Papers

A12

Synthesis and Characterization of Actinide Phosphates

C. E. BAMBERGER*, G. M. BEGUN and R. G. HAIRE

Oak Ridge National Laboratory, Tenn., U.S.A.

The immobilization of actinides by incorporation into synthetic monazite is an attractive concept for the long term storage of actinides. This stems from the known stability, over geological age, of natural monazites (which contain uranium and thorium) toward radiation and sea water. In seeking methods for the preparation of metal phosphates from insoluble metal compounds by simple reactions, we have identified both BPO_4 and SiP_2O_7 as convenient reagents for such a task. A large variety of reactions, involving compounds of Th, U, Np, Pu, Am and all the lanthanides were studied. The results obtained, based mainly on Raman spectroscopy and X-ray powder diffraction, allowed for postulating reaction mechanisms and for optimizing conditions for the preparation of ortho-, pyro- and trimeta-phosphates and actinide oxide phosphates. Some of the ternary phosphates thus prepared were used to prepare other phosphates, *e.g.*, $Pu(PO_3)_3$ and sodium-containing quaternary phosphates, *e.g.*, $Na_3Pu(PO_4)_2$ and $Na_3Ln(PO_4)_2$ (where Ln is a lanthanide element). Raman spectroscopy proved to be a very sensitive technique for identifying most of the compounds and for establishing their purity.

A13

Studies of Covalent Bonding to f Transition Elements

A. ALAN PINKERTON

Institut de chimie minérale et analytique, Université de Lausanne, Place du Château 3, 1005 Lausanne, Switzerland

In an effort to understand the bonding in lanthanide (Ln) and actinide (An) compounds, we have carried out a multidisciplinary study of their complexes with sulphur donor ligands.

Metals studied to date: Y(III), a Ln and An analogue with no available f orbitals; Ln(III), diamagnetic and paramagnetic 4f ions (Ln = La–Lu); Th(IV) and UO_2^{2+}, diamagnetic 5f ions.

Choice of ligands: Dithiophosphinate ions, $R_2PS_2^-$, were chosen as the polarisable nature of the donor atoms should enhance any covalent contribution to the bonding and these ligands also contain convenient nmr probes.

X-ray diffraction: Metal–sulphur bonding has been established in all systems studied with coordination numbers of 6 and 8 (Ln), 8 (Th) and 5 (uranyl), and the coordination polyhedra analysed.

Nmr of diamagnetics: Nuclear spin-spin coupling between ^{89}Y and ^{31}P demonstrates the presence of a covalent interaction without f orbital participation. Important spin-spin coupling, $^4J_{PP}$, through the uranyl center in the complexes $UO_2(S_2PR_2)_2 \cdot L$ may be understood on the basis of metal-ligand π interactions.

Nmr of paramagnetics: For the eight coordinate lanthanides a change in solution structure from dodecahedral (DOD) to square antiprismatic (SAP) is shown to occur at holmium. Hyperfine coupling to ^{31}P has been measured and shown to be twice as great for DOD structures as for the SAP analogues. Its variation with the substituents at phosphorus may be understood on the basis of changes in hybridisation due to the electronic requirement of the substituents.

Theoretical calculations: Preliminary results obtained from MS X_α calculations demonstrate an appreciable electron transfer from the ligands to the metal in the model compound $[Ce(S_2PH_2)_4]^-$. The calculated electron populations resulting from this donation are $6s^{0.18}6p^{0.56}5d^{1.03}4f^{0.77}$.

A14

The Stability of Coordination Compounds of Some Crown Ethers with Lanthanide(III) Ions

ZHOU JINZHONG*, WU XI and WANG DEXI

Institute of Atomic Energy, Beijing, China

Monocyclic polyethers, the 'crown ethers', are noted for their affinity and high selectivity towards alkali and alkaline earth elements, and a large amount of work has been published concerning the coordination chemistry of crown ethers with these elements. However, information about the coordination behavior of crown ethers towards the lanthanides is relatively scarce and is badly needed because of its practical as well as theoretical significance.

TABLE I. Stability Constants, β, of Coordination Compounds of Crown Ethers with Na^+ and Ln^{3+} (Solvent: MeOH; Ionic Strength: 0.1 *M* Me_4NCl).

Crown Logβ Ion	18C6				DB18C6	DCH18C6
	15 ± 0.5 °C	26 ± 0.5 °C	35 ± 0.5 °C	Izatt [2]	26 ± 0.5 °C	26 ± 0.5 °C
Na^+	4.37 ± 0.05	4.17 ± 0.02	4.01 ± 0.05	4.33	4.18 ± 0.01	3.32 ± 0.01
La^{3+}	3.21 ±0.05	3.25 ±0.01	3.31 ±0.03	3.29 ± 0.03	no	2.49 ±0.03
Ce^{3+}	2.76 ±0.02	2.81 ±0.01	2.93 ±0.04	3.57 ± 0.20	no	2.05 ±0.05
Pr^{3+}	2.36 ±0.02	2.47 ±0.01	2.57 ±0.04	2.63 ± 0.28	no	1.62 ±0.07
Nd^{3+}	2.05 ±0.11	2.16 ±0.01	2.30 ±0.09	2.44 ± 0.16	no	<1.3
Sm^{3+}	–	<1.6	–	2.03 ± 0.07	no	no
Eu^{3+}	–	<1.5	–	1.84 ± 0.14	no	no
Gd^{3+}	–	<1.5	–	1.34 ± 0.12	no	no
Tb^{3+}	–	<1.2	–	no	<1.5	no
Dy^{3+}	–	<1.2	–	no	<1.7	no
Ho^{3+}	–	<1.5	–	no	<1.7	no
Er^{3+}	–	<1.4	–	no	<1.5	no
Tm^{3+}	–	<1.3	–	no	<1.6	no
Yb^{3+}	–	no	–	no	<1.4	no
Lu^{3+}	–	no	–	no	<1.4	no

TABLE II. Thermodynamic Functions for the Coordination of 18-C-6 with Na^+ and Ln^{3+} in Methanol at 25 °C.

Ion	ΔG° (kcal/mol)	ΔH° (kcal/mol)	TΔS° (kcal/mol)
Na^+	–5.72	–8.01	–2.3
La^{3+}	–4.47	2.30	6.7
Ce^{3+}	–3.89	3.84	7.7
Pr^{3+}	–3.38	4.45	7.8
Nd^{3+}	–2.96	6.14	9.1

A pNa method is developed for the determination of the stability constants of the coordination compounds of crown ethers and lanthanide ions, Ln^{3+}, based on the competition between Na^+ and Ln^{3+} ions towards coordination with a given crown. It consists of setting up a cell using Na^+ as the competing ion, Na^+-selective electrode as the indicating electrode and Ag–AgCl electrode as the reference electrode. The electromotive forces of such a cell (C = drown ether)

$$\text{Ag–AgCl}\,|\,0.1\ M\ \text{Me4NCl},\ xM\ \text{Na}^+,\ yM\ \text{C},\ zM\ \text{Ln}^{3+}\,|\quad \text{Na}^+\text{-electrode}$$

are measured successively under these conditions: (1) only Na^+, but neither crown nor Ln^{3+} is present; (2) crown ether is present but not Ln^{3+} ion is present; (3) both crown ether and Ln^{3+} are present. From the electromotive forces measured, concentrations of free ions and then stability constants can be calculated. Details of this method were published in a short note [1].

With this method, stability constants of coordination compounds of 18-crown-6 (18-C-6), dibenzo 18-crown-6 (DB 18-C-6), dicyclohexyl 18-crown-6 (DCH 18-C-6), 15-crown-5 (15-C-5) and benzo 15-crown-5 (B 15-C-5) with all Ln^{3+} ions except Pm^{3+} in methanol are determined. The results are given in Table I and agree quite well with those reported by Izatt *et al.* [2] except for Ce^{3+}. It can be seen that for the lighter lanthanides, the stability constants of the coordination compounds with 18-C-6 or DCH 18-C-6 decrease with increasing atomic number of the lanthanides, a fact which can be explained by the better matching of the crown ether cavity size with cation diameter. The 18-C-6 also shows weak coordination with the heavier lanthanides whereas the DB 18-C-6 shows weak coordination only with the heavier lanthanides and no coordination is indicated for 15-C-5 or B 15-C5 with any lanthanides.

The stability constants of Na^+, La^{3+}, Ce^{3+}, Pr^{3+} and Nd^{3+} are determined at three different temperatures for the determination of ΔH° calculated by plotting log β against 1/T, ΔG° is calculated from the relation $\Delta G^\circ = -RT\ln\beta$ and then ΔS° calculated from the relation $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$.

The results obtained are given in Table II. From the ΔH° and ΔS° values it can be seen that the observed stability is entropic in origin.

1 Zhou Jingzhong and Wang Dexi, *J. Nucl. Radiochem., Beijing, 4,* 174 (1982).
2 R. M. Izatt *et al., J. Am. Chem. Soc., 99,* 8344 (1977).

A15

Solution and Solid State Structures of Lanthanide Complexes with Polyaza Polyacetic Macrocyclic Ligands: A Comparison of NMR and X-Ray Studies

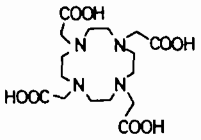
J. F. DESREUX*, M. F. LONCIN, M. R. SPIRLET

Laboratories of Analytical Chemistry and Radiochemistry and of Experimental Physics, University of Liège, Sart Tilman, B-4000, Liège, Belgium

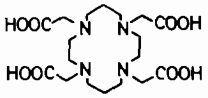
and J. REBIZANT

The European Institute for Transuranium Elements, Postfach 2266, D-7500 Karlsruhe, F.R.G.

Lanthanide complexes are known to form exceedingly labile species. Two rare exceptions to this rule are reported in the present paper.



DOTA



TETA

The ligand DOTA was found [1, 2] to form rigid lanthanide complexes in solution: the configuration of the ethylenediamine groups undergoes a very slow inversion as shown by NMR. Furthermore, the activation energy for this process is unusually large. An analysis of the solid state structure of Na$^+$(Eu-DOTA·H$_2$O)$^-$4H$_2$O has now been carried out, The metal ions lie between two planes made up respectively by the four nitrogens of the macrocycle and by the four carboxylate groups. The metal ion is also coordinated to one water molecule and its coordination polyhedron is a slightly distorted capped square antiprism. This structure exhibits an axial symmetry (C_4 axis) and the induced paramagnetic shifts can thus be reliably computed by the simple dipolar equation $\Delta\nu = 3\cos^2\theta - 1/r^3$. The calculated dipolar shifts of (YbDOTA)$^-$ are in excellent agreement with the experimental shifts, thus indicating that the DOTA complexes are highly symmetrical and have exactly the same structure in the solid and in solution.

The conformational properties of the paramagnetic lanthanide TETA complexes are no less surprising. Adding two $-CH_2-$ units to the DOTA structure brings about drastic changes in both the conformation and the structure of the macrocyclic complexes. As shown by a crystallographic investigation of Na$^+$(TbTETA)$^-$·5H$_2$O(NaCl)$_{1/2}$, the metal ion lies in a distorted dodecahedral environment of nitrogen atoms and carboxylate groups. This structure has an approximate C_2 axis and the induced paramagnetic shifts can no longer be calculated by the simpler form of the dipolar equation but have to be computed by the complete two-term dipolar equation. In this case, the calculated shifts are once again in excellent agreement with the experimental shifts. Moreover, the TETA complexes exhibit a quite unusual conformational behavior: the two orthogonal trapezoids in the dodecahedron are slowly moving up and down and are exchanging their position. This leads to profound alterations of the NMR spectra with temperature except for the two protons of the two propylenediamine carbon atoms in β positions. These protons lie on both sides of a near-plane of symmetry, the values of their dipolar geometric factors are not altered by the conformational changes and accordingly, their NMR peaks are not involved in exchange processes.

The DOTA and TETA complexes thus exhibit several intriguing features which have not been observed so far for other lanthanide complexes.

1 J. F. Desreux, *Inorg. Chem., 19,* 1319 (1980).
2 C. C. Bryden, C. N. Reilley and J. F. Desreux, *Anal. Chem., 54,* 610 (1982).

A16

Structure of the Pentahydrate of the Samarium(III) Perchlorate Complex with the Crown Polyether 1,4,7,10,13-Pentaoxacyclopentadecane, $[Sm(C_{10}H_{20}O_5)_2(H_2O)_4]^{3+}\cdot 3ClO_4^-\cdot H_2O$

T. J. LEE*, HRONG-ROANG SHEU, T. I. CHIU and C. T. CHANG

National Tsing Hua University, Hsinchu, Taiwan

The structure of samarium(III) perchlorate complex with the title ligand has been determined. This compound crystallizes in space group $P2_1/c$, a = 16.150(5), b = 14.898(5), c = 21.055(5) Å, β = 129.37(3)°, Z = 4, V = 3916.27 Å^3, D_c = 1.66, D_m = 1.62 g cm^{-3} (by floatation), μ = 18.30 cm^{-1} for MoKα radiation. The structure was mainly solved by heavy atom and Fourier method, and refined by full-matrix least squares techniques to a reliability index, R(F) of 0.061, based on 3540 reflections. The sama-