The architecture of dinuclear Ni and Cu complexes: twisted and parallel forms controlled by the self-assembly of Schiff base ligands

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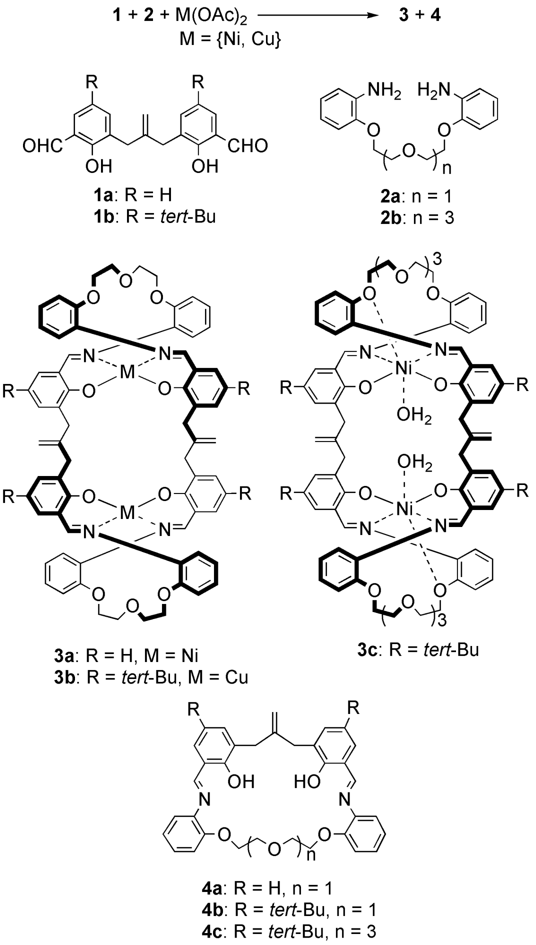
Received (in Montpellier, France) 10th December 2002, Accepted 22nd January 2003
First published as an Advance Article on the web 14th April 2003

Novel dinuclear complexes were synthesized through the self-assembly of macrocyclic Schiff base ligands and either nickel(II) or copper(II) ions. X-Ray structural analysis revealed that the complexes had either a double helix (twisted) structure in which each atom had a distorted square-planar coordination or a non-helical (parallel) structure in which the metals had octahedral coordination. The helical complexes were rather unusual in that their helicity originated not in the coordination centre, but mainly in the linker moieties in the ligand. Several factors influencing the formation of the helical structure are discussed.

Introduction

Well-defined inorganic architectures have been constructed by means of the self-assembly of suitably designed ligands whose programmed information is read out by given metal ions according to their coordination algorithm.[1a] The helix is one of the most attractive architectures to investigate, because it plays such an important role in supramolecular chemistry and biological systems.[1] There have been several attempts to construct helically arranged architectures[2–9] by using metal-induced self-assembly. The design of the linker connecting the chelating units is quite important, because the formation of the helical structure largely depends on the linker's shape and symmetry.[8] Comba *et al.* have detailed how the formation of helical and non-helical structures depends on the linker in dimetal complexes.[9]

We have investigated a variety of Schiff bases containing the isobutenylene chain [2-methylenepropane-1,3-diyl: $-CH_2-C(=CH_2)-CH_2-$] as a linker unit.[10] Recently, we demonstrated that a dinuclear titanium complex of one of these Schiff base ligands has a helical ("twisted") structure, which easily hydrolyses into a non-helical ("parallel") structure.[11] This change implies that the ligand has the potential to induce either a twisted structure or a parallel structure, depending on the coordination of the metal ion. In this paper, we report on novel dinuclear nickel(II) complexes with either twisted or parallel structures, as well as on an analogous copper(II) complex, which selectively emerged from the self-assembly of macrocyclic Schiff base ligands. Various factors influencing the formation of the helical structure are discussed.



Scheme 1

Experimental

Syntheses

Bis(hydroxybenzaldehyde)s **1** and diamines **2** (Scheme 1) were prepared according to reported methods.[10a,c]

DOI: 10.1039/b212285p

3a. To a solution of **1a** (0.148 g, 0.5 mmol) and **2a** (0.144 g, 0.5 mmol) in tetrahydrofuran (10 mL), a methanolic solution (30 mL) of nickel(II) acetate tetrahydrate (0.124 g, 0.5 mmol) was added. The resulting mixture was left at 25 °C without stirring for several days. Dark brown crystals of dinuclear Ni(II) complex **3a** separated out and were filtered and washed with chloroform and methanol (yield 0.203 g, 76%). Macrocycle **4a**,[10c] the 1:1 adduct of **1a** and **2a**, was a major by-product. The structure and purity of **3a** were confirmed by means of electrospray ionization mass spectroscopy (ESI-MS), Fourier transform infrared spectroscopy (FT-IR), and elemental analysis. Owing to the low solubility of the complex, NMR spectra could not be obtained. Anal. found: C, 58.29; H, 4.28; N, 3.78; calcd. for $C_{68}H_{60}N_4O_{10}Ni_2{\cdot}(CHCl_3)_2$: C, 58.00; H, 4.31; N, 3.87%. FT-IR (KBr) 1607 cm^{-1} (C=N). ESI-MS (positive mode) *m*/*z* 1233.1 (calcd. for $M + Na^+$: 1233.6). When chloroform was used as a solvent instead of THF, **3a** was obtained as a single crystal suitable for X-ray crystallography.

3b. When copper(II) acetate monohydrate was used instead of nickel(II) acetate, the reaction of **1b** with **2a** in chloroform–methanol afforded the dinuclear Cu(II) complex **3b**. The reaction was almost quantitative and little of the expected by-product, **4b**, was found. Recrystallization from THF gave a dark brown single crystal of **3b**. Anal. found: C, 69.83; H, 6.42; N, 3.88; calcd. for $C_{84}H_{92}N_4O_{10}Cu_2$: C, 69.79; H, 6.38; N, 3.78%. FT-IR (KBr) 1614 cm^{-1} (C=N). ESI-MS (positive mode) *m*/*z* 1445.7 (calcd. for $M + H^+$: 1445.7).

3c. Similarly, using nickel acetate tetrahydrate, the reaction of **1b** with **2b** in dimethylformamide–methanol afforded the dinuclear Ni(II) complex **3c**, together with **4c** as a by-product. Recrystallization from chloroform–methanol gave a dark brown single crystal of **3c**. Anal. found: C, 62.76; H, 6.55; N, 3.33; calcd. for $C_{92}H_{108}N_4O_{14}Ni_2{\cdot}(H_2O)_8$: C, 62.95; H, 7.12; N, 3.19%. FT-IR (KBr) 1616 cm^{-1} (C=N). ESI-MS (positive mode) *m*/*z* 1611.8 (calcd. for $M + H^+$: 1612.2).

X-Ray crystallography

For X-ray diffraction of a single crystal, the data were collected on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with λ(Mo-Kα) = 0.7107 Å radiation. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms' coordinates were refined anisotropically. Hydrogen atoms' coordinates were calculated. The final cycle of full-matrix least-squares refinement was based on the observed reflections of $I > 1.5\sigma(I)$ and the variable parameters, and the refinement converged with the unweighted and weighted agreement factors, R_1 and R_w, given below. ORTEP drawings were made with ellipsoids of 50% probability. All calculations were performed with the Molecular Structure Corporation's teXsan crystallographic software package.[12]

CCDC reference numbers 181644, 202477 and 204478. See http://www.rsc.org/suppdata/nj/b2/b212285p/ for crystallographic files in CIF or other electronic format.

Crystal data for 3a. $C_{34}H_{30}N_2O_5Ni{\cdot}CHCl_3$, $M_w = 724.70$, monoclinic, $a = 23.3866(8)$, $b = 10.9268(4)$, $c = 27.476(1)$ Å, $\beta = 112.0649(9)°$, $U = 6507.1(4)$ Å^3, $D_{calcd} = 1.479$ g cm^{-3}, $T = 193$ K, space group $C2/c$(#15), $Z = 8$, μ(Mo-Kα) = 8.88 cm^{-1}, 26 643 reflections measured and 7450 unique ($2\theta_{max} = 55.0°$, $R_{int} = 0.073$), which were used in all calculations. $R = 0.056$, $R_w = 0.066$.

Crystal data for 3b. $C_{84}H_{92}N_4O_{10}Cu_2{\cdot}C_4H_8O$, $M_w = 1516.87$, triclinic, $a = 15.1713(4)$, $b = 21.3550(5)$, $c = 12.5324(3)$ Å, $\alpha = 98.364(1)°$, $\beta = 92.0854(6)°$, $\gamma = 94.2007(9)°$, $U = 4001.8(2)$ Å^3, $D_{calcd} = 1.259$ g cm^{-3}, $T = 193$ K, space group P-1(#2), $Z = 2$, μ(Mo-Kα) = 5.93 cm^{-1}, 35 508 reflections measured and 17 688 unique ($2\theta_{max} = 55.0°$, $R_{int} = 0.053$), which were used in all calculations. $R = 0.063$, $R_w = 0.117$.

Crystal data for 3c. $C_{46}H_{54}N_2O_7Ni{\cdot}(H_2O)_4$, $M_w = 877.70$, monoclinic, $a = 15.5858(9)$, $b = 17.5726(9)$, $c = 17.4597(9)$ Å, $\beta = 99.845(2)°$, $U = 4711.5(4)$ Å^3, $D_{calcd} = 1.237$ g cm^{-3}, $T = 193$ K, space group $P2_1/a$(#14), $Z = 4$, μ(Mo-Kα) = 4.65 cm^{-1}, 39 260 reflections measured and 10 635 unique ($2\theta_{max} = 55.0°$, $R_{int} = 0.112$), which were used in all calculations. $R = 0.078$, $R_w = 0.110$.

Results and discussion

Dinuclear complexes of macrocyclic ligands and either nickel or copper were obtained by mixing the dialdehyde, diamine, and metal ion (Scheme 1). Mixing of **1a** and **2a** in the absence of a metal ion selectively afforded the macrocyclic adduct **4a**, which suggests that **3a** is formed by a template effect of the nickel ion. We would like to emphasize that these reactions afforded 48- or 60-membered macrocyclic rings, which have never been obtained in the absence of metal ions.

Fig. 1 shows an ORTEP drawing of **3a**. The ligand part of the complex is the 2:2 macrocycle of **1a** and **2a**, in which two phenolic oxygens and two imine nitrogens from the salicylideneaniline (SA) units are bound to each nickel atom in a slightly distorted square-planar geometry. The two SA units adopt an

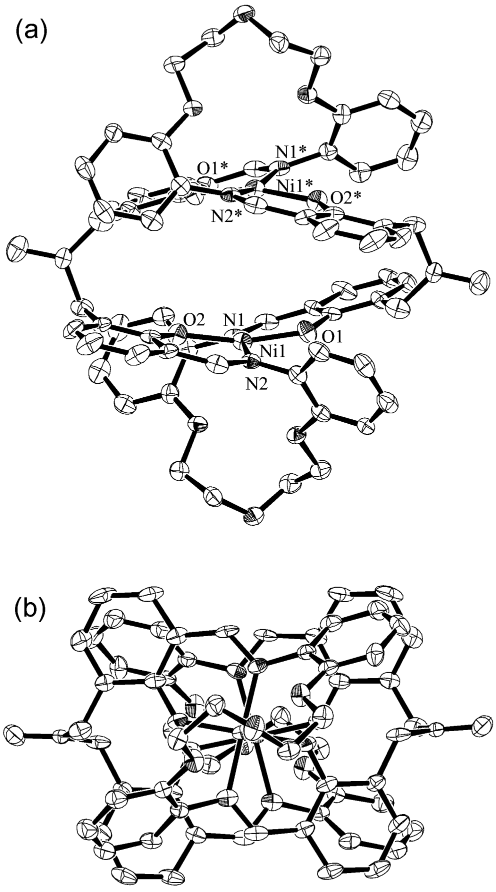


Fig. 1 ORTEP drawings of the dinuclear Ni(II) complex **3a**. (a) View nearly along the crystallographic C_2 axis. (b) View along a pseudo-C_2 axis (along the O4···Ni1···Ni1*···O4* line). Selected interatomic distances (Å) and bond angles (°): O1–Ni1 1.839(3), O2–Ni1 1.846(3), N1–Ni1 1.913(4), N2–Ni1 1.913(4), Ni1–Ni1* 4.426(1), O1–Ni1–O2 165.0(2), and N1–Ni1–N2 167.4(2). The solvent of crystallization (chloroform) and hydrogen atoms are omitted for clarity.

"anti-parallel" arrangement. As a result, the macrocyclic ligand is twisted into a double helix. We assume that structural restriction by the ethylene glycol chain and the coordination of the nickel atom result in the preference for the twisted structure over the parallel one. The symmetry of **3a** is approximately regarded as D_2. The complex is located around a crystallographic C_2 axis, perpendicular to which there are two pseudo-C_2 axes, one that passes through the C=C bonds and another that passes through O4···N1···N1*···O4*. The complex is intrinsically chiral and both enantiomers are present in the unit cell.

The crystal structure of **3b** is quite similar to that of **3a** (Fig. 2), although no crystallographic C_2 axis is present. The symmetry of **3b** is approximately D_2. Each copper atom sits in an anti-parallel pair of SA units and has a slightly distorted square-planar coordination. Since copper(II) strongly prefers the square-planar geometry, the higher yield of **3b** might be interpreted as a result of the efficiency of metal-templated self-assembly. In addition, Fig. 2(b) clearly shows that the *tert*-butyl group at the 5-position of the salicylidene moiety sticks out of the central part of the complex and therefore would not interfere with the formation of the twisted structure.

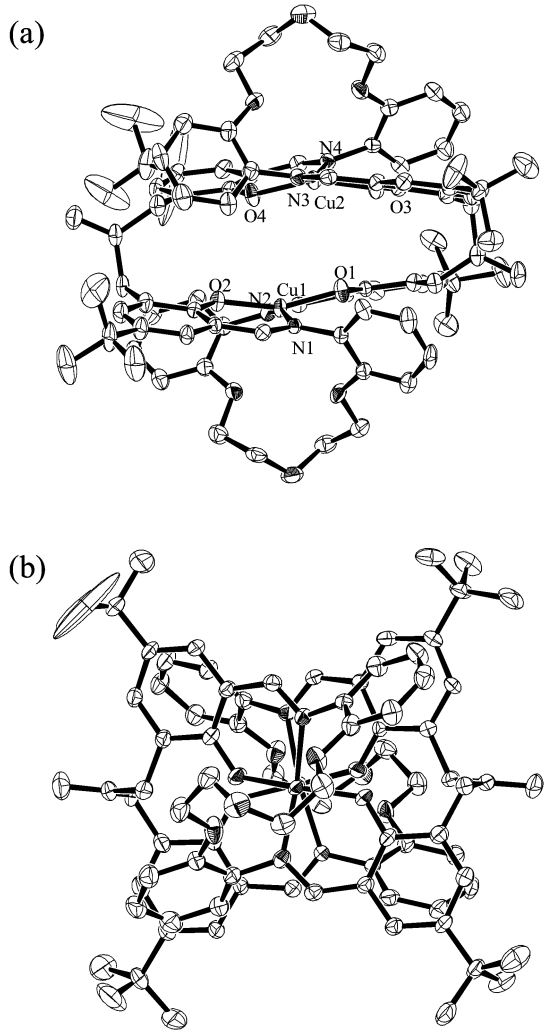


Fig. 2 ORTEP drawings of the dinuclear Cu(II) complex **3b**. (a) View along one pseudo-C_2 axis. (b) View along a second pseudo-C_2 axis (along the Cu1···Cu2 line). Selected interatomic distances (Å) and bond angles (°): O1–Cu1 1.875(3), O2–Cu1 1.874(3), N1–Cu1 1.995(3), N2–Cu1 1.999(3), O1–Cu1–O2 158.5(1), N1–Cu1–N2 160.3(1). O3–Cu2 1.884(3), O4–Cu2 1.883(3), N3–Cu2 1.991(3), N4–Cu2 1.982(3), Cu1–Cu2 3.8727(7), O3–Cu2–O4 159.7(1), and N3–Cu2–N4 161.3(1). The solvent of crystallization (THF) and hydrogen atoms are omitted for clarity.

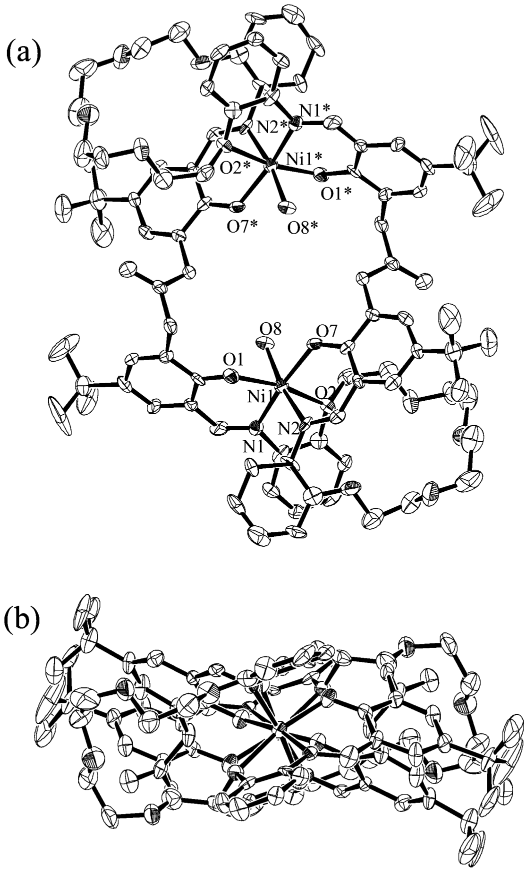


Fig. 3 ORTEP drawings of the dinuclear Ni(II) complex **3b**. (a) View from the direction perpendicular to the Ni1···Ni1* line. (b) View from the direction parallel to the Ni1···Ni1* line. Selected interatomic distances (Å): O1–Ni1 2.026(6), O2–Ni1 2.254(7), O7–Ni1 1.982(7), O8(H_2O)–Ni1 2.150(7), N1–Ni1 2.023(8), N2–Ni1 2.070(8), Ni1–Ni1* 7.733(3). Non-coordinated water molecules and hydrogen atoms are omitted for clarity.

Fig. 3 is an ORTEP drawing of **3c**. As with **3a**, the ligand part of the complex is the 2:2 macrocycle of **1b** and **2b**. Besides the two phenolic oxygens and two imine nitrogens from the SA units, one ether oxygen and one water molecule are bound to each nickel atom, which results in octahedral coordination.† In contrast to the ligand in **3a**, the ligand in **3c** is not helically twisted, but is folded in parallel and has a molecular point group of C_i. The difference in coordination may be attributed to the flexibility of ligand **2b**, which enables the ether oxygen atom of the tetraethylene glycol chain to coordinate to the nickel atom. The crystal structures [*cf.* Figs. 2(b) and 3(b)] clearly indicate that the *tert*-butyl groups of **3c** could have little influence on the folding of the complex.

It is notable that the helicity of complexes **3a** and **3b** does not originate from the coordination centre, which has nearly square-planar (pseudo-C_{2h}) symmetry. In contrast, other examples of double- and triple-stranded helicates have coordination centres with tetrahedral (pseudo-C_2) and octahedral (pseudo-C_3) symmetries, respectively.[5–9] In this regard, **3a** and **3b** are rather unusual helicates[13] and it is worth determining the origin of their helicity. Comparison of the crystal structures of **3a**–**c** indicates that a key factor related to the folding of the complex is the conformation of the isobutenylene linkage. There are three possible conformations for this linkage: skew-skew, *syn*-skew and *syn*-*syn*, depending on the dihedral

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† In more detail, three more water molecules are found in the unit cell, which are all involved in hydrogen bond interactions: O11···O1 (2.722 Å), O11···O7 (2.857 Å), O11···O8 (2.754 Å) and O9···O8 (2.883 Å).

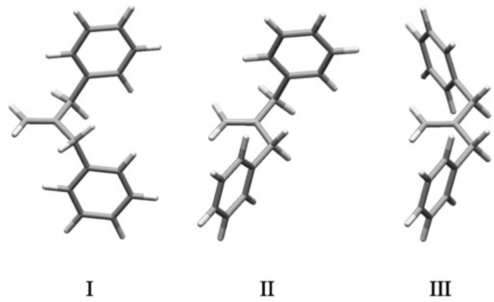

Fig. 4 Conformers of 2-benzyl-3-phenyl-1-propene as a model of isobutenylene linked compounds: I, skew-skew; II, *syn*-skew; and III, *syn*-*syn*.

angles (ϕ_1, ϕ_2) of the two C=C–C–C(Ar) moieties (Fig. 4).[10c] The isobutenylene chains in **3a** ($\phi_1 = 108.3°$, $\phi_2 = 108.9°$) and **3b** ($\phi_1 = 106.8°$, $\phi_2 = 107.2°$ and $\phi_1' = 89.0°$, $\phi_2' = 122.5°$) adopt the skew-skew form, whereas the chain in **3c** ($\phi_1 = 114.2°$, $\phi_2 = -11.8°$) adopts the *syn*-skew form. *Ab initio* molecular orbital calculations (MP2/6-311G** level) suggest that the skew-skew conformer is the most stable, by as much as 3 kcal mol^{-1}.[14] Therefore, the isobutenylene chain effectively affords C_2 axes in **3a** and **3b**, while inducing the helical structure. In contrast, complex **3c** adopts a *syn*-skew conformation because of distortion caused by the octahedral coordination, which prevents formation of the helix.

In summary, we have demonstrated that metal-templated self-assembly of ligands is influenced by several different variables, such as metal, substituents, linker length, and solvent. Although we have not examined all the combinations of these variables, our results indicate the preference of the structures (helical or non-helical) that will emerge under given conditions. First, metals with square-planar coordination, such as Ni(II) and Cu(II), are suitable for the helical form, but octahedral coordination may prevent the formation of the helix. Secondly, a substituent at the 5-position of the salicylidene group does not influence the formation of the helix. Thirdly, differences in the linker length may exert a considerable influence on helix formation. In this study, the replacement of **2a** by **2b** caused an unexpected change in the coordination of nickel, which resulted in non-helical folding. This effect of coordination change would compete with the conformational stability of the isobutenylene chains, which prefer a twisted geometry to some extent. Moreover, such energetic competition might be influenced by the solvent environment, by the presence of other ligands such as a water molecule, and even by crystal packing.

The above considerations on helix formation allow us to design a variety of molecules with helical moieties and to propose a supramolecular system, for example, in which a host molecule converts from helical structure to a non-helical structure in response to a guest molecule. These studies are now in progress.

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