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Stereoselective formation of a trinuclear hexa-stranded helicate-type zinc(II) complex

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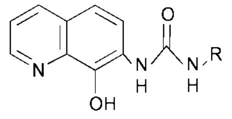
Received (in Cambridge, UK) 5th April 2001, Accepted 21st June 2001
First published as an Advance Article on the web 11th July 2001

8-Hydroxyquinoline derivatives HL[1] with urea moieties in the 7-position form hexa-stranded trinuclear coordination compounds with a helicate-type arrangement of the ligands; the chiral ligand HL[2] stereoselectively produces *P*-[Zn$_3$(L^2)$_6$].

Supramolecular architectures and molecular machines can be formed from simple components by self-assembly, which is controlled by the programming (‘molecular recognition’) which is encoded in the molecular building-blocks.[1] In this respect the control of stereo- and regio-chemistry during the self-assembly process is essential for the formation of specific, well-defined aggregates.[2]

Helicates are chiral di- or oligo-nuclear coordination compounds which are formed in self-assembly processes. One or more linear oligodonor ligand-strands wrap around the metal centers and thus possess a helical twist (left-handed *vs.* right-handed). Single-, double-, or triple-stranded helicates are obtained depending on the preferred coordination chemistry of the metal ions and on the kind of the ligands.[3] Only a few examples of analogous quadruple-stranded complexes are known.[4]

To our knowledge helicates with more than four ligand strands are not known although some complexes were described in which six ligands wrap around a metaloxo-cluster containing eight metal ions (M = Zn^{2+}, Cd^{2+}, Mn^{2+}) and two bridging μ_3-O^{2-} ligands.[5]



R = *n*-C$_8$H$_{17}$: H**L**^{1}
R = (*S*)-CH(Me)Ph: H**L**^{2}

The urea-substituted 8-hydroxyquinoline derivatives H**L** can be formed by reaction of 7-amino-8-hydroxyquinoline[6] with the *n*-octyl- or (*S*)-1-phenylethylisocyanate. Reaction of H**L** with zinc(II) acetate in methanol leads to zinc complexes which exhibit a metal/ligand ratio of 1:2. ^{1}H NMR spectroscopy (in CDCl$_3$) shows only one distinct set of signals for the coordinated ligand (Fig. 1) which possesses significant differences to those observed for the free ligand. For the zinc complex of **L**^{1} two signals are observed for the methylene unit which is attached to the urea-NH at δ 2.42 and 1.69 indicating diastereotopic behavior and thus a chiral environment. The remarkable high field shift of the protons in the 2- and 3-position of the alkyl chain [δ = 0.05 and 0.33 with $\Delta\delta$(ligand − complex) = 3.04 and 1.07] should be due to a close contact to the aromatic system of the hydroxyquinoline ligand. Indeed cross-peaks of alkyl signals with protons of the hydroxyquinoline can be observed by NOESY or ROESY NMR spectroscopy.

The complex of the chiral ligand **L**^{2} shows similar NMR spectroscopic features (Fig. 1) and a high optical rotation

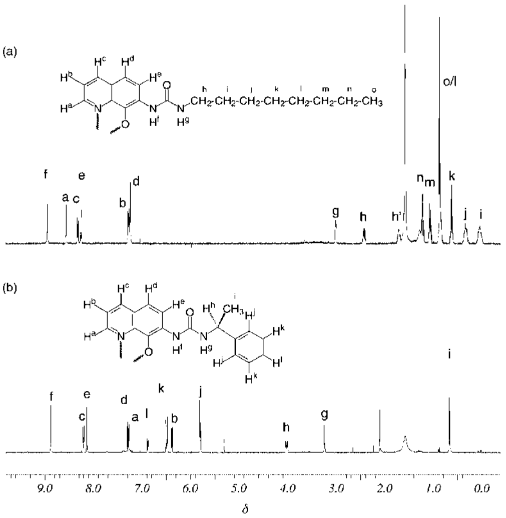


Fig. 1 ^{1}H NMR spectra of [Zn$_3$(**L**^{1})$_6$] (a) and *P*-[Zn$_3$(**L**^{2})$_6$] (b) in CDCl$_3$.

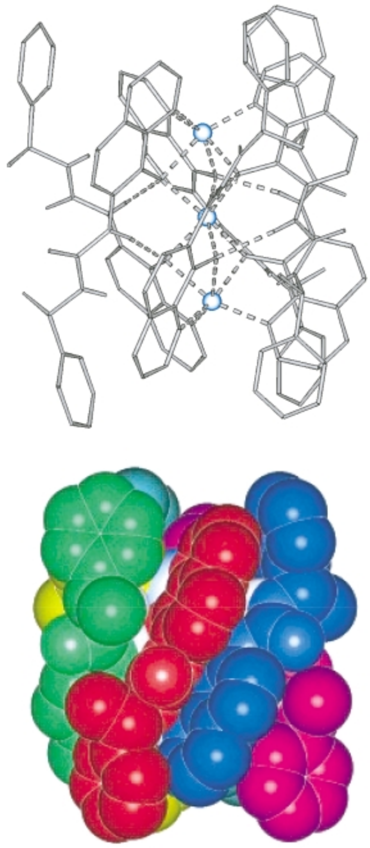


Fig. 2 Representations of the structure of *P*-[Zn$_3$(**L**^{2})$_6$] as found in the solid state, showing the helical arrangement of the six ligands around the three metal centers.

DOI: 10.1039/b103090f

{$[\alpha]_D = -1762$ (dioxane, $c = 0.1$); *cf.* $\mathbf{L^2}$: $[\alpha]_D = +27{,}6$ (dioxane, $c = 0.5$)} which indicates a helical arrangement of the ligands in the complex.[7] The ^{1}H and ^{13}C NMR spectra reveal that this complex is formed in a highly stereoselective fashion; only one stereoisomer is present. The enantiomeric trinuclear zinc(II) complex of the corresponding (*R*)-configurated ligand leads to $[\alpha]_D = +1815$ (dioxane, $c = 0.1$).

For the zinc(II) complex of the chiral ligand **L²** we obtained X-ray quality crystals from dioxane and the structural analysis shows that a trinuclear helicate-type complex $[Zn_3(\mathbf{L^2})_6]$ is formed.† Three zinc atoms are arranged linearly with the central atom possessing a separation of 2.884(3) and 2.879(3) Å to the two terminal ones. Six ligands are coordinating in a helical fashion to the metal centers with an alternating 'up' or 'down' orientation of the urea moieties (Figs. 2 and 3). Due to the chiral (*S*)-phenylethyl substituent *P*-helicity is induced at the hexa-stranded helix. This substituent at the urea is located close to the hydroxyquinoline units of a neighboring strand and thus leads to the anisotropic shifts found in the NMR spectra.

The complex $[Zn_3(\mathbf{L^2})_6]$ is made up from two terminal tris(8-hydroxyquinolinato) zinc complex units in which the chelating ligands are orientated *cis* to each other.[8] The three oxygen-donor atoms of each complex unit are located at facial positions and are able to bridge to the central zinc(II) ion (distances: O–$Zn_{terminal}$ 2.137–2.130 Å, O–$Zn_{central}$ 2.055–2.131 Å).[9,10] The trinuclear complex additionally is stabilized by interstrand hydrogen-bonding interactions between the aryl-NH protons and the quinolinato oxygen atoms. Thus, the oxygen-donors possess a tetracoordinated environment, bridging two metal centers and binding to one carbon and one hydrogen atom.

To summarise, we have presented the self-assembly of the first trinuclear hexa-stranded helicate-type complexes $[Zn_3(\mathbf{L})_6]$ from a total of nine components (six ligands and three metals). Alternatively, the compounds can be described as hexahelices made up from two interlocking triple-helical complexes '$[Zn(\mathbf{L})_3]^-$' connected by a zinc(II) ion and six hydrogen bonds. The unusual structure in the solid state is proven by an X-ray structure analysis of the chiral complex *P*-$[Zn_3(\mathbf{L^2})_6]$. NMR spectroscopy indicates that the same structure is present in solution and that the chiral complex *P*-$[Zn_3(\mathbf{L^2})_6]$ is formed highly stereoselective.

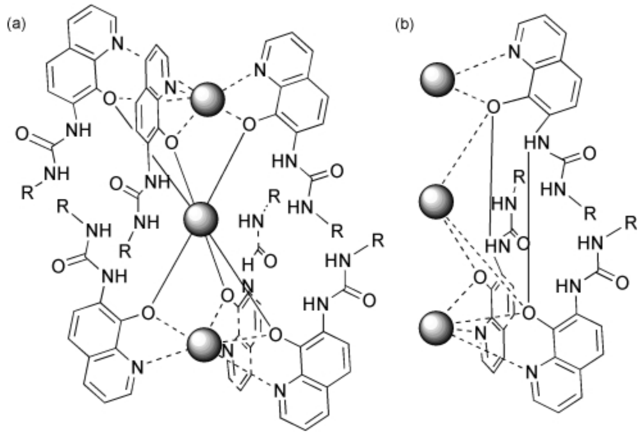


Fig. 3 Schematic representation of the structure of the complexes $[Zn_3(\mathbf{L})_6]$ (a), and the intramolecular interstrand hydrogen bonding (b).

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Notes and references

† *Crystal data* for $C_{108}H_{96}N_{18}O_{12}Zn_3\cdot 3C_4H_8O_2$, $M = 384.38$, monoclinic, space group $P2_1$ (No. 4), $a = 14.729(1)$, $b = 18.049(1)$, $c = 21.493(1)$ Å, $\beta = 108.50(1)°$, $V = 5418.5(5)$ Å^3, $D_c = 1.409$ g cm^{-3}, $\mu = 7.37$ cm^{-1}, $Z = 2$, $\lambda = 0.71073$ Å, $T = 198$ K, 13203 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin\theta)/\lambda] = 0.54$ Å^{-1}, 13203 independent and 8392 observed reflections [$I \geq 2\sigma(I)$], 1276 refined parameters, $R = 0.097$, $wR^2 = 0.182$, Flack parameter 0.07(2). CCDC reference number 157218. See http://www.rsc.org/suppdata/cc/b1/b103090f/ for crystallographic data in CIF or other electronic format.

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