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.

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

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

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

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By the X-ray diffraction method it has been established that the polyhedron of the aquo-dioxalateuranylate ion $[UO_2(C_2O_4)_2(OH_2)]^{2-}$ 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 $(CN_3H_6)_3[UO_2(C_2O_4)_2F]$ and $K(CN_3H_6)_2[UO_2(C_2O_4)_2(NCS)]\,2H_2O$.

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

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.

A44

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

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