)-phenoxy-*o*-xylene: This compound was prepared in 74% yield from

2,3-dihydroxybenzaldehyde and α,α′-dibromo-*o*-xylene according to our previously reported procedure.[4] M.p. 176−180 °C. IR (Nujol): $\tilde{\nu}$ = 1646 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): δ = 5.34 (s, 2 H), 6.84−7.51 (m, 5 H), 9.86 (s, 1 H), 11.03 (s, 1 H) ppm. $C_{22}H_{18}O_6$ (378.38): calcd. C 69.83, H 4.79; found C 69.62, H 4.61.

Preparation of the Ligand H_2L^4: This Schiff base was synthesised following standard procedures.[4] A mixture of dialdehyde (0.30 g, 0.79 mmol) and methylamine (40 wt.-% solution in water; 1 mL, 12.9 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 yielded a yellow crystalline material (0.26 g, 81%). M.p. 169−172 °C. IR (Nujol): $\tilde{\nu}$ = 1634 cm^{-1} (C=N). ^1H NMR ($CDCl_3$): δ = 3.47 (d, *J* = 1.6 Hz, 3 H, H8), 5.33 (s, 2 H, H9+H9′), 6.69 (dd, *J* = 7.6, 7.6 Hz, 1 H, H5), 6.84 (dd, *J* = 7.6, 1.6 Hz, 1 H, H6), 6.97 (dd, *J* = 7.6, 1.6 Hz, 1 H, H4), 7.28 (m, 1 H, H11), 7.51 (m, 1 H, H10), 8.29 (q, *J* = 1.6 Hz, 1 H, H7), 13.89 (s, 1 H, OH) ppm. $C_{24}H_{24}N_2O_4$ (404.46): calcd. C 71.27, H 5.98, N 6.93; found C 71.02, H 5.85, N 6.71. UV/Vis ($CHCl_3$): λ_{max} (10^{-3} ε) = 261 (24.6), 327 (6.53), 425 (0.85).

Preparation of the Complexes: A solution of H_2L^4 (0.74 mmol) in EtOH (20 mL) was added dropwise to a solution of $[Ni(CH_3COO)_2]\cdot 4H_2O$ or $[Cu(CH_3COO)_2]\cdot 4H_2O$ (0.74 mmol) in EtOH (20 mL). After stirring at room temperature for 2 h, solid complexes were collected by filtration, washed with diethyl ether and dried in vacuo. Yields ≥ 90%. Recrystallisation from $CHCl_3$ or $CHCl_3$/diethyl ether led to olive-green crystals of $[Ni_2(L^4)_2]\cdot CHCl_3$ or brownish-green crystals of $[CuL^4]$, respectively.

$[Ni_2(L^4)_2]\cdot CHCl_3$: M.p. 192−195 °C. IR (Nujol): $\tilde{\nu}$ = 1618 cm^{-1} (C=N). ESI-MS: *m*/*z* (%) = 405 (75) $[H_2L^4 + H]^+$, 461 (60) $[NiL^4 + H]^+$, 865 (40) $[Ni(L^4)_2 + 3H]^+$, 921 (100) $[Ni_2(L^4)_2 + H]^+$. ^1H NMR ($CDCl_3$): δ = 2.34 (s, 3 H, H8), 5.01 (d, *J* = 13.6 Hz, 1 H, H9), 5.21 (d, *J* = 13.6 Hz, 1 H, H9′), 6.36 (dd, *J* = 8.0, 7.6 Hz, 1 H, H5), 6.59 (dd, *J* = 8.0, 1.3 Hz, 1 H, H6), 6.78 (dd, *J* = 7.6, 1.3 Hz, 1 H, H4), 6.79 (br. s, 1 H, H7), 7.26 (m, 1 H, H11), 7.52 (m, 1 H, H10) ppm. $C_{48}H_{44}N_4Ni_2O_8\cdot CHCl_3$ (1041.65): calcd. C 56.50, H 4.35, N 5.38; found C 56.25, H 4.20, N 5.18. UV/Vis ($CHCl_3$): λ_{max} (10^{-3} ε) = 269 (88.1), 334 (15.9), 417 (7.05), 625 (0.10).

$[CuL^4]$: M.p. 210 °C (dec.). IR (Nujol): $\tilde{\nu}$ = 1628 cm^{-1} (C=N). ESI-MS *m*/*z* (%) = 405 (35) $[H_2L^4 + H]^+$, 466 (30) $[CuL^4 + H]^+$, 931 (60) $[Cu_2(L^4)_2 + H]^+$, 948 (50) $[Cu_2(L^4)_2 + NH_4]^+$, 953 (50) $[Cu_2(L^4)_2 + Na]^+$. $C_{24}H_{22}CuN_2O_4$ (465.99): calcd. C 61.86, H 4.76, N 6.01; found C 62.18, H 4.96, N 5.73. UV/Vis ($CHCl_3$): λ_{max} (10^{-3} ε) = 276 (42.8), 365 (14.7).

X-ray Crystallographic Study: X-ray diffraction measurements were carried out with a Bruker P4 diffractometer equipped with Mo-K_α radiation (λ = 0.71073 Å).

$[Ni_2(L^4)_2]\cdot CHCl_3$: olive green prismatic crystals, $C_{49}H_{45}Cl_3N_4Ni_2O_8$; *M* = 1041.66; *T* = 293(2) K, monoclinic, space group *C*2/*c* (No. 15); *a* = 50.056(15), *b* = 11.309(3), *c* = 16.340(5) Å, β = 95.92(2)°, *U* = 9201(5) Å^3; *Z* = 8; μ = 1.052 mm^{-1}; crystal size (mm) 0.22 × 0.18 × 0.15. 6604 reflections collected, 5631 independent, R_{int} = 0.1010. Such a high R_{int} value is probably due to the long *a* axis and the consequent difficulty in neatly resolving adjacent reflections and to the low diffraction power of the crystal characterised by a large fraction of weak intensities. The structure was solved by standard automatic direct methods and refined by full-matrix least-squares methods. Hydrogen atoms were located in calculated positions and in the final refinement cycles anisotropic thermal factors were used for all non hydrogen atoms. The solution and refinement were performed by means of the SHELX-97 program.[6] The final reliability factors for 595 refined parameters were: R_1 = 0.0954 calculated for 2606 reflections with $I > 2\sigma(I)$, wR_2 = 0.2818 for all 5631 reflections in the refinement; *GOF* = 1.076.

CCDC-171594 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] J.-M. Lehn, *Supramolecular Chemistry, Concepts and Perspectives*, VCH Verlagsgesellschaft, 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; 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, M. Neuburger, M. Zehnder, *J. Chem. Soc., Dalton Trans.* **2000**, 945−959; 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; J. J. Jodry, J. Lacour, *Chem. Eur. J.* **2000**, *6*, 4297−4304; H. Cheng, D. Chun-ying, F. Chenjie, M. Qing-jin, *J. Chem. Soc., Dalton Trans.* **2000**, 2419−2424; 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; C. R. Rice, S. Wörl, J. C. Jeffery, R. L. Paul, M. D. Ward, *J. Chem. Soc., Dalton Trans.* **2001**, 550−559; O. Mamula, F. J. Monlien, A. Porquet, G. Hopfgartner, A. E. Merbach, A. von Zelewsky, *Chem. Eur. J.* **2001**, *7*, 533−539; R. Annunziata, M. Benaglia, M. Cinquini, F. Cozzi, C. R. Woods, J. S. Siegel, *Eur. J. Org. Chem.* **2001**, 173−180; V. Amendola, L. Fabbrizzi, L. Gianelli, C. Maggi, C. Mangano, P. Pallavicini, M. Zema, *Inorg. Chem.* **2001**, *40*, 3579−3587.

[3] [3a] N. Yoshida, H. Oshio, T. Ito, *J. Chem. Soc., Perkin Trans. 2* **1999**, 975−983 and references therein. [3b] N. Yoshida, K. Ichikawa, M. Shiro, *J. Chem. Soc., Perkin Trans. 2* **2000**, 17−26. [3c] P. E. Kruger, N. Martin, M. Nieuwenhuyzen, *J. Chem. Soc., Dalton Trans.* **2001**, 1966−1970. [3d] M. Vázquez, M. R. Bermejo, M. Fondo, A. M. Gonzáles, J. Mahía, L. Sorace, D. Gatteschi, *Eur. J. Inorg. Chem.* **2001**, 1863−1868. [3e] E. J. Corey, C. L. Cywin, M. C. Noe, *Tetrahedron Lett.* **1994**, *35*, 69−72. [3f] G. Struckmeier, U. Thewalt, J. H. Fuhrhop, *J. Am. Chem. Soc* **1976**, *98*, 278−279. [3g] M. Albrecht, *Chem. Eur. J.* **2000**, *6*, 3485−3489, and references therein. [3h] B. Kersting, M. Meyer, R. E. Powers, K. N. Raymond, *J. Am. Chem. Soc.* **1996**, *118*, 7221−7222.

[4] L. Carbonaro, M. Isola, V. Liuzzo, F. Marchetti, F. Balzano, C. S. Pomelli, A. Raffaelli, *Eur. J. Inorg. Chem.* **2001**, 353−357.

[5] A copper(II) double-stranded tetranuclear helicate has been described in which the Cu^{II} adopts both square-planar and distorted tetrahedral geometries; see ref.[3a]

[6] G. M. Sheldrick, SHELXL-97, *A FORTRAN program for the solution and refinement of X-ray structures*, University of Göttingen, Germany, **1997**.

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