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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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 γ° 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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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 of the central ion through the sulfoxide oxygen. Conductivity and molecular mass measurements of the synthesized complexes verify that the acido ligand is included in the internal sphere of the complex.

Investigations of IR and electron absorption spectra of the nonhydrated nitrate and chloride lanthanide complexes with oil sulfoxides have shown the relative stability of electron donor–acceptor bonding in metal sulfoxide of the lanthanide series to grow with the increasing effective charge of a metal cation. The higher is the degree of hydration of the central ion the lower is the hydration value, which is dropping with increasing metal cation effective charge.

This paper presents the structures and some physical chemistry properties of the lanthanide chloride and nitrate complexes with different ligands, those complexes possessing internal and external spheres and being based upon dihexylsulfoxide and tributyl phosphate. In hydrocarbon solutions the internal sphere different ligand complexes have been found to undergo the process of disproportionation of the following type.

$$2[\mathrm{MeA_3\cdot DHSO\cdot 2TBP}] \rightleftarrows \mathrm{MeA_3\cdot 2DHSO\cdot TBP} + \mathrm{MeA_3\cdot 3TBP}$$

$$2[\mathrm{MeA_3\cdot 2DHSO\cdot TBP}] \rightleftarrows \mathrm{MeA_3\cdot 3DHSO} + \mathrm{MeA_3\cdot DHSO\cdot 2TBP}$$

Lanthanide nitrate complexes with aminosulfoxides and aminosulfides have been synthesized and investigated, the structures and some physical chemistry properties of the obtained complexes given. Complexing of the lanthanide nitrates with aminosulfides has revealed the central atom bonding with aminosulfide to proceed through a tertiary nitrogen. The complex formation of the lanthanide nitrates with aminosulfoxides has been supposed to form a chelate structure, for an aminosulfoxide molecule possesses two active groups – N–C and S=O. However, the obtained data have evidenced the coordination of the central atom in the complexes to proceed through the sulfoxide group oxygen only, and the tertiary nitrogen not to participate in the formation of the electron donor–acceptor bonding with metal ions. Further investigations of the pattern complexes of cobalt nitrates with aminosulfides and aminosulfoxides have shown that steric factors are, probably, the main barrier which prevents the tertiary nitrogen atom from the participation in the formation of electron donor–acceptor bonding with the central atom.

Dipole moments of the complexes synthesized have been measured and their thermal stabilities have been studied by the thermogravimetric technique. The thermal investigations have revealed the decomposition of the complexes not to depend on the metal nature, and the ligand nature to influence the thermal stabilities of the complexes. As a rule, complexes are more stable than ligands, for the decomposition temperatures of the former are 20–30 °C higher than those of the latter.

A43

Uranyl Mixed Compounds of the Dioxalate Series

R. N. SHCHELOKOV*, YU. N. MIKHAILOV, I. M. ORLOVA, A. V. SERGEEV, A. G. BEYRAHOV, A. S. KANISHCHEVA and G. M. LOBANOVA

Institute of General and Inorganic Chemistry of the Academy of Sciences of the U.S.S.R., Moscow, U.S.S.R.

By the X-ray diffraction method it has been established that the polyhedron of the aquo-dioxalateuranylate ion $[\mathrm{UO_2(C_2O_4)_2(OH_2)}]^{2-}$ is a pentagonal bipyramid in which two oxalate groups close five-membered cycles. The pentacoordination of the uranyl group is also preserved in the complexes $\mathrm{(CN_3H_6)_3[UO_2(C_2O_4)_2F]}$ and $\mathrm{K(CN_3H_6)_2[UO_2(C_2O_4)_2(NCS)]\,2H_2O}$.

The replacement of the aquo-group in the aquo-dioxalateuranylate ion by hydroxylaminate, N-methylhydroxylaminate and acetoxymate groups results in the formation of hexacoordinated compounds $\mathrm{(NH_4)_3[UO_2(C_2O_4)_2(NH_2O)]\,H_2O}$, $\mathrm{(NH_4)(CN_3H_6)_2[UO_2(C_2O_4)_2(CH_3NHO)]\,H_2O}$, $\mathrm{(CN_3H_6)_3[UO_2(C_2O_4)_2(CH_3)_2CNO]\,2H_2O}$.

It has been proved that in these compounds hydroxylamine, N-methylhydroxylamine and acetoxyme are coordinated by the uranyl ion through the nitrogen and oxygen atoms forming a three-membered metallocycle as a result.

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Mixed Ethylenediaminetetraacetic Compounds of Uranium(IV) and Thorium(IV)

R. N. SHCHELOKOV*, G. T. BOLOTOVA, A. V. SERGEEV, V. A. GILOV, YU. N. MIKHAILOV and G. M. LOBANOVA

N. S. Kurnakov's Institute of General and Inorganic Chemistry of the Academy of Sciences, Moscow, U.S.S.R.

Recently some uranyl mixed complexes, containing ethylenediaminetetraacetate (edta) and other anions have been synthesized and crystal structure