Papers

A12

Synthesis and Characterization of Actinide Phosphates

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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

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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

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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.