TABLE I.

	% mol			
	SiO_2	PbO	Na_2O	U
(1)	49.50	49.50	–	1.00 $UO_2(OAc)_2$
(2)	61.50	37.50	–	1.00 $UO_2(OAc)_2$
(3)	61.50	37.50	–	1.00 UO_3
(4)	61.50	37.50	–	1.00 Na_2UO_4
(5)	61.67	28.67	8.67	1.00 $UO_2(NO_3)_2$
(6)	61.67	24.67	12.67	1.00 $UO_2(NO_3)_2$
(7)	61.67	21.67	15.67	1.00 $UO_2(NO_3)_2$
(8)	61.67	19.67	17.67	1.00 $UO_2(OAc)_2$
(9)	59.50	–	39.50	1.00 $UO_2(OAc)_2$

TABLE II.

	ass. (cm^{-1})	fluor. (cm^{-1})
(1)	19850	–
(2)	19850	–
(3)	19850	–
(4)	19850	–
(5)	20195, 24100	18740
(6)	20012, 24190	18080, 18740, 19395
(7)	20200, 24230	18080, 18740, 19395
(8)	20350(sh), 24200	18080, 18740, 19395
(9)	20548, 21692(sh), 23873*	18080, 18740, 19395

*The spectrum has been measured at 4.2 K.

ferent temperatures. Their maxima are reported in Table II.

The analysis of the experimental data shows:

1) the absorption spectra of glasses with only PbO as network former are different from those containing also Na_2O, and only these show the presence of the UO_2^{2+} ion;

2) the intensity of the typical uranyl luminescence [2], using same thickness glasses, decreases with the increase of the PbO percentage and in the case of the lead silicate, the fluorescence completely disappears. Therefore, it is possible to deduce: a) the lack or a very low concentration of the UO_2^{2+} moiety in systems containing a high PbO percentage and b) the stabilization of the UO_2^{2+} ion in Na_2O rich systems, *i.e.* in strongly basic media (and this behaviour is very strange for Weyl [3] claimed the stabilization of U(VI) as UO_2^{2+} in acid glasses).

A possible explanation of the above observations could be given on the basis of structural considerations. In fact, in the case of silicate glasses, the structure (not completely defined, indeed) is made by SiO_4 tetrahedra linked in a three-dimensional network. In such a steric situation, it could be possible for the U(VI) ion to enter an interstitial site and form an UO_2^{2+} molecular ion. On the other hand, when we add PbO that enters as network former and network modifier, the system becomes much more distorted for the strong covalency of the Pb–O bond (obviously respect to the Na–O bond) with consequent formation of bidimensional chains or $(Si_2O_5)_n$ layers linked by Pb bridges [4]. This steric situation very probably is unfavourable to the formation of the UO_2^{2+} linear ion or to its presence in the interstices.

As concluding remarks, we can say that the development of this research in which we tried to understand the spectroscopic and structural behaviour of hexavalent uranium in some lead and sodium silicate glasses in which the ratio Na_2O/PbO is changed, will be the preparation and the study of the systems $xPbO/yNa_2O/zSiO_2/UO_2^{2+}/Ln^{3+}$ because, as well known, the energy migration from UO_2^{2+} to Ln^{3+} ions is very interesting and conceivably applicable to lasers.

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Emission Spectra of Europium(III) Complexes

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With the purpose to obtain reliable information on the microsymmetry around the central metal ion we have undertaken, lacking specific X-ray studies, the study of the following europium(III) complexes: $Eu(PU)_8X_3$ (I), $Eu(EU)_8X_3$ (II), $Eu(2\text{-}HAN)_8(ClO_4)_3$ (III), $Eu(biquO_2)_4(ClO_4)_3$ (IV), $Eu(HBPz_3)_3$ (V), $Eu(PA)_4(ClO_4)_3$ (VI), $Eu(PA)_3(NO_3)_3$ (VII), $Eu(PA)_3(NCS)_3$ (VIII), $Eu(biquO_2)_2(NO_3)_3$ (IX), $Eu(DMU)_3(NO_3)_3\cdot 2H_2O$ (X) $Eu(DEU)_3(NO_3)_3\cdot 2H_2O$ (XI), $Eu(PU)_3(NO_3)_3\cdot 3H_2O$ (XII), $Eu(pyO)_8X_3$ (XIII), $Eu(bipyO_2)_4(ClO_4)_3$ (XIV) and $Eu(bipyO_2)_2(NO_3)_3$ (XV) ($X = NO_3, ClO_4$).

Spectral and conductivity data suggested eight-coordination for the complexes I, II, III, IV, VI, XIV, nine-coordination for the complex VIII and ten-coordination for the complexes IX, XV, but doubt remained about the complexes VII, X, XI, XII, V.

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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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.

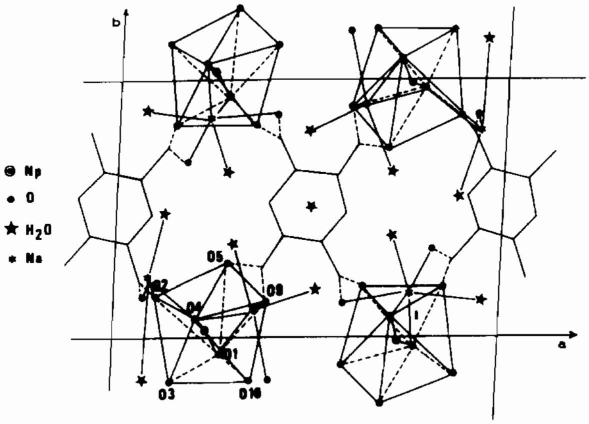

Fig. 1. Projection of the pyromellitate along the c axis.