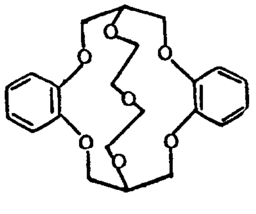
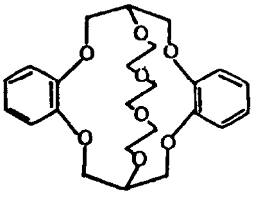
| Ln/Ligand | La | Nd | Sm | Gd |
|---|---|---|---|---|
| I | $LaCl_3 \cdot I \cdot 2H_2O$ | $NdCl_3 \cdot I \cdot H_2O$ | | $GdCl_3 \cdot I \cdot 2H_2O$ |
| II | $LaCl_3 \cdot II \cdot 2H_2O$ | | $SmCl_3 \cdot II \cdot H_2O$ | $GdCl_3 \cdot II \cdot H_2O$ |
| III | $LaCl_3 \cdot III \cdot 1.5H_2O$ | $NdCl_3 \cdot III \cdot 1.5H_2O$ | $SmCl_3 \cdot III \cdot ½H_2O$ | $GdCl_3 \cdot III \cdot H_2O$ |
| IV | $LaCl_3 \cdot IV \cdot H_2O$ | $NdCl_3 \cdot IV \cdot 0.3H_2O$ | | $GdCl_3 \cdot IV \cdot H_2O$ |



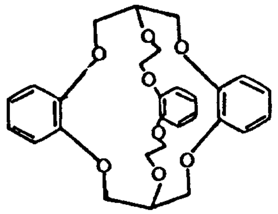
I

$C_{22}H_{26}O_7$



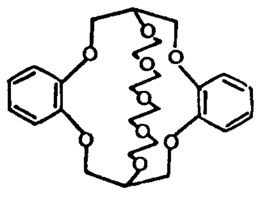
II

$C_{24}H_{30}O_8$



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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## A40

## Thermodynamics of Aquo 4f and 5f Trivalent Ions

F. DAVID*, B. FOUREST, J. DUPLESSIS

*Laboratoire de Radiochimie, Institut de Physique Nucléaire, B.P. No. 1, 91406 Orsay Cédex, France*

H. LATROUS

*Faculté des Sciences de Tunis, Tunisia*

J. OLIVER

*Transuranium Research Laboratory, Oak Ridge National Laboratory, Tenn., U.S.A.*

M. CHEMLA

*Laboratoire d'Electrochimie, Université Pierre et Marie Curie, 75230 Paris Cédex 05, France*

and J. M'HALLA

*Laboratoire d'Electrochimie, Faculté des Sciences de Monastir, Tunisia*

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 $4 \times 10^{-3}$ *M* < c < $5 \times 10^{-2}$ *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: $5.78 \times 10^{-6}$ $cm^2$ $s^{-1}$ and for trivalent actinides: Am: 6.25, Cm: 6.11, Cf: 5.87 and Es: $5.77 \times 10^{-6}$ $cm^2$ $s^{-1}$.

The S shaped change in the overall hydration of the cation across the considered series is correlated to the change in the primary hydration number N. Using the variation of N *versus* the crystallographic radius of the lanthanide and diffusion coefficient data for the actinides, we estimated N for each trivalent ion of the actinide series. A change of N from 9 to 8 should occur between Bk and Cf. Moreover, since entropy of trivalent lanthanide ions depends on their structure we obtained a new determination of the entropy of the $An^{3+}$ aqueous ions.

Finally we calculated hydration enthalpy of trivalent actinide ions with the same analytical expression we established for 37 monovalent, divalent, trivalent and tetravalent ions.

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### A41

## The Investigation of Mixed Actinide, Lanthanide and Pycrolonic Acid Complexes with Neutral Donor-Active Ligands

YU. KUVATOV, YU. I. MURINOV*, YU. E. NIKITIN, O. A. KOLYADINA and B. F. MYASOEDOV

*U.S.S.R. Acad. Sci. Inst. Chem., Bashkirian Branch, Ufa, U.S.S.R.*

The present paper reports the investigations on the complex formation of the actinide ions ($UO^{2+}$, $Tn^{4+}$, $Am^{3+}$) and lanthanide ions ($Ce^{3+}$, $Pr^{3+}$, $Nd^{3+}$, $Sm^{3+}$, $Eu^{3+}$, $Gd^{3+}$, $Tb^{3+}$, $Er^{3+}$, $Yb^{3+}$, $Lu^{3+}$) together with the picrolonic acid (1-nitrophenil-3-methyl-4-nitripyrazolone-5) and neutral donor-active ligands, *i.e.* tributylphosphate and the sulphoxides of oil origin or individual ones with different structures. The mixed complexes $UO_2A_2 \cdot S$, $UO_2A_2 \cdot 2S$, $AmA_3 \cdot 2S$, $ThA_4 \cdot S$, $LnA_3 \cdot S$, $LnA_3 \cdot 2S$, where A is a ligand anion and Ln a lanthanide ligand, have been found to form in the process of complexing. IR, PMR and electronic spectra have evidenced the formation of the above mentioned complexes. The constant values for the formation of the actinide and lanthanide complexes with pycrolonic acid have been determined. The stabilities of the complexes obtained of the following sequence $UO_2^{2+} < Ln^{3+} < Th^{4+}$ are of regular increasing character. IR investigations suggest the formation of a chelate structure of the central ion which acts as a complexing agent with the pycrolonic acid anion.

The constants of formating the mixed complexes $Ma_n \cdot mS$ of the sequence $UO_2^{2+} < Ln^{3+} < Th^{4+}$ increase as well. The organic diluent nature has been revealed to influence the mixed complex stabilities, the higher are the polarity and dielectric permeability of the hydrocarbon solvent the lower are the complex stabilities. The obtained data have been confirmed by the limited coefficients $\gamma^{\circ}$ of the hydrocarbons in the investigated complexes, those coefficients determined by GLC. The GLC analyses have revealed the parafin hydrocarbons to develop the positive non-ideal character in relation to the mixed actinides and lanthanides complexes. The dependence of the stabilities of the mixed complexes formed on the central ion effective charge which acts as a complex formating agent has been studied in the series $Ce^{3+}$–$Eu^{3+}$. The growth of the effective charge within this series should have led to increasing the acceptor properties of the chelate $MA_3$. In its turn it should have resulted in growing stability constants of the mixed complexes. Nevertheless, the things go quite the opposite way and it is probably due to the steric factors as well as to the mutual influence of the chelate and donor-active ligands in the coordination sphere of the metallic ion.

The influence of the basicity factor of the donor-active ligand upon the stabilities of the formed mixed complexes has been considered. Increasing basicities in the series diphenylsulfoxide < tributylphosphate < dihexylsulfoxide < oil sulfoxide < dicyclohexylsulfoxide < 2-amylthiophancyclohexylsulfoxide result in the stability regular growths of the complexes formed.

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### A42

## The Synthesis and Properties of Lanthanide Complexes with Different Neutral Ligands

YU. I. MURINOV*, V. I. DANILOV and YU. E. NIKITIN

*U.S.S.R. Acad. Sci. Inst. Chem., Bashkirian Branch, Ufa, U.S.S.R.*

The present paper reports the synthesis of new coordination complexes of lanthanide nitrates and chlorides with mono- and bidentate ligands. Dihexylsulfoxides (DHSO), tributylphosphate (TBP), aminosulfides, aminosulfoxides of various structures, and the sulfoxides of oil origin have been used as ligands.

The structures and some physical chemistry properties of chloride and nitrate lanthanide complexes with the sulfoxides of oil origin are presented. The complex compound structures have been shown to depend upon the process of producing and to correspond to the formula $LnA_3 \cdot mHCO \cdot NH_2O$, where LN–Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu, m = 3–5, n = 0–3.

All the IR spectra of the isolated compounds have shown a 10–60 $cm^{-1}$ band shift of sulfoxide group stretching vibrations towards the low frequency region as compared with that band position of a free sulfoxide. These data evidence the formation of electron donor–acceptor bonding