# Self-assembly of the First Heterodinuclear d–f Triple Helix in Solution

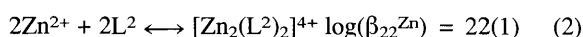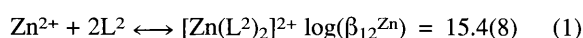Claude Piguet,*[a] Gérard Hopfgartner,[b] Alan F. Williams[a] and Jean-Claude G. Bünzli*[c]

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The segmental bidentate–tridentate ligand L^2 reacts with Ln^{III} and Zn^{II} in acetonitrile to give the first self-assembled heterodinuclear d–f triple-helical complexes $[LnZn(L^2)_3]^{5+}$ (Ln = La, Eu), as determined from solution-phase studies.

The preparation and study of supramolecular helical complexes has been the subject of considerable interest recently in order to unravel the intimate mechanisms of self-assembly processes.[1–3] Double-[1,2,4] and triple-helical[3,5,6] homopolynuclear structures have been generated by the complexation of tailored oligo-multidentate ligands with various d-block metal ions. However, it was realized only recently that luminescent lanthanide ions Ln^{III} could be introduced into self-assembled triple helices[7,8] and the development of new segmental ligands with different binding units connected by suitable spacers[9] offers promising possibilities for the synthesis of programmed heteropolynuclear complexes[10,11] which work as molecular light-converting devices.[8,12] It was shown recently that L^1 reacts with Fe^{II} and Ag^I to give the self-assembled heterodinuclear double-helical complex $[FeAg(L^1)_2]^{3+}$ where each cation occupies a site corresponding to its stereochemical preferences.[10] According to this strategy, the self-assembly of heterodinuclear helical d–f complexes requires the shift of the methyl group from the 6-position of the pyridine ring in L^1 to the 5-position in L^2, thus creating a ligand with a bidentate binding unit more suitable for efficient facial pseudo-octahedral coordination of d-block metal
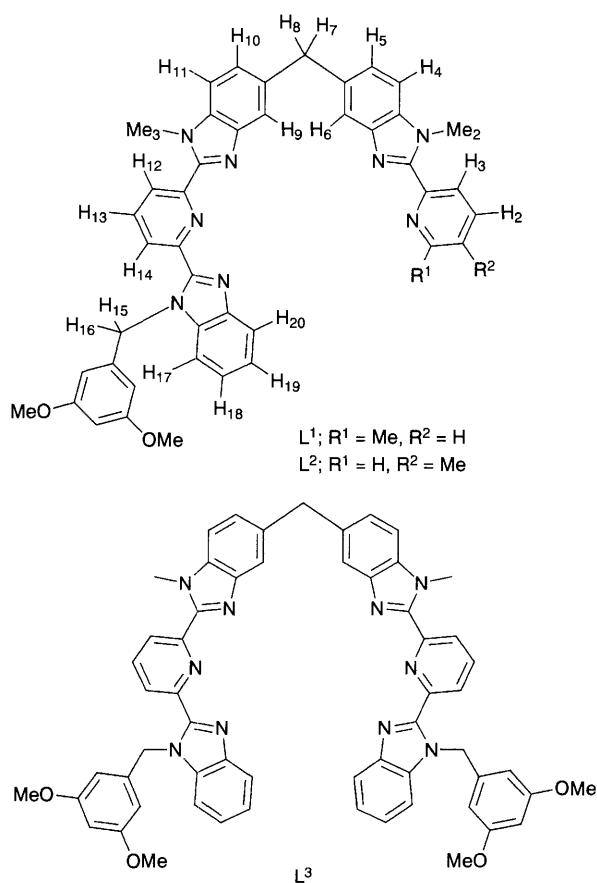
ions[6] and a tridentate unit suitable for pseudo-tricapped trigonal prismatic coordination of lanthanides.[7,8]

For homodinuclear d–d complexes, electrospray mass spectrometric (ES-MS) and spectrophotometric titrations of the ligand 2-{6-[1-(3,5-dimethoxybenzyl)-1H-benzimidazol-2-yl]-pyridin-2-yl}-1,1'-dimethyl-5,5'-methylene-2'-(5-methylpy-ridin-2-yl)bis[1H-benzimidazole] (L^2) with $Zn(ClO_4)_2·6H_2O$ in acetonitrile show the formation of $[Zn(L^2)_2]^{2+}$ (m/z 743.2) and $[Zn_2(L^2)_2]^{4+}$ (m/z 388.0), according to eqns. (1) and (2). Detailed ^1H NMR studies in CD_3CN (NOEDIFF and

$$Zn^{2+} + 2L^2 \longleftrightarrow [Zn(L^2)_2]^{2+} \; \log(\beta_{12}^{Zn}) = 15.4(8) \quad (1)$$

$$2Zn^{2+} + 2L^2 \longleftrightarrow [Zn_2(L^2)_2]^{4+} \; \log(\beta_{22}^{Zn}) = 22(1) \quad (2)$$

2D-NOESY)[10] show that $[Zn(L^2)_2]^{2+}$ adopts a C_2 head-to-head structure with both tridentate units meridionally coordinated to Zn^{II}, while $[Zn_2(L^2)_2]^{4+}$ displays the C_2 head-to-head double-helical structure (Fig. 1) reported for $[Zn_2(L^1)_2]^{4+}$.[10] This indicates that Zn^{2+} displays a stronger affinity for the tridentate coordinating units of L^1 and L^2 even though the bidentate unit is less constrained in L^2. Only traces of $[Zn(L^2)_3]^{2+}$ (m/z 1098.2) can be observed in the ES-MS spectrum in the presence of a large excess of ligand, as reported for L^1.[10]

For homodinuclear f–f complexes, spectrophotometric titrations of L^2 by $La(ClO_4)_3·7H_2O$ in acetonitrile show a sharp endpoint for a $La^{III}:L^2$ ratio of 0.65. Factor analysis[3] suggests the existence of a single absorbing complex and the spectrophotometric data can be satisfactorily fitted to eqn. (3).

$$2La^{3+} + 3L^2 \longleftrightarrow [La_2(L^2)_3]^{6+} \; \log(\beta_{23}^{La}) = 22.3(3) \quad (3)$$
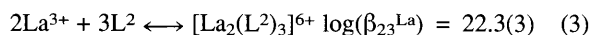
ES-MS spectra show only significant peaks corresponding to $[La_2(L^2)_3(ClO_4)_i]^{(6-i)+}$; i = 1–3 (m/z 501.8, 652.1, 902.6)[13] and ^1H NMR titrations confirm the formation of only one

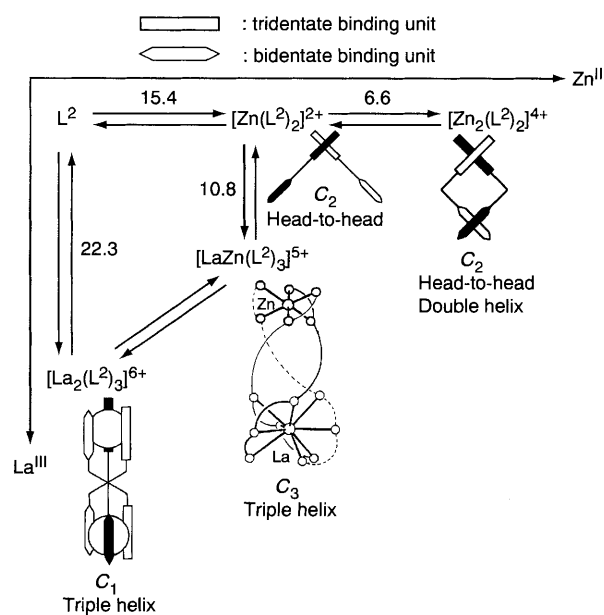L^1; R^1 = Me, R^2 = H
L^2; R^1 = H, R^2 = Me

L^3

Fig. 1 Equilibria of L^2 with La^{III} and Zn^{II} in acetonitrile

complex which displays a complex spectrum [Fig. 2(a)]. Detailed two-dimensional (^{1}H–^{1}H) correlation spectroscopy (COSY and NOESY) allows the complete assignment of the 78 signals arising from three different ligands L^2 coordinated to two La^{III} (two ligands L^2 adopt a head-to-head arrangement while the third ligand is oriented head-to-tail) and leading to the C_1 triple-helical structure depicted in Fig. 1.

For heterodinuclear d–f complexes, spectrophotometric titrations of L^2 with an equimolar mixture of $La(ClO_4)_3 \cdot 7H_2O$ and $Zn(ClO_4)_3 \cdot 6H_2O$ in the range $M_{tot} : L^2 = 0.1–2.5 : 1$, show a complicated variation of molar extinctions with two endpoints for metal : L^2 ratios of 0.3 and 1.0 : 1. These spectrophotometric data can be satisfactorily fitted with eqns. (1)–(4) [convergence was obtained with a root-mean-square (RMS) difference between observed and calculated absorbance of 0.002 unit] which strongly suggests that only one heterodinuclear complex $[LaZn(L^2)_3]^{5+}$ is formed during the titration. ES-MS spectra
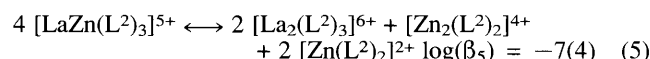
$$Zn^{2+} + La^{3+} + 3L^2 \longleftrightarrow [LaZn(L^2)_3]^{5+}$$
$$\log(\beta_{113}LaZn) = 26.2(3) \quad (4)$$
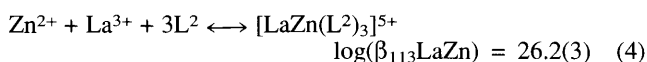
confirm this result and show the formation of $[LaZn(L^2)_3]^{5+}$ as the major product for a La : Zn : L^2 ratio of $1 : 1 : 3$ and a total concentration of $L^2 > 2 \times 10^{-4}$ mol dm^{-3} (m/z 467.3 together with adduct ions $[LaZn(L^2)_3 (ClO_4)_i]^{(5-i)+}$, $i = 1$–3). Other peaks corresponding to $[Zn(L^2)_2]^{2+}$ and free L^2 are also observed, and become the major peaks at lower concentrations. The ^{1}H NMR spectrum of a $1 : 1 : 3$ La : Zn : L^2 mixture in CD_3CN [Fig. 2(b)] shows a sharp spectrum implying the presence of one predominant species of high symmetry. Eqns. (1)–(4) predict that the concentration of $[LaZn(L^2)_3]^{5+}$ should be $ca.$ ten times greater than that of any other complex under these conditions. A detailed analysis of the NMR data (2D-COSY, 2D-NOESY and NOEDIFF) allows the complete assignment of the 26 signals which arise from three equivalent head-to-head ligands L^2 coordinated to La^{III} and Zn^{II} in an arrangement of the strands about the metal ions compatible with C_3 or C_{3v} symmetry on the NMR timescale. The two methylene groups H_7, H_8 and H_{15}, H_{16} give diastereotopic protons which precludes the existence of mirror planes,[4] leading to a C_3 triple-helical structure for $[LaZn(L^2)_3]^{5+}$. Detailed NOE measurements confirm that both bi- and tri-dentate units display cisoid conformations as a result of their coordination to Zn^{II} and La^{III} (NOE effects between Me_2–H_3 and Me_3–H_{12}) and that the diphenylmethane spacer adopts the characteristic conformation found for helical complexes[8,10] (intraligand NOE effects

between H_6–H_8, H_5–H_8, H_6–H_9). An interstrand NOE effect observed between Me_3–H_{15} implies the wrapping of the three tridentate units about the C_3 axis as previously reported[8] for $[Ln_2(L^3)_3]^{6+}$ (Ln = La, Eu, Gd, Tb, Lu) with an interstrand distance between Me_3–H_{15} of 3.5–3.8 Å as determined from the X-ray crystal structure of $[Eu_2(L^3)_3]$ $(ClO_4)_6]$.[14] Other significant interstrand NOE effects (H_{12}–H_5, Me_3–H_5, H_{12}–H_9) are only compatible with the packing of the ligands resulting from a triple-helical arrangement, confirming that $[LaZn(L^2)_3]^{5+}$ is a C_3 triple helix with La^{III} occupying the pseudo-tricapped trigonal prismatic site defined by the three wrapped tridentate units,[7,8,12] and Zn^{II} lies in the pseudo-octahedral site defined by the remaining bidentate units (Fig. 1). Slow diffusion of diethyl ether into a concentrated acetonitrile solution gives a high yield ($\geq 90\%$) of a beige microcrystalline powder whose elemental analysis corresponds to $[LaZn(L^2)_3](ClO_4)_5 \cdot 5H_2O$. The microcrystals are readily soluble in acetonitrile and give spectra (ES-MS, UV-VIS, ^{1}H NMR) identical to those obtained for $[LaZn(L^2)_3]^{5+}$ formed in $situ$. Similar behaviour is observed when Eu^{III} is substituted for La^{III}, leading to the self-assembly of the luminescent C_3 triple-helical complex $[EuZn(L^2)_3]^{5+}$ [m/z 469.8; $\log(\beta_{113}^{EuZn}) = 25.3(4)$].

The ligand luminescence at 77 K consists of an intense and structured band at 400 nm, with shoulders at 410 and 450 nm, arising from the $^1\pi\pi^*$ state, and of a double band centred at 530 nm corresponding to emission from a $^3\pi\pi^*$ state (lifetime 350 ms). Upon complexation, the $^1\pi\pi^*$ band undergoes bathochromic shifts of 45 (LaZn, lifetime 124 ms) and 60 nm (EuZn), respectively. A substantial antenna effect is observed in the Eu-containing complex. When excited at 340 nm, the emission spectrum of a microcrystalline sample displays, in addition to the triplet band, numerous sharp peaks which can be assigned as arising from the $Eu(^5D_J)$ levels ($J = 0$–2). The laser-excited excitation spectrum in the range of the $^5D_0 \leftarrow {}^7F_0$ transition contains only one, symmetrical but broad band (full width at half height 27 cm^{-1}), characteristic of a single metal ion site.[15] Under excitation at 400 nm, the $^5D_0 \rightarrow {}^7F_J$ emission spectrum obtained is typical of a substantially distorted C_3-symmetric species: the $^5D_0 \rightarrow {}^7F_1$ transition consists of three almost equally spaced components ($^7F_1$ crystal field levels at 314, 393, 438 cm^{-1}) and the relative, corrected and integrated intensities of the transitions to the ^7F_J levels are equal to 0.01, 1.0, 2.3, 0.2 and 2.3 for $J = 0, 1, 2, 3$ and 4, respectively. A similar, although less intense, luminescence spectrum arises when the excitation is achieved through the $^5D_0 \leftarrow {}^7F_0$ transition, which exemplifies the role played by the ligand in transferring energy onto the metal ion. The luminescence lifetime of the $^5D_0$ level (2.05 ± 0.1 ms) points to a europium ion well protected from deexcitation processes at low temp. (77 K). At room temp., however, the luminescence is much weaker and is non-measurable in 10^{-2} mol dm^{-3} solution.

In conclusion, the spectroscopic data show that the heterodinuclear complex $[LaZn(L^2)_3]^{5+}$ is the predominant product in solution when the ligand and metal ions are mixed in a stoichiometric ratio of $3 : 1 : 1$. Eqns. (1)–(4) allow calculation of eqn. (5) which, in spite of the large error, shows the stability

(a)

(b)

Fig. 2 ^{1}H NMR spectra of (a) $[La_2(L^2)_3]^{6+}$ and (b) $[LaZn(L^2)_3]^{5+}$ in CD_3CN (total concentration of L^2 1.5 × 10^{-2} mol dm^{-3})

$$4 [LaZn(L^2)_3]^{5+} \longleftrightarrow 2 [La_2(L^2)_3]^{6+} + [Zn_2(L^2)_2]^{4+}$$
$$+ 2 [Zn(L^2)_2]^{2+} \log(\beta_5) = -7(4) \quad (5)$$

of the heterodinuclear species. Although L^2 possesses only heterocyclic nitrogen donor atoms in both coordination sites, f- and d-block metal ions can be complexed selectively by the different coordinating units as a result of the low affinity of Ln^{III} for bidentate heterocyclic units.[12] This demonstrates that segmental heterocyclic multidentate ligands, which are particularly attractive for the preparation of homodinuclear luminescent devices with lanthanides (strong antenna effect, protection from external interactions, selective coordination of lanthanides)[7,12] are also suitable for the preparation of self-assembled heterodinuclear molecular light-converting devices.
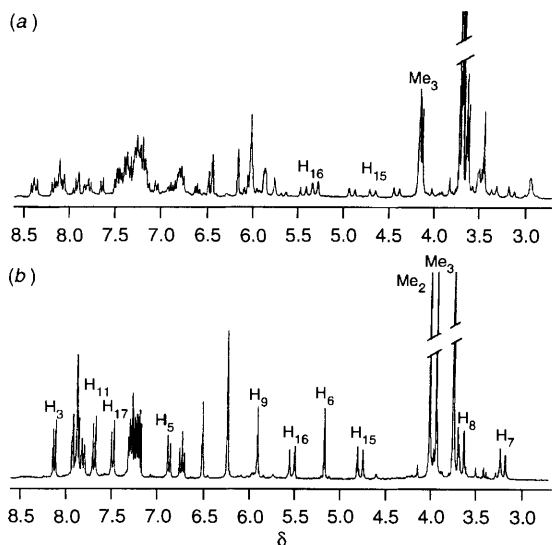
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