The structural analysis of the complex $Nd(pyO)_8(ClO_4)_3$ showed that the coordination polyhedron closely approximates to the square-antiprism (D_{4d}) while the complex $La(pyO)_8(ClO_4)_3$ has a geometry intermediate between a cube and a square-antiprism (D_4) [1]. The emission spectrum of the complex XIII agrees with that geometry found for the lanthanum complex; it closely approximates to the cube [2].

$BipyO_2$, $biquO_2$ and PA are chelating ligands which may give rise to octacoordinated species. The coordination polyhedron of the complex $La(bipyO_2)_4(ClO_4)_3$ has been found to be a cube [3]. The emission spectrum of the complex XIV well agrees with D_4 site symmetry [4]. Dodecahedron (D_{2d}) for complex IV and bicapped trigonal prism (C_{2v}) for complex VI, bicapped dodecahedron having D_2 symmetry for complex XV and C_{2v} symmetry for complex IX have been suggested by proper emission spectrum. In complex VIII the coordination polyhedron is made up of three oxygen and six nitrogen atoms. The emission spectrum suggests monocapped square-antiprismatic geometry and C_{4v} site symmetry for the europium(III) ion. On the basis of IR and conductivity data one must attribute twelve-coordination to europium(III) ion in complex VII. However, the emission spectrum agrees with bicapped dodecahedron and D_2 site symmetry. One nitrate group is thus ionic or two are monodentate.

Depending on the number of coordinated water molecules, the C.N. of europium in complexes X, XI, XII may be nine or greater. Monocapped square-antiprism (C_{4v}) and tricapped trigonal prism (D_{3h}) for nine-coordination and bicapped square-antiprism (D_{4d}) and bicapped dodecahedron (D_2 or C_{2v}) for ten-coordination are polyhedra encountered for lanthanide(III) complexes. The emission spectra of these complexes exclude C_{4v}, C_{2v}, D_{4d} symmetries. Tricapped trigonal prism and bicapped dodecahedron can be proposed as the polyhedra of these three complexes. This requires only one or no molecule of coordinated water. Square-antiprismatic geometry but lower than D_{4d} symmetries have been assigned on the basis of the emission spectra to the complexes I, II and III. X-ray study of the complex $Yb(HBPz_3)_3$ showed that the coordination polyhedron is a bicapped trigonal prism [5]. This requires that two molecules of ligand are tridentate whilst the third one is bidentate. The emission spectrum of the complex V is consistent with square-antiprismatic geometry having nearly perfect D_{4d} symmetry.

In general, no correlation exists between low symmetry and high intensity of the hypersensitive transitions or high symmetry and low intensity. This increases in the order: HBPz < 2-HAN < DMU < DEU < EU < PU < pyO < PA < $biquO_2$ < $bipyO_2$. In the same order increases the intensity ratio $^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$ in europium(III) complexes.

Abbreviations: PU = perhydropyrimidin-2-one; EU = imidazolin-2-one; DMU = N,N′-dimethylurea; DEU = N,N′-diethylurea; PA = picolinamide; pyO = pyridine-N-oxide; $bipyO_2$ = 2,2′-bipyridyl-N,N′-dioxide; $biquO_2$ = 2,2′-biquinolyl-N,N′-dioxide; 2-HAN = 2-quinolinecarboxylic acid; HBPz = hydrotrispyrazolylborate ion.

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B32

Crystal Structures and Mössbauer Studies of NpO_2^+ Complexes with Polycarboxylic Acids

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Complexes of neptunyl ($^{237}NpO_2^+$) with pyromellitic (benzene tetracarboxylic) and mellitic (benzene hexacarboxylic acids were prepared; their formula is: $(Na_3NpO_2C_{10}O_8H_2)_2\cdot 11H_2O$ and $Na_4(NpO_2)_2C_{12}O_{12}\cdot 8H_2O$ respectively. These solids were studied by X-ray diffraction, Mössbauer spectroscopy (^{237}Np) and magnetic susceptibility measurements.

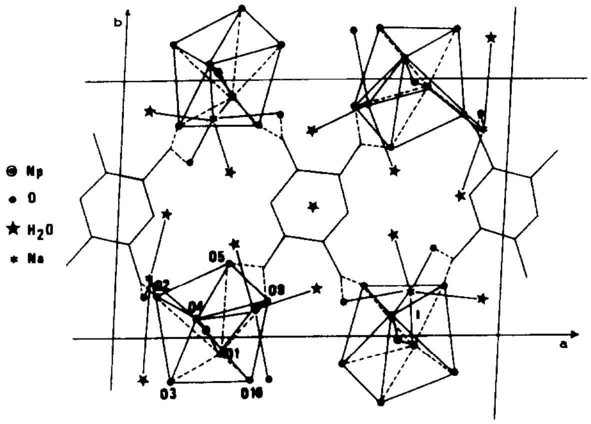

Fig. 1. Projection of the pyromellitate along the c axis.

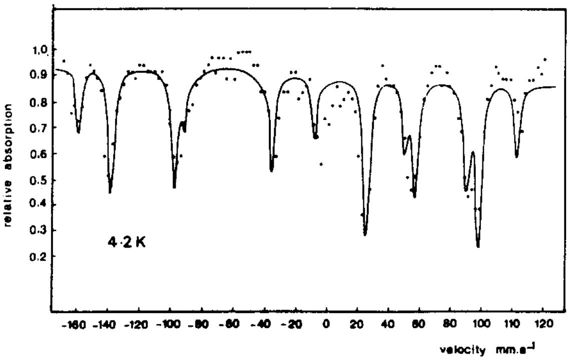

Fig. 2. Mössbauer spectrum (^{237}Np) of the mellitate.

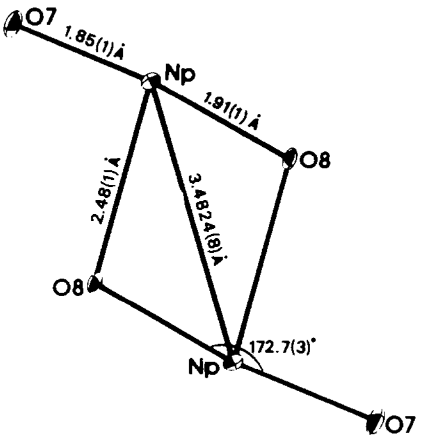

Fig. 3. Cation–cation complex of NhO_2^+.

The crystal structure of the Na_3NpO_2 pyromellitate was refined to R = 0,027 and R_w = 0.040 for 6793 independent reflexions. Crystal data are: $P\bar{1}$, a = 14.46(1) Å, b = 9.404(8) Å, c = 6.768(4) Å, α = 95.08°, β = 103.23°, γ = 87.47°, Z = 1. In this structure (Fig. 1), the NpO_2^+ ions are bonded to four pyromellitate anions whose carboxyl oxygens form the base of a pentagonal bipyramid surrounding the Np atom.

The Mössbauer spectrum recorded at 4.2 K and shown in Fig. 2, exhibited a magnetic hyperfine splitting attributed to paramagnetic relaxation phenomena [1, 2].

The crystal structure of the $Na_4(NpO_2)_2$ mellitate was solved by classical methods. R = 0.044 and R_w = 0.056 for 2372 independent reflexions. a = 12.53(1) Å, b = 11.58(2) Å, c = 17.81(2) Å, β = 105.79°, Z = 4, space group $C_{2/c}$. Two NpO_2^+ ions are connected to each other and coordinated to four mellitate anions. Figure 3 shows the 'cation–cation' complex of NpO_2^+. The χ curve for this complex follows the Curie–Weiss law. A magnetic transition occurs at about 10 K. The Mössbauer spectrum (^{237}Np) recorded at 4.2 K and then fitted [3] leads to the following hyperfine parameters: H_{eff} = 5490(10) kOe, e^2qQ = 97(2) mm s^{-1}. The isomer shift (δ = –19.2(5) mm s^{-1} ref. $NpAl_2$ [4]) corresponds to that of Np(V). Two Np atoms are at a distance shorter than 3.5 Å in this complex and this could explain the magnetic transition observed.

We wish to acknowledge the assistance of a NATO grant for collaboration research in making the cooperation between the Institut Curie and Florida State University (Prof. G. Choppin) possible.

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B33

Raman Spectroscopy of Neptunyl and Plutonyl in Aqueous Solutions: Hydrolysis of Np(VI) and Pu(VI) and Disproportionation of Pu(V)$^+$

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While the infrared and Raman spectra of the uranyl ion and its complexes have been the subject of considerable attention, there have been very few publications concerning the vibrational spectra of the plutonyl and neptunyl ions. For example Basile *et al.* [1, 2] have published values of the symmetrical stretching vibration, ν_1, of the PuO_2^{2+} and NpO_2^{2+} ions and of their carbonato complexes in 0.1 *M* Na_2CO_3 solutions. Madic *et al.* [3] published recently

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[+] Research sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under contracts W-7405-eng-26 with the Union Carbide Corporation and DE-AS05-76ER04447 with The University of Tennessee (Knoxville) and by the Centre d'Etudes Nucléaires, Fontenay-aux-Roses, France.

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