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Tridentate binding units as structural patterns for the design of nine-coordinate lanthanide building blocks with predetermined properties

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Abstract

The use of rigid receptors displaying preorganized cavities for the selective complexation of spherical ions has shown some limitations for trivalent lanthanide metal ions, Ln^{III}, because of the minor variation of their ionic radii. The recent development of semi-rigid ligands derived from macrocyclic platforms grafted with complexing pendant arms or from tripodal podands leads to an unprecedented fine tuning of the structural, thermodynamic and electronic properties of the lanthanide complexes, thus opening new perspectives for the design of functional molecular or supramolecular devices. The application of the *Induced fit* concept for the design of covalent and non-covalent nine-coordinate monometallic and polymetallic podates is emphasized together with applications as light-converters, thermal and electrochemical switches and template agents. The step-by-step evolution from rigidity to flexibility in lanthanide coordination chemistry is presented and the basic recognition processes responsible for the tuning of the metallic site are discussed. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Self-assembly; Podate; Lanthanide; Helicate; Recognition

1. Introduction

The lanthanide ions (4f block, Ln^{III}) offer attractive possibilities for the design of functional devices since the fascinating magnetic and spectroscopic properties of the free ion are essentially maintained in their complexes as a result of the minute mixing of 4f metal-centred and ligand-centred wave functions [1]. The resulting line-like emission of the metal-centred long-lived excited states find numerous applications in optics and analytical chemistry: (i) as luminescent probes in the visible [2] and near-IR [3] spectral domains, (ii) as light-emitting sensors for hetero- and homogeneous fluoroimmunoassays [4] and (iii) as labels for proteins and nucleic acids [5]. The magnetic properties associated with the $4f^n$ open-shell configurations of Ln^{III} have been extensively used for the design of paramagnetic contrast agents in Magnetic Resonance Imaging [6,7] and paramagnetic chiral shift reagents for the determination of enantiomeric excesses [8,9]. Finally, efficient homogeneous molecular catalysts for the hydrolysis of the phosphodiester bond involved in the sequence-specific cleavage of RNA take advantage of the strong acidic character of Ln^{III} [5,10]. The optimization of the final functions of these lanthanide complexes strongly depends on (i) the structural organization of the metallic site and its accessibility to ancilliary molecules or ions, (ii) the thermodynamic stability and kinetic inertness of the active device and (iii) the possible fine tuning of the electronic properties [11]; three crucial factors whose adjustment is severely limited by the poor stereochemical preferences inherent to spherical lanthanide cations with negligible ligand fields [12]. Except for a smooth contraction with increasing atomic numbers, the lanthanide metal ions display very similar coordination properties which make them particularly difficult to recognize and to introduce into organized molecular or supramolecular assemblies [11] (Scheme 1).

2. Macro(poly)cyclic receptors and preorganization

Inspired by the successful selective coordination of spherical s-block metal ions with preorganized macrobicyclic receptors (=cryptands) according to the *Lock*

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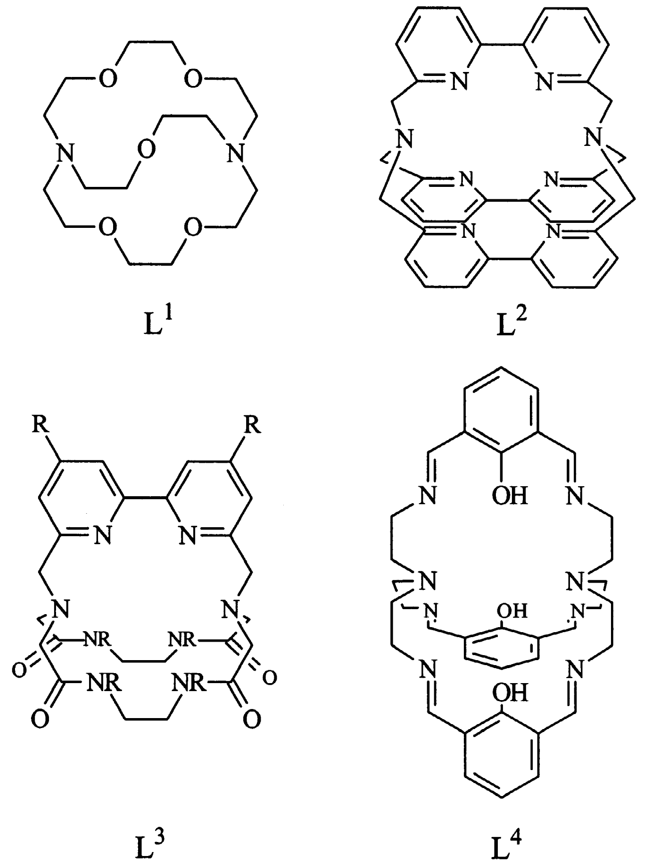


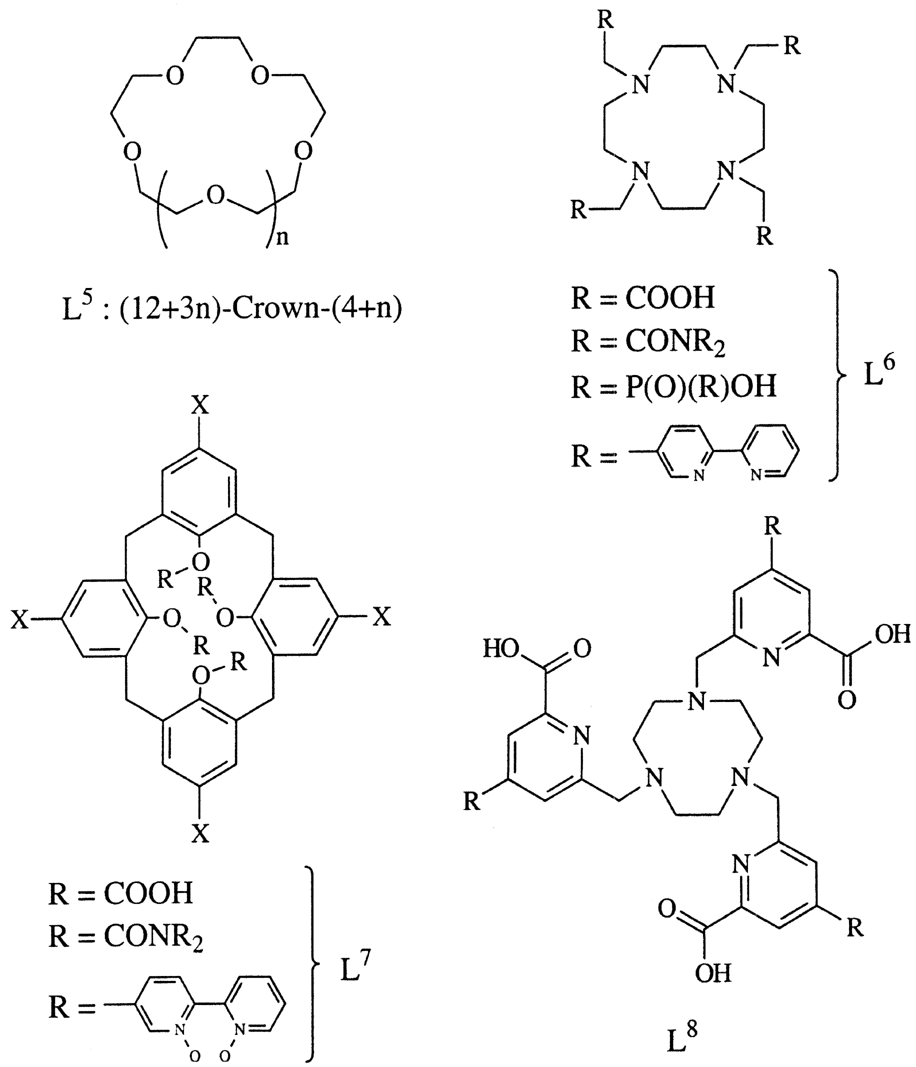
Scheme 1.

and key principle [13], related multidentate cryptands have been used for the complexation of Ln^{III}. In $[Ln(L^1)]^{3+}$ and $[Ln(L^2)]^{3+}$, the metal ions lie within the rigid macrobicyclic cavity which ensures kinetic inertness and protection against external interactions, two prerequisites for the design of efficient luminescent probes [14–16]. Moreover, the bidentate aromatic bipyridine chelating units in $[Ln(L^2)]^{3+}$ efficiently collect UV-light via ligand-allowed transitions, transfer this energy toward the metal ion which eventually re-emits in the visible spectral domain, thus leading to an efficient *Antenna* effect [14–16]. Various heterobiaryl groups have been introduced between the nitrogen bridgeheads (bithiazole, biimidazole, bipyrimidine, biisoquinoline, bipyridazine [14–16] and their N,N′ dioxydes [17]), but a significant improved protection of the metallic site results from the partial replacement of rigid aromatic cores with aliphatic diamide binding units leading to fascinating emission properties in $[Eu(L^3)]^{3+}$ [18,19]. However, the structural ultra-fine tuning required for the selective recognition of one particular Ln^{III} ion is strongly limited and only deceiving size-discriminating effects have been observed along the lanthanide series [20]. No improvement results from the introduction of tridentate chelating units between the nitrogen bridgeheads because strong distortions of the ligand backbone preclude the wrapping process required for the complexation of a single Ln^{III}. Dimetallic cryptates are then obtained in which each metallic site completes its coordination sphere with solvent molecules or anions as in $[Ln_2(L^4{-}3H)(NO_3)_2]^+$ [21].

Macromonocyclic ligands or coronands offer an alternative approach because the coordination sphere is only partially defined by the donor atoms of the rigid receptors as found for complexes with crown ethers $[Ln(L^5)]^{3+}$ which often coordinate ancilliary solvent molecules or anions [20,22]. An improved structural control is expected if coordinating side arms are grafted on the macrocylic platform and carboxylate, phosphonate, carboxamide or bipyridine binding units have been connected to crown ethers [20], cyclen (L^6) [23–26] and calixarenes (L^7) [27–29]. In these receptors, the heteroatoms of the ring (N for cyclen L^6 and O for calixarene L^7) and the coordinating atoms of the flexible side arms R form two parallel planes between which the lanthanide metal ion is efficiently eight-coordinated. Although significant size-selective effects are usually not observed along the Ln^{III} series, the thermodynamic, kinetic and electronic properties can be tuned by a judicious choice of the dimension of the platform and the nature of the side arms leading to application as luminescent probes and contrast agents [6,7,11,23–30]. As previously noticed for cryptands, tridentate chelating units are rarely connected to macrocyclic platforms because of the severe stereochemical limitations resulting from the complexation to nine-coordinate metal ions. To the best of our knowledge, L^8 represents the single case of a macrocyclic platform grafted with three bidentate dangling side arms, but in which the nitrogen atoms of the macrocycle coordinate to the metal leading to potentially tridentate chelating NNO units and producing the stable nine-coordinate complex $[Eu(L^8{-}3H)]$ according to luminescence measurements [30] (Scheme 2).

3. Podand-type receptors and predisposition

The restriction of the platform to a single point (=an atom) leads to podand-type receptors whose lack of strict structural rigidity prevents their description as preorganized ligands. However, the peculiar stereochemical constraints associated with the clipped podands *predispose* them for their selective complexation to metal ions [11]. Hexadentate podands made of three bidentate chelating units connected to nitrogen or carbon atoms are famous for efficiently encapsulating pseudo-octahedral d-block ions [31–34], but recent advances show that related receptors L^{9-1} display significant affinities for 4f-block ions [35–38]. 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^9 [37,38]. An intramolecular network of non-covalent N–H···O hydrogen bonds predisposes the deprotonated podand $[L^9{-}3H]^{3-}$ for its complexation to



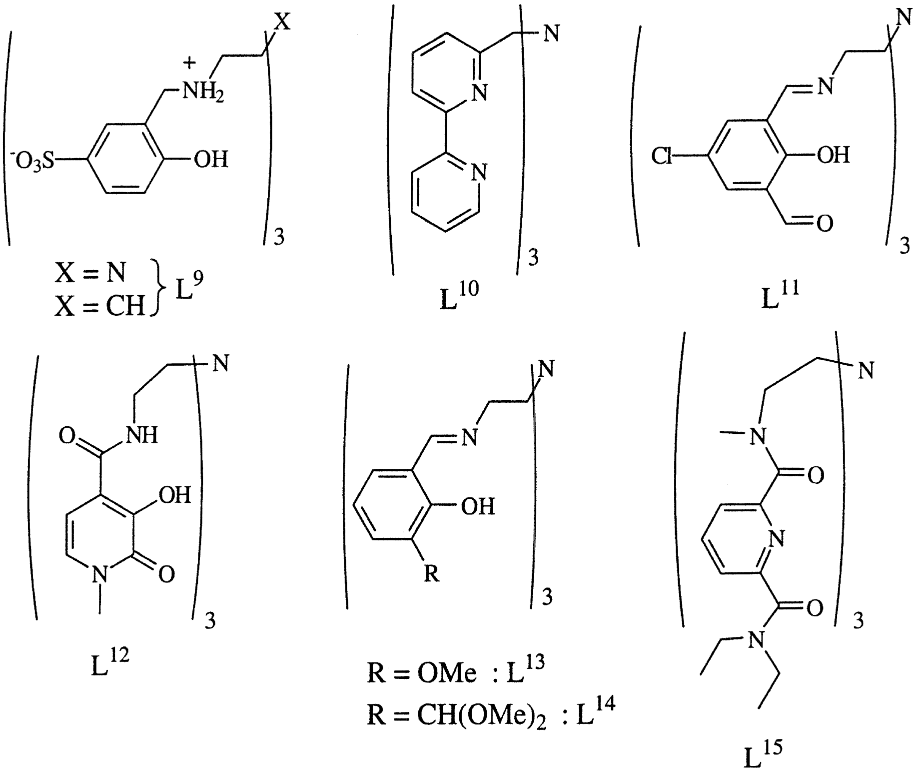
Scheme 2.

Ln^{III}. Stable 1:1 neutral podates $[Ln(L^9{-}3H)(H_2O)_6]$ are readily formed in which the ligand acts as a tridentate donor toward Ln^{III} via the phenolate groups. A second equivalent of podand $[L^9{-}3H]^{3-}$ displaces five water molecules and completes the coordination sphere to give the 1:2 podates $[Ln(L^9{-}3H)_2(H_2O)]^{3-}$ whose surprisingly large 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 $[Ln(L^9{-}3H)_2(H_2O)]^{3-}$ ($\log(\beta_2)=\log(K_1)+\log(K_2)$) shows an unprecedented selectivity for the small Ln^{III} ions ($\Delta\log(\beta_2)=\log(\beta_2^{Lu})-\log(\beta_2^{La})=5.5$) 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^9 with lipophilic aromatic groups reinforces the unusual trend of the stability constants $\log(K_2)>\log(K_1)$ because of the specific formation of a stabilizing equatorial hydrophobic belt made of six closely packed phenyl units in the 1:2 podates [37,38]. In both cases, secondary intramolecular non-covalent interactions (hydrogen bonds and dispersion forces) control the structural and thermodynamic properties of the final complexes according to the *Induced fit* principle [39]. Other hexadentate (=trisbidentate) podands using tris-aminoethylamine (L^{10}) [35,36] or tris-pyrazolylborate tripods [40,41] encapsulate Ln^{III} within their cavity, but the coordination of only seven donor atoms to Ln^{III} is insufficient to preclude the complexation of supplementary anions or solvents molecules as shown in the crystal structure of $[La(L^{10})(OH_2)(\eta^2{-}ClO_4)]^{2+}$ [35] and in the formation of twelve-coordinate lanthanide complexes in which two hexadentate podands are complexed to the same metal [40,41]. An improved match between the stereochemical preferences of Ln^{III} and the ligand binding possibilities should result from podands possessing three tridentate chelating arms since tricapped trigonal prismatic nine-coordinate Ln^{III} are common in 4f-block coordination chemistry. However, the wrapping of semi-rigid and bent tridentate binding units about a spherical ion induces severe structural constraints which strongly limit this approach [42]. This sentence is supported by the two following observations: (i) potentially tridentate chelating units in L^{11-13} are only dicoordinated to the same metal in $[La(L^{11}-3H)(DMF)_2$ [43], $[Gd(L^{12}-3H)(OH_2)_2]$ [44] and $[LaYb(L^{13}-3H)(NO_3)_2]^+$ [45] and (ii) Y^{III} is only coordinated to oxygen atoms in $[Y(L^{14}-3H)]$ [46]. Nevertheless, we notice that the podands L^{11-14} are designed to produce fused six-membered metallacycles upon complexation to Ln^{III} which is not optimum for the complexation of large metal ions [47] (Scheme 3).

The replacement of the central phenolate ring by a pyridine in L^{15} provides tridentate binding units coded for the formation of fused five-membered metallacycles leading to stable triple-helical nine-coordinate lanthanide complexes [48]. L^{15} exists as a mixture of four conformers which differ in the *cis-trans* orientation of their unsymmetrical tertiary amide functions. Upon protonation of the apical nitrogen atom in $[L^{15}+H]^+$, only two conformers remain in solution which are stabilized by the formation of intramolecular bi- and trifurcated hydrogen bonds respectively (Fig. 1) [49,50]. The complexation of L^{15} to Ln^{III} in acetonitrile gives nine-coordinate podates $[Ln(L^{15})]^{3+}$ ($\log(\beta)=6.7$–8.5; Ln=La–Lu) which are only marginally more stable than their protonated analogue $[Ln(L^{15}+H)]^{4+}$ ($\log(\beta)=6.4$–6.7) because the partial preorganization of the protonated ligand $[L^{15}+H]^+$ through intramolecular hydrogen bonding compensates the repulsive electrostatic contribution to the complexation process. The crystal structure of $[Eu(L^{15}+H)]^{4+}$ unambiguously confirms the existence of a trifuracted hydrogen bond which (i) rigidifies the complex, (ii) forces the metal ion to lie in the centre of the tricapped trigonal prismatic site and (iii) controls helicity within the covalent tripod. A good protection of the metallic site is achieved which provides a sizeable metal-centred emission upon UV-irradiation and an improved resistance toward hydrolysis compared to the non-podate analogue: two crucial points for the further development of organized and directional polymetallic systems [11].

A parallel approach uses facial pseudo-octahedral d-block complexes as helical non-covalent tripods for the organization of three unsymmetrical tridentate binding units around Ln^{III} [48]. The segmental ligand L^{16} possesses two different binding sites connected by a short methylene spacer which transmits the helicity along the ligand backbone. The bidentate chelating unit is analogous to 2,2′-bipyridine and coded for the coordination of soft six-coordinate d-block ions (M^{II}), while the tridentate binding unit has a significant affinity for hard f-block ions. A complete exploration of the energy hypersurface of the assembly process involving L^i (i=16, 17), Zn^{II} and La^{II} shows that the desired non-covalent podate $[LaZn(L^i)_3]^{5+}$ is formed quantitatively under stoichiometric conditions and using a total ligand concentration larger than 10^{-4} M (L^{16}) or 10^{-3} M (L^{17}; Fig. 2) [51,52].

The connection of an electron-attracting sulfonamide group at the five-position of the pyridine ring in L^{17} has



Scheme 3.

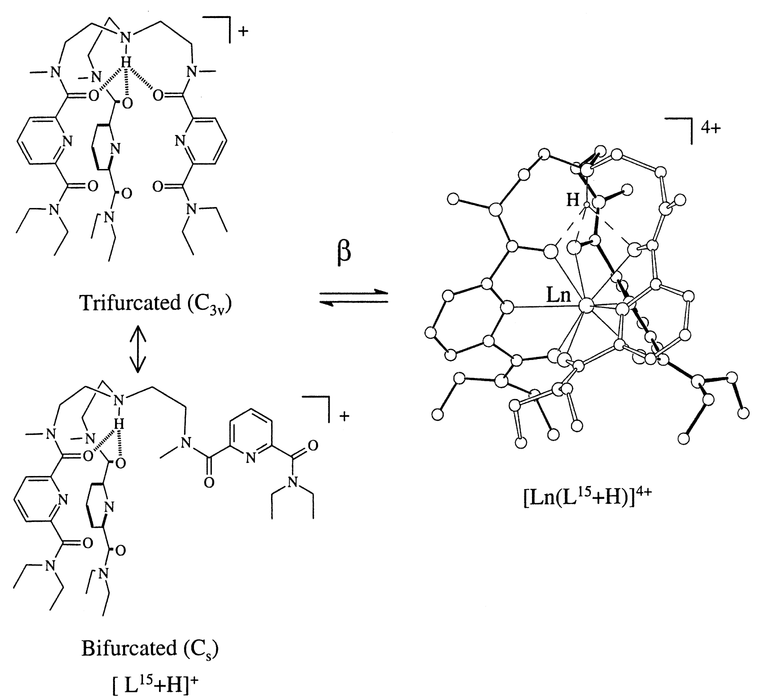


Fig. 1. Complexation of the protonated podand $[L^{15}+H]^+$ with Ln^{III} in acetonitrile. The structure of the complex corresponds to the crystal structure of $[Eu(L^{15}+H)]^{4+}$.

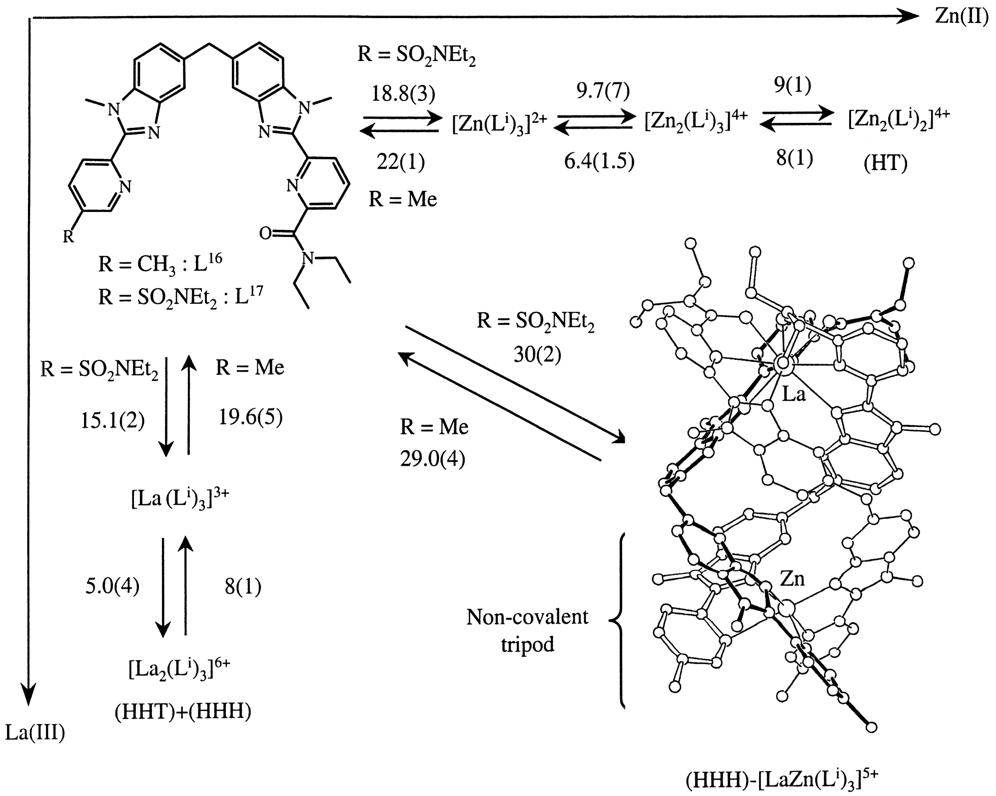


Fig. 2. Self-assembly of the non-covalent podates $[LaZn(L^i)_3]^{5+}$ in acetonitrile. Log(K) are given for each thermodynamic equilibrium.

only minor effects on the assembly process and on the luminescent properties of $[EuZn(L^i)_3]^{5+}$ (i=16, 17) which work as efficient UV→Vis light-converting devices [48,51,52]. However, the $^1A \rightleftharpoons {}^5T$ spin transition of Fe^{II} in $[LnFe(L^i)_3]^{5+}$ (i=16, 17) is sensitive to the sulfonamide substituent and a careful investigation of the thermodynamic and electronic parameters controlling this process demonstrates that entropic contributions are responsible for the increase of the critical temperature (=the temperature at which the mole fraction of high spin Fe^{II} is 0.5) when going from $[LnFe(L^{16})_3]^{5+}$ to $[LnFe(L^{17})_3]^{5+}$ [51,52]. Moreover, the effect of the size of Ln occupying the nine-coordinate site on the spin equilibria is maintained for both series of complexes leading to an ultra-fine tuning of the thermodynamic parameters; a remarkable point for the design of functional thermal switches (Fig. 3).

Temperature is not the only stimulus which can be used for switching processes and the non-covalent podate $[LnCo(L^{16})_3]^{5+}$ is sensitive to electric potentials [53]. As a result of the high spin d^7 electronic configuration of pseudo-octahedral Co^{II}, the non-covalent tripod is paramagnetic and labile, but its selective oxidation to Co^{III} (low spin d^6) at $E_{1/2}$=0.41–0.43 V (vs. SCE in acetonitrile +0.1 M NBu_4PF_6) produces a diamagnetic and kinetically inert tripod. This chemically reversible redox process corresponds to an electrochemical switching of the magnetic and kinetic properties of the non-covalent tripod which significantly affects the electronic and complexation properties of the lanthanide coordination site (Fig. 4) [53]. Treatment of $[LaCo(L^{16})_3]^{6+}$ with EDTA extracts Ln^{III} and gives quantitatively the complex *fac*-$[Co(L^{16})_3]^{3+}$ which is inert enough to work as a preorganized helical nine-coordinate receptor for the selective complexation of Ln^{III}.

X-ray crystal structures show that the non-covalent Co^{III} tripod in $[LnCo(L^{16})_3]^{6+}$ is distorted when Ln is a large lanthanide metal ion leading to a slight stretching of the Co–N bonds which is relaxed with smaller Ln^{III} ions. In solution, NMR data indicate the existence of a single isostructural series [54]. The high sensitivity of these non-covalent assemblies to minor structural variations offers promising possibilities for the selective complexation of Ln^{III} according to their size.

4. Acyclic tridentate receptors and secondary non-covalent interactions

The complexation of Ln^{III} by three symmetrical acyclic tridentate ligands L^{18-22} gives D_3-symmetrical complexes $[Ln(L^i\text{–}2H)_3]^{3-}$ (i=18, 19) and $[Ln(L^i)_3]^{3+}$ (i=20–22) [55–64]. Numerous crystal structures establish the formation of regular triple-helical complexes in which Ln^{III} is nine-coordinated in pseudotricapped trigonal prismatic sites formed by the wrapping of the bent chelating units about the spherical ion. Detailed studies of the electronic structure and optical properties of $[Ln(L^{18}\text{–}2H)_3]^{3-}$ confirm the threefold symmetry, but show that the expected contraction of the 4f orbitals along the lanthanide series suffers two exceptions for $Gd^{III}(4f^7)$ and $Tb^{III}(4f^8)$ which display larger crystal fields [57]. Since 4f electrons are essentially not involved in chemical bonding, this effect is not reflected by the thermodynamic data [58] which display a classical electrostatic trend (i.e. an increase of the formation constants with decreasing ionic radii [12]) from La to Dy. However, a subsequent slight decrease of the third successive stability constants ($\Delta\log(K_3)=\log(K_3^{Dy})-\log(K_3^{Lu})=0.77$) may be ascribed to the significant repulsive electrostatic interactions occurring between the negatively charged carboxylate groups of different strands

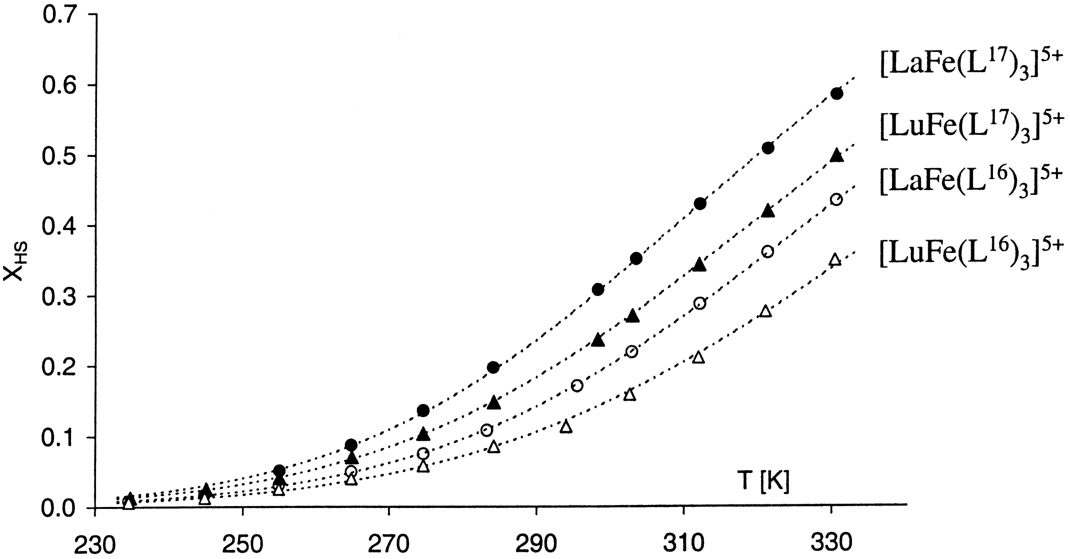


Fig. 3. Mole fraction (x_{hs}) of high spin Fe^{II} (^5T) for the thermal spin crossover transition occurring in $[LnFe(L^i)]^{5+}$ (i=16, 17; acetonitrile, 233–333 K).

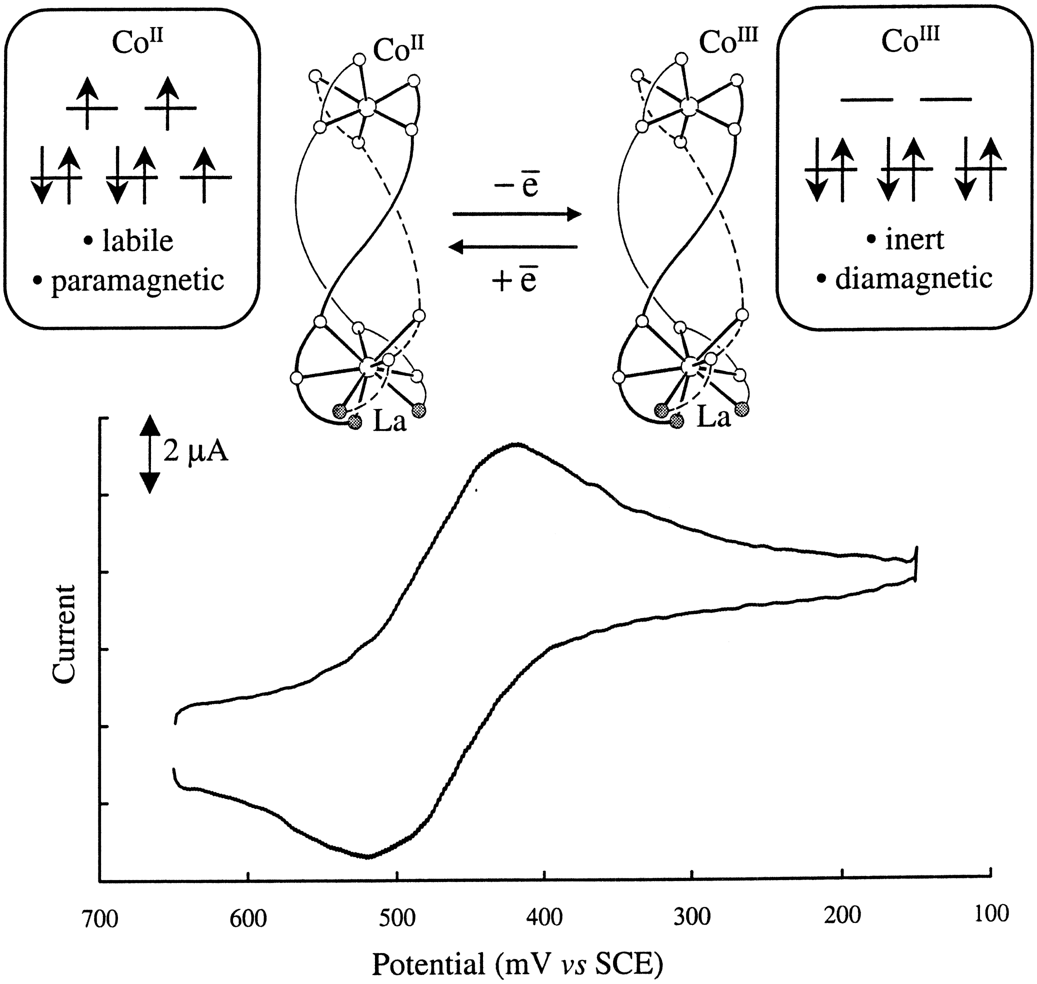
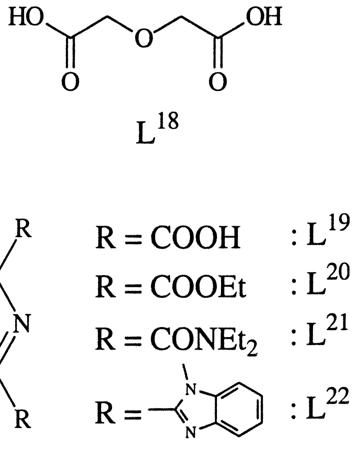


Fig. 4. Cyclic voltammogram of $[LaCo(L^{16})_3]^{5+}$ in acetonitrile showing the electrochemical switching of the magnetic and kinetic properties of the non-covalent podate.

which are put close together in the triple-helical complexes $[Ln(L^{18}{-}2H)_3]^{3-}$. A similar, but amplified effect is observed for the more rigid dipicolinate dianion $[L^{19}{-}2H]^{2-}$ which exhibits a larger size-discriminating effect in the complexes $[Ln(L^{19}{-}2H)_3]^{3-}$ ($\Delta\log(K_3)=\log(K_3^{Dy})-\log(K_3^{Lu})=1.27$; Fig. 5) [59,60] (Scheme 4).

These weak, but significant size effects are strong supports for the application of the *Induced fit* concept to the selective recognition of Ln^{III} in organized flexible molecular architectures. However, tridentate binding units containing two carboxylate termini cannot be introduced into extended segmental ligands for the design of more complicated polymetallic systems. We have thus developed a collection of symmetrical tridentate binding units possessing terminal alkyl or aromatic groups and in which secondary interstrand interactions can be implemented and modulated [61–64]. As a result of the weak affinity of ester groups for Ln^{III}, L^{20} gives only poorly stable and dynamically flexible complexes $[Ln(L^{20})_3]^{3+}$ in acetonitrile which cannot be used as building blocks for further developments [61]. On the other hand, the terminal carboxamide groups in L^{21} display an improved affinity for Ln^{III} and produce stable triple-helical complexes $[Ln(L^{21})_3]^{3+}$ in acetonitrile [62]. The formation constants exhibit a classical electrostatic trend along the complete lanthanide series within experimental error, but the wrapping of the



Scheme 4.

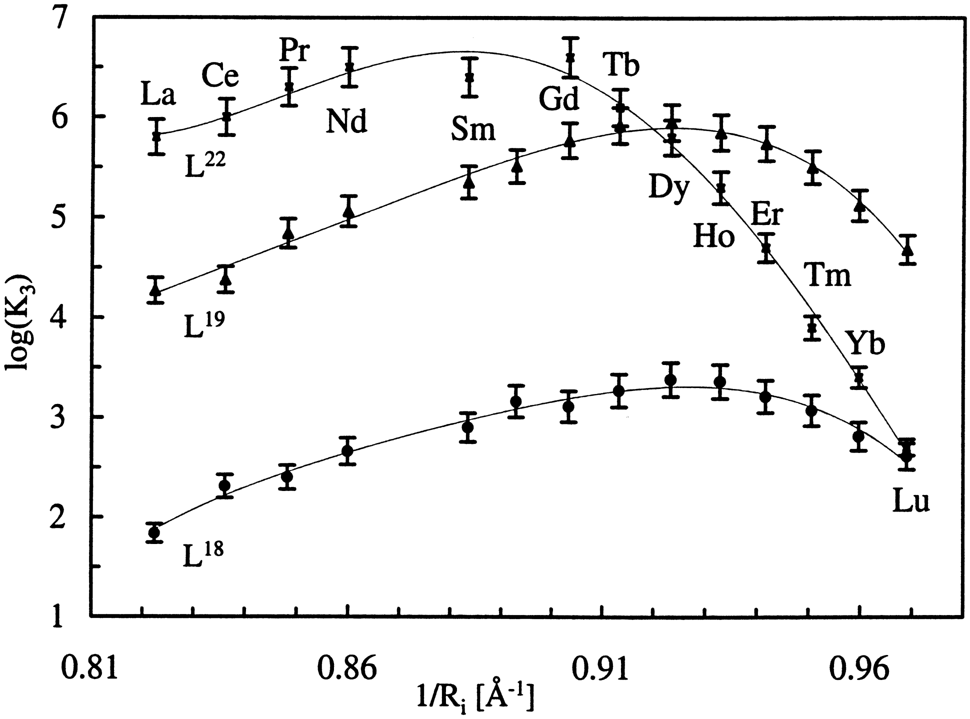


Fig. 5. Third successive stability constants ($\log(K_3)$) for the formation of triple-helical complexes $[\mathrm{Ln}(\mathrm{L}^{18}-2\mathrm{H})_3]^{3-}$ (in water), $[\mathrm{Ln}(\mathrm{L}^{19}-2\mathrm{H})_3]^{3-}$ (in water) and $[\mathrm{Ln}(\mathrm{L}^{22})_3]^{2+}$ (in acetonitrile) with respect to the inverse of the metallic ionic radii for nine-coordinate $\mathrm{Ln}^{\mathrm{III}}$ [12].

ligands brings closer the terminal alkyl residues of different strands, thus producing steric interstrand interactions which are responsible for the observation of two different isostructural series for $[\mathrm{Ln}(\mathrm{L}^{21})_3]^{3+}$ in solution [62]. Finally, the introduction of terminal benzimidazole groups in L^{22} produces efficient interstrand π-stacking interactions in the complexes $[\mathrm{Ln}(\mathrm{L}^{22})_3]^{3+}$ which are optimized for mid-range $\mathrm{Ln}^{\mathrm{III}}$ [63]. A detailed structural characterization shows that the compact triple-helical pattern found in the crystal structure of $[\mathrm{Eu}(\mathrm{L}^{22})_3]^{3+}$ is maintained in solution for the large $\mathrm{Ln}^{\mathrm{III}}$ (Ln=La–Tb) leading to a remarkable peak of selectivity around $\mathrm{Gd}^{\mathrm{III}}$ (Fig. 5). For smaller $\mathrm{Ln}^{\mathrm{III}}$, the close approach of the benzimidazole rings in $[\mathrm{Ln}(\mathrm{L}^{22})_3]^{3+}$ produces repulsive van der Waals contributions which strongly destabilize the triple-helical complexes ($\Delta\log(K_3)=\log(K_3^{\mathrm{Gd}})-\log(K_3^{\mathrm{Lu}})=3.9$) [64]. Several predictable modulations of this effect have been demonstrated with ligands analogous to L^{22}, but substituted with bulky and/or electroactive groups [64].

5. Conclusions and perspectives

The selective recognition and complexation of spherical s-block ions (alkali and alkaline earth) with preorganized macro(poly)cyclic receptors have been considered as a major success in coordination chemistry in the late sixties [13]. Thanks to the sizeable variation of the ionic radii within these groups, it was possible to design rigid receptors adapted for one particular spherical ion. Unfortunately, a related approach essentially failed with $\mathrm{Ln}^{\mathrm{III}}$ because the structural ultra-fine tuning required by the minor variation of the ionic radii between the trivalent metal ions along the lanthanide series is inaccessible to rigid systems. The introduction or removal of $-\mathrm{CH}_2-$ or $-\mathrm{CH}_2-\mathrm{O}-$ units within the macropolycyclic backbone produces at least 10 to 15% changes in the size of the cavity which are not compatible with the selection of one particular lanthanide. At first sight, the consideration of more flexible systems will suffer from less favourable enthalpic and entropic contributions to the complexation process [47], but the optimization of ligand–metal bonds associated with secondary non-covalent interstrand interactions may overcome this limitation as demonstrated by the modulable stabilities and size-discriminating effects obtained for triple-helical complexes with symmetrical acyclic tridentate ligands [61–64]. Moreover, the combination of secondary interactions with partial preorganization in podands has led to a new class of lanthanide complexes allowing the simultaneous tuning of structural, thermodynamic and electronic properties: a prerequisite for the development of functional devices. In this context, the controlled facial orientation of three unsymmetrical tridentate binding units via a tripod (covalent or non-covalent) gives complexes suitable for preliminary applications as luminescent probes, thermal and electrochemical switches. The extension toward a macrocyclic platform further increases the rigidity of the edifice and cylen and calixarenes grafted with strongly complexing pendant arms are useful precursors for obtaining paramagnetic contrast agents with Gd^{III} [6,7] and luminescent probes with Eu^{III} and Tb^{III} [3,5]. We believe that the emergence of the *Induced fit* principle as a leading concept in lanthanide coordination chemistry opens new perspectives for the selective recognition and incorporation of Ln^{III} into electronically and structurally organized architectures. Particular interest is now focused on the design of d–f and f–f polymetallic complexes displaying advanced functions and applications [11] such as directional energy transfer, synergetic activation of reactant and substrate and tunable building blocks for laser materials.

Acknowledgements

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