

EFFECT OF MIXED PENDANT GROUPS ON THE SOLUTION PROPERTIES OF 12-MEMBERED AZAPYRIDINOMACROCYCLES : EVALUATION OF THE PROTONATION CONSTANTS AND THE STABILITY CONSTANTS OF THE EUROPIUM (III) COMPLEXES

Alain Favre-Reguillon<sup>[a,b]</sup>, Jean-Michel Siaugue<sup>[b]</sup>, Fabienne Segat Dioury<sup>[b]</sup>, Gabriel Plancque<sup>[c]</sup>, Jacques Foos<sup>[b]</sup>, Charles Madic<sup>[d]</sup>, Christophe Moulin<sup>[c]</sup> and Alain Guy<sup>[b]</sup>

<sup>[a]</sup> Laboratoire de Catalyse et Synthèse Organique, UMR 5622, Université Claude Bernard, Lyon 1 France

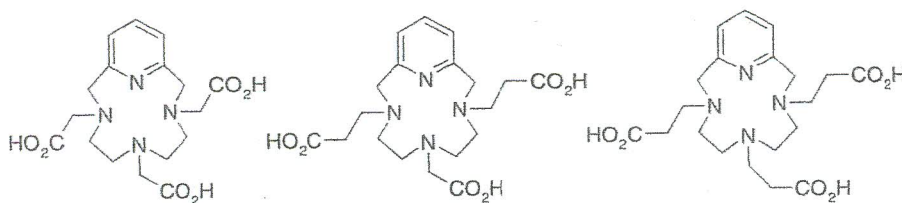
[alain.favre-reguillon@univ-lyon1.fr](mailto:alain.favre-reguillon@univ-lyon1.fr)

<sup>[b]</sup> Laboratoire de Chimie Organique et des Sciences Nucléaires, ESA 7084, CNAM, France

<sup>[c]</sup> Laboratoire d'Analyse, de Synthèse et de Spéciation Organométallique, CEA Saclay, France

<sup>[d]</sup> CEA, DEN, CEA Saclay, France

The protonation constants ( $\log K_i^{H^+}$ ) of new N-acetate or N-propionate substituted azamacrocycles derived from 12-membered azapyridinomacrocyclic were determined by potentiometric methods. The number of coordinated water molecules have been determined from the luminescence lifetime of the Eu(III) complexes indicating a tendency to decrease the degree of hydration upon increasing the ring size of the pendant arms. It has been shown that each ligand forms 1:1 complexes with Eu(III). The stability constants ( $\log K_{therm}$ ) of these complexes have been measured by time-resolved laser-induced europium luminescence. It appeared that the replacement of acetate pendant groups by propionate increases the overall basicity of the ligand but also decreases the stability constant of the Eu(III) complexes. The stability constants increase in the sequence  $\log K=21.1$  for  $[Eu-L^1] > \log K=13.7$  for  $[Eu-L^2] > \log K=10.7$  for  $[Eu-L^3]$ .



## PF-16

SPECTROSCOPIC INVESTIGATION OF URANIUM SUPERMOLECULES WITH OCTAACETATECALIX[8]ARENE AS LIGAND

9963 ✓

M.C.F.C. Felinto<sup>a</sup>, H.F. Brito<sup>b</sup>, D. F. Parra<sup>a</sup>, L.F.M. Maceta<sup>a</sup> and E.E. de S. Teotonio<sup>b</sup>

<sup>a</sup> Instituto de Pesquisas Energéticas e Nucleares, IPEN, Av Prof. Lineu Prestes 2242, Cidade Universitária, C.E.P. 05508-900 São Paulo, SP, Brazil. [mfelinto@net.ipen.br](mailto:mfelinto@net.ipen.br)

<sup>b</sup> Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo, C.P. 26077 São Paulo, SP, Brazil

The uranyl compounds ( $UO_2^{2+}$ ) present a great potential as luminescent materials, for instance, applied in technology laser, luminescent probes, cells for conversion of energy, etc. In this work it is reported synthesis, characterization and luminescent properties of the supermolecules of  $UO_2^{2+}$  and octaacetatecalix[8]arene. These compounds were characterized by complexation analyses for determining the  $U^{6+}$  concentration, infrared spectra, absorption in UV-VIS and luminescence spectroscopy. The results agree with the following composition  $UO_2(MS)_2 \cdot \text{octaacetate calix[8]arene}$  and  $UO_2(TFA)_2 \cdot \text{octaacetate calix[8]arene}$  (where MS is methane sulfonate and TFA is trifluoroacetate). The IR data show the coordination of counter ion and the inclusion into calixarene cavity. The luminescence spectra present the characteristic bands of the uranyl ion, attributed to the  ${}^3\Pi_u \rightarrow {}^1\Sigma_g^+$  transition. The emission spectrum of the supermolecule with MS recorded under excitation at 400 nm presents narrow bands different from that obtained with excitation at 255 nm that exhibits broaden bands. On the other hand, the emission spectra of the trifluoroacetate supermolecule system show identical profile under both excitation energies. Besides, it was observed a shifting of the bands in the emission spectra to shorter wavelengths for the precursor complexes as compared with those supermolecules system. The luminescence decay curves exhibit a mono-exponential behaviour presenting the lifetime for the  $UO_2(MS)_2 \cdot \text{octaacetatecalix[8]arene}$  ( $\tau = 413 \mu\text{s}$ ) higher than for the  $UO_2(TFA)_2 \cdot \text{octaacetatecalix[8]arene}$  ( $\tau = 168 \mu\text{s}$ ).