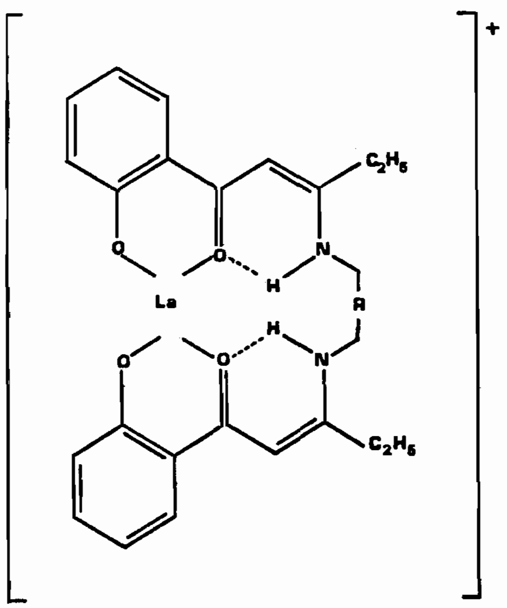

Fig. 5. NO_3^-, xH_2O.

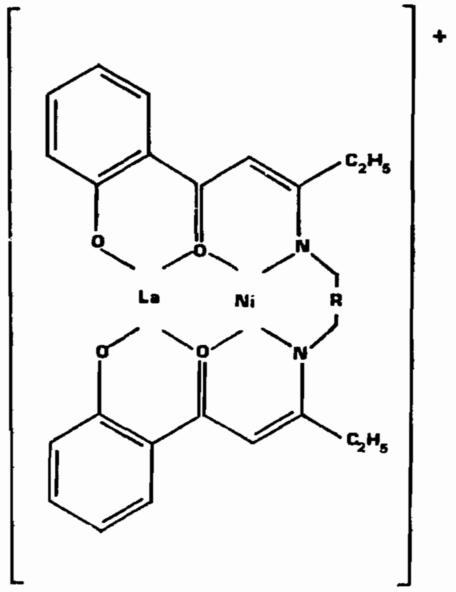

Fig 6. NO_3^-, xH_2O.

LiOH gave fine powdery products. The products analysed as $Ln_2(pap)_2(NO_3)(OH)$, nH_2O ($n = 2$ for La, 3 for Eu and 6 for Pr), and are assigned the *cis*-binuclear structure, III, by analogy with transition metal analogues [2].

Mononuclear Complexes of the Schiff Bases

The reaction of a chloroform solution of the Schiff base with a methanolic solution of $Ln(NO_3)_3 \cdot nH_2O$ gave fine, powdery products. For I complexes were available for Ln = La → Eu, and for II complexes were available for Ln = La → Sm. The complexes were of the form $Ln(H_2-L)NO_3 \cdot xH_2O$ and are assigned structure IV. Outer compartment occupancy is indicated by the absence, in the i.r., of ν_{OH} for the phenol and the presence of ν_{NH}. ^1H n.m.r. spectra of the La derivatives also support this proposition. The preference of lanthanide ions for oxygen donor environments would also suggest such an occupancy.

Binuclear Complexes of the Schiff Bases

Attempts to obtain homobinuclear lanthanide complexes have so far been unsuccessful as have been attempts to prepare heterobinuclear complexes by the reaction of the mononuclear lanthanum complexes with metal salts such as VO(IV), Th(IV), UO_2(VI) – all metals with strong $-O_2O_2$ preferences. The reaction of copper(II) ethanoate with IV gave the homobinuclear copper(II) derivative. The reaction of the mononuclear copper(II) complex of I having $-N_2O_2$ occupancy with $Ln(NO_3)_3$, nH_2O gave no heterobinuclear product but reaction of the corresponding nickel(II) complex with $Ln(NO_3)$, nH_2O did give heterobinuclear complexes of I (Ln = La, Pr, Eu).

1 U. Casellato, P. A. Vigato, D. E. Fenton and M. Vidali, *Chem. Soc. Rev.*, *8*, 199 (1979).
2 Y. Taguchi, F. Sagara, H. Kobayashi and K. Ueno, *Bull. Chem. Soc. Japan*, *43*, 2470 (1970).

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Complexes of Lanthanide Chlorides with Macrocyclic Polyethers

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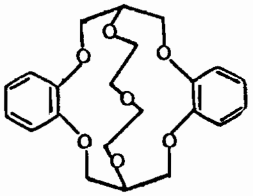
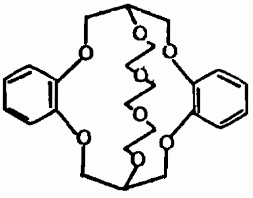
Macrobicyclic polyether ligands I, II, III and IV have been shown [1] to form complexes with alkali salts having high formation constants even in water (10^5 l mol^{-1}).

Ln/Ligand	La	Nd	Sm	Gd
I	$LaCl_3 \cdot I \cdot 2H_2O$	$NdCl_3 \cdot I \cdot H_2O$		$GdCl_3 \cdot I \cdot 2H_2O$
II	$LaCl_3 \cdot II \cdot 2H_2O$		$SmCl_3 \cdot II \cdot H_2O$	$GdCl_3 \cdot II \cdot H_2O$
III	$LaCl_3 \cdot III \cdot 1.5H_2O$	$NdCl_3 \cdot III \cdot 1.5H_2O$	$SmCl_3 \cdot III \cdot \frac{1}{2}H_2O$	$GdCl_3 \cdot III \cdot H_2O$
IV	$LaCl_3 \cdot IV \cdot H_2O$	$NdCl_3 \cdot IV \cdot 0.3H_2O$		$GdCl_3 \cdot IV \cdot H_2O$



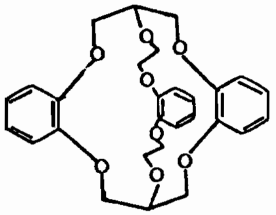
I

$C_{22}H_{26}O_7$



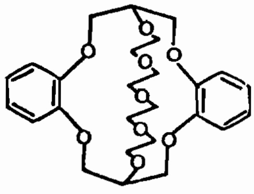
II

$C_{24}H_{30}O_8$



III

$C_{28}H_{30}O_8$



IV

$C_{26}H_{34}O_9$

These ligands provide potentially 7, 8, 8 and 9 oxygen atoms for coordination with a cation. We investigated the reaction between $LaCl_3$, $NdCl_3$, $SmCl_3$ and $GdCl_3$ and the four ligands. Crystalline compounds were obtained all of stoichiometry $LnCl_3$:ligand = 1:1, as deduced from elemental analysis. The existence of crystals depends upon the presence of water, evidence of this was obtained from infra red spectra particularly in the 3000–3500 cm^{-1} region and from analysis. Preliminary X-ray diffraction measurements and the densities of $LaCl_3 \cdot II \cdot xH_2O$ and $LaCl_3 \cdot III \cdot yH_2O$ gave values of x and y which are independent of elemental analysis.

Summary of the compounds obtained. *(see Table)*

A complete single crystal structure analysis of $LaCl_3 \cdot II \cdot H_2O$ has shown the crystals to contain $(LaCl_2 \cdot II)^+$ cations with the third chlorine ion and the water molecules occupying disordered sites in channels, similar to those in $KCl \cdot III \cdot 5H_2O$ [2].

1 D. G. Parsons, *J. Chem. Soc., Perkin, I,* 451 (1978).

2 I. R. Hanson and M. R. Truter, *J. Chem. Soc., Perkin II,* 1 (1981).

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Thermodynamics of Aquo 4f and 5f Trivalent Ions

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To get basic information on the complete actinide series radiochemical measurements are necessary. Since the structure of the aqueous trivalent ions is not known, we undertook a study of transport properties. These properties, like limit diffusion coefficient, are related to the size of the hydrated ion and therefore its variations along the 5f series should give informations on discontinuities in the size of the aquo ion and finally the number of water molecules surrounding the central ion.

Data have been obtained through a comparison of 4f and 5f elements with the open end capillary method.

Aqueous solutions were studied at 25.00 °C, pH 2.5, with LiCl or $Nd(ClO_4)_3$ as supporting electrolyte. For each investigated element, a linear variation of D *versus* $\sqrt{c}$ is observed in the LiCl concentration range 4×10^{-3} *M* < c < 5×10^{-2} *M*. After correction from the contribution of HCl, limit diffusion coefficients D^0 are obtained, for the studied lanthanides: Ce: 6.20, Gd: 5.74, Tb: 5.79, Tm: 5.80, Yb: 5.78×10^{-6} cm^2 s^{-1} and for trivalent actinides: Am: 6.25, Cm: 6.11, Cf: 5.87 and Es: 5.77×10^{-6} cm^2 s^{-1}.