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

J. F. LE MARECHAL, P. CHARPIN*, D. VIGNER and H. BRZEZINSKY

L.A. 331 – Département de Physico-chimie, Centre d'Etude Nucléaire de Saclay, Gif/Yvette 91191, France

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

M. TERESA VILHENA*, ÂNGELA DOMINGOS AND A. PIRES DE MATOS

Chemistry Dept., LNETI, Estrada Nacional 10, Sacavém, Portugal

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).

---

*On leave from DCEAI, LNETI, Lisbon.

A47

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

JEAN-PAUL SILVESTRE

Laboratoire de Physico-Chimie des Composés d'Eléments de Transition. ER C.N.R.S. 09, Université Pierre et Marie Curie, 4, place Jussieu, Tour 54, 2ème Etage, 75230 Paris Cédex 05, France

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