

likely that all these compounds have closely related structures.

A tetrahydrate $\text{LnM}(\text{ReO}_4)_4 \cdot 4\text{H}_2\text{O}$ ($\text{Ln} \cong \text{Eu-Lu}$ and $\text{M} = \text{Na, K, Rb, Ag}$) is disclosed for the $\text{LnM}(\text{ReO}_4)_4$ compounds. They are all isotypic and their structure (tetragonal $\overline{\text{P}4\text{n}2}$) is described for $\text{GdNa}(\text{ReO}_4)_4 \cdot 4\text{H}_2\text{O}$.

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 perhenates as $\text{Ln}(\text{ReO}_4)_3$ and $\text{Am}(\text{ReO}_4)_3$ or complex perhenates as $\text{Ln}(\text{MoO}_4)(\text{ReO}_4)$ are structurally linked up with these series, so they are mentioned with their relationships by isomorphous substitution.

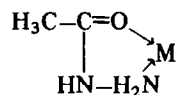
A48

Coordination Compounds of Lanthanides with Acetylhydrazine

V. S. PANGANI, R. I. MACHHOSHVILI, V. M. AGRE, V. K. TRUNOV and R. N. SHCHELOKOV*

N.S. Kurnakov Institute of General and Inorganic Chemistry, Academy of Sciences, All-Union Scientific Research Institute of Chemical Reagents and Ultra Pure Chemical Substances, Moscow, U.S.S.R.

Coordination compounds $\text{M}(\text{AH})_n\text{X}_3 \cdot m\text{H}_2\text{O}$, $\text{M} = \text{Pr, Nd, Eu, Gd, Dy, Ho, Er, Tm, Lu}$; $\text{X} = \text{Cl, NO}_3$, $n = 3, 4, 5$; $\text{X} = \text{NCS}$, $n = 3$; $m = 0, 1, 3$; $\text{AH} = \text{CH}_3\text{-CONHNH}_2$ 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.



($\text{M} = \text{Pr, Nd, Eu, Gd, Dy, Ho, Er, Tm, Lu}$).

The crystal structure of compounds $[\text{Dy}(\text{AH})_3(\text{H}_2\text{O})_3]\text{Cl}_3$ (I), $[\text{Ho}(\text{AH})_3(\text{H}_2\text{O})_3]\text{Cl}_3$ (II), $[\text{Er}(\text{AH})_4(\text{H}_2\text{O})](\text{NO}_3)_3$ (III), $[\text{Pr}(\text{AH})_5](\text{NO}_3)_3$ (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(I), 2.542 (III), 2.760 Å (IV); $\text{Ln-N}(\text{AH})$: 2.360 (I), 2.337 (III), 2.497 Å (IV); $\text{Ln-O}(\text{H}_2\text{O})$: 2.425 (I), 2.363 Å (III).

H-bonds type $\text{O-H}\cdots\text{O}(\text{Cl})$ and $\text{N-H}\cdots\text{O}(\text{Cl})$ in complexes observed.

A49

Complex Formation Between Trivalent Actinides and Pyrocatechol

A. S. STREZOV*

Bulgarian Academy of Sciences, Institute for Nuclear Research and Nuclear Energy, Sofia 1184, Bulgaria

and R. LUNDQVIST

Chalmers University of Technology, Department of Nuclear Chemistry, S-412 96 Gothenburg, Sweden

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

in detail to serve as a base for comparison with the complexation of some biologically active catechols.

This work is supported by the International Atomic Energy Agency and the Swedish Natural Science Council.

- 1 S. Sopen, S. Cooper and K. Raymond, *Inorg. Chem.*, **18**, 1611 (1979).
- 2 S. Sopen, K. Abu-Dari, D. Freyberg and K. Raymond, *J. Am. Chem. Soc.*, **100**, 7882 (1978).
- 3 A. Muscatello, J. Navratil and M. Killion, *Solvent Extr. and Ion Ex.*, **1**, 127 (1983).
- 4 K. Raymond, M. Kappal, V. Pecorato, W. Harris, C. Carrano, F. Weigl, P. Durbin, in N. M. Edelstein ed., 'Actinides in Perspective', *Proc. Actinides 1981 Conference, Pacific Grove Calif. Pergamon Press Oxford*, 1981 p. 491-507.
- 5 B. Myasoedov, Z. Karalova and L. Rodionova, *Proceedings International Solvent Extraction Conf. 1980, Liege, Belgium* vol. 3, sect. 14, paper 80.

A50

Stabilization of Novel Organouranium Compounds by the Bulky 1,3-Bis(trimethylsilyl)cyclopentadienyl Ligand

WILLIAM E. HUNTER* and JERRY L. ATWOOD

Department of Chemistry, University of Alabama, University, Ala. 35486, U.S.A.

The development and utilization of the 1,3-bis-(trimethylsilyl)cyclopentadienyl ligand (referred to as Cp^{''}) by Professor M. F. Lappert has resulted in the

preparation, isolation and X-ray characterization of several novel organolanthanide and -actinide compounds. This presentation will report the results of our X-ray structural studies of the following organouranium compounds: Cp₂UCl₂ (I), Cp₂U(BH₄)₂ (II), and Cp₂U(OAr)₂ (III) where OAr = 2,5-dimethylphenoxide.

Compound (I) crystallizes in the monoclinic space group C2/c with unit cell parameters $a = 27.037(9)$, $b = 7.084(3)$, $c = 22.327(9)$ Å, and $\beta = 131.83(4)^\circ$. Final agreement factors of $R = 0.020$ and $R_w = 0.026$ were obtained for 1701 observed reflections. The uranium atom resides on a crystallographic two-fold axis. The only unique U-Cl bond length is 2.579(2) Å. The average U-C distance is 2.72(1) Å.

Compound (II) crystallizes in the monoclinic space group C2/c with unit cell parameters $a = 27.731(9)$, $b = 7.138(4)$, $c = 22.561(9)$ Å, and $\beta = 132.45(5)^\circ$. The final R factor was 0.026 for 1199 observed reflections. (II) is isostructural with (I). The BH₄⁻ is coordinated to the uranium atom in a tridentate fashion. The U-H bond lengths are in the range of 2.37-2.42 Å.

Compound (III) crystallizes in the triclinic space group P1 with unit cell parameters $a = 10.236(5)$, $b = 10.830(6)$, $c = 19.767(7)$ Å, $\alpha = 90.25(4)$, $\beta = 92.20(4)$, and $\gamma = 103.09(6)^\circ$. The final agreement factor was 0.039 for 4518 observed reflections. The U-O bond distances are 2.12(6) and 2.109(6) Å.

A detailed discussion of the crystal and molecular structure of the above compounds will be presented and comparisons made with other organoactinide compounds already in the literature.