Institut de Chimie Minérale et Analytique

Spectrochemical Properties of Lanthanide Coordination and Supramolecular Compounds

Jean-Claude G. Bünzli*

Abstract. The work of the research group during the last 20 years in the field of lanthanide solvation, interaction with anions and neutral molecules, macrocyclic and supramolecular chemistry, and luminescent probes is briefly reviewed.

The series of 15 elements starting at lanthanum and extending to lutetium ($Z = 57–71$) is commonly referred to as lanthanides and as rare earths when the chemically similar scandium and yttrium are added. Their history started in the summer of 1787 when a Swedish army captain, *Karl Arrhenius* discovered a strange black mineral in a quarry near Waxholm fortifications, on a small island in the vicinity of Stockholm. He named the black stone 'ytterbite', after the nearby town of Ytterby [1]. *Johan Gadolin*, a Finnish professor of chemistry working at the University of Åbo (presently Turku), analyzed the mineral and separated a yet unknown element, today referred to as yttrium [2]. The other rare-earth elements have been characterized between 1803 and 1907 except for promethium which was artificially synthesized in 1947. Their history is a chronicle of conflicting and often incorrect claims because the changes in the chemical and physical properties are small as the atomic number increases. Two elements were discovered in Geneva by *J.C. Galissard de Marignac*, ytterbium in 1878 and gadolinium in 1880 [3]. Rare earths started their industrial fate rather modestly in 1891 when the Austrian entrepreneur *Karl Auer von Welsbach* invented the incandescent mantle bearing its name and composed of 99% thorium oxide and 1% of cerium oxide [4]. The *Auer* mantle was superior to electric light for more than four decades and an estimated five billions were sold until 1935. Today, major uses of rare earths are still related to light, for instance in lasers, in the manufacture of energy-saving incandescent lamp bulbs, and in luminescent probes. Numerous other applications for rare earths have now evolved, ranging from nuclear industry to petroleum industry, optics, electronics, magnetism, and medicine.

The importance of lanthanide ions in biochemistry and medicine is linked to their peculiar spectroscopic and magnetic properties [5]. The large energy gaps between the ground and first excited states of Eu^{III} and Tb^{III} limits nonradiative deexcitation processes, enabling the use of these ions as luminescent structural probes and long-lived emitting stains for homogenous fluoroimmunoassays. The large magnetic moment and the short electronic relaxation rate of Gd^{III} is ideal for the preparation of contrast agents in NMR imaging while Eu^{III}-containing complexes are effective shift reagents for the interpretation of intricate NMR spectra. More recently, lanthanide complexes have proved to be efficient catalysts for the specific cleavage of DNA and RNA while the development of photosensitizers for cancer therapy offers new hope for an improved treatment of this disease. All these applications require a precise knowledge of the coordination properties of the lanthanide ions and carefully tailored ligands able to encapsulate these ions while preserving or enhancing some of their spectroscopic and magnetic properties. Keeping this background in mind, we initiated 20 year ago a research program centered on the coordination chemistry of the trivalent lanthanide ions in nonaqueous solution and on the relationship between the composition of the inner-coordination shell of the metal ion and its photophysical properties.

Anion and Solvent Interactions in Nonaqueous Solutions

The geometrical arrangement of ligands around Ln^{III} ions essentially depends upon the steric properties of the ligand and coordination numbers (CN) between 3 and 12 are obtained with suitable design of the ligating molecules [6]. We have inves-

Correspondence: Prof. J.-C. G. Bünzli
Université de Lausanne
Institut de chimie minérale et analytique
BCH 1402
CH–1015 Lausanne

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tigated the interaction between the entire series of Ln[III] ions and perchlorate, nitrate, acetonitrile, and dimethylsulfoxide under strictly controlled anhydrous conditions by means of several spectroscopic methods, in particular FT IR. Coordination numbers vary widely with both the nature of the ligands bonded in the inner-coordination sphere and the composition of the solutions [7], although CN = 9 is often found [8]. This demonstrates that the inner-coordination sphere of the Ln[III] ions is easily adjustable to the environment to which these ions are exposed. Henceforth the versatility and adaptability of these metal ions which give them a great advantage when used as spectroscopic probes in biological or environmental systems. On the other hand, we have established that perchlorate penetrates into the inner-coordination sphere of the Ln[III] ions, the apparent stability constant $\log K_1$ being around 2.

Host-Guest Complexes with Macrocyclic Ligands

The luminescent $^5D_0$(Eu) and $^5D_4$(Tb) states are easily quenched by high-energy vibrations, in particular O–H stretching. One way to prevent interaction with solvent molecules when they are used as luminescent probes (e.g. in fluoroimmunoassays), and to enhance their ability to capture excitation light through energy transfer via the ligand states, is to insert them into macrocyclic receptors. As a follow-up of our work on crown and aza-crown ethers [9], and on Schiff bases [10], we are presently investigating the ability of calixarenes to provide a suitable coordination environment for Ln[III] ions [11]. Our main interest is focused on dinuclear edifices with substituted calix[8]arenes (Fig. 1) since in the solid state the complex molecules are fairly well isolated and are therefore good model molecules for the

study of Ln[III] to Ln[III] energy-transfer mechanisms. In addition, the photophysical properties of the dinuclear complexes [LnLn'(LH$_2$)(solv)$_n$] (Ln = Eu, Tb) can be easily tuned by changing the substituent in the para-position. When R = t-Bu, the Eu-containing complexes possess a low-lying ligand-to-metal charge-transfer (LMCT) band inducing unusually large f-f oscillator strengths (e.g., 5 $l\cdot mol^{-1}\cdot cm^{-1}$ for $^5D \rightarrow {}^7F_0$) and an efficient quenching of the Eu-centered luminescence. On the other hand, the Tb[III] luminescence is conveniently excited and not quenched. Replacing t-Bu by NO$_2$ shifts the LMCT state at higher energy and the ligand $^1\pi\pi^*$ and $^3\pi\pi^*$ states at lower energy. As a consequence, the Eu[III] luminescence is less quenched and better excited through the ligand levels, but the Tb[III] ion can no more be excited [12].

Self-assembled Mono- and Dinuclear f-f and d-f Triple Helicates

The development of lanthanide complexes with tailored chemical, structural, and physico-chemical properties represents a challenge to the synthetic chemists in view of the large coordination numbers, the high lability, and low steric requirements of the Ln[III] ions. In addition to preformed macrocyclic receptors and metal-induced template reactions, the chemists may turn to self-assembly processes leading to so-called supramolecular edifices. Supramolecular chemistry relies on H-bonds, ion-dipole, hydrophobic, and van der Waals interactions to construct large


R = H
    n=1 : calix[4]arene
    n=5 : calix[8]arene

R = C(CH$_3$)$_3$
    n=5 : b-LH$_8$

R = CH(CH$_3$)$_2$
    n=5 : p-LH$_8$

R = NO$_2$
    n=5 : n-LH$_8$

R = SO$_3$H
    n=5 : s-LH$_8$
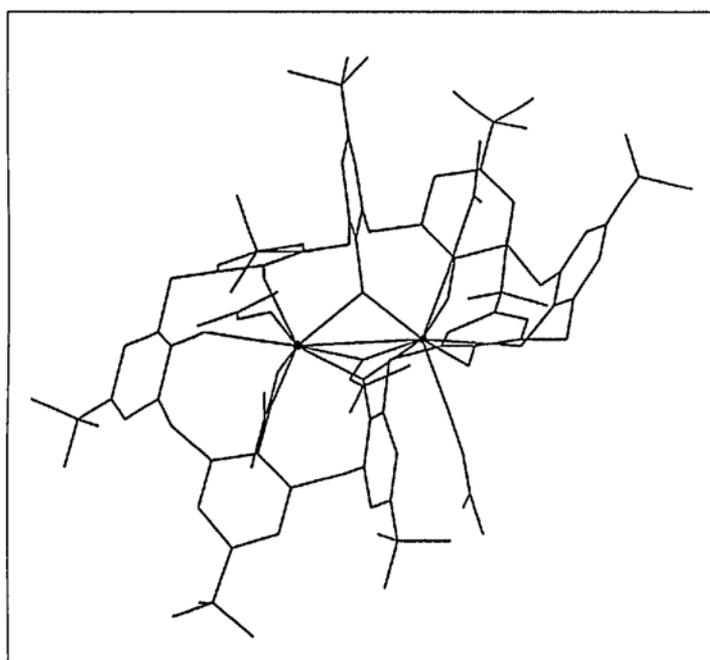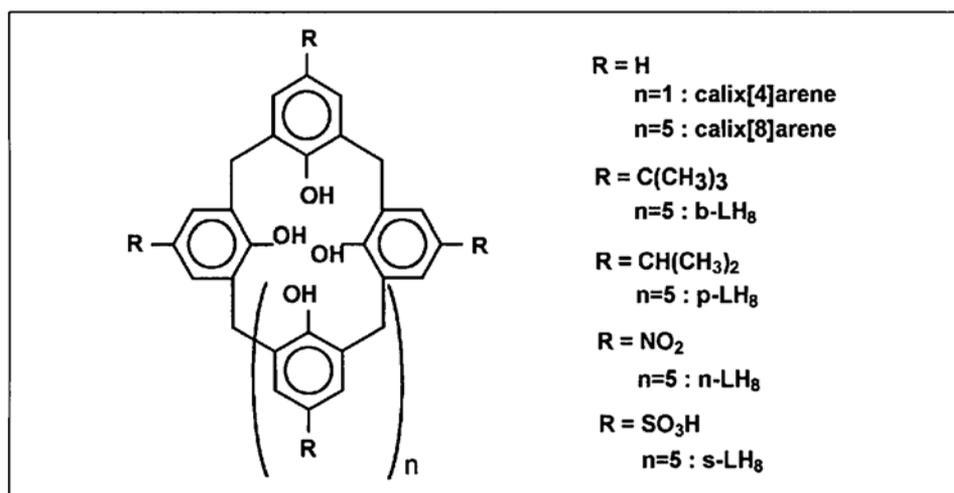
Fig. 1. *Dinuclear complex [Eu(LH$_2$)(DMF)$_5$]·4DMF*
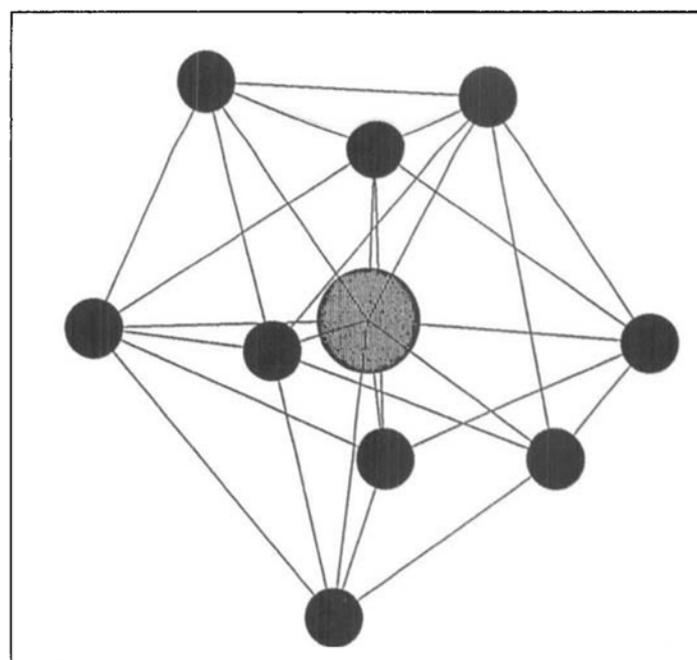
Fig. 2. *Coordination polyhedron in [Eu(L^5)$_3$]^3*

L	R^1	R^2	R^3
L^0	H	H	H
L^1	H	Me	H
L^2	H	Et	H
L^3	H	Oct	H
L^4	H	Bz(OMe)$_2$	H
L^5	H	Et	Me
L^6	Phe	Bz(OMe)$_2$	H
L^7	PheNO$_2$	Bz(OMe)$_2$	H
L^8	PheNEt$_2$	Bz(OMe)$_2$	H

L^9 R = X, R' = H, R" = Me
L^{10} R = Y, R' = H, R" = Me
L^{11} R = R' = X, R" = H
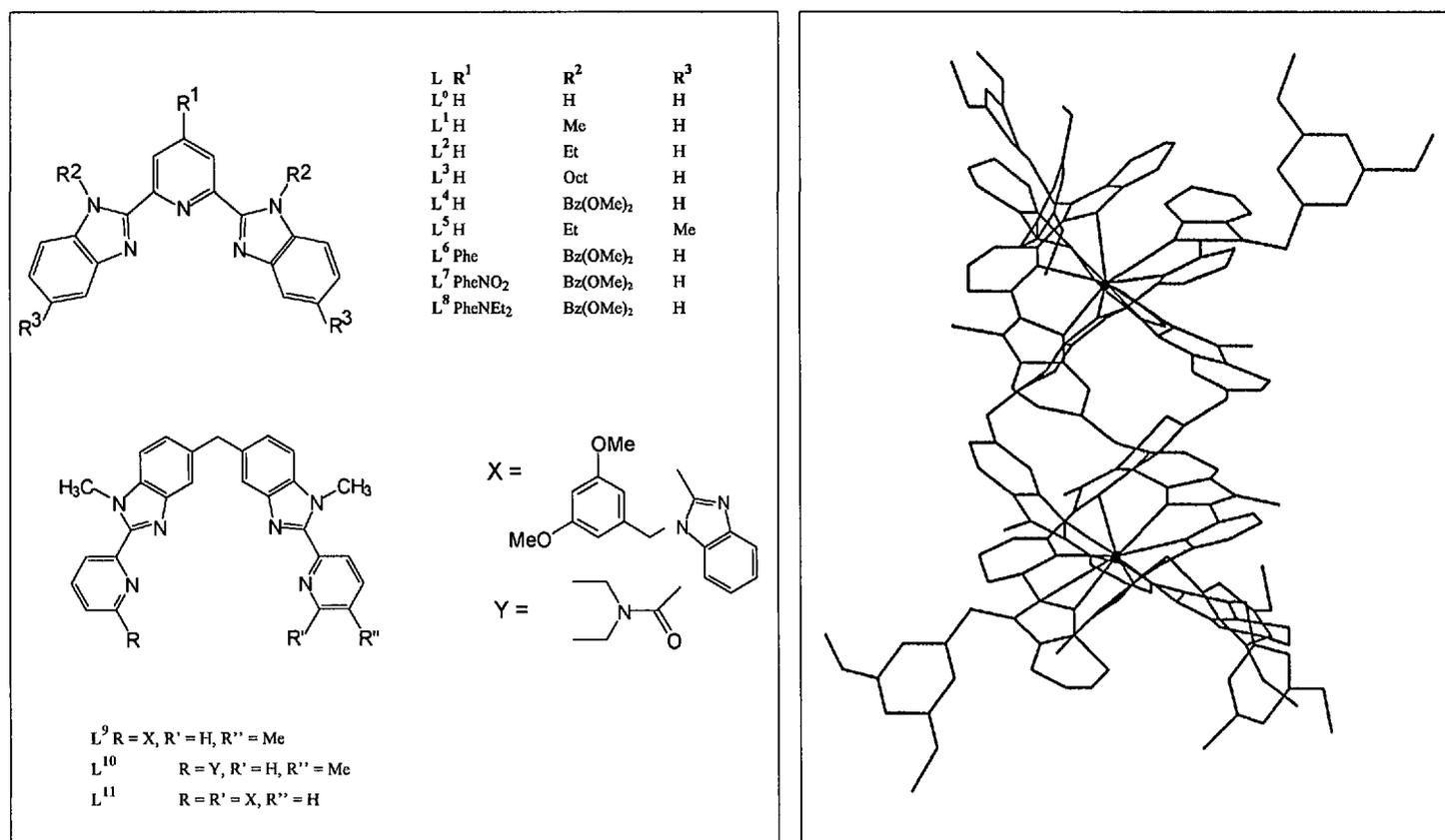
Fig. 3. *Dinuclear triple helicate [Eu$_2$(L^{10})]$^{6+}$*

supramolecular assemblies. In collaboration with Dr. *C. Piguet* from the University of Geneva, we are developing a strategy aimed at synthesizing lanthanide-containing building blocks for the design of materials with predetermined physicochemical properties. We use the basic synthons L^i, which provide a tridentate cavity for complexation of the Ln^{III} ions. In [Ln(L^i)$_3$]$^{3+}$ complexes [13][14], the 9-coordinate Ln^{III} ion lies in an environment close to the ideal tricapped trigonal prismatic arrangement (*Fig. 2*). Both the quantum yield of the metal-centered luminescence and the stability of the edifices can be controlled by a careful choice of the substituents R^1 through R^3. In particular, a large size-discriminating effect is obtained with 2,6-bis(1'-methylbenzimidazole-2'-yl)pyridine between Gd^{III} and Lu^{III}, the stability constant dropping by a factor of 10^4.

The binucleating ligands L^j are coded for the complexation of two lanthanide ions and effectively self-assemble to yield binuclear f-f edifices held together by 18 noncovalent ion-dipole bonds and several stacking interactions between the ligand strands [15] (*Fig. 3*). The asymmetric ligands L^k selectively self-assemble with mixtures of Ln^{III} and M^{II} (M = Zn, Fe) ions leading to triple-stranded noncovalent heterodinuclear podates [EuM(L)$_3$]$^{5+}$ [16] [17]. The Fe^{II}-containing edifices display

a spin-crossover behavior between 20 and 60°, the parameters of which can be tuned by the choice of the Ln^{III} ions. Moreover, the supramolecular assemblies with ligands bearing a carboxamide binding unit are water-resistant and possess better luminescent properties [17]. We are presently modifying ligands L^i, L^j, and L^k to improve both their complexing ability and the photophysical and magnetic properties of their supramolecular edifices with Ln^{III} ions.

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