



Trivalent lanthanide ions: versatile coordination centers with unique spectroscopic and magnetic properties

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Abstract

At first sight, trivalent lanthanide ions Ln^{III} are not very attractive to the chemist: the spherical entities with “inner” 4f valence electrons interact electrostatically with their surroundings, display little stereochemical preferences, and have very similar chemical behavior. On the other hand, these ions exhibit rich and unique spectroscopic and magnetic properties that can be taken advantage of either for spectroscopic and magnetic probes, or to construct materials with specific physico-chemical properties. Moreover, the intrinsic chemical drawbacks of the Ln^{III} ions can be turned into a benefit since the ions adapt easily to almost any chemical environment and can therefore be readily introduced into a variety of ionic, molecular, and supramolecular edifices where they act as functional centers. We will first outline the historical aspects of Ln^{III} coordination chemistry. Fundamental properties of the Ln^{III} ions, including coordination numbers and geometries, solvation, hydrolysis and thermodynamic aspects of complexation, are then briefly reviewed. We finally focus on the several methods developed by inorganic chemists to trap the elusive lanthanide ions into environments preserving or even enhancing their physical properties, or increasing the differences in their chemical characteristics. © 2000 Elsevier Science S.A. All rights reserved.

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1. Ln^{III} coordination chemistry: the success stories

1.1. A slow start

Coordination chemistry of the trivalent lanthanide ions Ln^{III} has long stayed in the shadow of d-transition element chemistry. The latter, developed after Alfred Werner's investigation of two different compounds with the same chemical composition, $\text{CoCl}_3 \cdot 4\text{NH}_3$, led him to propose new ideas on the chemical bond in metal-containing compounds: a metal ion surrounds itself with several *ligands*. The physical and chemical properties of the resulting assembly are determined by the nature of the ion-to-ligand chemical bonds and by the geometrical arrangement of the ligands around the metal ion. The main group transition elements have a rich coordination chemistry essentially governed by a combination of steric and electronic requirements dictated by the shape of the d orbitals and the associated ligand-field effects. The coordination number (CN), which is the number of metal-to-

ligand bonds, usually ranges between 4 and 6 and it was long thought by analogy that Ln^{III} ions have also $\text{CN}=6$. The first break in this consensus came from Ketelaar [1], who suggested that rare earth ethylsulfates have $\text{CN}=9$ based on X-ray diffraction experiments. This initial work was soon followed by a report on the crystal structure of Nd^{III} bromate, which also pointed to a metal ion surrounded by nine water molecules and lying in a site with C_{3v} (pseudo- D_{3h}) symmetry [2]. Despite this evidence, the old ideas continued to prevail until the 1960s when Schwarzenbach started to study Ln^{III} polyaminocarboxylates and when Hoard showed that edta complexes contain Ln^{III} ions with $\text{CN}=10$ [3]. Nowadays, it is common knowledge that large coordination numbers (7–12) dominate the coordination chemistry of Ln^{III} ions.

1.2. Success stories

Academic curiosity for the chemical properties of the lanthanide ions has been a constant driving force for the development of their coordination chemistry. But, in addition, practical applications soon emerged, first in the field of analytical chemistry [4], separation sciences (for a recent account, see Ref. [5]), and more recently in various

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aspects of modern technology, particularly in the analysis of biomedical materials. We shall concentrate on the latter applications only since they have been the main thrust for the fast development of Ln^{III} coordination chemistry during the last two decades. One initial landmark was the discovery in 1942 of what is known today as the antenna effect by Weissman [6], who demonstrated that energy transfer occurs from the bound ligands to the metal ion, providing an excellent way for the sensitization of the Ln^{III} ion luminescence. This discovery contributed to the belief that Ln^{III} -containing liquid lasers were feasible. However, too stringent requirements both on the chemical and photophysical properties of such devices prevented commercial development.

The first success story came in 1969 when Hinckley [7] showed that the NMR spectrum of a large molecule such as cholesterol can be simplified by adding a shift reagent, namely the phenanthroline adduct of $[\text{Eu}(\text{dpm})_3]$ (dpm, dipivaloylmethane, Fig. 1). The interaction of the β -diketonate reagent with the investigated molecule leads to paramagnetic shifts which vary essentially with the inverse third power of the distance between the paramagnetic

metal center and the proton. This effect, along with further developments in which the induced paramagnetic shift is separated into its two contact (through-bond) and pseudo-contact (through-space) contributions, allows one to use the paramagnetic Ln^{III} ions as structural reporters for large organic molecules and metallosupramolecules [8], while chiral shift reagents probe the absolute configuration of amino acids [9,10].

Fifteen years after Hinckley's paper, other aspects of NMR and of Ln^{III} paramagnetism made the headlines when Carr demonstrated that $[\text{Gd}(\text{dtpa})]^{2-}$ (Fig. 1) acts as a contrast agent in magnetic resonance imaging, enhancing the contrast of cerebral tumor images. While shift reagents essentially have an academic interest, contrast agents are the heart of a multibillion dollar medical imaging industry and several contrast agents based on the high spin ($S = 7/2$) Gd^{III} ion have been and are still being engineered.

Almost at the same time, a small Finnish company, Wallac Oy, located in Turku where Professor Johan Gadolin discovered the first rare-earth element, yttrium, in 1794, proposed a new type of immunoassay which met immediate success. In a first step (Fig. 2), an antibody

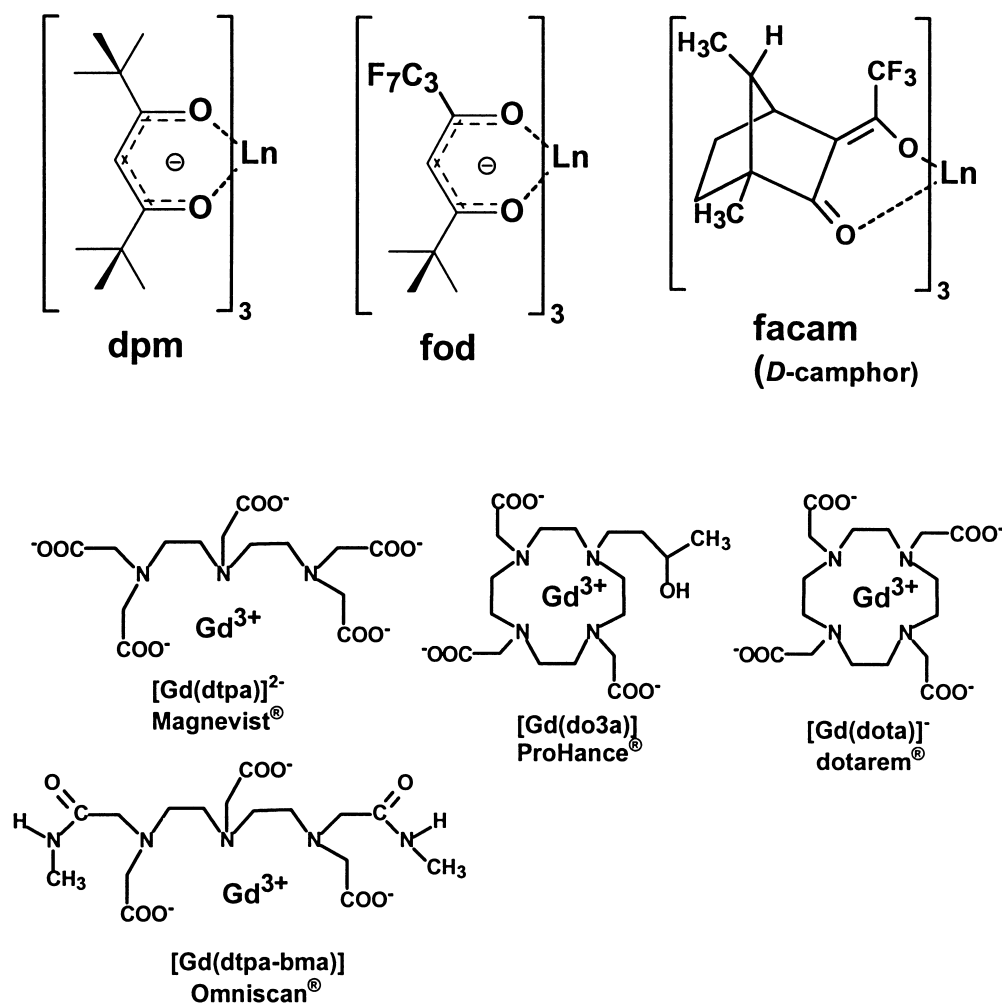


Fig. 1. Commonly used shift reagents (top) and first generation commercial contrast agents for magnetic resonance imaging (bottom).

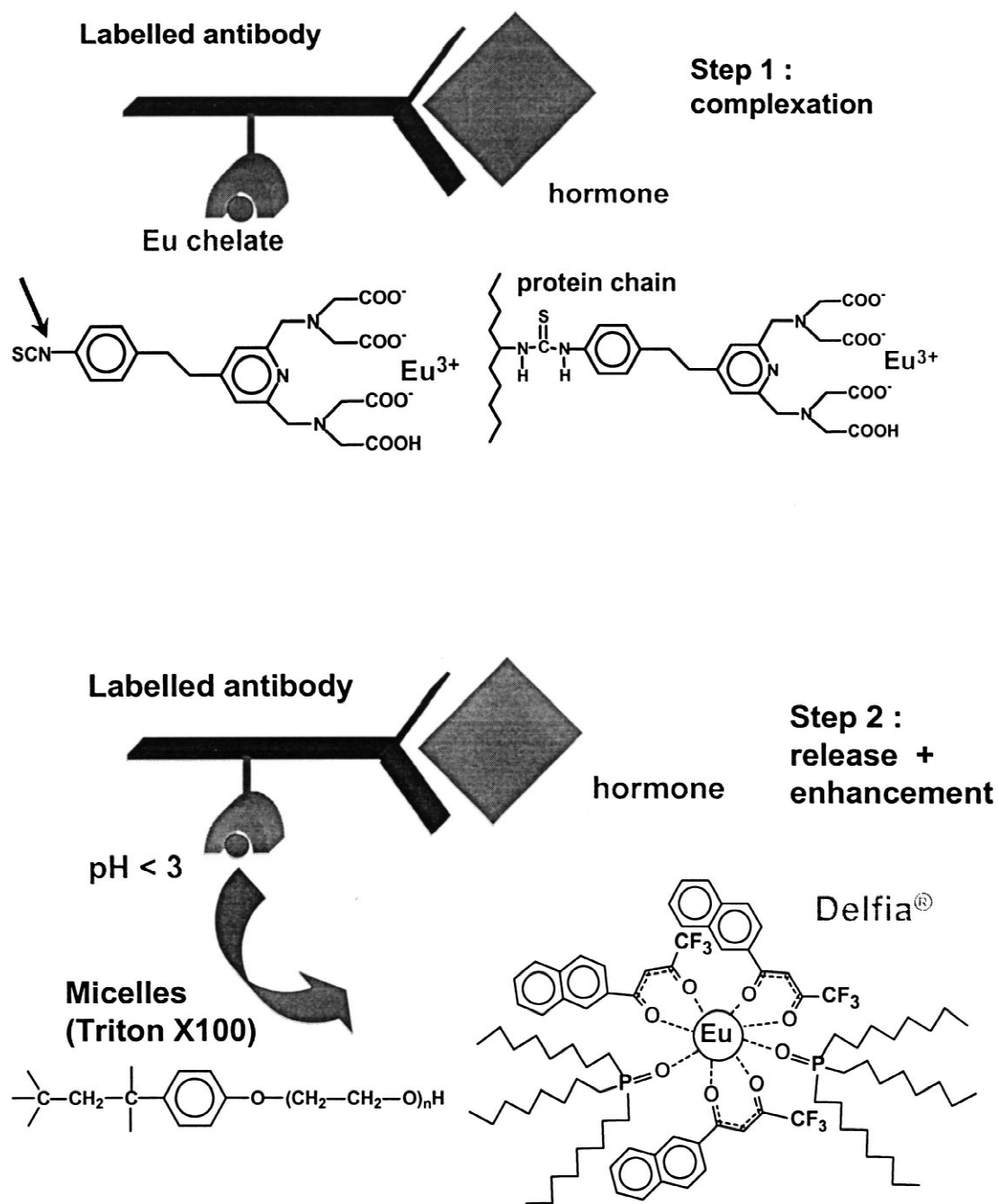


Fig. 2. Delfia[®] technology for immunoassays. Redrawn from Ref. [11].

labeled with an Eu^{III} chelate is reacted with a surface-immobilized analyte. The pH is then lowered, the Eu^{III} ions are released and inserted into a protective micellar environment consisting of β -diketonates, trioctylphosphine oxide and Triton[®] X-100. The metal-centered luminescence of the resulting assembly displays a large quantum yield (70%) and time-resolved measurements of this luminescence, to separate it from the luminescence of the

biological material, leads to very sensitive assays. The detection limit (10^{-14} M) is comparable to or even better than that attained by radioactive-based assays [11]. More recently, coordination compounds have been used for designing analytical sensors [12], catalysts for specific cleavage of DNA and RNA [13] and agents for cancer radio- [14,15] and photo-therapy [16]. All these applications have produced unprecedented interest in Ln^{III} coordi-

nation chemistry and have led to very imaginative strategies for inserting the functional Ln^{III} ions into stable chemical environments.

2. Fundamental properties of Ln^{III} ions [17]

While ligand-field effects in d-transition metal complexes commonly extend from 15 000 to 25 000 cm^{-1} (180–300 kJ mol^{-1}), they are much smaller in 4f-element compounds with hard donors, approximately 500 cm^{-1} (6 kJ mol^{-1}). This is due to the shielding of the 4f orbitals by filled subshells of higher principal quantum number. The coordination chemistry of 4f elements, and associated Sc^{III} and Y^{III} , is therefore subtle, with geometrical arrangements of the ligands essentially determined by steric effects.

2.1. Ionic radii and coordination numbers

One characteristic property of Ln^{III} ions is their large ionic radius, which decreases monotonically between La^{III} and Lu^{III} . The main point here is that the difference $r_i(\text{La}) - r_i(\text{Lu})$ amounts to only 0.18 Å (for CN=9), a figure only slightly larger than the difference between Ca^{II} ($r_i = 1.18$ Å) and Sr^{II} ($r_i = 1.31$ Å). This situation makes the tailoring of a receptor specifically designed to recognize one particular Ln^{III} ion difficult, especially if other Ln^{III} ions are present. On the other hand, the ionic radius largely depends upon CN, with an increase of about 0.3 Å between CN=6 and 12. As a consequence, Ln^{III} ions easily adapt to many different coordination environments, making them the “chameleons” of coordination chemistry. As a matter of fact, every coordination number between 3 and 12 has been evidenced in the solid state (Fig. 3) [18]. In solution, Ln^{III} ions have the tendency to adopt large coordination numbers. Investigation of lanthanide perchlorates and nitrates in acetonitrile in the presence of a strong donor such as dimethylsulfoxide has revealed a decrease in CN of about two units in going from La^{III} (CN \approx 10) to Lu^{III} (CN \approx 8) and, moreover, an increase in the CN of a specific ion upon addition of a larger quantity of the donor. This exemplifies the ability of the Ln^{III} ions to expand their coordination shell when required. In general, fractional CNs are obtained, indicating the presence of equilibria between species with different CN [19]. In water, the same trend is observed (Fig. 4): after several decades of thorough studies, it is now well established that larger Ln^{III} ions have CN=9 while smaller ions have CN=8 [20].

2.2. Hydrolysis and hydration enthalpies

One factor to take into account when attempting to complex Ln^{III} ions is their large hydrolysis constants, $^*\beta_{11}$ values ranging between -9 (La) and -8 (Lu) [21]. For

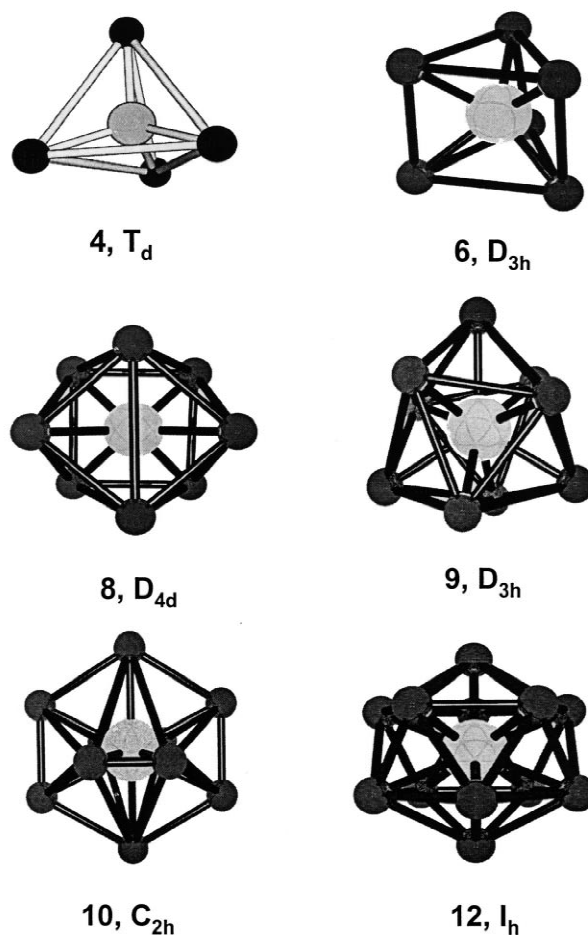


Fig. 3. The versatility of Ln^{III} ions: some coordination polyhedra evidenced in the solid state with their idealized symmetry: CN=4, $[\text{Lu}(\text{t-but})_4]^-$ [50]; CN=6, $[\text{Er}(\text{dpm})_3]^{3+}$ [51]; CN=8, $[\text{Lu}(\text{H}_2\text{O})_8]^{3+}$ [52]; CN=9, $[\text{Eu}(\text{dipic})_3]^{3+}$ [53]; CN=10, $[\text{Nd}(\text{NO}_3)_2(18\text{-crown-6})]^+$ [54]; CN=12, $[\text{Sm}(\text{tppb})_2]^+$ (tppb, tris[3-(2-pyridyl)-pyrazol-1-yl]borate) [38]. Redrawn using the PACHA program [55].

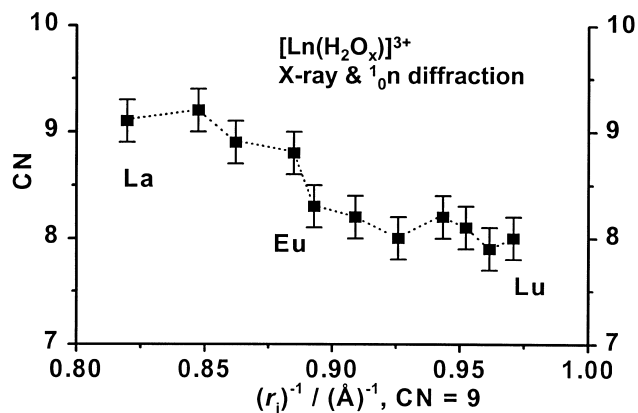


Fig. 4. Hydration number of Ln^{III} ions in solution. Redrawn after Ref. [20].

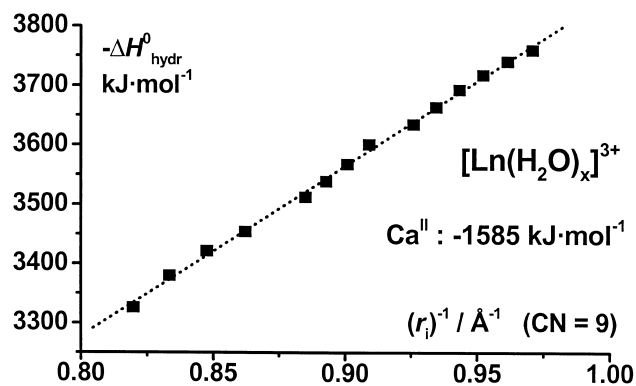


Fig. 5. Hydration enthalpies of Ln^{III} ions. Redrawn from Ref. [20].

instance, if the stability of a Lu^{III} complex with L is $\log K_1 = 3$, the following distribution of species occurs at pH 7 in the presence of 10^{-3} M free L: $[\text{LnL}]/[\text{LnOH}]/[\text{Ln}_{\text{aq}}] = 45/45/10$

$$*\beta_{l,m} = \frac{[\text{Ln}_m(\text{OH})_l(\text{H}_2\text{O})_{n-1}]^{(3m-l)+} \cdot [\text{H}^+]^l}{[\text{Ln}(\text{H}_2\text{O})_n]^{3+}]^m} \quad (1)$$

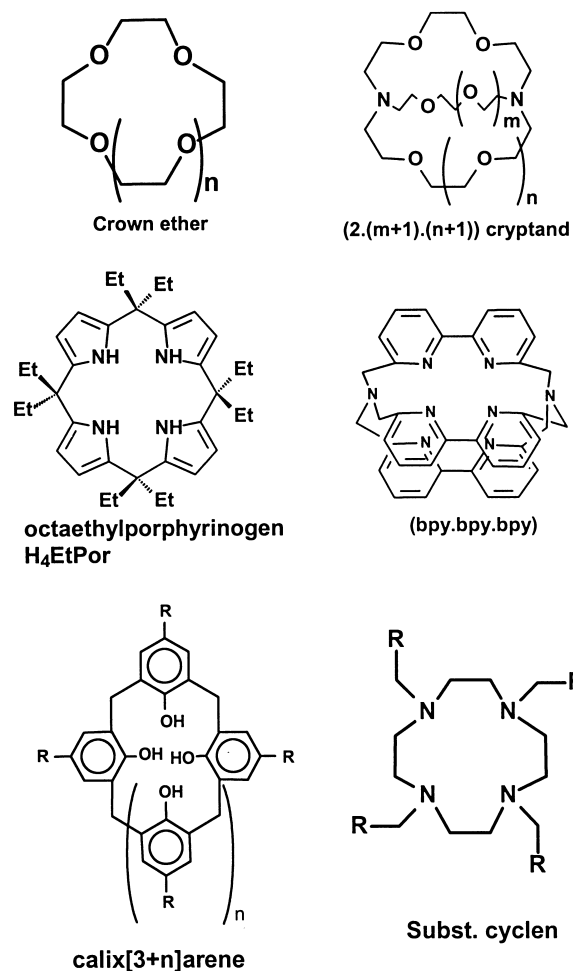
The complexation process of a hydrated (solvated) ion can be decomposed into two steps. The first involves the de-solvation of both the metal ion and the ligand and is highly enthalpy unfavorable since ΔH_{hydr} is very large for Ln^{III} ions. Values decrease from -3326 kJ mol⁻¹ for La^{III} to -3759 kJ mol⁻¹ for Lu^{III} (Fig. 5) [21], as compared to -1585 kJ mol⁻¹ for the otherwise chemically similar Ca^{II} ion. As a consequence, the enthalpy favorable second step in which the two de-solvated species combine to form the complex cannot compensate the dehydration enthalpy and most of the complexes are entropy stabilized. This “compensation model” predicts a linear relationship between ΔH_r and ΔS_r , which is effectively often observed. Moreover, it is responsible for the increase in the formation constant with decreasing size of the Ln^{III} ion.

3. Inserting functional Ln^{III} ions into chemical edifices

During the last decades, inorganic chemists have come up with several very imaginative strategies to insert the spherical hard Ln^{III} ions into functional architectures with predetermined properties. A brief account is given below.

3.1. Rigid receptors (Scheme 1)

Since 4f ions are spherical, one idea is to apply the *lock and key* principle put forward by Fischer in 1894, as has been done for the selective complexation of s ions: a monocyclic (coronand) or polycyclic (cryptand) receptor is engineered, which bears enough donor atoms to fulfil most of the coordination requirements of the metal ion and the



Scheme 1.

cavity of which perfectly matches the ionic diameter (Fig. 6). Application of this principle to the selective complexation of 4f ions has, however, been somewhat deceptive: the discriminating effect of a coronand (e.g., a crown ether) of a given cavity size being small, with $\Delta \log K(\text{La-Lu}) \approx 0.5-1.5$ only [22]. Moreover, a stability difference of the same order of magnitude is recorded between complexes with two successive macrocycles. In fact, adding one $-\text{CH}_2-\text{CH}_2-\text{O}-$ group enlarges the mean cavity of a crown ether by about $0.5-0.7$ Å [23], a difference greater than the ionic diameter variation between La^{III} and Lu^{III}. In other words, the size of the coronand cavity cannot be tuned finely enough to accommodate a given Ln^{III} ion. This does not mean that

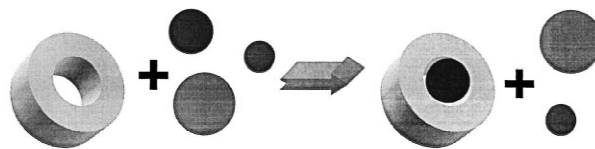


Fig. 6. Schematic illustration of the lock and key principle (Emil Fischer, 1894).

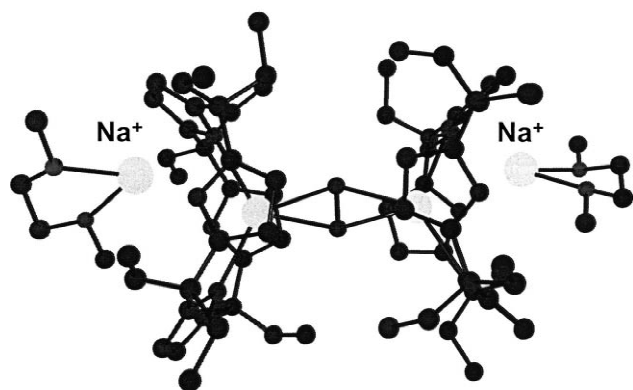


Fig. 7. Activation of dinitrogen by octaethylporphyrin complexes of Pr^{III} . Redrawn from Ref. [24] using the PACHA program [55].

interesting coronand-based systems cannot be designed, as demonstrated by a recent example where a combination of two porphyrinogen complexes of Pr^{III} or Nd^{III} activates dinitrogen, reducing it to its N_2^{2-} anion (Fig. 7) [24]. Moving to tridimensional receptors does not solve the problem of fine-tuning the cavity. For instance, cryptates with [2.2.1] display almost the same stability in water, around $\log K = 6.5$, for the entire Ln^{III} series [22]. The reason is that the cavity is slightly too small for lighter Ln^{III} ions and slightly too large for the heavier ions. Moreover, the side chains grafted onto the N bridgehead atoms are somewhat flexible and adapt the cavity to the actual size of the metal ion. Introducing more rigidity into these chains, for instance by using bipyridyl groups, may help, as exemplified by the stable and luminescent $[\text{Eu}(\text{bpy}.\text{bpy}.\text{bpy})]^{3+}$ cryptate used in homogeneous fluoroimmunoassays (Fig. 8). In these analyses, an antigen is specifically reacted with two different antibodies, one labeled with the Eu cryptate and the other with an energy acceptor having a large absorption coefficient (a chemically engineered allophycocyanin). Upon UV excitation,

energy is transferred first onto the Eu^{III} ion (antenna effect) and second onto the organic acceptor which emits strong luminescence at 660 nm. Since the product of the quantum yield of the latter by the efficiency of the second energy transfer is larger than the quantum yield of the Eu cryptate, amplification is obtained [25].

3.2. Designing induced cavities

To overcome the difficult application of the lock and key principle, one may resort to the *induced fit* concept [26]. Some flexibility is introduced into the ligand, allowing the receptor to wrap around the metal ion forming an induced cavity specifically adapted to the size of the metal ion. Use of this principle led to the design of several families of receptors (Fig. 9).

3.2.1. Large flexible macrocycles

Since crystal structure determinations pointed to many middle-sized macrocycles displaying some flexibility, an obvious way of introducing more versatility into the receptors was to resort to large macrocycles, especially for the synthesis of dimetallic edifices. Interest in the latter [27] arose because of the potential applications: (i) as luminescent probes, since two different luminescent centers can be helpful in imaging techniques; (ii) as precursors for doped materials where metal centers must be implemented at a fixed distance; (iii) as catalysts for the specific cleavage of DNA and RNA [28]; and (iv) as analytical sensors, for instance for *in vivo* mapping of Ca^{II} concentration [29]. Several classes of large macrocycles have been developed, including Schiff bases [30], cryptands [31], and calixarenes, particularly calix[8]arenes. For instance, we have shown that the photophysical properties of dimetallic calix[8]arene complexes can be easily tuned by minor modification of the substituents on the upper rim, leading to selective sensitization of either

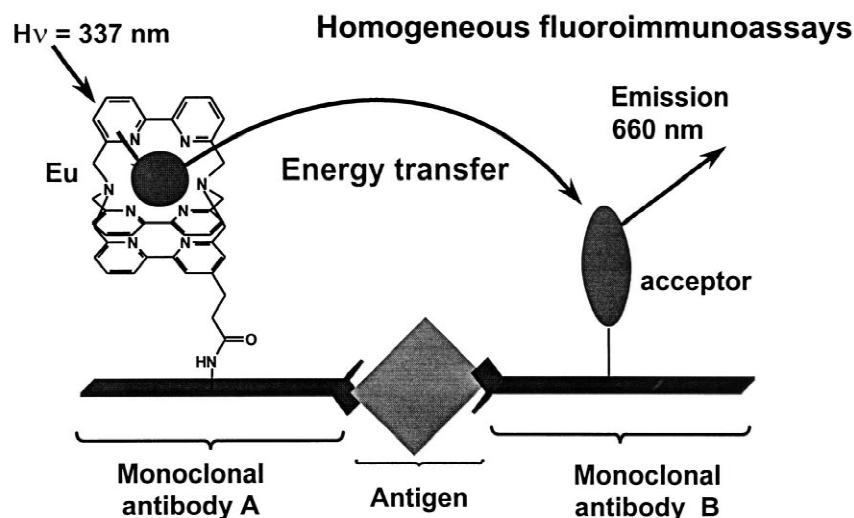
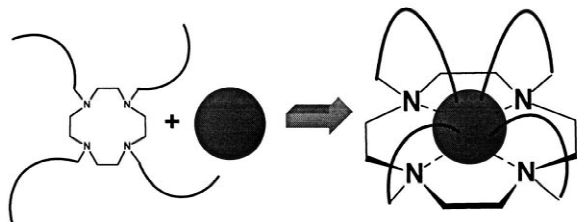
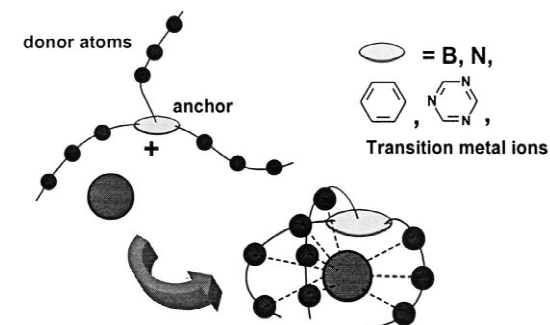


Fig. 8. Homogenous fluoroimmunoassays. Redrawn after Ref. [25].

Ligands with pendant arms



Podands



Self-assembly processes

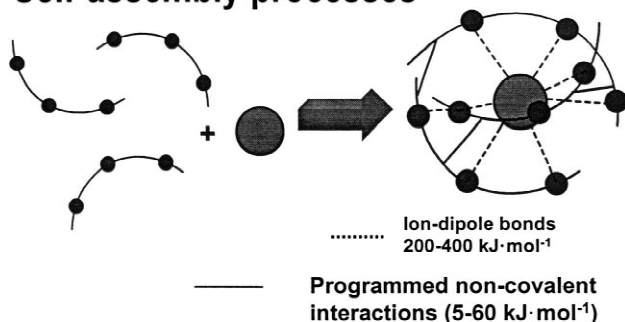


Fig. 9. Designing induced cavities for Ln^{III} ions: schematic representation.

Eu^{III} or Tb^{III} [32]. It is noteworthy that the formation of the dimetallic edifices usually requires a large reorganization of the ligand conformation, a factor which is energetically unfavorable.

3.2.2. Ligands bearing pendant arms

To minimize the reorganization energy, coordinating pendant arms have been grafted onto small macrocycles such as cyclen or calix[4]- and calix[5]arenes. In the first case, the coordination cavity is achieved by the four N donor atoms of the ring and by additional (usually four) donor atoms located on the dangling arms. With respect to the commonly observed nine coordination of Ln^{III} ions, one position remains free for interaction with solvent molecules, an essential feature in the design of MRI contrast agents [10,33]. Large stabilities are obtained:

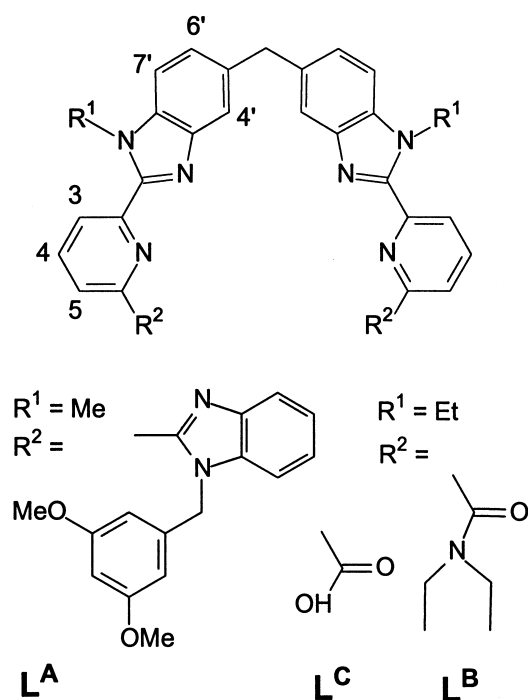
$\log K$ for the $[\text{Ln}(\text{dota})]^-$ complexes (Fig. 1) in water are in the range 23–26, that is 17–20 orders of magnitude larger than the stability of the aforementioned [2.2.1] cryptates. Luminescent probes and analytical sensors based on these systems are presently also being developed [34,35]. On the other hand, the phenoxy donor groups of calix[4]- and calix[5]arenes do not necessarily participate in the binding of Ln^{III} ions, depending on which rim is substituted. These ligands also induce highly stable edifices and are frequently used in the design of efficient extraction agents, particularly for nuclear waste management [36], or of lanthanide-based luminescent probes [37].

3.2.3. Podands

When the design of an edifice with given functionalities requires the presence of bidentate or tridentate arms, their grafting onto a relatively large macrocyclic platform is not always optimum and podands constructed from a smaller size anchor are more efficient. Ligands with four arms are built from small aromatic rings, while tri-armed receptors are simply engineered from a single atom, usually nitrogen, boron, or a transition metal ion. One example of such a podand is tppb, tris[3-(2-pyridyl)pyrazolyl]hydroborate, which yields 1:2 complexes in which the Ln^{III} ions lie in a 12N coordination site with a symmetry close to I_h (Fig. 3) [38]. One advantage of podands is that the number of donor atoms can easily be changed by varying both the number of the arms and their denticity. On the other hand, these ligands are less pre-disposed than the macrocycles fitted with pendant arms, so that the correct orientation of the arms upon complexation may require more conformational work. A remedy to this drawback is the use of weak non-covalent interactions, such as H-bonding, to position the arms so that the donor atoms are organized in the required orientation before complexation [39,40]. There are numerous examples of Ln^{III} podates described in the literature and a short review is given in Ref. [41].

3.2.4. Self-assembly processes

Molecular recognition, which is the heart of life processes, is often based on self-assembly, an action in which carefully tailored particles spontaneously assemble around the selected guest. The application of these processes in coordination chemistry is relatively recent [23], but has produced fascinating bi- and tridimensional functional architectures [42]. The key to self-assembly in coordination chemistry is that the formation of the host cavity not only relies on strong ion-dipole bonds to spatially organize the ligand strands but also on the presence of programmed weak non-covalent interactions between these strands. In our laboratories, we have produced a large library of monotopic and ditopic ligands which self-assemble with Ln^{III} ions to yield monometallic and dimetallic 3d–4f and 4f–4f edifices with predetermined luminescent or magnetic



properties [43]. As an example, our work on triple stranded dimetallic 4f–4f helicites is briefly summarized. Ligand L^A (Scheme 2) was first designed to form dimetallic edifices in organic solutions, to minimize the desolvation energy of the Ln^{III} ions. The resulting helicites [44] are highly stable in acetonitrile ($\log K \approx 20\text{--}22$ for the larger Ln^{III} ions) [45], but they proved to be rather sensitive to hydrolysis and, moreover, the quantum yield of the Eu helicite is extremely small, probably because of the presence of a too low-lying ligand-to-metal charge transfer state [46]. Diethylamido groups were therefore substituted to the terminal benzimidazole moieties to yield ligand L^B . Helicites with the latter are more stable than the bimetallic complexes with L^A and less sensitive to hydrolysis, surviving the addition of 3 M water in CH_3CN . Moreover, the quantum yield of the Eu helicite is 40 times larger than that of $[\text{Eu}_2(\text{L}^A)_3]^{6+}$ and luminescent properties are not altered by the addition of water [47]. These data encouraged us to further modify the ditopic ligand, introducing a terminal carboxylic acid function which enabled it to self-assemble in water with Ln^{III} ions (Fig. 10). The resulting edifices are the first bimetallic 4f–4f helicites self-assembled in water and they are highly stable [48]: the pEu value is around 21 as compared to 25 for $[\text{Eu}(\text{dota})]^-$ [49]. Moreover, the Ln^{III} ions are well protected from water interaction, resulting in quite long lifetimes of the excited $\text{Eu}(^5\text{D}_0)$ and $\text{Tb}(^5\text{D}_4)$ levels (2.1 and 2.5 ms, respectively). The quantum yield of the metal-centered luminescence is sizable for the Eu-helicite, but small for the Tb edifice because of a back transfer process. This new

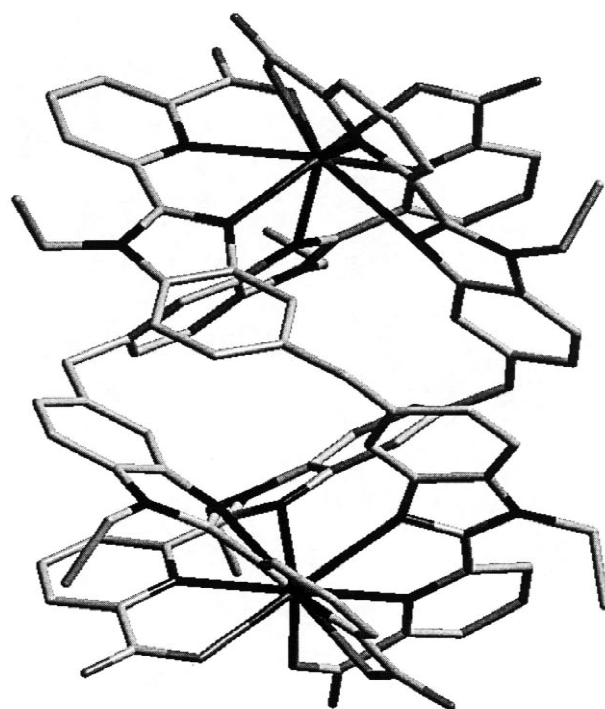


Fig. 10. Molecular structure of the triple stranded dimetallic helicite $[\text{Eu}_2(\text{L}^C\text{-}2\text{H})_3] \cdot 20.5\text{H}_2\text{O}$. Redrawn from Ref. [48].

class of lanthanide carboxylates are promising compounds for the development of water-soluble luminescent stains and we are in the process of testing new ligands based on a modification of L^C which should enable easy coupling with biological material, provide a better antenna effect and lead to even more stable edifices.

4. Conclusion

The characteristic magnetic and photophysical properties of trivalent lanthanide ions are well known and used in many practical devices and analytical processes. The versatility of their coordination properties makes them ideal ions to introduce into edifices with programmed physico-chemical properties. Due to the minute variation in both ionic radius and chemical properties between consecutive Ln^{III} ions, the tailoring of coordination environments specific to a given ion has to rely on ligands able to induce adaptable cavities around the metal ion. This may be achieved either using large flexible macrocyclic ligands, ligands with dangling arms, podands or self-assembly processes. The variety of approaches used to date shows that ligand engineering is only limited by the imagination of inorganic chemists and there is no doubt that cutting-edge improvements will lead to the design of even better functional lanthanide-containing architectures in the near future.

Acknowledgements

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