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.

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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 $[\mathrm{UO_2(C_2O_4)_2(OH_2)}]^{2-}$ 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 aquodioxalateuranylate 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)

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Recently some uranyl mixed complexes, containing ethylenediaminetetraacetate (edta) and other anions have been synthesized and crystal structure of the $(CH_3H_6)_4[(UO_2)_2edtaF_4]$ has been determined [1]. The edta group is shown to be a bridge hexadentate ligand with planar conformation of the $N{-}CN_2{-}CH_2{-}N$ fragment. As continuation of this work some other complexes of the U(IV) and Th(IV), namely $M_4[U(Th)edta(CO_3)_2]$; $M_4[Uedta(C_2O_4)_2]\cdot 3H_2O$; $M_3[U(Th)edta\cdot F_3]$; $M_2[UedtaCl_2\cdot 4H_2O]$; $U(Th)edta\cdot 6H_2O$ ($M = CN_3H_6^+$) were synthesized and their properties such as conductivity in water solutions, IR-spectra, thermostability were investigated.

The structure of the $(CN_3H_6)_3[UedtaF_3]$ and isomorphous $(CN_3H_6)_3[ThedtaF_3]$ was determined by X-ray analysis. The coordination polyhedron of these compounds was shown to be a distorted square antiprism with the cap over one base (C.N.9). The edta group is hexadentate and ethylenediamine fragment has gosh-conformation. The structure is constituted by the separate complex $[U(Th)edtaF_3]^{3-}$ anions and $(CH_3H_6)^+$ cations. The hydrogen bonds NH···O and NH···F are between anions and cations.

1 R. N. Shchelokov, I. M. Orlova, G. V. Podnebesnova, A. V. Sergeev and A. G. Beyrahov, *Abstracts of XXII ICCC*, Budapest, 1982, v. 1, p. 285.

A45

Reaction of UCl_4 with Triphenyl Phosphine in Aprotic Solvent: Formation and Structure of an Ionic Complex

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An unexpected compound has been obtained in reacting uranium tetrachloride and triphenyl phosphine in tetrahydrofuran. Infra-red spectra and single crystal structural determination identified the reaction product as $UCl_6(HP(C_6H_5)_3)_2(THF)_2$. The crystal belongs to Pa_3 high symmetry group with $a = 17.137(6)$ Å, $Z = 4$.

The hexachlorouranate(IV) is a nearly perfect octahedron and the P–H bond lies on the threefold axis. Similar complexes have already been synthesized in protic solvents [1–3]. The outcoming of the phosphonium hydrogen in our experimental conditions will be discussed.

1 P. Gans and B. C. Smith, *J. Chem. Soc.*, 4172 (1964).
2 B. W. Fitzsimmons, P. Gans, B. Hayton and B. C. Smith, *J. Inorg. Nucl. Chem., 28*, 915 (1966).
3 J. Selbin and J. D. Ortego, *J. Inorg. Nucl. Chem., 29*, 1449 (1967).

A46

Reactions of Uranium Metal with Alcohols

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S. H. Pitts, Jr. [1] has reported reactions of uranium metal in mixtures of alcohols/carbon tetrachloride. We report the reaction of the uranium metal with ethanol/carbon tetrachloride at room temperature. After evaporation of the solution, a compound formulated as $UCl_2(C_2H_5O)_2$ was obtained as confirmed by elemental analysis and i.r. spectroscopy. The ^1H n.m.r. spectra are also discussed.

Preliminary results were also obtained for the anodic dissolution of uranium metal in alcohols. Evidence for alkoxide U(IV) species is shown by U.V./visible and i.r. spectroscopy.

1 S. H. Pitts, Jr., *Canadian Patent, 963024* (1975).

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A47

Crystal Chemistry of the Lanthanide-Alkaline or Alkaline-Earth Perrhenates and Some Related Compounds with Ag, Pb and Actinides

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The lanthanide-alkaline and lanthanide-alkaline-earth perrhenates $LnM(ReO_4)_4$, $LnM'_3(ReO_4)_9$ and $LnM'(ReO_4)_5$ (M = Li, Na, K, Rb; M' = Ca, Sr, Ba) and some related compounds (M = Ag; M' = Pb) are disclosed by the study of some phase diagrams.

The synthesis of a large number of these compounds (most frequently carried out in solid state by heating $Ln(ReO_4)_3$ and $M(ReO_4)$ or $M'(ReO_4)_2$ together) shows that they crystallize preferently with a cubic structure (a ≅ 15 Å) and particularly with an hexagonal structure ($P6_3/m$, a ≅ 10 Å; c ≅ 6 Å). This last structure was determined by the X-ray diffraction study of a monocrystal of the isotypic compound $ThCd(MoO_4)_3$. It is somewhat related to the apatite structure. Other structures are possible but whatever the system is (cubic, orthorhombic, hexagonal), the different unit cells are connected by simple geometrical relations, so it is more than