A "MASTER KEY" TO CHEMICAL SEPARATION PROCESSES

One of the keys to sorting nuclear waste is extracting minor actinides – the most "troublesome" long-lived elements – from the flow of waste by separating them from lanthanides, which have very similar chemical properties to actinides, for possible transmutation into shorter-lived elements. Thanks to a European initiative coordinated by CEA, this key is now available: its name is Sanex. There now remains to develop tough, straightforward industrial processes to integrate it into a new nuclear waste management approach by 2005. Sanex joins the Diamex process, used for the combined separation of lanthanides and minor actinides from fission products. A third process, Sésame, designed to separate americium, completes the list of available separation processes.

Glove box tests at the CEA/Valrhô-Marcoule Atalante facility, where new molecules are developed for the advanced separation of long-lived radionuclides by liquid–liquid extraction.

Thierry Foulon/CEA

Actinides and lanthanides: close neighbors

Separating **minor actinides**, neptunium (Np), americium (Am), and curium (Cm), from high-level **radioactive** waste generated by spent nuclear-**fuel reprocessing** or **recycling** operations involving the Purex process is at the heart of a major CEA research initiative. Although Np can be extracted in combination with uranium (U) and plutonium (Pu) using a modified version of the **Purex** process, new processes seem necessary to separate Am and Cm.

Let us consider the example of a fuel containing uranium oxide, **enriched** with 3.5% uranium-235, that has remained in an EDF nuclear reactor for three years, and was reprocessed three years after its removal from the reactor. The high-level liquid effluent remaining after the U and Pu extraction cycles contains a high concentration of nitric acid (3–4 mol/L(1)). For an initial metric ton of U, it contains some 28 kilograms (kg) of **fission products**, including 10 kg of **lanthanides** (Ln) and 0.35 kg of actinide (An) mixture composed of Am + Cm. The Ln/(Am + Cm) mass ratio in the waste is thus very high, in the area of 30. These two series of elements, Ln and An, are found in this effluent in their + III oxidation state, i.e. in an ionic form created after the removal of three electrons from the atom's electron cloud.

There are many similarities between the properties of Ln(III) and An(III) ions from the two series of homologous elements. They are strongly hydrated in aqueous solution and have similar ionic radii. They bind directly with a variable number of electron-donor atoms depending on the chemical system considered. The number of bonds that they can form, or the **coordination numbers** observed, vary from 6 to 12. In addition, according to the theory used to rationalize the reactivity of metal ions with **ligands** in aqueous solution, Ln(III) and An(III) ions are hard acids(2). They therefore tend to react with hard bases(2), such as ligands with electron-donor oxygen atoms. The interaction between these Ln(III) and An(III) ions, and these oxygenated ligands, is thus primarily electrostatic(3). As these metal ions all have the same charge + 3, the reactivities of the Ln(III) and An(III) ion series with this type of hard ligand are very close.

(1) Moles per liter. One mole of any substance contains 6.02×10^{23} (Avogadro's number) atoms or molecules.
(2) The term "hard" refers to partners, the **cation** (acid) and ligand (base) of a **complexation** reaction that do not change the size of their electron cloud when they are associated. In such cases, the bond between the cation and the donor atom of the ligand is essentially of an electrostatic type.
(3) Involving only Coulomb forces of attraction.
(4) A polydentate ligand is one that bonds with a metal ion via several donor atoms (the ligand "bites" the ion with several "teeth").

The distribution of electrons in the electron cloud of An(III) ions does, however, present a greater spatial extension than that observed in Ln(III) ions. It is hoped that this difference can be exploited to obtain a difference in reactivity by selecting ligands with electron-donor atoms that are not so hard as oxygen, and thus capable of separating these two families of ions. The metal-ion/ligand bonds formed could have a certain covalent nature, meaning that in this type of chemical bond, partial interpenetration occurs between the electron clouds of the metal ion and the donor atom of the ligand, which could help to promote reactions with An(III) ions.

In addition, separation techniques of the kind discussed here require very high performance levels, tolerating very little loss of Am and Cm in waste, and demanding an extremely high degree of purity in the separated Am and Cm.

Separating actinides by selective extraction

Considering the type of waste to be processed (aqueous effluent), the high-performance separation processes required, and the industrial maturity of the Purex hydrometallurgical process, it seemed only logical to develop **hydrometallurgical** processes for Am(III) and Cm(III) separation based on liquid–liquid extraction. The first separation stage, the **Diamex** process, is aimed at separating the mixture of An(III) and Ln(III) ions from the rest of the waste – 2/3 of the fission products – and most of the nitric acid. The second stage, the **Sanex** process, aims to separate the groups of An(III) and Ln(III) ions from each other. This is achieved through selective extraction of the An(III) ions, which are a minor ingredient of the mixture, and products that the operator wishes to recover. The mixture of An(III) + Ln(III) ions to be separated should preferably be in a nitric acid solution with a concentration of 0.1 to 1 mol/L, to avoid the possible formation of unwanted precipitates, which would hinder extraction operations.

What type of molecules should be developed?

In order to promote the affinity of extractant molecules for An(III) rather than Ln(III) ions, and avoid generating secondary solid waste from the use of new chemical reagents, the molecules defined are all ligands with several electron-donor nitrogen atoms (polydentate[(4)] N-donor). The greater the number of electron-donor nitrogen atoms in direct contact with the metal ion, the greater the difference between the reactivity of An(III) and Ln(III) ions is likely to be. The ligands studied at the CEA are either bi- or tridentate, almost planar, nitrogen-bearing molecules, or tripod molecules with nitrogen-bearing "arms" (table). These nitrogen-bearing molecules are generally used in a synergetic mixture with an acid extractant. Nonetheless, in the case of *bis*-triazinylpyridines (BTP), these extractants can be used on their own.

The research conducted in this field includes fundamental studies of the properties of these nitrogen-bearing molecules, as well as development studies concerning separation processes tested on high-level radioactive effluent in the shielded cells of the **Atalante** facility at CEA/Valrhô-Marcoule.

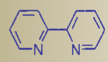
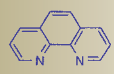
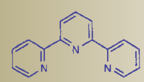
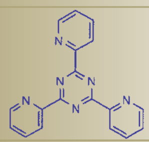
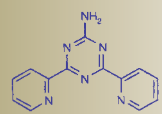
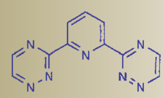
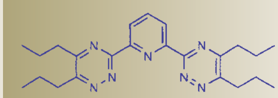
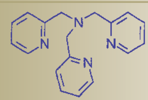
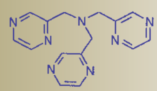
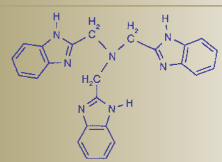
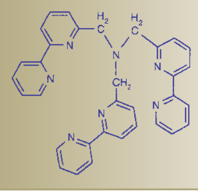
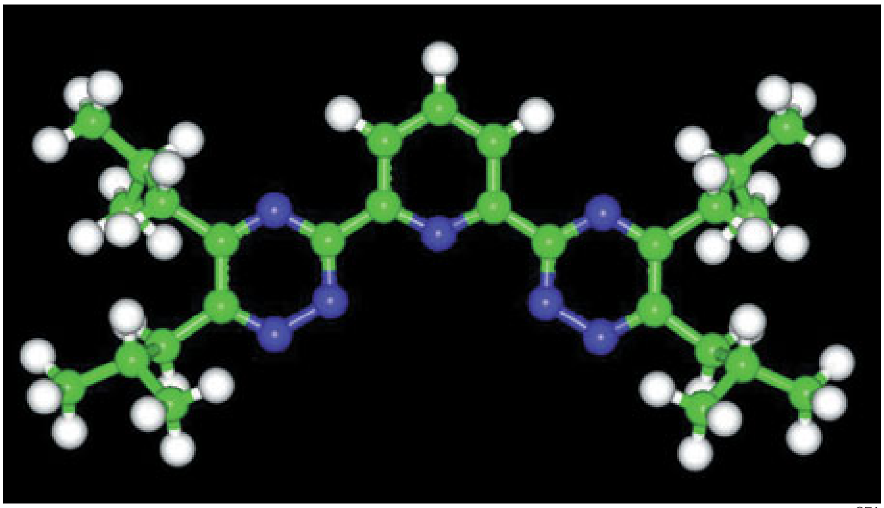
name and (acronym)	semi-developed formula	research laboratories
2,2'-bipyridine (Bipy)		DSM/SCM/Saclay
1,10-o-phenanthroline (o-phen)		DSM/SCM/Saclay
2,2':6',2"-terpyridine (tpy)		DEN/DRCP/SCPS/Marcoule and DSM/SCM/Saclay
2,4,6-tri-(pyridine-2-yl)-1,3,5-triazine (TPTZ)		DEN/DRCP/SCPS/Marcoule and DSM/SCM/Saclay
2-amino-4,6-di-(pyridin-2-yl)-1,3,5-triazine (ADPTZ)		DEN/DRCP/SCPS/Marcoule and DSM/SCM/Saclay
2,6-*bis*-(1,2,4-triazine-3-yle)-pyridine (BTP)		DEN/DRCP/SCPS/Marcoule and DSM/SCM/Saclay
2,6-*bis*-(5,6-di-*n-propyl*-1,2,4-triazine-3-yle)-pyridine (n-prop.BTP)		DEN/DRCP/SCPS/Marcoule and DSM/SCM/Saclay
tris-[(2-pyridyl)methyl] amine (tpa)		DSM/LRI/Grenoble
tris-[(2-pyrazinyl)methyl] amine (tpza)		DSM/LRI/Grenoble
nitrilotris-(benzimidazol-2-yl-methyl) (ntb)		DSM/LRI/Grenoble
tris-[(2:2'-bipyridin-6-yl) methyl]-amine (tbpa)		DSM/LRI/Grenoble

***Table.** Main polydentate, nitrogen-bearing molecules studied at the CEA Nuclear Energy Division (DEN) and Physical Sciences Division (DSM) as part of the work on An(III) and Ln(III) ion separation.*

The great affinity of actinides for nitrogen-bearing molecules

Fundamental studies into the behavior of nitrogen-bearing molecules with respect to Ln(III) and An(III) ions has involved determining the formula, stability, and structure of the **complexes** formed, both in aqueous solution and in various **solvent** media, using a wide range of experimental methods,

Iso-butyl-bis-triazinyl-pyridine (iBu-BTP) molecule studied as part of the development work on the Sanex process. The affinity of BTP molecules for actinides is more than a hundred times greater than for lanthanides, making them very promising extractants.



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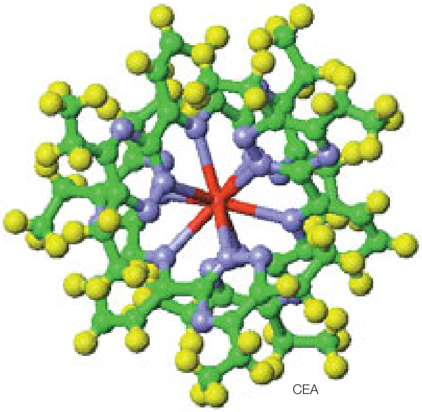


Crystalline structure of a complex formed between a lanthanide ion, gadolinium Gd, and an extractant molecule called 2,6-bis-(5,6-diethyl-1,2,4-triazin-3-yl)-pyridine.

including spectroscopy. This work has led to the discovery of why polydentate, nitrogen-bearing ligands have a greater affinity for An(III) than Ln(III) ions. It has been demonstrated that bonds between the nitrogen atoms of these ligands and Ln(III) and An(III) ions include some definite covalence, particularly visible in the fact that enthalpy is the driving force behind reactions. This results in heat being released during the reaction. The covalence observed in bonds with the electron-donor nitrogen atoms of ligands seems higher for An(III) ions than for Ln(III) ions, thus explaining the greater affinity of these ligands for An(III). Theoretical studies in the fields of quantum chemistry and molecular mechanics have provided greater insight into certain crucial aspects of reactions between these metal ions and nitrogen-bearing ligands (box). In particular, the synergetic extraction mechanism of Ln(III) ions using a mixture of nitrogen-bearing ligand and carboxylic acid has been identified by computer calculations. The calculated synergetic complex seems consistent with the experimental result.

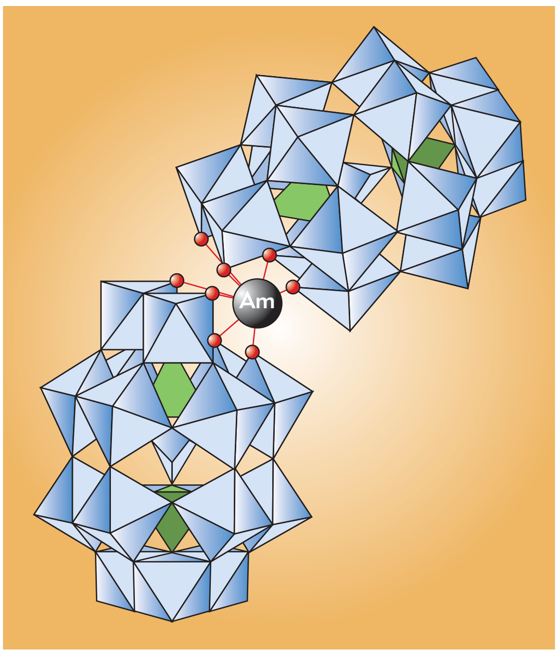


Figure. ***Complexation of the Am^{3+} metal ion by the $P_2W_{17}O_{61}^{10-}$ ligand. The structure is a lacunary heteropolyanion, composed of phosphates (green) and tungstates (blue), and has a vacant site at one of its ends which Am can fill (two ligands are required for one Am).***

Satisfactory test in favor of the Sanex process

BTP molecules have proved to be among the most suitable nitrogen-bearing extractants for developing an An(III) separation process. Their affinity for An(III) ions is more than a hundred times greater than for Ln(III) ions. In addition, An(III) ions can be separated using an An(III) + Ln(III) mixture in a nitric acid medium with a concentration of about 1 mol/L. Lastly, BTP molecules extract An(III) ions as nitrates, thereby dispensing with the need for an acid extractant to act as a synergetic agent. A process has been developed and successfully tested on a high-level radioactive effluent in the Atalante facility. On the basis of these highly promising results, CEA has placed the development of this system among its top priorities.

Once separated from the Ln(III) ions, the Am(III) + Cm(III) mixture can then be put through the **Sésame** process to separate these two elements. This process is based on extractive selection of Am by tri-*n*-butyl phosphate. The operation requires prior selective **oxidation** of Am in the form of AmO_2^{2+}. This is made possible by the electrolysis[5] of solutions containing the Am(III) + Cm(III) mixture and a specific ligand, a lacunary heteropolyanion (figure).

Working towards rugged, straightforward industrial processes

Significant advances were made in the CEA's development work on processes for separating Am(III) and Cm(III) from Ln(III) ions, when the BTP family was discovered in Karlsruhe (Germany) within the context of the European **Newpart** contract

The contribution of theoretical chemistry

Basic studies concerned with designing molecules for use in separating long-lived **radioelements** are still largely dependent on experimental approaches based on chemists' experience. Today, however, they are also backed up and improved by theoretical approaches[1]. These seek to rationalize research with two objectives: firstly, to provide more insight into the **complexation** or extraction mechanisms of extractant systems already known, then, in the longer term, to help develop new molecules or new extractant systems.

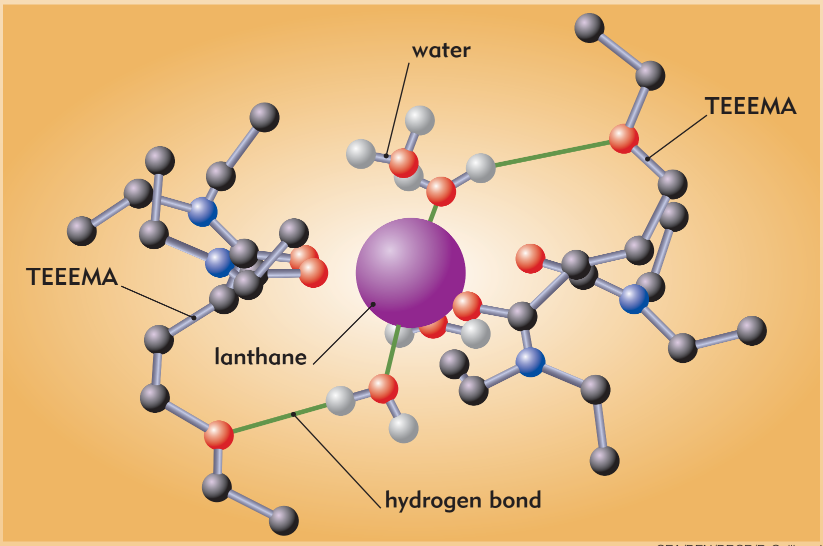
These objectives were used as a guide in setting up an approach in which one key stage entails defining the relations between the structure of the molecule (or molecular system) and extraction properties. The term molecule structure refers not only to the arrangement of atoms in space, but also to all the dependent calculated properties, such as the *electronic properties* (e.g. the atoms' charges) or the *orbital properties* (such as the type and energy level of the molecular orbitals, i.e. the spatial distribution of bonding electrons in the molecules).

The methods used to calculate these properties can be divided into two categories:

- **quantum-chemical methods**, which can be applied to small systems (typically containing several tens of atoms), are used to study the electronic structure of the molecular systems in question (isolated molecules) and the interactions between the species to be extracted and the extractant molecules (**cations-ligands**). They provide means to assess the length of chemical bonds and the angles between these bonds, and calculate the most likely conformations. Quantum-chemical methods also shed light on chemical reactivity by analyzing several possible reaction mechanisms. In addition, they play an important role in determining parameters used in molecular dynamics. These methods are divided into several categories depending on the theory used (*ab initio* or semi-empirical methods and density-functional methods). The first two methods are distinguished by the approximations used to solve the Schrödinger equation[2].
- **molecular-mechanics and -dynamics methods**, based on conventional mechanics, are used to study complex systems (containing several thousand atoms), such as a cation, one or more ligands surrounded by **solvent** molecules. Molecular mechanics calculates the structure and energy of molecular systems, whereas molecular dynamics simulates the movement of atoms using conventional mechanical momentum equations, and offers structural properties as well as thermodynamic variables, such as energy variations associated with complexation.

Quantum chemistry and molecular mechanics thus offer two perfectly complementary approaches. Quantum-chemical studies are, however, difficult to conduct on **actinides** because of the very nature of the elements concerned (high number of electrons) and the specific properties of experimental characterizations (**radioactive** medium) required to construct and validate models. Furthermore, despite ongoing progress in computer technologies, a great deal of fundamental work remains to be done.

(1) Refer to *Clefs CEA* No. 42 (autumn 1999), p. 14.
(2) This equation must be solved to determine the energy of the system, and a function, called the wave function, from which all the properties of the system can be deduced. It was proposed by Erwin Schrödinger in 1926.



CEA/DEN/DRCP/P. Guilbaud

Instantaneous view of a hydrated complex of the La^{3+} ion (shown in purple) with two TEEEMA molecules, a complex-forming agent from the malonamide family, during a molecular dynamics trajectory. Water plays a key part in the combined extraction of minor actinides and lanthanides (Diamex process) owing to the hydrogen bonds (in green).

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(1996–1999), coordinated by CEA. In addition, fundamental experimental or modeling studies have helped to specify the concepts on which these results are based, together with the new studies in progress at Marcoule. These are conducted jointly with teams from the CEA Physical Sciences Division in Grenoble and Saclay, and with the scientists of the **Practis** research group. Most of the studies at Marcoule are also part of the European **Partnew** contract (2000–2003), coordinated by CEA/Valrhô-Marcoule, involving eleven laboratories from six EU member states. In view of the inroads made, it now seems reasonable to predict that rugged, straightforward Sanex processes could be proposed in the relatively short term as part of the initiative to optimize nuclear waste management.

(5) Change in the oxidation state of a dissolved ion induced by electrodes allowing electrical current to circulate. In this example, the Am(III) ion loses electrons and is finally oxidized as Am(VI) (the AmO_2^{2+} ion).

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