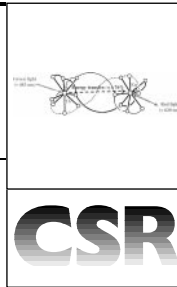


Mono- and polymetallic lanthanide-containing functional assemblies: a field between tradition and novelty



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Received 19th May 1999

The variable and versatile co-ordination behaviour of lanthanide metal ions, Ln^{III}, limits their selective introduction into organised molecular or supramolecular architectures. The design of lanthanide-based devices is thus a special challenge since their specific electronic, magnetic or spectroscopic properties result from a precise control of the co-ordination sphere around the metal ions. The *lock-and-key* principle associated with the preorganisation of rigid macropolycyclic multidentate ligands tailored for one particular Ln^{III} only partially fulfils these structural requirements. The development of less constrained macrocyclic ligands or macrocycles bearing pendant arms allows a smooth transition toward flexible (predisposed) receptors leading to the application of the *induced fit* principle in lanthanide co-ordination chemistry. According to this concept, programmed secondary non-covalent interstrand interactions (π -stacking, hydrogen bonds, electrostatic re-

pulsion) assist the complexation process leading to an ultra-fine tuning of the metallic co-ordination sites. These two complementary approaches are discussed and evaluated for the design of organised mono-, di- and polymetallic lanthanide complexes together with the consideration of new semi-rigid multidentate podands which combine both aspects.

1 Mono- versus polymetallic lanthanide-containing functional devices

The lanthanides correspond to the first period of the f-block elements starting at lanthanum ($Z = 57$) and ending at lutetium ($Z = 71$). As a result of the low energy of the 4f orbitals, one 5d and two 6s electrons are easily removed leading to a complete series of stable Ln^{III} cations possessing characteristic 4fⁿ open-

Claude Piguet was born in 1961. He studied chemistry at the University of Geneva and obtained his PhD thesis with felicitations in 1989 in the field of biomimetic copper–dioxygen complexes. He pursued his formation as a postdoctoral fellow in the group of Prof. J.-M. Lehn (University of Strasbourg, 1989–1990) and then collaborated as Maître-assistant with Prof. A. F. Williams (University of Geneva, 1990–1994) and Prof. J.-C.G. Bünzli (University of Lausanne, 1995). In 1995 he received the Werner Medal of the New Swiss Chemical Society for his research in the field of supramolecular chemistry of d- and f-block metal ions. Recipient of the Werner grant for the project 'Toward Organized Luminescent Materials' and Lecturer at the University of Geneva (1995–1998), he was nominated full Professor in Inorganic Chemistry in 1999. His



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research interests and topics include the design of controlled self-assembled supramolecular complexes with d-block and f-block metal ions, the development of functional lanthanide probes and sensors, the preparation of lanthanide-containing metallomesogens and the application of paramagnetic NMR for characterizing co-ordination complexes in solution.

Jean-Claude Bünzli was born in 1944. He earned a degree in chemical engineering in 1968 and a PhD in 1971 (Swiss Federal Institute of Technology, Lausanne) for his work on the kinetic behaviour of Nb and Ta pentachloride adducts. He spent two years at the University of British Columbia as a teaching postdoctoral fellow (photoelectron spectroscopy) and one year at the Swiss Federal Institute of Technology in Zürich (physical organic chemistry). He was appointed assistant-professor at the University of Lausanne in 1974 and started a research program on the spectrochemical properties of f-elements. He was promoted as a full Professor of Inorganic and Analytical Chemistry in 1980. He acted as the elected Dean of the Faculty of Sciences (1990–1991) and as one of the elected Vice-Rectors of the University (1991–1995). He held positions of invited



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professor at the Université Louis Pasteur, Strasbourg in 1996 and at the Science University of Tokyo in 1998. He is a member of the Finnish Academy of Sciences and Letters and of the editorial boards of *Spectroscopy Letters* and *Acta Chemica Scandinavica*. His present research focuses on supramolecular chemistry of lanthanide ions, with a special emphasis on the design of luminescent devices.

shell configurations ($n = 0$ for La $\rightarrow n = 14$ for Lu). These 4f orbitals have less radial extension than the filled 5s² and 5p⁶ orbitals and are thus shielded from external perturbations¹ and the 4f electrons are little involved in covalent interactions upon the formation of chemical bonds, leading to a poor stereochemical control in lanthanide-containing edifices. Consequently, the Ln^{III} ions display large and variable co-ordination numbers (CN = 8–12)² which are difficult to predict because the hard Ln^{III} ion will complete its co-ordination sphere by binding small molecules or anions (water, chloride, hydroxide, *etc.*) if the number of available sites offered by the host is too low. On the other hand, steric constraints strongly influence the coordination sphere, so that a given multidentate receptor may impose a particular co-ordination number around the metal. Finally, when one realises that the fine tuning of the fascinating electronic, spectroscopic and magnetic Ln^{III} properties required for the design of functional molecular building blocks with potential uses in biology, medicine, and materials sciences results from a precise structural control of the metal ion sites (accessibility, geometry, symmetry, type and number of the donor atoms, nature of the different ions in polymetallic assemblies),³ it is obvious to conclude that the selective incorporation of Ln^{III} ions into highly organised architectures is the limiting step for designing programmed functional devices.

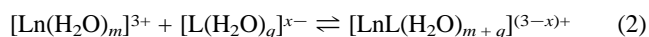
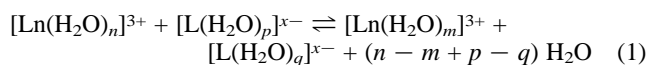
Most of the systems of practical use today rely on monometallic lanthanide complexes with optimised structural and electronic properties. Some homodi- and homotrimetallic complexes have been tested too, with their designs based on the principles prevailing for monometallic species. Prospects for the development of such systems are good as far as chemical properties are concerned, for instance hydrolytic catalysts for biological systems⁴ or porphyrinogen complexes for the fixation and reduction of dinitrogen.⁵ On the other hand, physico-chemical properties of homodimetallic species are often not much enhanced compared to those of the monometallic systems and the development of heteropolymetallic architectures in which a judicious combination of different 4f ions imbedded at specific locations would offer new perspectives for programming advanced functional devices such as (i) micelles or polymers in which the luminescent ion is sensitised by light-harvesting ligands organised around a non-luminescent ion, (ii) vectorial devices for energy and/or electron migration, (iii) systems acting both as luminescent probes and contrast agents, (iv) precursors for doped materials in which the lanthanide ions have to be inserted at given distances. Such heteropolymetallic complexes create an additional task for the chemist since they require the recognition of specific lanthanide ions by the different compartments of a polytopic receptor. This represents a real challenge because as far as co-ordination chemistry is concerned the only difference between Ln^{III} ions is a small monotonous contraction of the ionic radius with increasing atomic numbers. In going from La^{III} to Lu^{III}, the total relative contraction amounts to only *ca.* 16%, a figure that can be compared to the difference in ionic radius observed between Na⁺ and K⁺ (26%) and careful attention has therefore to be given to the design of polytopic receptors for preparing pure heteropolymetallic lanthanide-containing devices.

In this paper, we review the various methods adopted so far to master the chemical environment of the lanthanide ions in monometallic systems and we explore ways to produce polytopic receptors for heteropolymetallic 4f–4f edifices based on the experience gained with homodimetallic 4f–4f and heterodimetallic 4f–3d complexes.

2 Underlying concepts for the control of the Ln^{III} co-ordination sphere

Detailed thermodynamic investigations of lanthanide complexation processes in water point to a remarkable compensa-

tion effect responsible for the emergence of the well-known electrostatic trend, *i.e.* a monotonous increase of the formation constants of the complexes with the decreasing size of Ln^{III}.⁶ Two successive steps can be written for the net complexation reaction of a Ln^{III} ion with a ligand L corresponding to dehydration [eqn. (1)] followed by the combination of the desolvated partners [eqn. (2)].



Opposite enthalpic and entropic contributions are expected for each reaction, but the compensation effect assumes that the free energy for the dehydration process [eqn. (1)] is negligible at room temperature because $\Delta H_1 \approx T\Delta S_1$. The global free energy of the complexation process is thus dominated by the enthalpy-driven combination step ($\Delta G_{\text{global}} = \Delta G_1 + \Delta G_2 \approx \Delta G_2$) leading to increased formation constants with increasing charge density on the cation. Although this simple approach is often used as a guideline for interpreting thermodynamic data for lanthanide complexes, the introduction of steric constraints, preorganisation and/or chelate effects within sophisticated receptors may alter the expected electrostatic trend because specific intramolecular interactions and solvation effects are not considered in this simple model. Some selectivity (= deviation from the electrostatic trend) for the complexation of Ln^{III} has been evidenced for polycarboxylates and related acyclic polydentate receptors, but the rationalisation of these observations is difficult and the associated structural control is limited.⁶ On the other hand, the recently emerging applications of lanthanide-containing systems in chemistry, biology and medicine require a high degree of structural and electronic control, as demonstrated by the following three examples.

(a) Luminescent sensors and molecular light-converters can take advantage of the specific properties associated with 4f^{*n*} open-shell configurations of Ln^{III} ions (narrow emission lines in the visible or IR range, long-lived excited states) if the following requirements are fulfilled in the final devices: (i) a precise structural and geometrical arrangement of the donor atoms around Ln^{III}, (ii) a good protection of the metallic site from solvent molecules possessing high-frequency C–H, N–H or O–H vibrations which deactivate the metal-centred excited states, (iii) sufficient thermodynamic stability and kinetic inertness and (iv) suitable ligand- and metal-centred excited levels for efficient intramolecular energy transfers.⁷ The design of a receptor satisfying these criteria is difficult for monometallic complexes and becomes a stimulating challenge for extended heteropolymetallic assemblies working as directional light-converting devices or logic gates (Fig. 1a).⁸

(b) Similar considerations apply to contrast agents used in magnetic resonance imaging (MRI, Fig. 1b) and based on Gd^{III}-containing edifices in view of the ⁸S_{7/2} electronic configuration of this paramagnetic ion. The accessibility to the metal ion has to be strictly controlled since water molecules must enter the first co-ordination sphere to maximise inner-sphere relaxivity, but no de-complexation is tolerated because of the high toxicity of the aquo-ion.⁹ Moreover, the exchange rate between co-ordinated and bulk water should be optimised to ensure an efficient transfer of the paramagnetic information. The development of successful contrast agents again relies on the careful engineering of organised architectures, as recently exemplified by the design of a calcium-sensitive magnetic resonance imaging contrast agent based on a dimetallic Gd^{III} supramolecular edifice.¹⁰

(c) The catalytic sequence-specific cleavage of phosphodiester bridges in RNA and DNA is required in antisense technology used for the development of new therapies. Recent developments have shown that co-ordination of water mole-

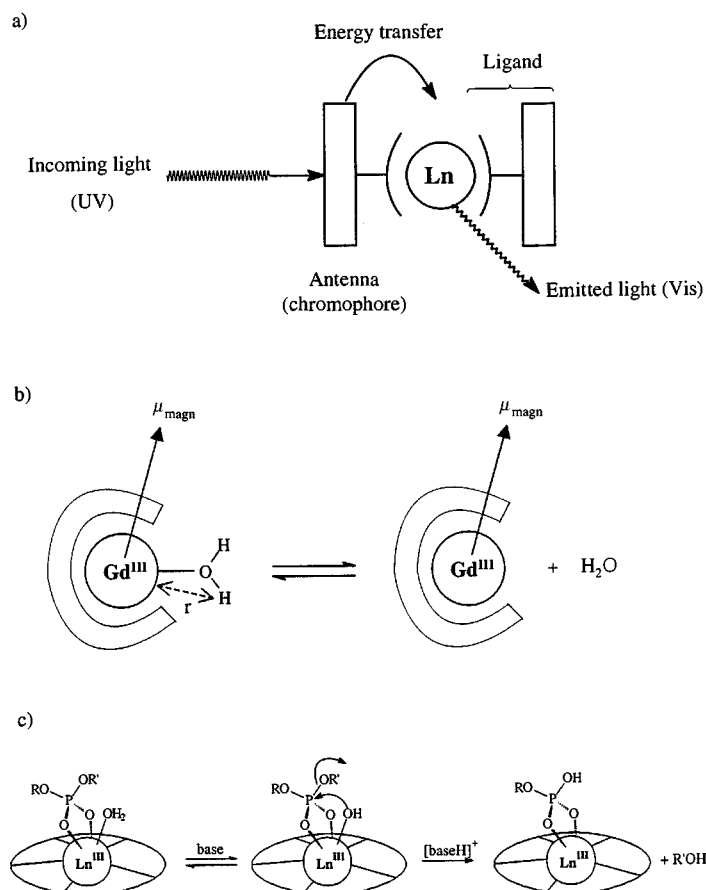


Fig. 1 Schematic representation of lanthanide-containing functional devices working as a) a UV–vis light converter, b) a MRI contrast agent and c) a catalyst for the hydrolysis of the phosphodiester bond.

cules and phosphate residues to Ln^{III} respectively assists the deprotonation of the nucleophile and activates the substrate providing the needed catalytic effect which has been first demonstrated with monometallic macrocyclic Ln^{III} complexes conjugated to oligonucleotides (Fig. 1c).¹¹ Interestingly, impressive accelerations have been observed for homodimetallic lanthanide complexes in which the metal ions activate simultaneously the nucleophile (water) and the electrophile (phosphate residue).⁴

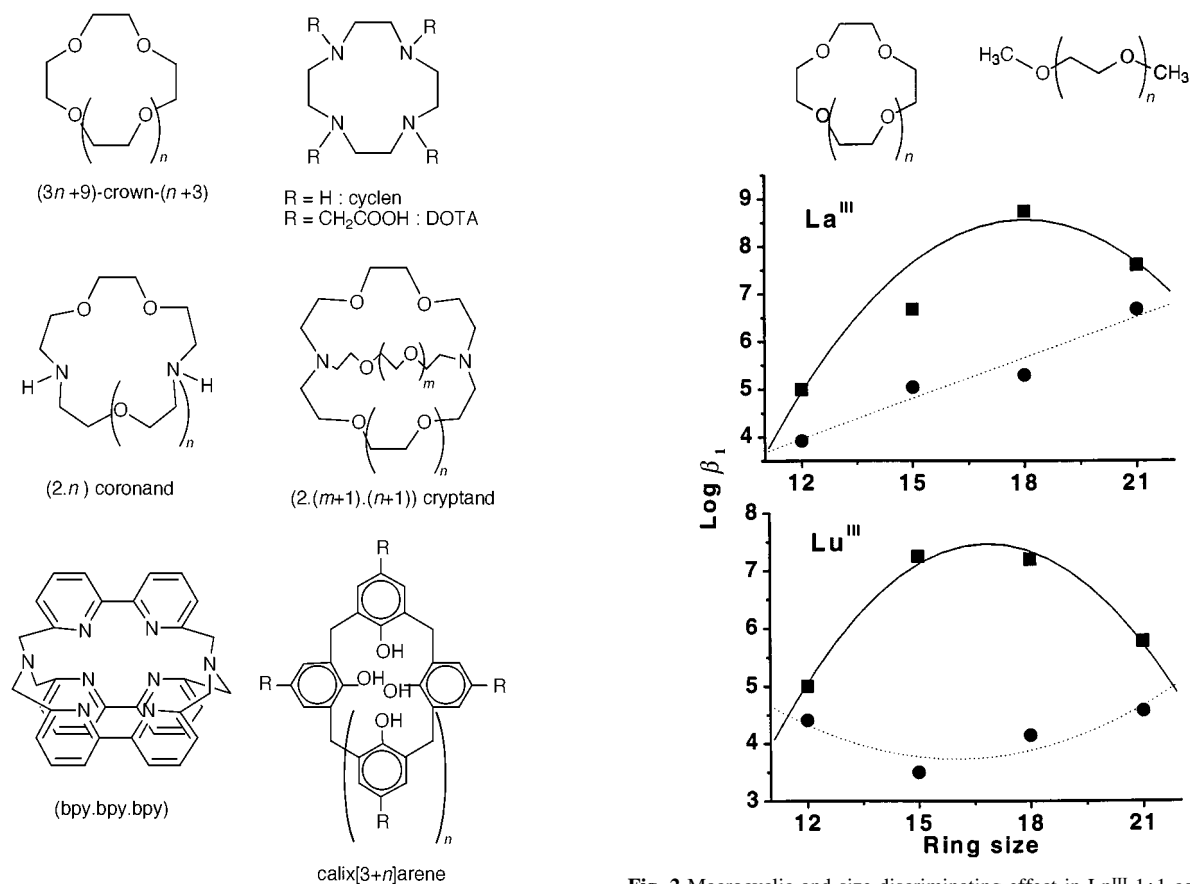
This brief survey reveals that a considerable gap exists between the molecular organisation provided by usual multidentate ligands bound to Ln^{III} and the precise structural and electronic control required for programming lanthanide-containing functional devices. For more than two decades, the *lock-and-key* principle¹² combined with preorganisation of rigid receptors has been extensively investigated for solving this problem, but the recent consideration of more flexible systems has led to the (re)discovery of the *induced fit* principle associated with the predisposition of the receptor.¹³ From a thermodynamic point of view, the preorganisation of the receptor according to the *lock-and-key* concept aims at minimising the entropy cost of the complexation process while maximising the enthalpy-favourable ligand–metal interactions and related work on the encapsulation of Ln^{III} ions by rigid macrocyclic and macropolycyclic ligands is presented below. This approach is critically compared with the parallel development of less rigid receptors: (i) macrocycles with grafted pendant arms and (ii) multidentate ligands and podands which tend to overcome the increased entropy cost of the assembly process through optimisation of convergent non-covalent interactions according to the *induced fit* concept.

3 Structural, thermodynamic and electronic control in monometallic lanthanide complexes

3.1 The *lock-and-key* principle

The principle has deep roots in biological processes in which molecules can only be chemically active if they are attached onto a receptor. According to Emil Fischer (1894), the fixation must be selective, which implies a strict steric match between the receptor and the host, hence the “lock-and-key” image to illustrate the requirements of molecular recognition. These notions (fixation, molecular recognition) together with the concept of co-ordination brought forward by Werner at the turn of the 20th century are the basis of supramolecular chemistry.¹⁴ The simplest example of molecular recognition is the selective complexation of a spherical entity, for instance a spherical metal ion (Na^{I} , Ca^{II} , Al^{III} , Cu^{I} , Ln^{III} , *etc.*) and to meet this challenge, several types of monocyclic (coronands) and polycyclic (cryptands) receptors have been developed. The receptor contains the necessary chemical information stored in its structure and the relevant properties for the recognition process are its form, its size and the number and nature of the anchor sites (donor atoms). The characteristics of the latter include their position in the receptor, their electronic properties (charge density, polarisability, ability to engage in van der Waals interactions) and their chemical reactivity upon coupling with the host (acid–base or redox processes).

Following the initial work on alkaline and alkaline earth cations, crown ethers were chosen to test size-discriminating effects along the Ln^{III} series (Scheme 1).¹⁵ In propylene carbonate, the maximum stability of the coronates is gradually shifted from 18-crown-6 for the lighter Ln^{III} ions to 15-crown-5



Scheme 1

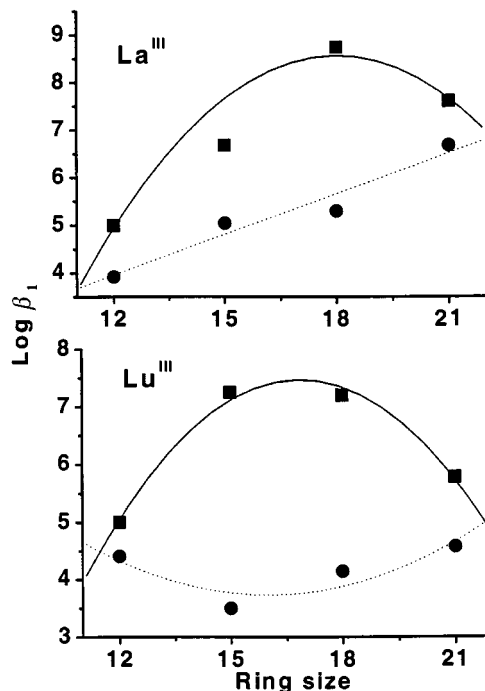


Fig. 2 Macrocyclic and size-discriminating effect in Ln^{III} 1:1 complexes with crown ethers (■) and with the corresponding open-chain analogues (●) (adapted from ref. 16).

for the heavier ones. The entropy-driven macrocyclic effect (the difference in stability between the coronate and the complex with the open-chain analogue) is usually at a maximum for the best adjusted macrocycle. The discriminating effect is nevertheless small, with $\Delta\log K = 1\text{--}2$ between two consecutive macrocycles, as shown in Fig. 2, mainly because the cavity size cannot be tuned finely enough.¹⁶ Adding one $-(\text{CH}_2)_2\text{-O}$ group enlarges the mean cavity diameter by more than $0.5\text{--}0.7$ Å,¹⁴ a difference 2–3 times as large as the contraction of the ionic radius along the entire Ln^{III} series! Moreover, the macrocycles are not completely rigid and they adapt their conformation when the ionic radius decreases. Combined with the electrostatic trend, this leads to almost identical stability constants for the Lu^{III} coronates with 15-crown-5 and 18-crown-6 ethers. If the macrocycle is too small, sandwich 1:2 complexes form and differentiation between the Ln^{III} ions is now determined by steric repulsion of the ligands when the Ln–O distance becomes shorter: complexes with lighter Ln^{III} ions are more stable but, again, $\Delta\log K_{\text{La-Lu}}$ is only of the order of 1–2. Better discrimination can be achieved by rigidifying the ligand upon fusion with benzyl rings ($\Delta\log K_{\text{La-Lu}} = 2.6$ for dibenzo-18-crown-6), at the cost of the overall stability which drops by almost 4 orders of magnitude for La^{III}. On the other hand, adding more flexibility into the ring by replacing two ether functions in 18-crown-6 with two amine groups results in an increased stability of over 8 orders of magnitude, while any size-discriminating effect is lost.

Moving to macrobicyclic receptors such as cryptands does not improve the situation since the addition of a $-(\text{CH}_2)_2\text{-O}$ group in one of the side chains also enlarges the cavity too much to get a fine tuning adapted to the small size difference between two consecutive Ln^{III} ions. As a matter of fact, there is almost no gain in stability over the diazapolyoxyocycloalkanes and the stability remains almost constant along the Ln^{III} series or has the tendency to be governed by electrostatic effects, depending on

the solvent. In addition, small particles such as water, fluoride, or even an oxygen atom from a perchlorate group can slide between the arms and interact with the metal ion. However, interesting bicyclic receptors have been designed, which provide high stability and good energy transfer for the sensitization of the Eu^{III} and Tb^{III} ions. One example is the tris(bipyridine) cryptand (bpy.bpy.bpy) used in homogeneous immunoassays.¹⁷

In parallel to this work, and to circumvent some of the limitations encountered with rigid monocyclic and bicyclic receptors, ionisable macrocycles have been developed, bearing pendant arms fitted most frequently with carboxylic or phosphorous-containing acid functions. The presence of the latter leads to the formation of strong complexes, owing to a hard ion–ion interaction between Ln^{III} and the carboxylate anions. The ligands are intermediate between preorganised and predisposed entities, since the complexed pendant arms usually have a different conformation than in the free ligand and since they can adapt to the varying size of the Ln^{III} ions. Several platforms have been used to graft these arms: crown ethers, diazapolyoxyocycloalkanes, cyclen and other polyazacycloalkanes, and more recently calixarenes. Although significant size-selective effects are usually not observed within the Ln^{III} series, these ionisable macrocycles proved to be good chelating agents for the selective complexation of lanthanides over alkali and alkaline earth cations.¹⁸ A general trend is that the stability can be slightly tuned by adjusting the ring size and the number of donor atoms of the platform as well as the number of arms to form a suitable cage structure for the Ln^{III} ion. Among all the ligands tested, DOTA (1,4,7,10-tetrakis(carboxymethyl)-1,4,7,10-tetraazacyclododecane) proved to be one of the best sequestering agent for Ln^{III} ions, with $\log K$ in the range 22–26 and non-cyclic ligand behaviour: *i.e.* the stability of the complexes increases with the increase in charge density. Thanks to its high stability, the complex $[\text{Gd}(\text{DOTA})]^-$ has been

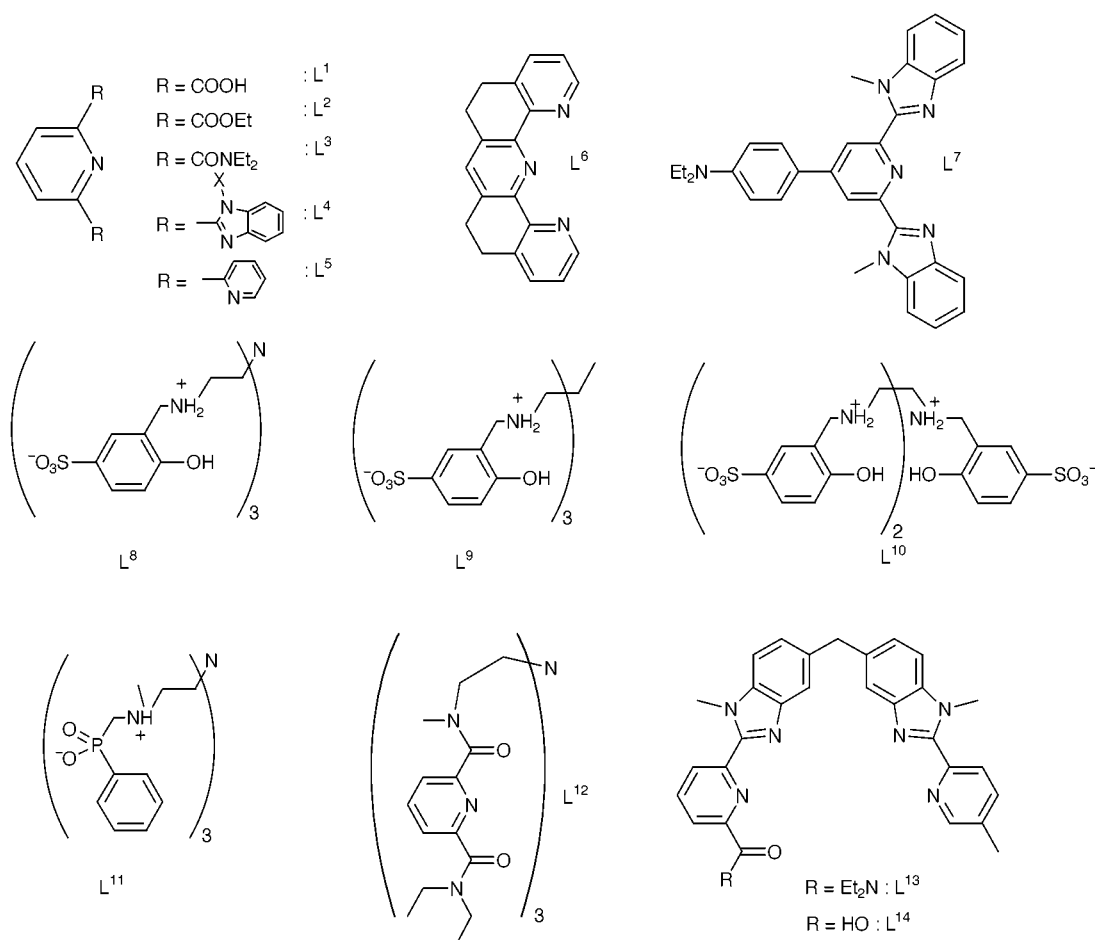
developed as an efficient contrast agent for magnetic resonance imaging.

3.2 The induced fit principle

The ever-increasing demand for improved selectivity in the complexation of lanthanide metal ions has led to the consideration of the *induced fit* principle which uses flexible receptors in order to optimise the interactions with the metal ions which act as template agents. The increased entropic cost of the complexation process compared with preorganised systems is overcome by the programming of stabilising intramolecular non-covalent interstrand interactions which can be modulated by judicious design of the receptor. The coding of suitable structural and electronic information in a receptor which will be expressed in the final complex and optimised for one particular metal ion is not an easy task, especially for 4f ions.¹⁹ To the best of our knowledge, Grenthe described the first lanthanide complexes $[\text{Ln}(\text{L}^1\text{-}2\text{H})_3]^{3-}$ exhibiting secondary intramolecular interactions affecting the thermodynamic trend along the lanthanide series according to the *induced fit* concept (Scheme 2).²⁰ The cumulative formation constants $\log(\beta_3)$ for $[\text{Ln}(\text{L}^1\text{-}2\text{H})_3]^{3-}$ in water display the classical electrostatic trend for large Ln^{III} ($\text{Ln} = \text{La-Tb}$), reach a plateau around Dy–Er which corresponds to a weak peak of selectivity for these ions and then decrease for the smaller Ln^{III} ($\text{Ln} = \text{Tm-Lu}$; Fig. 3). In the crystal structures of $[\text{Ln}(\text{L}^1\text{-}2\text{H})_3]^{3-}$, the de-protonated dipicolinate ligands are wrapped around Ln^{III} to give triple-helical complexes in which the metal ion is nine co-ordinate in a pseudo-tricapped trigonal prismatic site. This D_3 -symmetrical structure is maintained in solution along the complete lanthanide series and the decrease of $\log(\beta_3)$ for the heavy Ln^{III} ($\text{Ln} = \text{Tm-Lu}$) cannot be attributed to different co-ordination numbers

in the final complexes. Steric constraints were invoked in the original paper,²⁰ but a careful consideration of the molecular structure of $[\text{Ln}(\text{L}^1\text{-}2\text{H})_3]^{3-}$ shows that the building of the metal ion cavity brings the negatively charged carboxylate side arms of one ligand very close to those belonging to the neighbouring strands (Fig. 3a). For large Ln^{III} ions, the contact distance remains sufficient to produce minor electrostatic repulsion (minimum average O...O distance = 3.46 Å for $[\text{La}(\text{L}^1\text{-}2\text{H})_3]^{3-}$), but the contraction of the Ln^{III} radius induces an increased repulsion between the carboxylate groups (average O...O distance = 3.26 Å for $[\text{Lu}(\text{L}^1\text{-}2\text{H})_3]^{3-}$) which eventually destabilises the complexes with the heavy Ln^{III} ions. Although these secondary interactions remain limited and β_3 decreases by a factor less than 10 between $[\text{Er}(\text{L}^1\text{-}2\text{H})_3]^{3-}$ and $[\text{Lu}(\text{L}^1\text{-}2\text{H})_3]^{3-}$, these preliminary observations suggest that the *induced fit* principle can be applied for the selective recognition of Ln^{III} ions.

In order to substantiate this interpretation, a series of neutral symmetrical tridentate ligands containing a central pyridine ring connected to variable side arms $\text{L}^2\text{-}5$ has been investigated for the complexation of Ln^{III} ions.^{21–23} The diester derivative L^2 is structurally similar to L^1 , but it reacts with 4f ions to give thermodynamically unstable and kinetically labile cationic complexes $[\text{Ln}(\text{L}^2)_3]^{3+}$ which exist as an intricate mixture of conformers in dynamic equilibria in solution.²¹ Formation constants in acetonitrile $[\log(\beta_3)]$ are small compared to those measured for $[\text{Ln}(\text{L}^1\text{-}2\text{H})_3]^{3-}$ in water (a more competing solvent!) and follow the typical electrostatic trend (Fig. 4). A related behaviour is observed for 2,2':6',2''-terpyridine (L^5) which provides unstable and labile triple-helical complexes $[\text{Ln}(\text{L}^5)_3]^{3+}$ in acetonitrile,²² but no reliable stability constants have been determined for these complexes. Improving the affinity of the neutral side arms for Ln^{III} is the key feature for preparing stable cationic nine co-ordinate triple-helical com-



Scheme 2

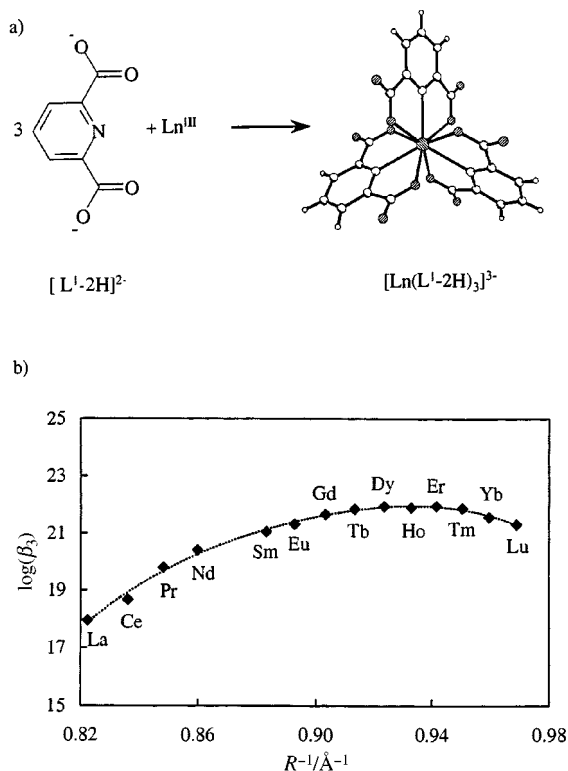


Fig. 3 a) Formation and structure of the triple-helical complexes $[\text{Ln}(\text{L}^1\text{-}2\text{H})_3]^{3+}$ and b) cumulative formation constants $\log(\beta_3)$ for $[\text{Ln}(\text{L}^1\text{-}2\text{H})_3]^{3+}$ in water ($I = 0.5 \text{ M}$, 298 K) given versus the inverse of the ionic radii of nine-coordinate Ln^{III} .

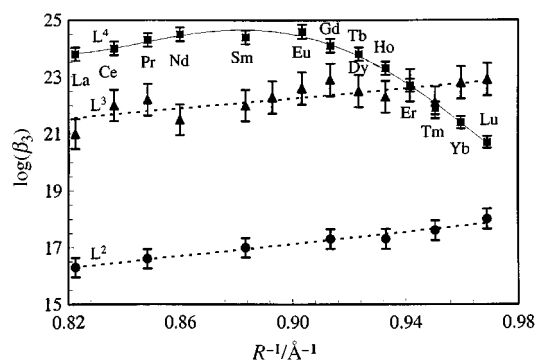


Fig. 4 Cumulative formation constants $\log(\beta_3)$ of $[\text{Ln}(\text{L}^2)_3]^{3+}$ (●), $[\text{Ln}(\text{L}^3)_3]^{3+}$ (▲) and $[\text{Ln}(\text{L}^4)_3]^{3+}$ (■) in acetonitrile (298 K) given versus the inverse of the ionic radii of nine-coordinate Ln^{III} .

plexes with defined structural properties. Three parallel approaches have been explored. Firstly, Thummel and co-workers have introduced rigid ethylene bridges in L^6 which force the three connected pyridine units to adopt a cisoid conformation preorganised for their meridional trico-ordination to Ln^{III} in the triple-helical complexes $[\text{Ln}(\text{L}^6)_3]^{3+}$.²² NMR data point to a remarkable increase in stability and an improved resistance toward water hydrolysis, but no size-discriminating effects for specific lanthanide metal ions have been reported. Secondly, Piguet and co-workers have increased the electronic density on the co-ordinating oxygen atom of the side arms by replacing ester functions with carboxamide groups in L^3 . The affinity of the side arms for the hard lanthanide metal ions is significantly improved leading to the formation of inert D_3 -symmetrical complexes $[\text{Ln}(\text{L}^3)_3]^{3+}$ which are stabilised by a factor of 10^5 – 10^6 compared to $[\text{Ln}(\text{L}^2)_3]^{3+}$.²¹ A detailed study of their solution structure demonstrates the existence of two different isostructural series controlled by secondary steric constraints between the terminal diethylamino groups which are brought

close together by the wrapping of the strands about Ln^{III} . For the large lanthanide metal ions ($\text{Ln} = \text{Ce-Tb}$), the central pyridine is weakly bound to Ln^{III} leading to dynamically averaged D_{3h} -symmetrical complexes $[\text{Ln}(\text{L}^3)_3]^{3+}$ in solution. For the small lanthanides ($\text{Ln} = \text{Er-Yb}$) a compact, rigid and inert D_3 -symmetrical triple-helical structure is obtained. This structural segregation between large and small Ln^{III} is encouraging, but the incriminated constraints are too weak to affect significantly the thermodynamic data which display the typical electrostatic trend within experimental error for the complete lanthanide series (Fig. 4). Thirdly, the extension of the aromatic planes on going from pyridine in L^5 to benzimidazole side arms in L^4 produces triple-helical complexes $[\text{Ln}(\text{L}^4)_3]^{3+}$ in which the benzimidazole rings of neighbouring strands are closely packed along the C_3 axis. Strong intramolecular interstrand π -stacking interactions are evidenced with large Ln^{III} leading to an optimal stabilisation around Gd^{III} . A further contraction of the cavity with smaller Ln^{III} results in a strong destabilisation of the triple-helical structure because of the repulsive van der Waals interactions occurring between interpenetrating electronic shells.²³ Thermodynamic studies in acetonitrile support this interpretation and show that the third cumulative formation constants $[\log(\beta_3)]$ of $[\text{Ln}(\text{L}^4)_3]^{3+}$ decrease by a factor of 10^3 between Gd^{III} and Lu^{III} when the relative contraction of the ionic radii amounts only to 7%! (Fig. 4). Since the origin of the peak selectivity is firmly established, specific structural variations of the receptors give predictable modulations in the final complexes. The attachment of bulky groups to the benzimidazole side arms in L^4 ($X = 3,5$ -dimethoxybenzyl) prevents a regular wrapping of the three strands thus removing the close packing between benzimidazole rings and leading to a complete loss of selectivity and an impressive decrease in stability.²³ On the other hand, the introduction of the strong 4-(diethylamino)-phenyl donor group in the 4-position of the pyridine ring in L^7 strengthens the N(pyridine)- Ln^{III} bond and shifts the wrapped strands in the final triple-helical complexes $[\text{Ln}(\text{L}^7)_3]^{3+}$ leading to a new peak of selectivity centred around Tb^{III} .²³

This fine and predictable tuning of structural and thermodynamic properties in monometallic complexes justifies the efforts focused on the development of predisposed ligands for programming organised lanthanide-containing architectures, but the simultaneous implementation of predetermined functions (e.g. light-conversion, energy transfer, paramagnetic relaxation) requires better control and adjustment of electronic properties. In order to improve the structural and electronic properties in the final complexes, two different side arms have been connected to the central pyridine units leading to unsymmetrical tridentate binding units. However, the co-ordination of three unsymmetrical strands to a spherical Ln^{III} provides a mixture of two isomers depending on the relative orientations of the bound chelating units. According to a statistical distribution, we expect the formation of 25% of the facial isomer (HHH)- $[\text{LnL}_3]$ (C_3 -symmetry) and 75% of the meridional isomer (HHT)- $[\text{LnL}_3]$ (C_1 -symmetry), but only the facial isomer possesses the structural and electronic characteristics compatible with the development of advanced functional devices (high symmetry and vectorization). The quantitative preparation of the desired facial complex may be achieved through the connection of three unsymmetrical strands to a semi-flexible covalent tripod. A very elegant approach has been described by Orvig and co-workers who have connected hydrophilic sulfonated bidentate aminophenolate strands to various constrained tripods in L^8 - 10 .²⁴ An intramolecular network of non-covalent N-H...O hydrogen bonds predisposes the deprotonated podand $[\text{L}^8\text{-}3\text{H}]^{3-}$ for its complexation to Ln^{III} . Stable 1:1 neutral podates $[\text{Ln}(\text{L}^8\text{-}3\text{H})(\text{H}_2\text{O})_6]$ are readily formed in which the ligand acts as a tridentate donor toward Ln^{III} via the phenolate groups (Fig. 5a). A second equivalent of podand $[\text{L}^8\text{-}3\text{H}]^{3-}$ displaces five water molecules to give the 1:2 podates $[\text{Ln}(\text{L}^8\text{-}3\text{H})_2(\text{H}_2\text{O})]^{3-}$ whose surprisingly large

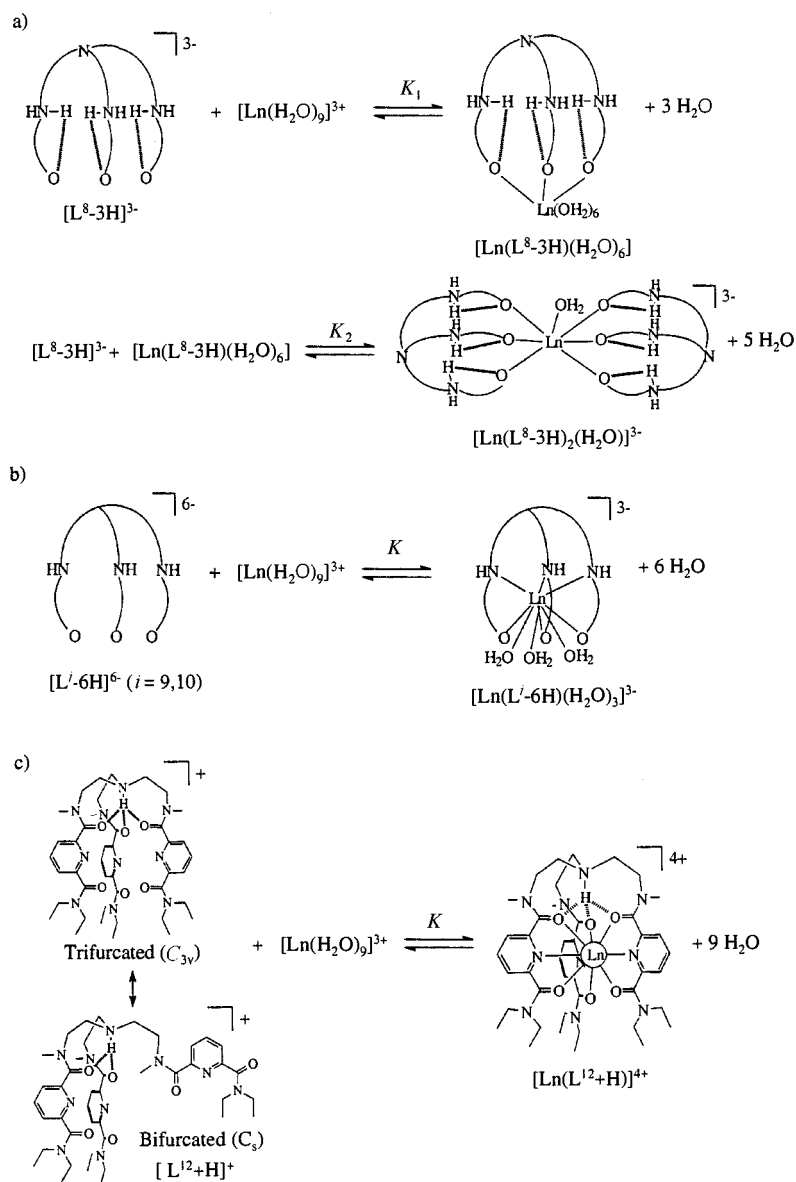


Fig. 5 a) Formation of the lanthanide podate $[\text{Ln}(\text{L}^8\text{-3H})_2(\text{H}_2\text{O})]^{3-}$ controlled by intramolecular hydrogen bonds.²⁴ b) Encapsulation of Ln^{III} by the constrained hexadentate podates L^{9-10} .²⁴ c) Encapsulation of Ln^{III} by a predisposed nonadentate podand $[\text{L}^{12+\text{H}}]^+$.²⁵

stability $[\log(K_2) > \log(K_1)]$ results from the considerable contribution of the second step (K_2) to the translational entropy. Moreover, the observed electrostatic trend for the cumulative formation constants of $[\text{Ln}(\text{L}^8\text{-3H})_2(\text{H}_2\text{O})]^{3-}$ $[\log(\beta_2) = \log(K_1) + \log(K_2)]$ shows an unprecedented selectivity for the small Ln^{III} ions $[\Delta\log(\beta_2) = \log(\beta_2^{\text{Lu}}) - \log(\beta_2^{\text{La}}) = 5.5]$ whose origin is enthalpic and probably associated with the tightening of the intramolecular hydrogen bond network. The replacement of terminal hydrophilic phenolate rings in L^8 with lipophilic aromatic groups in L^{11} produces similar 1:2 complexes $[\text{Ln}(\text{L}^{11})_2]^{3+}$ in which the metal is six co-ordinate by three negatively charged phosphinato donor groups of each podand. The cumulative formation constants $\log(\beta_2)$ are significantly reduced because of the weaker affinity of the binding groups for Ln^{III} , but the unusual order of the successive stability constants $\log(K_2) > \log(K_1)$ is reinforced because of the specific formation of a stabilising equatorial hydrophobic belt made of six closely packed phenyl units in the 1:2 podates $[\text{Ln}(\text{L}^{11})_2]^{3+}$.²⁴ In both cases, secondary intramolecular non-covalent interactions (hydrogen bonds in $[\text{Ln}(\text{L}^8\text{-3H})_2(\text{H}_2\text{O})]^{3-}$ and dispersion forces in $[\text{Ln}(\text{L}^{11})_2]^{3+}$) control the structural and thermodynamic properties of the final complexes. A contraction of the covalent tripod in L^{9-10} hinders the intramolecular hydrogen bond network and reaction with Ln^{III} produces

classical encapsulated complexes $[\text{Ln}(\text{L}^i\text{-6H})(\text{H}_2\text{O})_3]^{3-}$ ($i = 9, 10$) in which the chelating units are bidentate; the co-ordination sphere being completed by three water molecules (Fig. 5b).²⁴ The logical extension toward tridentate chelating units connected to a covalent tripod to give nonadentate podands is strongly limited by the severe structural requirements resulting from the helical wrapping of three bent tridentate chelating units around a spherical metal ion. The partial co-ordination of potentially nonadentate podands to Ln^{III} and/or the formation of interpenetrated dimers are generally observed except for the protonated podand $[\text{L}^{12+\text{H}}]^+$ which produces regular nine co-ordinate C_3 -symmetrical podates $[\text{Ln}(\text{L}^{12+\text{H}})]^{4+}$ in the solid state and in solution (Fig. 5c).²⁵ Prior to complexation, $[\text{L}^{12+\text{H}}]^+$ exists as a mixture of two conformers which are stabilised by an intramolecular trifurcated (respectively bifurcated) $\text{N-H}\cdots(\text{O}=\text{C})_n$ hydrogen bond involving the protonated apical nitrogen atom of the tripod and the proximal carbonyl groups. The resulting preorganisation of the receptor overcomes the large electrostatic repulsion between $[\text{L}^{12+\text{H}}]^+$ and Ln^{3+} leading to stable and rigid podates $[\text{Ln}(\text{L}^{12+\text{H}})]^{4+}$. Compared with the non-clipped triple-helical analogues $[\text{Ln}(\text{L}^3)_3]^{3+}$, the podates are stabilised by entropic effects and the protection of the metal ion is improved; two crucial points for the development of luminescent lanthanide-containing devices. However,

$[L^{12+}H]^+$ and L^3 do not exhibit significant size-discriminating effects along the lanthanide series and further secondary interactions must be encoded to improve structural control in nine co-ordinate lanthanide podates if such an effect has to be implemented.

An alternative approach uses facial octahedral d-block complexes as non-covalent helical tripods for controlling the facial co-ordination of three unsymmetrical tridentate binding units about Ln^{III} .²⁶ The segmental ligand L^{13} has been designed for this purpose and possesses a bidentate domain analogous to 2,2'-bipyridine coded for the recognition of octahedral d-block ions connected to an unsymmetrical tridentate binding unit coded for f-block ions. A complete characterisation of the energy hypersurface of the thermodynamic assembly process between L^{13} , M^{II} and Ln^{III} ($M = Fe, Co, Zn$; $Ln = La-Lu$) predicts the quantitative formation of the non-covalent podates $[LnM(L^{13})_3]^{5+}$ for stoichiometric conditions and a total ligand concentration larger than 5×10^{-5} M. This is indeed observed and the structures of the final self-assembled complexes $[LnM(L^{13})_3]^{5+}$ have been characterised both in solution and in the solid state. The d-block ions are facially pseudo-octahedrally co-ordinated by the three bidentate binding units thus forming a non-covalent tripod which arranges the tridentate binding units for their facial complexation to nine-coordinate Ln^{III} ions (Fig. 6).²⁶ The spectroscopically inactive Zn^{II} ion in

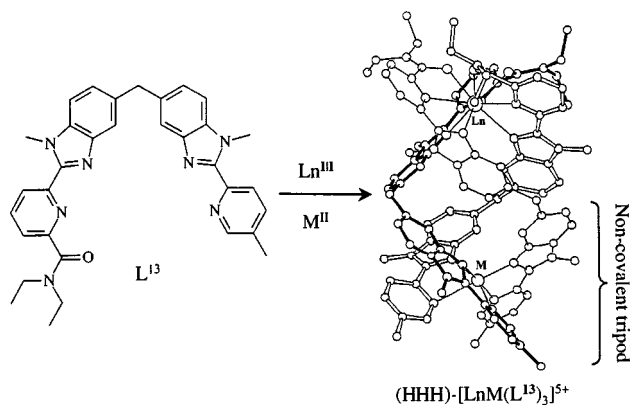


Fig. 6 Self-assembly of the non-covalent podates $[LnM(L^{13})_3]^{5+}$. The structure on the right corresponds to the X-ray crystal structure of $[EuZn(L^{13})_3]^{5+}$.

$[LnZn(L^{13})_3]^{5+}$ acts as a structural organiser and has no effect on the electronic and spectroscopic properties associated with Ln^{III} . In $[EuZn(L^{13})_3]^{5+}$, a strong red luminescence is detected upon irradiation with UV light which can be optimised by minor structural changes in $[EuZn(L^{14}-H)_3]^{2+}$. The latter complex is strongly emissive and stable in water which opens up new perspectives for the development of self-assembled luminescent stains in aqueous media.

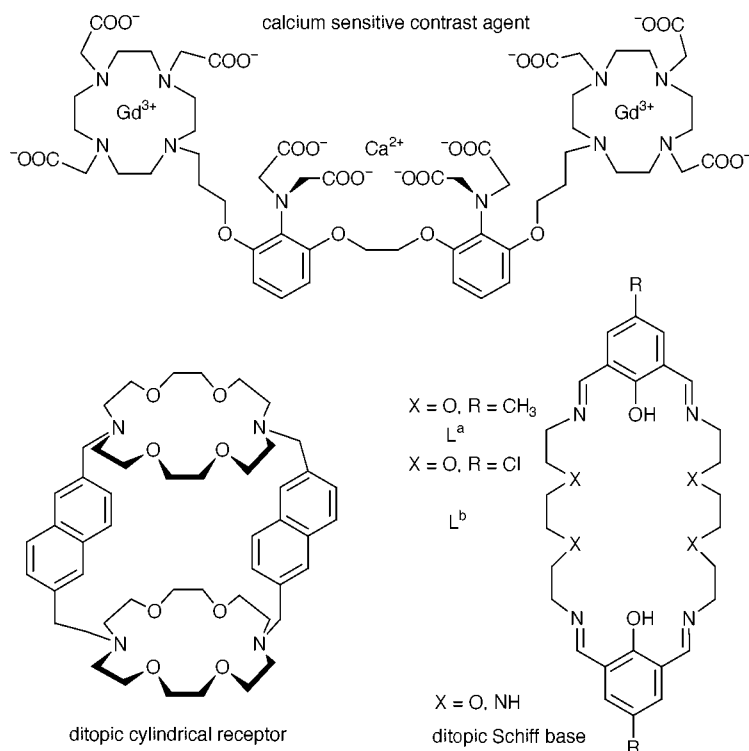
The introduction of d-block ions with predictable electronic and kinetic properties into the non-covalent tripod is the starting point for the preparation of lanthanide-containing molecular devices with predetermined properties. Co^{II} and Fe^{II} give structurally similar non-covalent podates $[LnCo(L^{13})_3]^{5+}$ and $[LnFe(L^{13})_3]^{5+}$ which display different functions. The light-yellow complexes $[LnCo(L^{13})_3]^{5+}$ act as templates for the selective preparation of kinetically inert Co^{III} podates $[LnCo(L^{13})_3]^{6+}$ which can be decomplexed to give the chiral inert preorganised nonadentate receptor $FAC-[Co(L^{13})_3]^{3+}$. The dark purple complexes $[LnFe(L^{13})_3]^{5+}$ work as tunable thermal switches which simultaneously change optical (dark purple \leftrightarrow orange) and magnetic (diamagnetic \leftrightarrow paramagnetic) properties.²⁶ These self-assembled complexes can be described as lanthanide-containing anchors whose structures, solution behaviour and electronic properties can be modulated by the choice of the non-covalent tripod: a first step toward the development of vectorial heterodimetallic f-f assemblies.

4 Toward functional polymetallic f-f supramolecular complexes

Considering the difficulties inherent in the preparation of organised monometallic lanthanide complexes, it is not surprising that only limited research work has been focused on the preparation of polymetallic lanthanide-containing molecular or supramolecular complexes. Homodimetallic f-f complexes based on symmetrical bis-compartmental ligands represent simple cases which have been tested for improving the efficiency of paramagnetic MRI contrast agents²⁷ and luminescent probes,^{7,8} but the new properties associated with the weak intramolecular intermetallic f-f interactions occurring in these complexes introduce essentially limiting factors for their use as functional devices: (i) relaxivity of water molecules bound to Gd^{III} is limited at high magnetic field by the increased electron-spin relaxation induced by dipolar coupling,²⁷ (ii) paramagnetism is modified by weak antiferromagnetic coupling^{28,29} and (iii) emission properties are affected by intermetallic energy transfers, energy migration and/or emission/re-absorption processes.^{7,8} The related heterodimetallic f-f complexes have been much less investigated because their preparation requires the recognition of each metal ion by a specific site and we are aware of a single report describing the quantitative formation and complete characterisation of a pure heterodimetallic complex $[(L^{15}-3H)(Yb(C_3H_6O))(La(NO_3)_2)]^+$ in the solid state.²⁸ In order to overcome this limitation, statistical mixtures of complexes containing homo- and heteropairs have been synthesised and spectroscopically characterised, but the interpretation of the data and their potential applications are obviously limited.⁸ On the contrary, a large amount of heterodimetallic d-f complexes have been synthesised by taking advantage of the pronounced stereochemical preferences of soft 3d-block ions (Fe^{II} , Co^{II} , Ni^{II} , Cu^{II} and Zn^{II}) which strongly contrast with those of hard Ln^{III} ions. Compartmental ligands (macrocycles or podands) possessing different binding units adapted for the recognition of one particular type of metal ions have been systematically developed leading to isolated d-f heteropairs in the solid state and in solution.³⁰ Magnetic interactions between d- and f-block metal ions is a current theme of interest, but less attention has been focused on intramolecular d \leftrightarrow f energy transfers.³⁰ Many efforts dedicated to the preparation of polymetallic lanthanide complexes involve macrocyclic receptors and the *lock-and-key* principle, but recent advances in metallosupramolecular chemistry have led to the design of self-assembled lanthanide complexes according to the *induced fit* concept. Both aspects are briefly considered in the two following sections.

4.1 The lock-and-key principle

In order to make use of the *lock-and-key* principle for embedding two identical 4f ions in a single receptor, host molecules have to be designed which are comprised of two compartments each able to strongly bind one metal ion (Scheme 3). Basically, two approaches can be used. The first relies on two macrocycles linked together. One of the few examples is the recent design of a calcium-sensitive magnetic resonance contrast agent based on a homodimetallic Gd^{III} complex. A selective complexing agent for Ca^{II} , 1,2-bis(o-aminophenoxy)ethane-*N,N,N',N'*-tetraacetic acid, has been modified by grafting two Gd^{III} receptors (Scheme 3). In the absence of calcium, the iminodiacetates of the calcium-binding compartment interact with Gd^{III} , hindering water coordination onto the paramagnetic ion. In the presence of calcium, the iminodiacetates bind this ion, thereby allowing water to interact more efficiently with Gd^{III} and the relaxivity of the polymetallic assembly increases by 80%.¹⁰ Another category of potential hosts would be molecules in which two macrocycles are held at a suitable



Scheme 3

distance by two bridging units to form a cylindrical macrotricyclic receptor similar to the hosts used to selectively complex organic amines.¹⁴ Attempts to use this concept in our laboratories failed because oligomeric species were formed. To design heterodimetallic edifices, similar host molecules could be engineered, bearing macrocycles with different cavity sizes and/or pendant arms. To the best of our knowledge, this synthetic way has not been attempted, probably in view of the difficulty encountered for the fine tuning of each compartment to the requirements of a specific 4f ion, and also in view of the work required for synthesizing such a non-symmetric receptor.

The second approach makes use of a macrocycle with a large cavity and possessing two compartments each coded for the coordination of one 4f ion. Several homodimetallic 4f–4f edifices have been isolated, mainly with macrocyclic Schiff bases³⁰ (Scheme 3) and with calixarenes²⁹ (Scheme 1). Macrocyclic Schiff bases are derived from the condensation of a substituted 2,6-diformylphenol with an appropriate diamine, and Ln^{III} ions often play the role of template agents. The homodimetallic [Gd₂(NO₃)₄(L^a-2H)]·H₂O complex displays a propeller conformation with pseudo *D*₂ symmetry; the metal ions are ten coordinate being bound to four oxygen atoms from two bidentate nitrate ions, to two oxygen and two nitrogen atoms from the macrocycle and to the two phenolate functions acting as bridging groups. The metal–metal distance is short, 3.97 Å, but not unusual for this type of compound.³⁰ Both homo- and heterodimetallic 4f–4f complexes have been isolated with L^b, but the hetero compounds probably consist of a mixture of homo- and heterodimetallic complexes. The ligand displays some size-discriminating effect: when equimolar quantities of La^{III} and Sm^{III} or Dy^{III} are reacted, the isolated compounds contain respectively 20% or 90% La^{III}. Moreover directional intramolecular Tb^{III}→Eu^{III} energy transfer occurs in the heterodimetallic material while the sensitization of the metal ion luminescence by energy transfer from the triplet state of the ligand is reasonably good.³⁰ The interest in the field seems now to turn on iminophenolate cryptates obtained by template synthesis in which the metal–metal distance is particularly short, 3.45 Å.⁸ Calixarenes result from the condensation of

substituted phenols and formaldehyde and they offer a rich chemistry with almost unlimited possibilities since functions or functional arms can be grafted both on their upper and lower (phenolic) rims. Calix[8]arenes (H₈L) have a cavity large enough to accommodate two Ln^{III} ions and in the presence of a sufficiently strong base (triethylamine) they react in DMF or DMSO with 4f ions to give neutral dimetallic [Ln₂(H₂L)(solv)₅]·x solv entities. In the case of *p*-*tert*-butylcalix[8]arene (b-H₈L) and *p*-nitrocalix[8]arene (n-H₈L), available crystal structures show the Ln^{III} ions being eight coordinate, two deprotonated phenol groups and one solvent molecule acting as bridging ligands. The overall symmetry is C₂, with the symmetry axis perpendicular to the intermetallic Eu–Eu axis. A striking feature is the two-bladed propeller conformation adopted by the ligand upon coordination, which requires a substantial rearrangement energy. Indeed, the free ligand has a somewhat flat and “ondulated” conformation which is retained in the 1:1 complexes with Ca^{II} or Ln^{III} ions. In the dimetallic complexes, the ligand can be described as two calix[4]arenes with cone conformation and placed side by side in a “transoid” configuration. The large conformational change sustained by the ligand upon the transformation of the 1:1 complexes into the 1:2 complexes is reflected in the half-lives of this reaction step: 5500 s while the reaction leading to the 1:1 complex occurs in the ms range. From this point of view, it is clear that calix[8]arenes cannot not be viewed as strictly preorganised macrocycles but, rather, as flexible receptors able to adapt somewhat to the changing size of the host metal ions. A slight size-discriminating effect has been reported for b-H₂L⁶⁻, which has a preference for cations in the middle of the lanthanide series, but this effect is too small to be used for selective complexation. The dimetallic complexes with calix[8]arenes present interesting functionalities in that the energy transfer from the ligand onto the trivalent Ln^{III} ions can be easily tuned by simple changes in the *para* substituent of the phenol groups. For instance, Fig. 7 clearly points to b-H₂L⁶⁻ being a good sensitizer for Tb^{III} (the detection limit in DMF upon luminescence monitoring is < 10⁻¹⁰ M) but transferring very poorly to Eu^{III}, while n-H₂L⁶⁻ behaves as a good Eu^{III} sensitizer but the energy of its ³ππ* state is lower than the

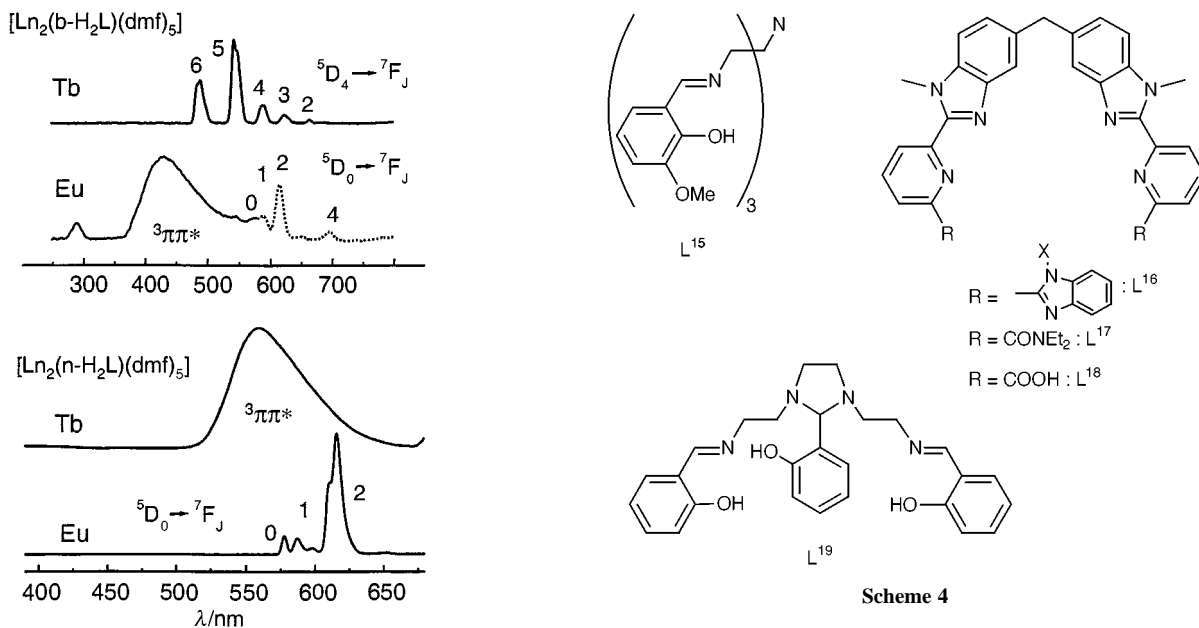


Fig. 7 Luminescence spectra showing how the sensitisation of Eu^{III} and Tb^{III} ions can be tuned by changing the substituent in the *para* position of the phenol groups of calix[8]arenes.

energy of the excited $^5\text{D}_4(\text{Tb}^{\text{III}})$ level, preventing any ligand-to-metal energy transfer. The close proximity of the two ions in $[\text{Ln}_2(\text{H}_2\text{L})(\text{DMF})_5]$, about 3.6–3.9 Å, allows magnetic interaction to take place between the two ions. At $T < 20$ K, the magnetic susceptibility of the Gd^{III} dimetallic edifice with $\text{b-H}_2\text{L}^{6-}$ deviates from the Curie law and the temperature dependence can be fitted with a simple model taking into account two weakly anti-ferromagnetically coupled $S = 7/2$ ions, with $J = -0.063 \text{ cm}^{-1}$.²⁹ Given the extensive efforts made presently to graft arms with various functional groups on calixarenes, both on the lower and upper rims, there is no doubt that some of the resulting dimetallic edifices will be of considerable interest in several applied fields.

4.2 The induced fit principle

Until now, the only pure and fully characterised heterodimetallic f-f complex $[(L^{15}\text{-3H})(\text{Yb}(\text{C}_3\text{H}_6\text{O}))(\text{La}(\text{NO}_3)_2)]^+$ results from the incorporation of two different lanthanide metal ions into a flexible nonadentate podand according to the *induced fit* principle. Yb^{III} is seven co-ordinate by the podand (four nitrogen atoms of the tripod and three oxygen atoms of the bridging phenolate groups) and occupies the upper part of the cavity of the podate, while La^{III} is co-ordinated by the three bridging phenolates and the terminal methoxy groups.²⁸ However, no reliable solution study has been reported and we cannot conclude that the final heterodimetallic podate is the thermodynamic product of a strict self-assembly process because kinetic factors and/or selective crystallisation of one particular species within a mixture of equilibrating complexes cannot be excluded.

In order to preliminarily explore the mechanism of directional intramolecular $\text{Ln}^1 \rightarrow \text{Ln}^2$ energy transfers, the symmetrical bis-tridentate ligands L^{16-18} have been synthesized.³¹ Self-assembly with Ln^{III} provides homodimetallic triple-stranded helicates $[\text{Ln}_2(L^i)_3]^{6+}$ ($i = 16, 17$) and $[\text{Ln}_2(L^{18}\text{-2H})_3]$ in which the nine co-ordinate metal ions are facially co-ordinated by three wrapped tridentate chelating units and separated by 8.8–9.1 Å (Fig. 8). The electronic and thermodynamic characteristics can be tuned by a judicious choice of the terminal donor group of the tridentate binding units. $[\text{Eu}_2(L^{16})_3]^{6+}$ is luminescent upon UV irradiation, but energy back-transfer processes

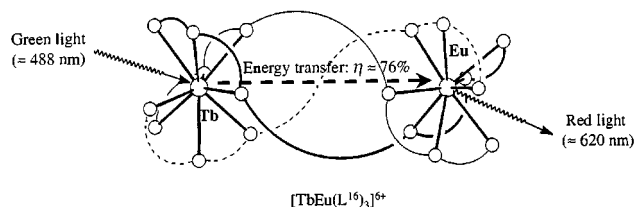
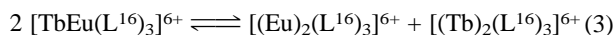


Fig. 8 Schematic representation of the heterodimetallic triple-stranded helicate $[\text{TbEu}(\text{L}^{16})_3]^{6+}$ working as a directional light-converter.

involving ligand-centred excited states quench the emission of the analogous Tb-complex. This drawback is removed for $[\text{Ln}_2(L^{17})_3]^{6+}$ and $[\text{Ln}_2(L^{18}\text{-2H})_3]$ ($\text{Ln} = \text{Eu}, \text{Tb}$) leading to efficient UV-vis light-converting devices in acetonitrile and water respectively.³¹ Under stoichiometric conditions, the assembly processes are highly selective and the reaction of L^{16} (3 equiv.) with an equimolar mixture of $\text{Ln}^1(\text{III})$ and $\text{Ln}^2(\text{III})$ ($\text{Ln}^1 \neq \text{Ln}^2$ and $\text{Ln} = \text{La}, \text{Eu}, \text{Tb}, \text{Lu}$) produces only three complexes: two homodimetallic helicates $[(\text{Ln}^1)_2(\text{L}^{16})_3]^{6+}$ and $[(\text{Ln}^2)_2(\text{L}^{16})_3]^{6+}$ and the heterodimetallic analogue $[(\text{Ln}^1)(\text{Ln}^2)(\text{L}^{16})_3]^{6+}$.³¹ Systematic deviations from the statistical distribution $\{[(\text{Ln}^1)_2(\text{L}^{16})_3]^{6+}$ (25%), $[(\text{Ln}^2)_2(\text{L}^{16})_3]^{6+}$ (25%) and $[(\text{Ln}^1)(\text{Ln}^2)(\text{L}^{16})_3]^{6+}$ (50%)} are observed when Ln^1 and Ln^2 have different sizes and at least one Ln^{III} is smaller than Gd^{III} . These results imply a destabilisation of the heterodimetallic complex produced by subtle interstrand interactions, relevant to the *induced fit* concept, which favours the formation of triple-stranded helicates possessing two identical metallic cavities. The speciation of the thermodynamic mixture for the $\text{Eu}^{\text{III}}/\text{Tb}^{\text{III}}$ pair leads to a disproportionation constant $K_{\text{dis}} = 0.94$ [eqn. (3)] which can be compared to the expected statistical value of 0.25.



The extra destabilisation of the heterodimetallic complex amounts to 1.6 kJ mol^{-1} , compared to a complex possessing two independent metallic sites, which demonstrates the sensitivity of flexible self-assembled architectures to minor variations in the size of the metal ions ($R_{\text{NC-9}}^{\text{Eu}} = 1.120 \text{ \AA}$, $R_{\text{NC-9}}^{\text{Tb}} = 1.107 \text{ \AA}$). Evidence for an efficient intramolecular $\text{Tb} \rightarrow \text{Eu}$ energy transfer has been found ($\eta = 76\%$) which provides a directional light-converting supramolecular device if pure heterodimetallic complexes can be prepared (Fig. 8). Similarly, the podand L^{19} reacts with Ln^{III} to give the side-by-side homodimetallic complexes $[\text{Ln}_2(L^{19}\text{-3H})_2]$ in which each Ln^{III} is eight-co-ordinate in a pseudo-square antiprism; one phenolate

of each ligand strand bridges the two metal ions which are held 3.918 Å apart.³² This structure is maintained in solution and the use of statistical Tb/Eu mixtures exhibits an efficient intramolecular directional Tb→Eu energy transfer in the heterodimetallic complex [TbEu(L¹⁹-3H)₂], but no speciation has been determined which prevents the evaluation of a possible thermodynamic control of the assembly process. A few extensions toward organised polymetallic lanthanide complexes have been reported for aesthetically appealing solid state networks using lanthanide as connectors between divergent bidentate ligands,³³ but their electronic, spectroscopic or magnetic properties have not been considered. Recently, monometallic lanthanide building blocks have been tentatively introduced into liquid crystals displaying calamitic mesophases and macroscopic structural ordering.³⁴ Binnemans and co-workers have demonstrated that the intermolecular interactions responsible for the emergence and stability of the mesophases depend on the size of the lanthanide metal ions encapsulated in the cavity of the lipophilic receptors. The resulting control of the fusion and isotropization processes suggests that non-covalent intermolecular interactions may also obey the *induced fit* principle leading to lanthanide-containing organised macroscopic materials with predetermined properties.

5 Summary and outlook

This short overview compares two fundamental principles in metallosupramolecular chemistry: the *lock-and-key* and the *induced fit* which are apparently antagonistic in their essences and definitions. As far as lanthanide co-ordination complexes are concerned, the *lock-and-key* approach is difficult to apply in a strict sense since the high level of rigidity associated with a satisfying preorganisation of the receptor is not compatible with the ultra-fine tuning required for the recognition of Ln^{III} ions and their subsequent selective incorporation into specific co-ordination sites. The selectivity or size-discriminating effect observed for rigid macrocyclic ligands remains modest along the lanthanide series, in contrast with the remarkable selectivity established for spherical alkali and alkaline earth ions. More flexible macrocyclic receptors lead to improved stability and the associated easy control of the arrangement and orientation of the donor atoms in macrocycles is a considerable advantage for programming lanthanide complexes which is counter-balanced by the loss of selectivity. The *induced fit* principle explores the reverse approach in which the flexibility of acyclic ligands is used to build a cavity around the metal ions whose size and geometry is optimised by secondary interstrand interactions. The thermodynamic and structural properties of the resulting lanthanide complexes can be finely tuned, but the relative orientation of unsymmetrical binding units around Ln^{III} is limited. This represents a severe drawback for the simultaneous tuning of electronic and spectroscopic properties.

In this context, semi-rigid podands combine some of the advantages of the two approaches. The orientation and the geometric arrangement of the binding units co-ordinated to Ln^{III} in the final complexes is ensured by the tripod (covalent or non-covalent) while the intrinsic flexibility of the dangling side arms allows the programming of non-covalent secondary interactions (π -stacking, hydrogen bonding, steric repulsion). It is thus not so surprising that the only well characterised heterodimetallic f,f' complex is a podate,²⁸ but only a few examples of well-defined lanthanide podates have been reported because of the difficulty to fulfil the large co-ordination number requirement of Ln^{III} ions with flexible side arms. The development of nonadentate podands containing three tridentate binding units is a logical solution to this problem, although structural restrictions induced in the tripod generally prevent the formation of organised and predictable assemblies. Nevertheless, pioneer work in that

field^{24–26} suggests that the association of a carefully designed tripod with specific dangling chelating units may overcome these limitations leading to vectorial lanthanide-containing anchors acting as fundamental building blocks for the design of functional polymetallic lanthanide-containing devices.

6 Acknowledgments

This work is supported through grants from the Swiss National Science Foundation and the Werner Foundation.

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Review 8/04240C