

(P $\bar{1}$) with a lattice comparable to a pseudo-lamellar structure, intercalated water molecules occupying the interlayer spaces.

The substitution of Pd, Pt, Cu to Ni (with Ln = Eu) gives rise to isostructural compounds.

Change of solvent (Solvent = (CH₃)₂SO) does not modify the geometry of the neutral centrosymmetric heteropentanuclear entity, dmsol molecules substituting to water molecules. Compounds obtained with M' = Ni, Ln = Ce, Eu, Er crystallize in the triclinic system (P $\bar{1}$), with CN = 9, n = 5.

A32

Synthesis and Structure of Uranyl Complexes with Carboxylic Acids and Oxygen Containing Neutral Ligands

V. I. SPITSYN*, R. N. SHCHELOKOV, YU. N. MIKHAILOV, K. M. DUNAEVA, I. M. ORLOVA, V. E. MISTRJUKOV, A. V. SERGEEV, V. V. KOLESNIK and Z. R. ASHUROV

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

Complexes [UO₂Ac₂CH₃CON(CH₃)₂]₂, [UO₂·(C₆H₅COO)·2(CH₃)₂SO₂] and [UO₂Ac₂·1.5CO(NH₂)₂] were obtained by the interaction of the aquadiacidouranyl complexes with the neutral ligands.

Single crystal X-ray diffraction studies show that [UO₂Ac₂CH₃CON(CH₃)₂]₂ has dimeric structure and uranyl ion here is pentacoordinated. Crystal structure of the [UO₂(C₆H₅COO)₂·2(CH₃)₂SO]₂ is built of monomeric complexes where uranyl ion is hexacoordinated, and structure of the [UO₂Ac₂·1.5CO(NH₂)₂] is formed by the isolated complex [UO₂Ac₂·3CO(NH₂)₂]⁺ cations and [UO₂Ac₃]⁻ anions. Complex [UO₂Pr·1.5CO(NH₂)₂] is built in the same way, uranyl ions are penta- and hexacoordinated. The uranyl complex with dicarboxylic succinic acid and DMSO [UO₂COOCH₂CH₂COO·(CH₃)₂SO] is built of chains where each acidoligand is bound in a bidentate way to one pentacoordinated uranyl ion, forming 4-membered cycle, and in a monodentate way to two other pentacoordinated uranyl ions. The crystal structure of the NH₄[UO₂·Pr₃] is built of isolated complexes, each bidentate propionate ion forms a 4-membered cycle. The growth of the chains of monocarboxylic acids leads to predominance of the isolated forms of uranyl complexes.

A33

Equivalent Conductivities and First Hydrolysis Constant Determination of Aqueous Trivalent Lanthanide Ions by Conductance Data Fitting

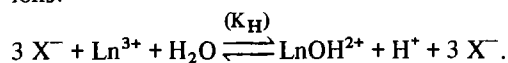
F. DAVID*, R. GUILLAUMONT

Laboratoire de Radiochimie, Institut de Physique Nucléaire, B.P. No. 1, 91406 Orsay Cédex, France

and J. M'HALLA

Laboratoire d'Electrochimie, Faculté des Sciences de Monastir, Tunisia

Conductance measurements by Spedding *et al.* [1] were obtained with halide solutions at pH \cong 6.4 without taking into account hydrolysis of M³⁺ ions:



Since the aqueous solution should contain several ions (and small quantities of carbonate) we developed [2] a generalized Robinson-Stokes equation which is applicable to mixture of ions. Therefore observed equivalent conductivities can be derived as:

$$\Lambda_{obs} = \Lambda_{obs}^o - \frac{\{2A'I + B'\Lambda_{obs}^o \sum_p (S^p)^2 (1 - \sqrt{q_p})\} \sqrt{I}}{1 + Ba\sqrt{I}} \quad (1)$$

with $\Lambda_{obs}^o = (\sum_i C_i |Z_i| \lambda_i^o) / 3C$; A' = A/3 C; A = 30.32; B' = 0.7852; I: ionic strength; C_i and Z_i: concentration and charge of 'i' ion; S^p and q_p are eigen vectors and eigen values of the Onsager–Kim matrix.

Taking into account hydrolysis, eqn. (1) is linearized and we fitted the experimental conductance data. The agreement between calculated and experimental data is 0.2%.

We deduce the first hydrolysis constant (log K_H \cong 7) and values of the hydrated radius for 13 lanthanides and we will consider the variations of these interesting parameters along the 4f series. Moreover the obtained limiting equivalent conductivities λ_o are 5% less than those which are generally tabulated.

1 F. H. Spedding, P. E. Porter and J. M. Wright, *J. Am. Chem. Soc.*, **74**, 2055 (1952).

2 J. M'Halla and F. David, to be published.