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 likely that all these compounds have closely related structures.

A tetrahydrate $LnM(ReO_4)_4 \cdot 4H_2O$ (Ln ≅ Eu–Lu and M = Na, K, Rb, Ag) is disclosed for the $LnM(ReO_4)_4$ compounds. They are all isotypic and their structure (tetragonal $P\bar{4}n2$) is described for $GdNa(ReO_4)_4 \cdot 4H_2O$.

The lanthanide contraction is well observed for each series and in some cases the tetrad effect is also observed.

A large number of related compounds, for example simple perrhenates as $Ln(ReO_4)_3$ and $Am(ReO_4)_3$ or complex perrhenates as $Ln(MoO_4)(ReO_4)$ are structurally linked up with these series, so they are mentioned with their relationships by isomorphous substitution.

A48

Coordination Compounds of Lanthanides with Acetylhydrazine

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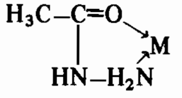
Coordination compounds $M(AH)_nX_3 \cdot mH_2O$, M = Pr, Nd, Eu, Gd, Dy, Ho, Er, Tm, Lu; X = Cl, NO_3, n = 3, 4, 5; X = NCS, n = 3; m = 0, 1, 3; $AH{=}CH_3CONHNH_2$ were isolated from water or ethanol solutions by reactions of lanthanide salts with acetylhydrazine. On the basis of IR and Raman spectra investigations of the normal and deuterated complexes it was shown that all these compounds contain chelate metal-hydrazide rings.



(M = Pr, Nd, Eu, Gd, Dy, Ho, Er, Tm, Lu).

The crystal structure of compounds $[Dy(AH)_3(H_2O)_3]Cl_3$ (I), $[Ho(AH)_3(H_2O)_3]Cl_3$ (II), $[Er(AH)_4(H_2O)](NO_3)_3$ (III), $[Pr(AH)_5](NO_3)_3$ (IV) were determined.

The coordination numbers were found 9 in I–III and 10 in IV. The polyhedron of metals has the configuration of threecapped trigonal prism in I and II, the configuration of monocapped square antiprism in III and configuration of twocapped square antiprism in IV.

The metal–ligand bond lengths (mid.) in complexes are: Ln–N: 2.571(1), 2.542 (III), 2.760 Å (IV); Ln–N(AH): 2.360 (I), 2.337 (III), 2.497 Å (IV); Ln–O(H_2O): 2.425 (I), 2.363 Å (III).

H-bonds type O–H···O(Cl) and N–H···O(Cl) in complexes observed.

A49

Complex Formation Between Trivalent Actinides and Pyrocatechol

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A continuous research work was done for the development of powerful chelating agents specific for trivalent and tetravalent actinide ions. In the recent years intensive investigations were carried out using some catecholate chelating ligands connected with the strong complexing power of the catecholate group [1–3]. The catecholate ligand is essential for the metabolism in biological systems especially some substituted catechol derivatives. They can be used as specific sequestering agents for removal of actinides from biological systems [4], which is important for environmental research and nuclear medicine as well.

It was found also that some substituted pyrocatechols act as effective extractants for both tracer and macroquantities of transplutonium elements as well as rare earths from strong alkaline solutions [5]. While most of the research was performed studying tetravalent actinides, little is known about the complexation between pyrocatechol and actinides in the trivalent state.

Thus, we have chosen to investigate the catecholate reactions with trivalent actinides by the means of the solvent extraction method.

We found out that hydrolysis and sorption of Am^{3+} prevail from pH higher than 6 and because pyrocatecholate ligand is not stable in the alkaline region the experiments have to be performed in argon atmosphere. The complex formation between americium and pyrocatechol is obviously stronger than both sorption and hydrolysis at pH higher than 9. There is also experimental evidence that the ligand itself is extracted by the TBP agent which further complicates the system.

The mechanism of complex formation and the stability of the complexes formed will be investigated