Hetero-dinuclear sodium–lanthanide(III) complexes with an asymmetric compartmental macrocycle

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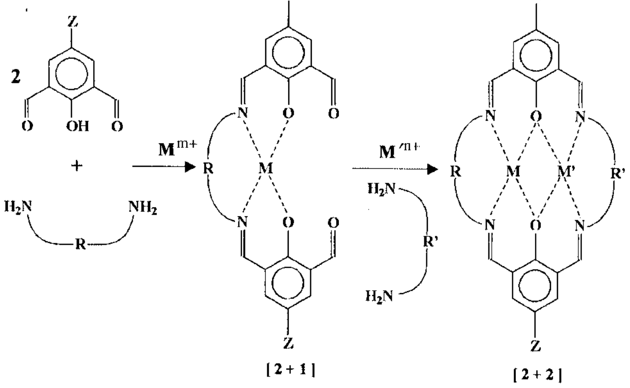
A heterodinuclear macrocyclic complex containing both Yb^{3+} and Na^+ ions has been synthesized and characterized by X-ray crystallography and ^1H and ^{23}Na solution NMR; at room temperature the coordinated Na^+ ion is in slow chemical exchange with free Na^+ ions and its NMR resonance is strongly shifted.

In recent years asymmetric compartmental ligands have been under intense scrutiny because it is expected that well defined bimetallic systems may find interesting applications in several areas of chemical research.[1–4] The synthesis of compartmental macrocycles is commonly pursued by a step-by-step condensation of 2,6-diformyl-4-substituted phenols with polyamines which may also contain other donor atoms. Heterodinuclear (M,M′) complexes may be conveniently prepared by reacting the intermediate [2 + 1] acyclic complex, obtained by template synthesis in the presence of M^{m+} ions, with a suitable polyamine in the presence of M'^{n+} ions.[5]

A marked difference in the set of donor atoms of the two adjacent chambers favours the formation of heterodinuclear complexes (with respect to homodinuclear complexes) thus limitating the possibility of positional heterodinuclear isomers.[6,7]

Here, we investigate the synthesis and characterisation of a Yb–Na dinuclear complex which represents the first example of macrocyclic compartmental complex containing a lanthanide and an alkali metal ions.

On the basis of the above considerations, it was thought that a suitable ligand should contain a Schiff base chamber for the lanthanide coordination and a crown-ether moiety for the coordination of the alkali metal ion. As diformyl precursor we used 3,3′-(3-oxapentane-1,5-diyldioxy)-bis(2-hydroxybenzaldehyde) which, upon reaction with 1,5-diamino-3-azamethylpentane (Scheme 1) yields the asymmetric compartmental macrocycle shown in Fig. 1.[8,9]



Scheme 1

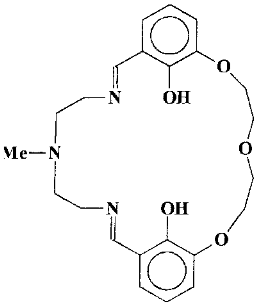


Fig. 1 Schematic representation of the compartmental macrocycle (L) designed for coordinating a lanthanide(III) ion into the Schiff base (N_3O_2) chamber and an alkali metal ion into the crown-ether moiety.

Rather surprisingly it was found that this macrocyclic ligand coordinates lanthanide(III) ions into the crown-ether chamber rather than into the N_3O_2 Schiff base.[9,10] On the other hand the same crown-ether chamber is involved in the coordination of alkali ions in the case of homonuclear alkaline metal containing species.[11] Thus, although both ions prefer coordination at the O_2O_3 chamber, we surmise that the use of the Na^+ containing complex may force the coordination of the lanthanide(III) ion into the Schiff-base chamber.

This synthetic strategy was successful as shown by the spectroscopic properties and X-ray structure of the obtained $YbNa(L)Cl_2$ derivative (Fig. 2).†

The ytterbium ion is coordinated by two chlorine atoms in *trans* positions and by three nitrogen and two negatively charged phenyl oxygen atoms of the ligand, reaching heptacoordination with a pentagonal bipyramidal geometry. The sodium ion is coordinated by the three etheric oxygen atoms and the same two phenyl oxygens that act as a bridge. A methanol molecule is also coordinated in the apical position of the resulting pentagonal pyramidal polyhedron. The oxygen atom of the methanol is disordered and two positions have been found. The Yb···Na contact distance is 3.555(2) Å.

The high temperature ^1H NMR spectrum (65 °C, CD_3OD) of $YbNa(L)Cl_2$ (Fig. 3) is consistent with the occurrence of a motion in the macrocyclic ring which reduces to half (twelve) the number of the observed resonances. Although the spectrum covers a range of *ca.* 70 ppm, the resonances associated with the two N_3O_2 and O_2O_3 chambers can be unambiguously assigned. In fact, the paramagnetic Yb(III) ion causes a large spread of the five protons (and of the methyl group) associated with the Schiff base compartment (−15 to −57 ppm) whereas the proton associated with the crown ether and aromatic moieties fall in the region +7 to −8 ppm *i.e.* they 'feel' only in part the paramagnetism of the lanthanide ion.

The ^{23}Na NMR spectrum at ambient temperature consists of the broad absorption of the bound ion (Na^b) at *ca.* 40 ppm

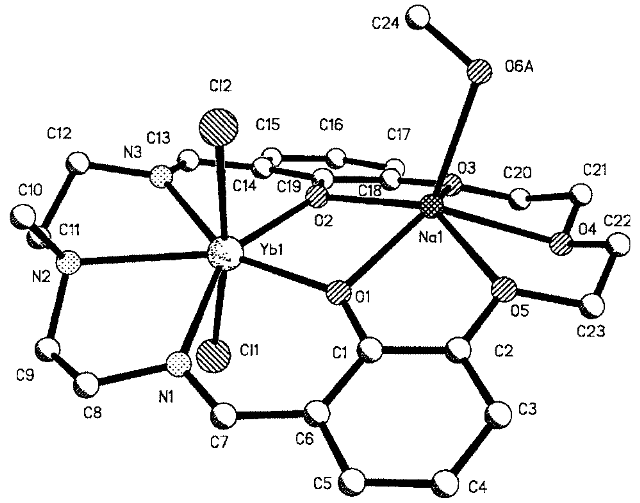


Fig. 2 ORTEP drawing of $[YbNa(L)Cl_2]\cdot MeOH$ with ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (°): Yb–O(1) 2.204(3), Yb–O(2) 2.226(3), Yb–N(1) 2.459(4), Yb–N(2) 2.593(4), Yb–N(3) 2.474(4), Yb–Cl(1) 2.582(1), Yb–Cl(2) 2.638(1), Na–O(1) 2.343(4), Na–O(2) 2.296(4), Na–O(3) 2.370(5), Na–O(4) 2.444(5), Na–O(5) 2.316(4), Na–O(6)(methanol) 2.35(mean); Cl(1)–Yb–Cl(2) 172.14(4), Yb–O(1)–Na 102.2(1), Yb–O(2)–Na 103.0(1).

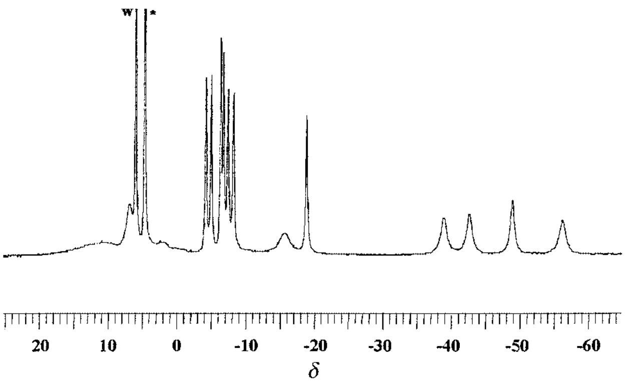


Fig. 3 400 MHz ^1H NMR spectrum of $YbNa(L)Cl_2$ at 65 °C in CD_3OD. The water and methanol resonances have been labelled with the symbols w and *, respectively.

upfield from that of the free ion (Na^f) [Fig. 4]. Upon increasing the temperature the exchange between Na^f and Na^b becomes fast on the NMR timescale [Fig. 4] and, at 65 °C, a relatively narrow absorption at *ca.* −16 ppm is observed. It seems reasonable to suggest that the release of Na^+ ion from the crown-ether chamber induces an overall flexibility of the macrocycle as the ^1H NMR spectrum recorded at ambient temperature is more complex than that obtained at 65 °C.

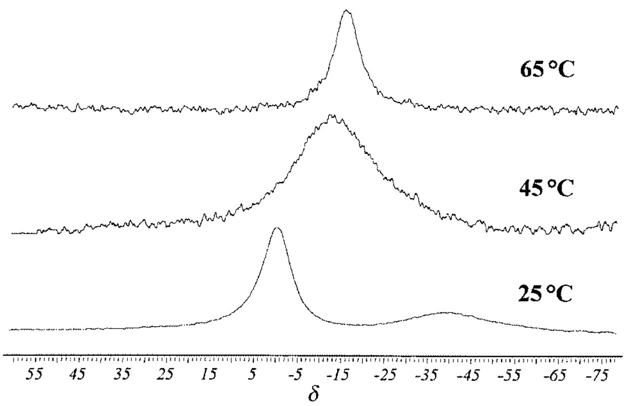


Fig. 4 Variable temperature ^{23}Na NMR spectra of $YbNa(L)Cl_2$ (25 mM) at 9.4 T in the presence of NaCl (30 mM) in CD_3OD.

The high and negative paramagnetic ^{23}Na NMR shift observed for Na^b strongly suggests that the principal axis of the magnetic susceptibility tensor associated with the Yb(III) ion lies along the Yb–Na direction rather than along an axis perpendicular to the macrocyclic plane. This finding may be highly relevant to development of a novel class of ^{23}Na-shift reagents which could be very useful in separating the ^{23}Na NMR resonances for intra- and extra-cellular components.[12]

Notes and references

† *Crystal data* for $YbNa(L)Cl_2\cdot MeOH$: $C_{24}H_{30}Cl_2N_3NaO_6Yb$, yellow crystal, 0.30 × 0.35 × 0.25 mm, M = 723.44, monoclinic, space group $P2_1/n$, a = 12.586(3), b = 13.127(3), c = 16.690(3) Å, β = 101.08(3)°, U = 2706(1) Å^3, Z = 4, D_c = 1.776 g cm^{-3}, μ(Mo-Kα) = 3.713 mm^{-1}, T = 293(2) K, 7338 reflections measured, 6903 reflections with $I > 4\sigma(I)$ used in all calculations, $R(F^2)$ = 0.0411, $wR(F^2)$ = 0.112. The structure was solved using direct methods and refined by full-matrix least squares on F^2. CCDC 182/1503.

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