

# STEREOCHEMISTRY OF SOME HIGH COORDINATION COMPOUNDS OF DIOXOURANIUM(VI) WITH THIOSEMICARBAZONES

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## كيمياء فراغية لبعض المركبات التناسقية العالية لليورانسيوم السداسي مع الثيوسيميكرbazون

رام أجراول - هيمنش أجراول - اندرانيل اشكرابورتى

لأيون اليورانسيوم السداسي سلوك شاذ حيث يكون له رقم تناسقي عالي في مركباته. تم تحضير عدد من المتراكبات التناسقية من الادي اكسو يورانسيوم السداسي مع مشتقات الثيوسمي كر بازون مع الأنتي بيرين حيث يدخل في تركيب المتراكبات أيضاً أيونات البروميد واليوديد والثيوسيانات والخلات أو النترات. ولقد حضرت المتراكبات في المذيبات غير المائية وتم التعرف عليها بالطرق الفيزيوكيميائية المختلفة، وكان ارتباط المرتبطات ثلاثي المخلب عن طريق نتروجين - نتروجين - كبريت. وقد استخدمت مصفوفة ولسن لتعيين ثابت القوة والتردد لطول الرابطة بين اليورانسيوم - أكسجين وتم أيضاً دراسة الثبات الحراري لتلك المتراكبات.

Key Words: Coordination compounds, Dioxouranium, Stereochemistry, Thiosemicarbazone

### ABSTRACT

The  $UO_2^{2+}$  ion is peculiar in its coordination behaviour, because of its inherent capacity of forming compounds with higher coordination number. In the present work we describe the synthesis of a series of eight, nine and ten coordinated compounds of dioxouranium(VI) with 4[N-(2'-nitrobenzalidene)- amino] antipyrinethiosemicarbazone (2'-NO<sub>2</sub>BAAPT) and 4[N-(3'-nitrobenzalidene) amino] antipyrinethiosemicarbazone (3'-NO<sub>2</sub>BAAPT) with the general composition  $UO_2X_2.nL$  (X = Br, I, NCS or ClO<sub>4</sub>, n=2; X = NO<sub>3</sub> or CH<sub>3</sub>COO, n = 1; L = 2'-NO<sub>2</sub>BAAPT or 3'-NO<sub>2</sub>BAAPT). These compounds were synthesized in non-aqueous solvents, and were characterized by various physico-chemical techniques. The ligands behave as tridentate N<sub>2</sub>S-donors. Wilson's G-F matrix method was used to determine the stretching and interaction force constants from which the U-O bond distances were calculated. Thermal stabilities of these complexes were also investigated.

### INTRODUCTION

Actinide ions generally present very high coordination numbers and the type of polyhedron obtainable is influenced by the nature of the ligands. Many good reviews on the coordination chemistry of the actinides have appeared in literature[1]. But there is a lack of information on the polyhedra obtainable with polydentate ligands. Thus in the present paper, some eight, nine and ten-coordinated compounds of  $UO_2^{2+}$  with 4[N(2'-nitrobenzalidene) amino]

antipyrinethiosemicarbazone (2'-NO<sub>2</sub>BAAPT) (I) and 4[N(3'-nitrobenzalidene) amino] antipyrinethio-semicarbazone (3'-NO<sub>2</sub>BAAPT) (II) are reported.

### EXPERIMENTAL

#### Reagent

Dioxouranium(VI) nitrate was used as received from B. D. H. and was dehydrated by keeping it over conc. H<sub>2</sub>SO<sub>4</sub>[2]. UO<sub>2</sub>Br<sub>2</sub> was prepared from UO<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub> by treating it

with hydrobromic acid. After evaporating most of the solvent, the solution was kept over conc.  $\text{H}_2\text{SO}_4$  till yellow crystals separated out[3] and dioxouranium(VI) iodide was obtained by treating dioxouranium(VI) nitrate with barium iodide in dry ether[4]. Dioxouranium(VI) thiocyanate was prepared by mixing an alcoholic solution of anhydrous dioxouranium(VI) nitrate and potassium thiocyanate[5].  $\text{UO}_2(\text{ClO}_4)_2$  was prepared by digesting  $\text{UO}_2(\text{NO}_3)_2$  with the calculated amount of perchloric acid and evaporating the mixture to dryness. Dioxouranium(VI) perchlorate formed was crystallized until free from nitrate ions[6].

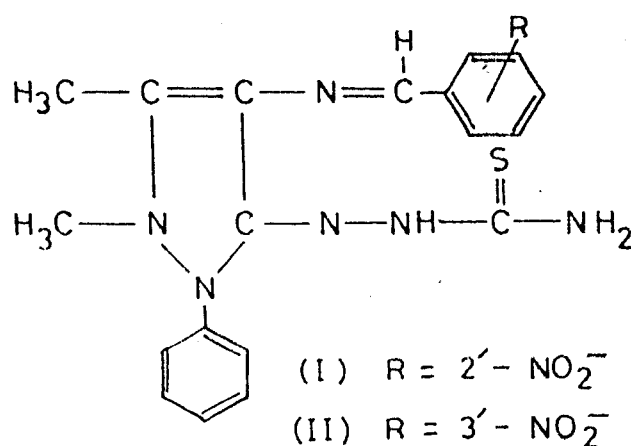
The ligands were synthesized[7] in two steps. In the first step, a solution of the aromatic aldehyde (1 mmol) in absolute ethanol was mixed with 4-aminoantipyrine (1.1 mmol) in the same solvent and the mixture was refluxed for ~ 3 hrs. On cooling, a yellow crystalline product was separated, which was filtered and recrystallized in the same solvent. In the

second step, the corresponding Schiff base as obtained in the first step, was dissolved in hot ethanol and refluxed with an equimolar ratio of thiosemicarbazide for ~ 3 hrs. On cooling the coloured crystalline thiosemicarbazone is obtained.

### Synthesis of the Complexes

All the complexes were isolated by the following general method. An ethanolic solution of metal salt was added to a hot ethanolic solution of the ligand in the required molar ratio. The reaction mixture was refluxed on a steam bath for 2-3 hrs and left for overnight. Coloured solids separated were filtered, washed successively with ethanol and ether and dried in air (yield ~ 75--82%).

The chemical analyses and physico-chemical measurements were done as reported earlier [8,9].



### RESULTS AND DISCUSSION

The reaction of  $\text{UO}_2^{2+}$  salts in ethanol with 4[N-(2'-nitrobenzalidene) amino] antipyrinethio-semicarbazone (2'- $\text{NO}_2$ BAAPT) and 4[N-(3'-nitrobenzalidene) amino] antipyrinethiosemicarbazone (3'- $\text{NO}_2$ BAAPT) resulted in the formation of the complexes of the general composition  $\text{UO}_2(\text{L})_n\text{X}_2$  ( $n=2$ ,  $\text{X} = \text{Br}, \text{I}, \text{NO}_3, \text{NCS}, \text{CH}_3\text{COO}$ ;  $n=3$ ,  $\text{X} = \text{ClO}_4$ ,  $\text{L} = 2' - \text{NO}_2\text{BAAPT}$  or  $3' - \text{NO}_2\text{BAAPT}$ ). The analytical data of these complexes are presented in Table 1. The complexes are fairly stable and can be stored for long

period at room temperature. The complexes are generally soluble in common organic solvents. The molar conductance value (Table 1) determined in nitrobenzene at room temperature suggest that except perchlorato complexes, all other complexes are non-electrolytic in nature, while the perchlorato complexes are ionic in nature and both the perchlorato ions are present outside the coordination sphere. The molecular weight of the complexes as determined cryoscopically in freezing nitrobenzene are in good agreement with the conductance values.

**Table 1.**  
Analytical data of  $\text{UO}_2^{2+}$  complexes of thiosemicarbazones

Complex	Yield (%)	Found (Calculated) %					Formula Wt. (Experimental Values)	$\Omega \text{ M (Ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$
		U	C	H	N	S		
$\text{UO}_2\text{Br}_2 \cdot 2(2' - \text{NO}_2\text{BAAPT})$	75	18.89	36.24	2.96	15.56	5.07	1234	3.2
		(19.07)	(36.53)	(3.04)	(15.70)	(5.12)	(1248)	
$\text{UO}_2\text{I}_2 \cdot 2(2' - \text{NO}_2\text{BAAPT})$	80	17.56	33.63	2.79	14.48	4.71	1327	3.3
		(17.73)	(33.97)	(2.83)	(14.60)	(4.76)	(1342)	

Table 1 Contd.

Complex	Yield (%)	Found (Calculated) %					Formula Wt. (Experimental Values)	$\Omega M (\text{Ohm}^{-1} \text{cm}^2 \text{mole}^{-1})$
		U	C	H	N	S		
UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ·(2'-NO <sub>2</sub> BAAPT)	81	29.40 (29.63)	28.15 (28.39)	2.31 (2.36)	15.56 (15.69)	3.93 (3.98)	790 (803)	3.1
UO <sub>2</sub> (NCS) <sub>2</sub> ·2(2'-NO <sub>2</sub> BAAPT)	78	19.58 (19.76)	39.59 (39.86)	3.10 (3.15)	18.47 (18.60)	10.52 (10.63)	1183 (1204)	3.6
UO <sub>2</sub> (CH <sub>3</sub> COO) <sub>2</sub> ·(2'-NO <sub>2</sub> BAAPT)	85	29.64 (29.86)	34.37 (34.62)	3.08 (3.13)	12.17 (12.29)	3.97 (4.01)	781 (797)	3.9
(UO <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ·2(2'-NO <sub>2</sub> BAAPT)	80	18.33 (18.49)	35.29 (35.43)	2.91 (2.95)	15.10 (15.22)	4.91 (4.97)	417 (1287)	52.9
UO <sub>2</sub> Br <sub>2</sub> ·2(3'-NO <sub>2</sub> BAAPT)	77	18.88 (19.07)	36.22 (36.53)	2.96 (3.04)	15.55 (15.70)	5.07 (5.12)	1232 (1248)	2.9
UO <sub>2</sub> I <sub>2</sub> ·2(3'-NO <sub>2</sub> BAAPT)	80	17.55 (17.73)	33.62 (33.97)	2.78 (2.83)	14.49 (14.60)	4.70 (4.76)	1326 (1342)	3.1
UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ·(3'-NO <sub>2</sub> BAAPT)	81	29.42 (29.63)	28.17 (28.39)	2.30 (2.36)	15.56 (15.69)	3.93 (3.98)	788 (803)	3.1
UO <sub>2</sub> (CH <sub>3</sub> COO) <sub>2</sub> ·(3'-NO <sub>2</sub> BAAPT)	79	19.57 (19.76)	39.60 (39.86)	3.09 (3.15)	18.46 (18.60)	10.53 (10.63)	1181 (1204)	2.8
UO <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ·2(3'-NO <sub>2</sub> BAAPT)	81	18.34	35.29	2.91	15.11	4.92	413	53.6

The magnetic measurements of the dioxouranium(VI) complexes are independent of field strength and temperature[10] and the ground states of dioxouranium (VI) compounds contain no unpaired electrons, the compounds are therefore weakly diamagnetic as observed by previous workers[11].

#### Infrared spectra and nature of coordination

A study and comparison of infrared spectra of free ligands and their UO<sub>2</sub><sup>2+</sup> complexes (Table 2) imply that these ligands behave as neutral tridentate and the UO<sub>2</sub><sup>2+</sup> also coordinated through N, N of two azomethine groups and through thioketo-S.

The strong bands observed at 3440-3270 cm<sup>-1</sup> region in the free ligands have been assigned to  $\nu$  (NH) vibrations. Practically no affect on these frequencies after complexation

precludes the possibility of complexation at this group. The absorptions at ~ 1600 cm<sup>-1</sup> in the free ligands can be attributed to (C=N) stretching vibrations of imine nitrogen, which is in agreement with the observations of previous workers[12-14]. On complexation, these frequencies were observed to be shifted to lower wave number (Table 2). These observations suggest involvement of unsaturated nitrogen atoms of the two azomethine groups in bonding with the UO<sub>2</sub><sup>2+</sup> ion.

The spectra of present ligands, the bands observed in 1300-1125 cm<sup>-1</sup>, 1120-1095 cm<sup>-1</sup> and 840-730 cm<sup>-1</sup> region are assigned to [ $\nu$  (C=S) +  $\nu$  (C=N) +  $\delta$  (C=N)], [ $\delta$  (N-C-S) and  $\delta$  (C=S)] and  $\nu$  (C=S) stretching respectively, following the observations of Irving et al.[15] and other workers[16-18]. Coordination of sulphur with the metal ion would result in the displacement of electrons toward the latter, thus resulting in weakening of (C=S) bond. Hence, on complexation (C=S) stretching vibrations should decrease and that of (CN) should

increase[18-19]. In all the present complexes of  $UO_2^{2+}$  with 2'-NO<sub>2</sub>BAAPT and 3'-NO<sub>2</sub>BAAPT, the frequencies in the region 1300-1125 cm<sup>-1</sup> get an increase by nearly 50-60 cm<sup>-1</sup>. Similarly bending modes of (N-C-S) and (C=S) also get increase but in lesser amount. On the other hand, on complexation, the frequencies in the region 840-730 cm<sup>-1</sup> are shifted to lower wave numbers and the intensities of the bands are also reduced. All these particular changes on

complexation confidently preclude any unambiguity concerning the presence of a metal- sulphur bond.

The possibility of thione-thiol tautomerism (H-N-C=S) ⇌ (C=N-SH) in these ligands has been ruled out for no bands around 2500-2700 cm<sup>-1</sup>, characteristics of thiol group are displayed in the infrared absorption[20-21].

**Table 2**  
Partial IR data (cm<sup>-1</sup>) of dioxouranium (VI) complexes of thiosemicarbazones

Complex	v(NH)	v(C=N)	v(C=S) + v(C=N) + δ(CN)	δ(NCS) + δ(C=S)	v(C=S)	v(U-N)	v(U-S)
2'-NO <sub>2</sub> BAAPT	3440s	1600s	1300s	1120m	840 s	-	-
	3270m		1290s	1095m	750vs		
UO <sub>2</sub> Br <sub>2</sub> .2(2'-NO <sub>2</sub> BAAPT)	3440s	1570s	1355s	1155m	800s	430m	380m
	3272m		1330s	1130m	735m		
UO <sub>2</sub> I <sub>2</sub> .2(2'-NO <sub>2</sub> BAAPT)	3440s	1572s	1358s	1158m	812s	435m	382m
	3270m		1332s	1132m	740m		
UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> .2(2'-NO <sub>2</sub> BAAPT)	3442s	1565s	1350s	1155m	802s	438m	385m
	3270m		1320s	1132m	740m		
UO <sub>2</sub> (NCS) <sub>2</sub> .2(2'-NO <sub>2</sub> BAAPT)	3442s	1572s	1355s	1158m	803s	432m	390m
	3272m		1305s	1135m	730s		
UO <sub>2</sub> (CH <sub>3</sub> COO) <sub>2</sub> .2(2'-NO <sub>2</sub> BAAPT)	3440m	1570m	1358s	1155m	805s	435m	385m
	3270m		1325m	1140m	725s		
UO <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> .2(2'-NO <sub>2</sub> BAAPT)	3442m	1562s	1355m	1162m	802s	440m	370m
	3270m		1320m	1145m	730s		
3'-NO <sub>2</sub> BAAPT	3435s	1598s	1305s	1120m	837s	-	-
	3285m		1270s	1090m	730s		
UO <sub>2</sub> Br <sub>2</sub> .2(3'-NO <sub>2</sub> BAAPT)	3430s	1565s	1358s	1155m	812s	435m	370m
	3290		1310s	1130m	715s		
UO <sub>2</sub> I <sub>2</sub> .2(3'-NO <sub>2</sub> BAAPT)	3438m	1570s	1355s	1157m	805s	440m	375m
	3285m		1315s	1132m	718s		
UO <sub>2</sub> (NCS) <sub>2</sub> .2(3'-NO <sub>2</sub> BAAPT)	3435s	1570m	1358s	1155m	805s	432m	382m
	3282m		1312s	1132m	712s		
UO <sub>2</sub> (CH <sub>3</sub> COO) <sub>2</sub> .2(3'-NO <sub>2</sub> BAAPT)	3430s	1568s	1360s	1158m	802s	438m	385m
	3280m		1322s	1130m	705s		
UO <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> .2(3'-NO <sub>2</sub> BAAPT)	3432s	1565m	1365s	1162m	802s	435m	382m
	3287m		1325s	1135m	710s		

The far IR spectral bands in the ligands are practically unchanged in the complexes. However some new bands with medium to weak intensity in this region in all the complexes under study are assigned to  $\nu$  (U-N) and  $\nu$  (U-S) in accordance with various other reports[22-24].

### Anions

The perchlorato complexes exhibited bands at  $\sim 1100$  ( $\nu_3$ ) and  $625 \text{ cm}^{-1}$  ( $\nu_4$ ), both of which showed no signs of splitting and thus perchlorate is present as free ion of  $T_d$  symmetry[25-27]. This view has already been confirmed by conductance measurements.

The very intense  $\nu(\text{C}=\text{N})$  band at  $\sim 2120 \text{ cm}^{-1}$  suggests that the thiocyanato group in the present complexes are nitrogen bonded[28-30]. The frequency of the (C-S) stretching vibration at  $820 \text{ cm}^{-1}$  is also in agreement with a nitrogen

bonded isothiocyanate[28-30]. A medium intensity band at  $\sim 480 \text{ cm}^{-1}$  may be assigned as  $\delta$  (NCS) absorption.

The infrared spectra of the nitrate complexes in KBr pellets showed the absence of a band at  $\sim 1360 \text{ cm}^{-1}$  suggesting that all the nitrate ions are covalently bonded to the metal ion. In both nitrate complexes the occurrence to two strong absorptions at  $\sim 1520$  and  $1310 \text{ cm}^{-1}$  is attributed to  $\nu_1$  and  $\nu_4$  modes of vibrations of the covalently bonded nitrate group respectively, suggesting that the nitrate groups are inside the coordination sphere[31]. The nitrate groups seem to be bidentate in these complexes, since the infrared frequencies due to this group occur in almost the same frequency ranges[32] ( $1520, 1310, 1030, 805$  and  $740 \text{ cm}^{-1}$  as  $\nu_1, \nu_4, \nu_2, \nu_6$  and  $\nu_3/\nu_5$ , respectively) as in  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ .

**Table 3**  
Various force constants (m dynes/Å), U-O bond distance (Å) and frequencies ( $\text{cm}^{-1}$ )  $\nu_1$  and  $\nu_3$  of  $\text{UO}_2^{2+}$  complexes of thiosemicarbazones.

Complex	$\nu_1$	$\nu_3$	U-O force constant	Force constant due to interaction between bonds	distance
$\text{UO}_2\text{Br}_2 \cdot 2(2'\text{-NO}_2\text{BAAPT})$	832	925	6.8172	-0.2921	1.7399
$\text{UO}_2\text{I}_2 \cdot 2(2'\text{-NO}_2\text{BAAPT})$	828	928	6.8090	-0.3465	1.7399
$\text{UO}_2(\text{NO}_3)_2 \cdot 2(2'\text{-NO}_2\text{BAAPT})$	830	925	6.8016	-0.3078	1.7405
$\text{UO}_2(\text{NCS})_2 \cdot 2(2'\text{-NO}_2\text{BAAPT})$	840	930	6.9188	-0.2676	1.7369
$\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2(2'\text{-NO}_2\text{BAAPT})$	825	920	6.7242	-0.3085	1.7423
$\text{UO}_2(\text{ClO}_4)_2 \cdot 2(2'\text{-NO}_2\text{BAAPT})$	830	920	6.7632	-0.2695	1.7411
$\text{UO}_2\text{Br}_2 \cdot 2(3'\text{-NO}_2\text{BAAPT})$	835	925	6.8793	-0.3071	1.7378
$\text{UO}_2\text{I}_2 \cdot 2(3'\text{-NO}_2\text{BAAPT})$	837	928	6.8796	-0.2759	1.7378
$\text{UO}_2(\text{NO}_3)_2 \cdot 2(3'\text{-NO}_2\text{BAAPT})$	835	920	6.8025	-0.2302	1.7402
$\text{UO}_2(\text{NCS})_2 \cdot 2(3'\text{-NO}_2\text{BAAPT})$	827	930	6.8166	-0.3698	1.7399
$\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2(3'\text{-NO}_2\text{BAAPT})$	825	927	6.7779	-0.3622	1.7408
$\text{UO}_2(\text{ClO}_4)_2 \cdot 2(3'\text{-NO}_2\text{BAAPT})$	830	932	6.8556	-0.3618	1.7384

### Complexation affect on uranyl ion spectra

Uranyl ion  $\text{UO}_2^{2+}$  is quite peculiar both in its own structure and in its coordination compounds[33-35]. The ions retains its identity over a wide range of vibrations in experimental conditions and can be considered from the geometric point of view, as a single particle. In the present investigation, the  $\nu$  (U=O) in all the complexes has been

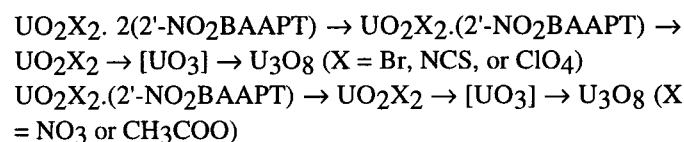
assigned in  $930\text{-}920 \text{ cm}^{-1}$  and  $840\text{-}825 \text{ cm}^{-1}$  region as  $\nu_3$  and  $\nu_1$  respectively (Table 3). A group theoretical consideration[36] shows that a linear and symmetrical triatomic  $\text{UO}_2^{2+}$  ion possessing  $D_{\infty h}$  symmetry gives rise to three fundamental modes of vibrations. Wilson's GF matrix method[37] has been used to determine the stretching and interaction force constants. The results are in turn used to evaluate U-O bond distances following Badger's formula [38].

The force constants, bond distances and spectral data used herein are presented in Table 3. It is apparent from Table 3, that the bond length decreases with the increase in the value of symmetric stretching frequency ( $\nu_1$ ) [38]. Another observation is that a plot of ( $\nu_1 + \nu_3$ ) versus force constant gives a straight line with the increase in the symmetric stretching vibration on complexation, the U-O force constant and the force constant due to the interaction between the bonds have also been found. Further the U-O bond distance of uranyl salts generally varies from 1.60 to 1.92 Å depending on the equatorial ligands [39]. The calculated values of the U-O bond distances of the present complexes are well within the range 1.7369-1.7423 Å.

### Thermal Studies

The thermal data are given in Table 4. The thermogravimetric curves of  $\text{UO}_2(2'\text{-NO}_2\text{BAAPT})_n\text{X}_2$  ( $n = 2$ ,  $\text{X} = \text{Br}$ ,  $\text{NCS}$  or  $\text{ClO}_4$ ;  $n = 1$ ,  $\text{X} = \text{NO}_3$  or  $\text{CH}_3\text{COO}$ ) clearly indicate the absence of water molecules in the

complexes. The pyrolysis curves of bromo, thiocyanato and perchlorato complexes behave similarly and show that the decomposition of these complexes starts at  $\sim 235^\circ\text{C}$  and is completed at  $\sim 480^\circ\text{C}$ . The break in the curves at  $\sim 330^\circ\text{C}$  indicates that at this stage only one molecule of organic ligand has been lost ( $\sim 33\%$ ). In the temperature range  $380\text{-}480^\circ\text{C}$  there is an additional decrease in weight due to loss of the second organic ligand molecule. In the case of nitrate and acetato complexes the loss at  $\sim 330^\circ\text{C}$  is found to be  $\sim 52\%$ . At this stage only organic ligand molecule is lost. The oxide  $\text{U}_3\text{O}_8$  is formed around  $725^\circ\text{C}$  via the formation of  $\text{UO}_3$ , following which there is no measurable change in weight [40]. In brief, these changes can be shown as:



**Table 4.**  
Thermoanalytical results of dioxouranium(VI) complexes of 2'-NO<sub>2</sub>BAAPT

Complex	Sample weight (mg)	Residual weight (mg)	Ligand Mass Loss (%)				Residual (%)	
			235-330° C		380-480° C		725° C	
			Theor. <sup>a</sup>	Exp.	Theor. <sup>b</sup>	Exp.	Theor. <sup>c</sup>	Exp.
$\text{UO}_2\text{Br}_2 \cdot 2(2'\text{-NO}_2\text{BAAPT})$	25.00	5.57	32.77	33.21	65.54	66.36	22.48	21.59
$\text{UO}_2\text{Br}_2 \cdot 2(2'\text{-NO}_2\text{BAAPT})$	27.20	9.21	50.93	51.69	-	-	34.95	33.89
$\text{UO}_2\text{Br}_2 \cdot 2(2'\text{-NO}_2\text{BAAPT})$	26.40	5.94	33.97	34.82	67.94	68.79	23.31	22.52
$\text{UO}_2\text{Br}_2 \cdot 2(2'\text{-NO}_2\text{BAAPT})$	28.60	10.00	52.36	52.98	-	-	35.93	34.98
$\text{UO}_2\text{Br}_2 \cdot 2(2'\text{-NO}_2\text{BAAPT})$	24.20	5.07	31.77	32.34	63.55	64.26	21.80	20.96

a-Calculated for loss of 1 mole of ligand.

b-Calculate for total loss of ligand.

c-Calculated as  $\text{U}_3\text{O}_8$ .

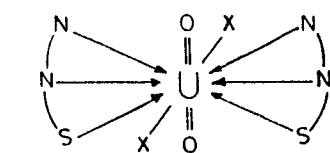
### Stereochemistry and the Structure of the Complexes

In the complex  $\text{UO}_2(\text{H}_2\text{O})_4(\text{NO}_3)_2$ , Misra et al [11] suggested that dioxouranium (VI) nitrate forms covalent complexes possibly involving the 5f-orbitals. The IR data of dioxouranium (VI) nitrate complexes of 2'-NO<sub>2</sub>BAAPT/3'-NO<sub>2</sub>BAAPT suggest the bivalent nature of the nitrate groups in these complexes [32]. Thus  $[\text{UO}_2\text{L}(\text{NO}_3)_2]$  it may be considered to have a nine-

coordinated uranium atom with four oxygen atoms from the two bidentate nitrate groups, two nitrogen atoms of azomethine groups and one thioketo-sulphur atom in a plane perpendicular to the linear OUO group. Similarly in  $[\text{UO}_2\text{L}(\text{CH}_3\text{COO})_2]$ , with the tridentate nature of the organic ligand and bidentate chelating acetato groups, nine-coordinated structures are suggested. In halo and thiocyanato complexes, both the anions are covalently bonded. In these cases, all the complexes are ten coordinated. In  $[\text{UO}_2\text{L}_2](\text{ClO}_4)_2$ , both perchlorato groups are ionic in

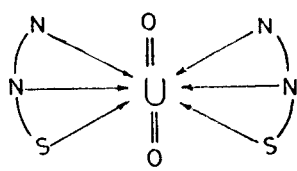
nature, thus it is revealed that the coordination number of U(VI) is eight in these complexes. The proposed structures

of the complexes are given in Figs. (III), (IV), (V) and (VI).



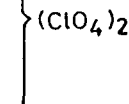
(X = Br, I or NCS) (C.N=10)

(III)



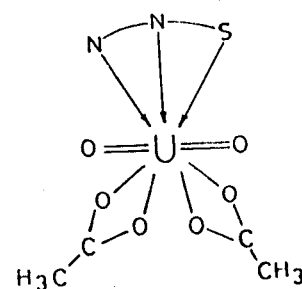
(C.N=8)

(IV)



(C.N=9)

(V)



(C.N.=9)

(VI)

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