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Lanthanide Complexes with Macrocyclic and Macroacyclic Schiff Bases[*]

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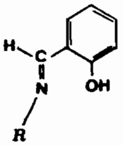
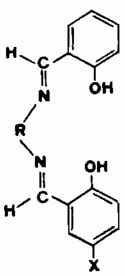
Many mononuclear lanthanide complexes with simple or cyclic Schiff bases of the type **I**, **II** and **III** have been obtained and characterized by X-ray determination [1]. However, less attention has been paid to binuclear lanthanide complexes in spite of much interest in their physicochemical properties.



I



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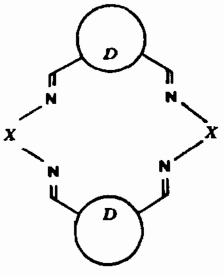
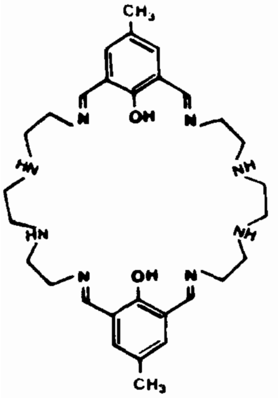


III

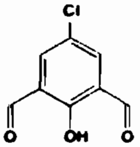
Head unit: D = pyridine, furan, thiophen, pyrrole
Lateral unit: X = 1,*n*-diamine

Recently the synthesis of homodinuclear lanthanide complexes with the large binucleating macrocyclic ligand **IV** (H_2L_A) obtained by condensation of 2,6-diformyl-4-methylphenol and triethylenetetramine, has been reported [2]. With the preparation of complexes of this type it is becoming feasible to study the interactions between lanthanide ions.

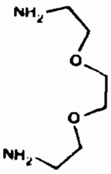


H_2L_A

IV



V



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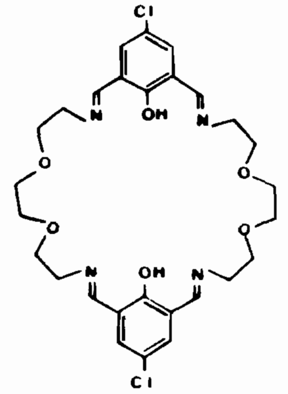
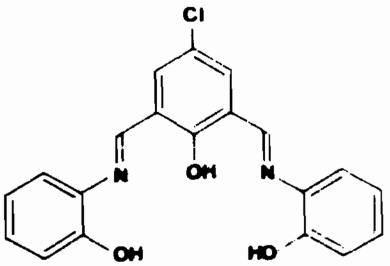


H_2L_B

VII

We have extended the binucleating systems by using the keto-precursor 2,6-diformyl-4-chlorophenol **V** and the polyamine **VI** for the formation of the macrocycle **VII** (H_2L_B). In addition, the coordination ability toward lanthanides of the compartmental ligand **VIII** (H_3L_C), which can be seen as the half unit of the macrocycle **VII**, has been tested.



H_3L_C

VIII

With the macrocylic ligand H_2L_B complexes with the formulae $Ln_2L_B(NO_3)_4 \cdot nH_2O$ (Ln = lanthanide = La, Tb, Dy; n = 2–4) have been obtained, while with the potentially pentadentate compartmental ligand H_3L_C complexes such as $LnL_C \cdot H_2O$ (Ln = La, Pr, Sm, Gd, Dy, Yb) have been obtained. The present paper reports the preparation and characterization of these lanthanide complexes, together with their physicochemical properties.

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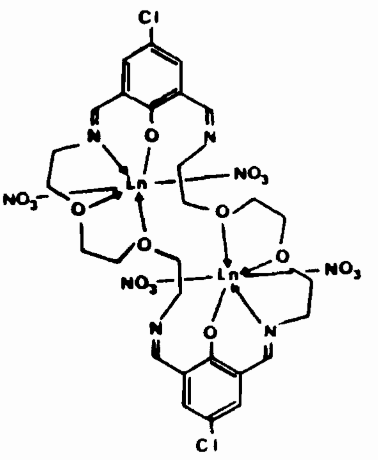
Results and Discussion

The homodinuclear lanthanide complexes of the macrocycle H_2L_A have the composition $Ln_2(L_A)(NO_3)_4 \cdot nH_2O$ or $Ln_2(L_A)(NO_3)_{4-x}OH_x$ ($x = 1$ or 2). The dinuclear nature of the complexes was established by FAB mass spectra [2]. The complexes with H_2L_B have the formula $Ln_2(L_B)(NO_3)_4H_2O$, similar to that obtained with H_2L_A.

The magnetic moment of the terbium complex (13.42 BM, 9.5 per terbium atom) shows that it is substantially unaffected by metal–metal interaction, being due to two magnetically dilute terbium(III) ions (Table I). To explain the results, it is possible that in these, and possibly in the above complexes, the ligand does not behave as a compartmental but as a macrocyclic binucleating ligand where the two ions are coordinated at a very long distance from each other with no heteroatoms shared between metal ions. A possible coordination about the metal ions might be that shown in **IX**. A different shape of these complexes cannot, however, be ruled out, as found for the complex $La_3(L_D)(NO_3)_6 \cdot 3MeOH$, synthesized by reaction of $La(NO_3)_3 \cdot 6H_2O$ with diacetylpyridine and 1,3-diamino-2-hydroxypropane in methanol [3].

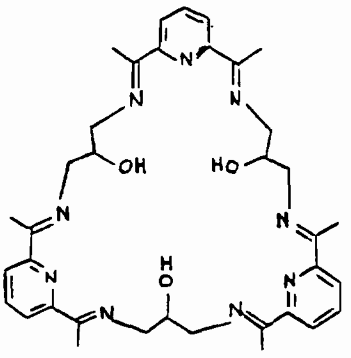
TABLE I. Magnetic Moments (BM) at Room Temperature for the Prepared Compounds

Compound	μ_{eff} (per metal atom)	μ (per free ion)
$DyL_C \cdot H_2O$	9.65	10.6
$GdL_C \cdot H_2O$	7.27	7.94
$SmL_C \cdot H_2O$	1.32	1.65
$PrL_C \cdot H_2O$	3.03	3.62
$YbL_C \cdot H_2O$	4.10	4.5
$TbL_C \cdot H_2O$	8.95	9.7
$EuL_C \cdot H_2O$	3.06	3.40
$Tb_2L_B(NO_3)_4$	9.5	9.7



IX

The reaction of H_3L_C with the appropriate lanthanide(III) nitrate in the presence of the stoichiometric amount of base (LiOH) produces the complexes $LnL_C \cdot nH_2O$ ($n = 0$, 1). In these complexes there is the difficulty (found also with the models) that H_3L_C should behave as a pentadentate ligand towards one lanthanide ion. Although this should occur, there is a coordination unsaturation about the metal ion, also considering the solvent molecules present, and consequently an oligomerization of the complex could be suggested.



X

(H_3L_D)

The binucleating ability of H_3L_C, also with f-block ions, was recently demonstrated for the complex $Mg[Th_2(L_C)_3] \cdot 6H_2O$, obtained by reaction of the preformed ligand or of the keto and amino precursors with thorium nitrate in the presence of LiOH and magnesium acetate. Each anion is a dinuclear unit, in which two Th atoms are bridged by three oxygen atoms from three different ligands [4].

We suggest that similar compartmental behaviour may be present for the lanthanide complexes derived from H_3L_C. In addition, the magnetic moments are lower than those expected (see Table I) (this could be caused, however, by oligomerization only) and it was possible to prepare complexes of the type $Mg_3[Ln_3(L_C)_3]_2 \cdot nH_2O$ or $Li_3[Ln(L_C)_3] \cdot nH_2O$ where the anionic stoichiometry is the same as that of the thorium complex.

References

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