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Complexes of Imidazole with Dioxouranium(VI) Nitrate and Acetate

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The imidazole group of L-histidine provokes considerable interest due to its biological role in mechanisms of enzymatic catalysis and in metal bonding to proteins and enzymes [1].

The mode of bonding between metal ions and imidazole may involve both the pyridine (N-3) and pyrrole (N-1) nitrogen atoms. The ambidentate nature of imidazole ring has been proved by Tovrog and Drago on the basis of NMR data [2].

In our laboratory studies on the interaction of dioxouranium(VI) with aminoacids, peptides and proteins have been undertaken in order to contribute to the mapping of binding sites in metal–protein interactions [3–7]. We report here, in addition to the few data already reported [8], ir, ^{1}H NMR and conductivity studies on the complex formation occurring when dioxouranium(VI) is reacted with imidazole.

Experimental

Synthesis of the Complexes

A solution of 1 mmol of $UO_2(NO_3)_2 6H_2O$ or $UO_2(CH_3COO)_2 2H_2O$ in ethyl acetate was added dropwise to a solution of 2 mmol imidazole in ethyl acetate under stirring and heating at 50 °C. Yellow crystalline products were obtained within few hours by cooling the solution. The compounds were filtered, washed and dried under vacuum. *Anal.* Found: C, 13.63; N, 15.82; H, 1.62; U, 44.57. Calcd. for $C_6H_8N_6O_8U$: C, 13.58; N, 15.84; H, 1.51; U, 44.90. Found: C, 14.37; N, 6.80; H, 2.02; U, 57.14. Calcd. for $C_5H_8N_2O_5U$: C, 14.49; N, 6.76; H, 1.93; U, 57.48%.

Infrared Spectra

IR spectra (4000–400 cm^{-1} region) of the solid compounds were taken as KBr pellets or as hexachlorobutadiene mulls using a Perkin-Elmer spectrophotometer model 621. Far IR spectra (400–150 cm^{-1} region) were recorded as Nujol mulls between polyethylene plates with a Beckman IR 11 instrument.

^{1}H NMR Measurements

The spectra were measured in CD_3OD at 28 °C using a Varian T60 spectrometer. Chemical shifts in δ/ppm were related to TMS as internal standard.

Conductivity Measurements

The measurements were carried out in ethanol at 23 °C by means of an Amel model 131 instrument. Λ_M values are expressed in ohm^{-1} cm^2 mol^{-1}.

Results and Discussion

The isolated compounds are crystalline powders of yellow colour. The elemental analysis is in agreement with the formation of $UO_2(C_3H_4N_2)_2(NO_3)_2$ (I) and $UO_2(C_3H_3N_2)(CH_3COO)H_2O$ (II) complexes when imidazole is reacted with uranyl nitrate and acetate respectively. Complex (I) is slightly soluble in most solvents while complex (II) exhibits a very low solubility.

Table I reports some IR characteristic frequencies of the free ligand and complexes in the solid state. The spectrum of the free ligand shows strong absorption bands at 3013, 1540 and 620 cm^{-1}, assigned to the stretching, bending and torsion modes respectively of the N–H bond [9]. These frequencies are shifted to 2980, 1548 and 623 cm^{-1} in the complex I. The lowering of the N–H stretching frequency in the complex can be associated with resonance contribution and intermolecular hydrogen bonding [10]. The absence of the strong peak at 1380 cm^{-1}, typical of an ionic nitrato group, observed when the spectrum is recorded as hexachlorobutadiene mull, and the presence of absorption bands at 1490, 1290 and 1034 cm^{-1}, characteristic of coordinated nitrato groups [11], are consistent with the coordination of nitrato groups to dioxouranium(VI). Furthermore, the infrared combination frequencies at 1782, 1758, 1742 and 1730 cm^{-1} support the hypothesis of nitrato groups acting both as bidentate and monodentate ligands to the uranyl group, in agreement with the results of Lever *et al.* [12]. These data are corroborated by the peaks near 250 cm^{-1} where δ(O–U–O) of nitrato complexes is known to occur [13, 14].

In the spectrum of the complex II no N–H bands of the imidazole ring are detectable, and peaks are present at 1536, 1476, 1430, 677 and 612 cm^{-1} which have been assigned by Jones [15] to the asymmetric and symmetric stretching, deformation and torsion modes respectively of acetato groups coordinated to dioxouranium(VI). These frequencies are coincident with those found for $NaUO_2(CH_3COO)_3$ where the acetato groups are coordinated as bidentate to uranium(VI) [16]. The intensity of the peaks due to $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ and the

TABLE I. Some Significant IR Frequencies (cm^{-1}) of the Dioxouranium(VI) Complexes of Imidazole.

Vibration Modes	$C_3H_4N_2$	$UO_2(C_3H_4N_2)_2(NO_3)_2$	$UO_2(C_3H_3N_2)(CH_3COO)H_2O$
ν(N–H)	3013	2980	–
Nitrate		1782	
Combination		1758	
Frequencies		1742	
		1730	
ν(C=N)	1664	1632	1625
δ(N–H)	1540	1548	–
$\nu_{as}(COO^-)$			1536
$\nu_s(COO^-)$			1476
			1430
$\nu_{as}(NO_2)$		1490	
$\nu_s(NO_2)$		1290	
ν(N–O)		1034	
ν_{as}(O–U–O)		900	910
$\delta(COO^-)$			677
γ(N–H)	620	623	–
$\gamma(COO^-)$			612
δ(O–U–O)		277	276
		263	262
		253	
		246	

TABLE II. ^{1}H NMR Spectra of the Imidazole Complexes in CD_3OD at 28 °C. Chemical shifts are given as δ/ppm from TMS as internal standard.

Compound	–CH	–CH –CH	$-CH_3$
$C_3H_4N_2$	7.71, 1H	7.10, 2H	
$UO_2(C_3H_4N_2)(NO_3)_2$	8.50 1H	7.42, 2H	
$UO_2(C_3H_3N_2)(CH_3COO)H_2O$	7.98, 1H	7.27, 2H	2.55, 3H

separation value between them are consistent with the coordination of the acetato group as bidentate ligand [17] better than bridging adjacent uranium atoms [18].

The asymmetric stretching (ν_3) of the O–U–O group in the complexes occurs as intense band near 900 cm^{-1} and the broad peak centered at 262 cm^{-1} with a shoulder at 276 cm^{-1} is attributed to the doubly-degenerated UO_2^{2+} deformation (ν_2), in agreement with the results of the literature [19–21].

Table II reports the chemical shifts of the C–H resonances of imidazole and complexes. The ^{1}H NMR spectrum of the free ligand exhibits two singlets at 7.71 and 7.10 ppm, 1 and 2 in intensity, assigned to the ring protons in position 2 and 4,5 respectively. The signals are broad and show a significant downfield displacement in the complexes. In the spectrum of the complex II a singlet of intensity 3 occurs at 2.55 ppm, due to the acetato $-CH_3$ protons. The resonance value is indicative of an acetato group coordinated to uranium(VI) since an ionic acetato group resonates at higher field values (*ca.* 2 ppm).

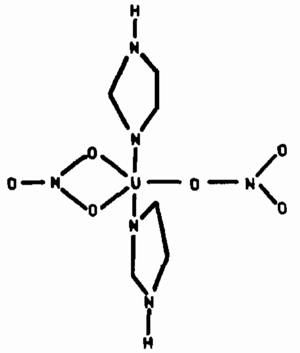
Table III shows the conductivity values Λ_M found for the complexes. The relatively high value observed for complex I indicates a certain tendency of such a complex to ionize in ethanol. In fact, a Λ_M value of 50, near to that measured, is exhibited by an equimolar ethanolic solution of uranyl nitrate, in which both nitrato groups act as bidentate to the uranyl group [22]. On the other hand, the low Λ_M value shown by complex I is consistent with

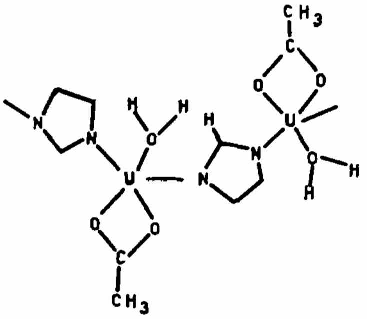
TABLE III. Conductivity Values of the Complexes in Ethanol (C = 10^{-4} *M*, T = 23 °C).

Compound	Λ_M(Ohm^{-1} cm^2 mol^{-1})
$UO_2(C_3H_4N_2)_2(NO_3)_2$	60.0
$UO_2(C_3H_3N_2)(CH_3COO)H_2O$	3.4

the non-ionic nature of this compound also in solution.

In conclusion, the present ir, pmr and conductivity data support the coordination of the imidazole ring to dioxouranium(VI) and are in agreement with the formulation of the structure of the complexes proposed in scheme *a* and *b*:





In complex I the bonding takes place at the pyridine nitrogen (N-3) (scheme *a*) and in complex II at both nitrogen atoms, N-1 and N-3 (scheme *b*). The latter coordination changes the monodentate imidazole molecule into the bidentate imidazolate anion with two nitrogen atoms indistinguishable, thus promoting the formation of a polymeric structure as found for imidazole complexes of Co(II) and Zn(II) [23]. Such a view is also in agreement with the formula and the very low solubility and conductivity values.

Finally, in the complexes the favourite pentacoordination of the uranyl ion in the equatorial plane is completed by nitrato groups or an acetato group and a molecule of water.

References

1 R. J. Sundberg and R. B. Martin, *Chem. Rev., 74,* 471 (1974).
2 B. S. Tovrog and R. Drago, *J. Am. Chem. Soc., 99,* 2203 (1977).
3 A. Marzotto and O. Traverso, *Ann. Univer. Ferrara, 3,* 197 (1974).
4 A. Marzotto, *J. Cryst. Mol. Struct., 6,* 259 (1976).
5 A. Marzotto, *Chem. Biol. Interact., 14,* 383 (1976).
6 A. Marzotto, *J. Inorg. Nucl. Chem., 39,* 2193 (1977).
7 A. Marzotto and F. Braga, *Xe Conv. Naz. Chim. Inorg., Bressanone* (1977); and *J. Inorg. Biochem.,* in press.
8 A. Marzotto, *XI Congr. Naz. Chim. Inorg., 20A, Arcavacata di Rende* (1978).
9 M. Cordes De N.D. and J. L. Walter, *Spectrochim. Acta, 24A,* 237 (1968).
10 T. J. Lane C.S.C., I. Nakagawa, J. L. Walter C.S.C., and A. J. Kandathil, *Inorg. Chem., 1,* 267 (1962).
11 B. M. Gatehouse, S. E. Livingstone and R. S. Nyholm, *J. Chem. Soc.,* 4222 (1957).
12 A. B. P. Lever, E. Mantovani and B. S. Ramaswamy, *Can. J. Chem., 49,* 1957 (1971).
13 F. A. Hart and J. E. Newbery, *J. Inorg. Nucl. Chem., 30,* 318 (1968).
14 J. I. Bullock and F. W. Parrett, *Can. J. Chem., 48,* 3095 (1970).
15 L. H. Jones, *J. Chem. Phys., 23,* 11 (1955).
16 W. H. Zachariasen and H. A. Pdettinger, *Acta Cryst., 12,* 526 (1959).
17 K. Nakamoto, Y. Morimoto and A. Martell, *J. Am. Chem. Soc., 83,* 4528 (1961).
18 G. Bor, L. Magon, L. Maresca and G. Natile, *J. Chem. Soc. Dalton,* 1308 (1973).
19 J. E. Newbery, *Spectrochim. Acta, 25A,* 1699 (1969).
20 A. Marzotto, *J. Inorg. Nucl. Chem., 35,* 3403 (1973).
21 A. Marzotto, *Inorg. Nucl. Chem. Letters, 10,* 915 (1974).
22 J. C. Taylor and M. H. Mueller, *Acta Cryst., 19,* 536 (1965).
23 M. Goodgame and F. A. Cotton, *J. Am. Chem. Soc., 84,* 1543 (1962).