TABLE IV. ^{13}C NMR[a] chemical shifts (δ/ppm) of free Pyridoxal hydrochloride and UO_2 acetate containing solutions in CD_3OD.

Compound	C-3	C-2	C-4	C-5	C-6	C-4′	C-5′	C-2′
Pyridoxal	151.13	145.13	141.01	140.28	126.20	105.92	71.14	14.74
Pyridoxal + UO_2acetate 1:1	148.50	142.70	140.15		122.49	107.00	71.07	15.49
Pyridoxal + UO_2acetate 1:2	148.53	142.83	140.18		122.41	107.10	71.13	15.53
Δ ppm =	−2.60	−2.30	−0.83	−0.10	−3.79	+1.18	−0.01	+0.79

[a] ^{13}C nmr chemical shifts are measured downfield from TMS used as an internal standard.

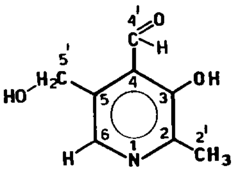

Fig. 1. Pyridoxal.

(VI)/pyridoxal system in aqueous and methanol solutions.

NMR spectra in aqueous solutions. Tables I and II show the ^1H and ^{13}C NMR chemical shifts of free pyridoxal and uranyl acetate/pyridoxal solutions at varying molar ratios. The presence of uranyl acetate in the aqueous solutions containing pyridoxal (PL) at pH 3.25 causes changes of the proton and carbon chemical shifts which may indicate the direct involvement of uranyl ion in the binding to the ligand. The major chemical shifts variations are observed for 2′-CH_3, C-4′-H and C-6-H protons (Table I) and C-2, C-3, C-6 and C-4 carbons (Table II). Since such carbons were found to be sensitive on the deprotonation process of the phenolic group C-3-OH [7] it is conceivable that uranyl ion binds the pyridoxal molecule *via* the C-3-O^- donor.

The ^1H as well as ^{13}C NMR spectra of the solutions at different UO_2^{2+}/PL molar ratios indicate that the major species formed at this pH is the equimolar complex.

The hemiacetal form, under which pyridoxal exists both in aqueous and methanol solutions, appears to be preserved in the complexed ligand molecule since no variation of the chemical shifts is observed for C-4′ and C-5 carbons upon metal binding.

NMR spectra in methanol solutions. Tables III and IV report the ^1H and ^{13}C chemical shifts for the free pyridoxal and its methanol solutions with uranyl acetate.

The chemical shifts variation of the C-6-H and 2′-CH_3 protons and C-2 and C-3 carbons upon metal ion binding to pyridoxal are quite similar to those found in aqueous solutions. This could indicate the same C-3-O^- binding of pyridoxal to UO_2^{2+} in methanol solution as well.

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Spectroscopic Behaviour of U(VI) Containing Glasses

M. BETTINELLI

Ist. Chim. Generale, Univ. of Padova, Padua, Italy

G. INGLETTO*

Ist. Biochimica, Univ. of Parma, Italy

A. MONTENERO

Ist. Strutturistica, Univ. of Parma, Italy

and F. FERMI

Ist. Fisica, Univ. of Parma, Italy

The aim of our research is to study materials that can have applications as lasers. For this reason, as preliminar work, we prepared in our laboratory some glasses whose composition is $xPbO/yNa_2O/zSiO_2$, doped with U(VI) salts (Table I), to understand the PbO influence on the formation of the UO_2^{2+} moiety, especially because the U(VI) coordination in silicate and in particular lead silicate glasses is not yet completely clarified [1]. Then we measured the absorption and emission spectra at dif-

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

A. SEMINARA* and A. MUSUMECI

Istituto Dipartimentale di Chimica e Chimica Industriale dell'Università, viale A. Doria 8, 95125 Catania, Italy

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.