

**SYNTHESIS AND STRUCTURAL INVESTIGATIONS OF  
DIOXOURANIUM(VI) COORDINATION COMPOUNDS OF  
4-[N-(*p*-DIMETHYLAMINO BENZALIDENE)AMINO]  
ANTIPYRINE THIOSEMICARBAZONE<sup>1</sup>**

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**ABSTRACT.** This paper reports the isolation of some solid coordination compounds of dioxouranium(VI) with a 4-[N-(*p*-dimethylaminobenzalidene)amino]antipyrine thiosemicarbazone (DABAAPT). The analytical data indicate that the complexes have the general composition  $UO_2X_{2.n}(DABAAPT)$  ( $X = Br, I, NCS^-$  or  $ClO_4^-$ ,  $n = 2$ ;  $X = NO_3^-$  or  $CH_3COO^-$ ,  $n = 1$ ). These compounds were characterized by various physico-chemical techniques. The ligand behaves as tridentate N,N,S-donor. The probable coordination number of uranium is found to be 8, 9 or 10 depending on the nature of anionic ligand. 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 compounds were also investigated.

**KEY WORDS:** Dioxouranium(VI) coordination compounds, 4-[N-(*p*-Dimethylaminobenzalidene)amino]antipyrine thiosemicarbazone, Tridentate N,N,S-donor

## INTRODUCTION

Dioxouranium ion,  $UO_2^{2+}$ , is quite peculiar both in its own structure and in its coordination chemistry. It can be considered from a geometric point of view as a single particle. Since coordination occurs in the plane normal to the O-U-O axis and the numbers of ligands in the equatorial plane can be up to six, there is a large number of geometric structures which are not found in the usual coordination chemistry of d-block transition metal ions. This peculiarity is of great interest because of the various possible applications involving the technology and uses of uranium derivatives. We have published a number of papers on dioxouranium(VI) complexes of various Schiff bases [1-4]. To our knowledge no report has been published on  $UO_2^{2+}$  coordination compounds of 4-[N-(*p*-dimethylaminobenzalidene)amino]antipyrine thiosemicarbazone (DABAAPT) (Figure 1). The present work reports the synthesis and characterization of some 8, 9 and 10-coordinated compounds of dioxouranium(VI) with this ligand.

## EXPERIMENTAL

**Reagents.** Dioxouranium(VI) nitrate was used as received from B.D.H. Dioxouranium(VI) nitrate was dehydrated by keeping it over concentrated sulphuric acid [5].  $UO_2Br_2$  was prepared from  $UO_2(CH_3COO)_2$  by treating it with hydrobromic acid. After evaporating most of the solvent, the solution was kept over concentrated sulphuric acid till yellow crystals separated out

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[6]. Dioxouranium(VI) iodide was obtained by treating dioxouranium(VI) nitrate with barium iodide in dry ether [7]. Dioxouranium(VI) thiocyanate was prepared by mixing an alcoholic solution of anhydrous dioxouranium(VI) nitrate and potassium thiocyanate [8].  $\text{UO}_2(\text{ClO}_4)_2$  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 recrystallized until free of nitrate ions [9].

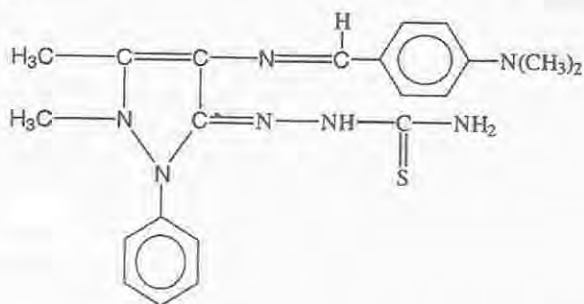


Figure 1. 4-[N-(*p*-Dimethylaminobenzalidene)amino]antipyridine thiosemicarbazone (DABAAPT).

The ligand DABAAPT was synthesized in two steps [10]. (i) A solution of *p*-dimethylaminobenzaldehyde (1 mmol) in absolute ethanol (20 mL) was mixed with 4-aminoantipyridine (1.1 mmol) in the same solvent and the mixture was refluxed for 2-3 h. On cooling a yellow crystalline product was separated, which was filtered and recrystallized in the same solvent. (ii) In the second step, the Schiff base of 4-aminoantipyridine was dissolved in hot ethanol and refluxed with an equimolar ratio of thiosemicarbazide for ~3 h. On cooling the yellow colored crystalline thiosemicarbazone is obtained (m.f.  $\text{C}_{21}\text{H}_{25}\text{N}_7\text{S}$ , m.p. 213 °C, yield ~72%).

*Synthesis of complexes.* All the complexes of  $\text{UO}_2^{2+}$  with DABAAPT 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 ~3 h and left for overnight at 30 °C, colored solids separated were filtered, washed successively with ethanol and diethylether and dried in air (yield ~70-80%).

*Analyses.* The microanalysis of C, H and N were performed in the micro-analytical laboratory of the Chemistry Department, University of Delhi, Delhi, India. The sulphur content was determined gravimetrically as  $\text{BaSO}_4$  [11]. Uranium was estimated by decomposing the compounds with concentrated nitric acid, diluting with distilled water, precipitating the metal as hydroxide with aqueous dilute ammonia, washing the precipitate with distilled water, finally igniting it in air and weighing the insoluble as  $\text{U}_3\text{O}_8$ .

The molecular weights of the complexes were determined cryoscopically in freezing nitrobenzene using a Beckmann thermometer of  $\pm 0.01$  °C accuracy. Conductivity measurements were carried out using a Toshniwal Conductivity Bridge (type CL 01/01) and a dip type cell operated at 220 volts AC. All measurements were made at room temperature in nitrobenzene. Magnetic measurements were carried out with a Gouy balance and  $\text{Hg}[\text{Co}(\text{SCN})_4]$  was used as a calibrant. IR spectra of the complexes were recorded on a Perkin-Elmer Model-521 infrared spectrophotometer in CsI in the range 4000-200  $\text{cm}^{-1}$ . Thermogravimetric analyses were carried out in static air, with open sample holders and a small boat. The heating rate was 6 °C/min.

## RESULTS AND DISCUSSION

The reactions of dioxouranium(VI) salts with DABAAPT gave complexes of the general composition  $\text{UO}_2(\text{DABAAPT})_n\text{X}_2$  ( $n = 2$ ,  $\text{X} = \text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NCS}^-$  or  $\text{ClO}_4^-$ ;  $n = 1$ ,  $\text{X} = \text{NO}_3^-$  or  $\text{CH}_3\text{COO}^-$ ). The analytical data of these complexes are presented in Table 1. Except for the iodo complex, all the complexes are fairly stable and can be stored for long periods at room temperature. The iodo complex decomposed to a sticky mass after a few weeks. The complexes generally are soluble in common organic solvents.

The molar conductances of the complexes determined in nitrobenzene at room temperature are given in Table 1. The results suggest the halo, pseudohalo, nitrate and acetate complexes are essentially non-electrolytes while the perchlorate complex dissociates in nitrobenzene and behaves as 1:2 electrolyte [12]. The molecular weights of the complexes as determined cryoscopically in freezing nitrobenzene are consistent with the conductance values.

The magnetic behavior of the dioxouranium(VI) complexes are independent of field strength and temperature [13]. The ground states of dioxouranium(VI) compounds contain no unpaired electrons and the compounds are weakly diamagnetic, as observed by previous workers [14, 15].

Table 1. Analytical, conductivity and molecular weight data of  $\text{UO}_2^{2+}$  complexes of DABAAPT.

Complex	Yield %	Found (calc.) %					Mol. wt. Found (calc.)	$\Omega \text{ M}^{-1} \text{ cm}^2 \text{ mole}^{-1}$
		U	C	H	N	S		
$\text{UO}_2\text{Br}_2 \cdot 2(\text{DABAAPT})$	75	18.99 (19.13)	40.03 (40.51)	3.97 (4.01)	15.62 (15.75)	5.08 (5.14)	1236 (1244)	3.1
$\text{UO}_2\text{I}_2 \cdot 2(\text{DABAAPT})$	70	17.65 (17.78)	37.46 (37.66)	3.69 (3.73)	14.45 (14.64)	4.73 (4.78)	1330 (1338)	3.4
$\text{UO}_2(\text{NO}_3)_2 \cdot (\text{DABAAPT})$	75	29.59 (29.71)	31.28 (31.46)	3.08 (3.12)	15.57 (15.73)	3.93 (3.99)	792 (801)	3.3
$\text{UO}_2(\text{NCS})_2 \cdot 2(\text{DABAAPT})$	75	19.70 (19.83)	43.88 (44.00)	4.11 (4.16)	18.53 (18.66)	10.60 (10.66)	1187 (1200)	3.7
$\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot (\text{DABAAPT})$	81	32.19 (32.33)	40.53 (40.76)	4.16 (4.21)	13.18 (13.31)	4.30 (4.34)	727 (736)	3.9
$\text{UO}_2(\text{ClO}_4)_2 \cdot 2(\text{DABAAPT})$	75	18.42 (18.55)	39.13 (39.28)	3.84 (3.89)	15.15 (15.27)	4.95 (4.98)	419 (1283)	54.6

*Infrared spectra.* Comparison of infrared spectra of the free ligand and its respective  $\text{UO}_2^{2+}$  complexes (Table 2) indicates that the ligand behaves as neutral tridentate and that the  $\text{UO}_2^{2+}$  is coordinated through N and N of two azomethine groups and S of the thioketo group.

The strong bands observed at  $3440\text{--}3270 \text{ cm}^{-1}$  in the free ligand have been assigned to  $\nu(\text{NH})$  vibrations. Practically no effect on these frequencies after complexation precludes the possibility of complexation at this group. The absorption at  $\sim 1600 \text{ cm}^{-1}$  in the free ligand can be attributed to  $(\text{C}=\text{N})$  stretching vibrations of imine nitrogen, which is in agreement with the observations of previous workers [16, 17]. On complexation, these frequencies shifted to lower wave numbers (Table 2). These observations suggest involvement of unsaturated nitrogen atoms of the two azomethine groups in bonding with the metal ion.

In substituted thioureas, the  $(\text{C}=\text{S})$  stretching bonds vibration are strong with other vibrations such as  $(\text{CN})$  stretching and bending as well as  $(\text{N}-\text{C}-\text{S})$  bending modes [18]. In the spectra of present ligand, the bands observed in  $1300\text{--}1125 \text{ cm}^{-1}$  region,  $1120\text{--}1095 \text{ cm}^{-1}$  and  $840\text{--}730 \text{ cm}^{-1}$  region are assigned to  $[\nu(\text{C}=\text{S}) + \nu(\text{C}=\text{N}) + \nu(\text{C}-\text{N})]$ ,  $\delta(\text{N}-\text{C}-\text{S}) + \delta(\text{C}=\text{S})$  bending and  $\nu(\text{C}=\text{S})$  stretching, respectively, following the observations of Irving *et al.* [19] and other



workers [20, 21]. Coordination of sulphur with the metal ion would result in the displacement of electrons towards the sulfur, thus weakening the C=S bond. Hence, of S-coordination C=S stretching vibrations should decrease and that of (CN) should increase [21, 22]. In all the present complexes of  $\text{UO}_2^{2+}$  with DABAAPT, the frequencies in the range  $1300\text{-}1125\text{ cm}^{-1}$  increased by nearly  $50\text{-}60\text{ cm}^{-1}$  compared to the free ligands. Similarly, bending mode frequencies (N-C-S) and (C=S) also increased but to a lesser extent. On the other hand, on complexation the frequencies in the  $840\text{-}730\text{ cm}^{-1}$  range are shifted to lower wave numbers and the band intensities also are reduced. All these specific changes on complexation are fully consistent with formation of a metal-sulfur bond. The possibility of thione-thiol tautomerism ( $\text{H-N-C=S} \rightleftharpoons \text{C=N-SH}$ ) in this ligand can be ruled out because no bands around  $2700\text{-}2500\text{ cm}^{-1}$  that are characteristic of the thiol group are displayed in the infrared spectra [23, 24]. The far infrared bands in the free ligand are practically unchanged in the complexes. Some new bands with medium to weak intensity in the  $350\text{-}315\text{ cm}^{-1}$  region in all the complexes tentatively are assigned to  $\nu(\text{U-N})$  and  $\nu(\text{U-S})$  in accordance with other reports [25, 26].

Table 2. Key IR frequencies ( $\text{cm}^{-1}$ ) of  $\text{UO}_2^{2+}$  complexes of DABAAPT.

Complex	$\nu(\text{NH})$	$\nu(\text{C=N})$	$\nu(\text{C=S}) + \nu(\text{C=N}) + \delta(\text{CN})$	$\delta(\text{NCS}) + \delta(\text{C=S})$	$\nu(\text{C=S})$	$\nu(\text{U-N})/\nu(\text{U-S})$
DABAAPT	3360 s 3330 s	1600 vs	1310 m 1290 m	1115 m 1095 w	830 s 730 m	-
$\text{UO}_2\text{Br}_2 \cdot 2(\text{DABAAPT})$	3362 s 3320 m	1572 m	1365 m 1340 m	1165 m 1132 m	782 m 710 m	342 m 310 w
$\text{UO}_2\text{I}_2 \cdot 2(\text{DABAAPT})$	3360 m 3335 m	1570 m	1370 m 1330 m	1172 m 1138 m	775 s 710 m	350 m 315 w
$\text{UO}_2(\text{NO}_3)_2 \cdot (\text{DABAAPT})$	3360 s 3332 m	1575 m	1365 m 1342 m	1160 m 1142 m	770 s 705 m	337 m 320 w
$\text{UO}_2(\text{NCS})_2 \cdot 2(\text{DABAAPT})$	3362 s 3330 m	1565 m	1372 m 1345 m	1165 m 1130 m	775 m 722 m	345 m 325 w
$\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot (\text{DABAAPT})$	3365 s 3335 m	1565 m	1370 m 1340 m	1162 m 1135 m	770 m 715 m	350 m 320 w
$\text{UO}_2(\text{ClO}_4)_2 \cdot 2(\text{DABAAPT})$	3360 s 3340 m	1570 m	1372 m 1335 m	1170 m 1130 m	775 m 710 m	345 m 322 w

Uranyl ion  $\text{UO}_2^{2+}$  retains its identity over a wide range of vibrations and can be considered from the geometric point of view as a single particle. It has four fundamental vibrations [27-30]. (i) Non-degenerate symmetric stretching ( $\nu_1$ ) occurs in the range  $900\text{-}800\text{ cm}^{-1}$ . (ii) Non-degenerate asymmetric stretching ( $\nu_2$ ) occurs at  $\sim 1000\text{-}900\text{ cm}^{-1}$  region. (iii) Doubly degenerate O-U-O bending vibration ( $\nu_3$ ) appears at  $\sim 250\text{ cm}^{-1}$ . In the present investigation the  $\nu(\text{U=O})$  in all the complexes has been assigned in the range  $930\text{-}920\text{ cm}^{-1}$  and in the  $840\text{-}825\text{ cm}^{-1}$  region as  $\nu_3$  and  $\nu_1$ , respectively (Table 3).

*Complexation effect on uranyl ion spectra.* The infrared absorption spectra of uranyl(VI) compounds give valuable information regarding the various vibrations due to uranyl ion, anions and crystal lattice. The available structural data indicate that the uranyl bond length is not constant in different uranyl compounds. In general, single crystal X-ray or neutron diffraction studies are required to have accurate bond lengths. Due to the poor X-ray diffracting power of oxygen as compared with uranium, only a few compounds have been studied by these techniques. Hence alternate methods have become essential to have an idea of the bond lengths

from force constants which can be calculated from the vibrational data. Although both linear  $D_{\infty h}$  and bent ( $C_{2v}$ ) structures have been suggested for the uranyl ion, it generally is conceded that in the ground state the uranyl ion has a linear structure in the solid phase and probably also in solution. Conn and Wu [31], Lecomte and Freymann [32] and Sevchenko and Stepanov [33] from their infrared studies confirmed the three fundamental frequencies of uranyl ion  $\nu_1$  asymmetric stretching,  $\nu_2$  bending and  $\nu_3$  anti-symmetry stretching vibrations. From X-ray studies Zachariassen [29] has predicted that the U-O bond distance varies from 1.60 Å in  $\text{Na}[\text{UO}_2(\text{CH}_3\text{COO})_2]$  to 1.92 Å in  $\text{MgU}_2\text{O}_7$ . Such a large range of U-O bond distances in different uranyl salts should produce a very large range of uranyl frequencies; Jones [28] has suggested the determination of bond lengths from infrared spectral data calculating the force constants by valence force field. Narasimhan [34] has calculated the various force constant of the uranyl ion in calcium uranyl nitrate using Wilson's G.F. matrix method [35]. Hoekstra has calculated bond lengths in uranyl fluoride and uranyl carbonate using Badger's rule [36].

In the present studies of  $\text{UO}_2^{2+}$  complexes of DABAAPT, it has been observed that the  $\nu_1$  mode of uranyl ion appears with weak intensity and the  $\nu_3$  mode with strong intensity in the IR spectra (Table 3). A group theoretical consideration [37] 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 G.F. matrix method [35] 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 [36].

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

Complex	U-O force constant	Force constant due to interaction between bonds	U-O bond distance	$\nu_1$	$\nu_3$
$[\text{UO}_2(\text{DABAAPT})_2\text{Br}_2]$	6.80	-0.230	1.74	835 m	920 m
$[\text{UO}_2(\text{DABAAPT})_2\text{I}_2]$	6.82	-0.292	1.74	835 w	925 m
$[\text{UO}_2(\text{DABAAPT})(\text{NO}_3)_2]$	6.92	-0.268	1.74	840 m	930 m
$[\text{UO}_2(\text{DABAAPT})_2(\text{NCS})_2]$	6.88	-0.276	1.74	837 w	928 m
$[\text{UO}_2(\text{DABAAPT})(\text{CH}_3\text{COO})_2]$	6.76	-0.270	1.74	830 m	920 m
$[\text{UO}_2(\text{DABAAPT})_2(\text{ClO}_4)_2]$	6.88	-0.307	1.74	835 m	930 m

The force constants, bond distances and spectral data used herein are presented in Table 3. It is apparent from Table 3 that the bond lengths decrease with 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. The U-O bond distance or uranyl salts generally vary from 1.60 to 1.92 Å depending on the equatorial ligand [29]. The calculated values of the U-O bond distances of the present complexes are 1.74 Å.

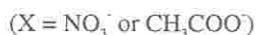
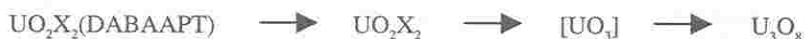
**Anions.** In  $[\text{UO}_2(\text{DABAAPT})_2(\text{ClO}_4)_2]$ , the presence of the  $\nu_1$  ( $1090 \text{ cm}^{-1}$ ) and  $\nu_3$  ( $620 \text{ cm}^{-1}$ ) bands indicate that the  $T_u$  symmetry of  $\text{ClO}_4^-$  is maintained in this complex and suggests the presence of  $\text{ClO}_4^-$  outside the coordination sphere [39, 40]. In the  $[\text{UO}_2(\text{DABAAPT})_2(\text{NCS})_2]$  complex, the three fundamental absorption C-N stretch ( $\nu_1$  at  $2070 \text{ cm}^{-1}$ ), C-S stretch ( $\nu_3$  at  $855 \text{ cm}^{-1}$ ) and N-C-S bending ( $\nu_2$  at  $475 \text{ cm}^{-1}$ ) are identified. These frequencies are associated with terminal N-bonded isothiocyanate ions [41, 42].

The infrared studied of dioxouranium(VI) nitrate complexes have been carried out since 1941 [32], but detailed proposals for the assignment of bands were first reported by Gatehouse and Comyn [5]. McGlynn *et al.* [27] and then Topping [43] reported the infrared spectra of a series of complexes of dioxouranium(VI) nitrate, but no satisfactory explanation has been made for deciding between monodentate and bidentate nitrate complexes. However, Curtis *et al.* [44] showed that the overtone and combination bands of the nitrate group sometimes might be used to distinguish monodentate and bidentate nitrate complexes.

Many infrared data on dioxouranium(VI) complexes can be found in a work of Bullock [45]. These data are inconsistent with the presence of bidentate nitrate groups. The fundamental vibrational modes of the nitrate group in  $[\text{UO}_2(\text{DABAAPT})(\text{NO}_3)_2]$  complex occur at 1520 ( $\nu_4$ ), 1295 ( $\nu_1$ ), 1030 ( $\nu_2$ ), 805 ( $\nu_6$ ), 740 ( $\nu_3$ ) and 710  $\text{cm}^{-1}$  ( $\nu_5$ ). The nitrate groups seem to be bidentate in this complex, since the IR frequencies due to this group occur in almost the same frequency ranges as in  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{Apy}$  and  $\text{UO}_2(\text{NO}_3)_2 \cdot \text{AcApy}$  [46, 47].

Similar to nitrate, the acetate ion also is a potentially bidentate ligand towards the uranyl group. A number of complexes of uranyl acetate with neutral monodentate ligands like TPPO, TPAsO, TMAO, HMPA or DPSO are reported in the literature [48]. In these complexes the acetate ion behaves as covalent bidentate and the coordination number is found to be seven or eight, depending on whether the complexes are monomeric or dimeric. In the present case the complex  $[\text{UO}_2(\text{DABAAPT})(\text{CH}_3\text{COO})_2]$  is monomeric and the infrared spectra of this complex shows two bands at 1550 and 1460  $\text{cm}^{-1}$  attributed to asymmetric and the symmetric stretching vibrations of  $\text{COO}^-$ , respectively [49, 50]. A difference,  $\Delta\nu(\text{COO}^-)$ , of  $\sim 90 \text{ cm}^{-1}$  suggests bidentate  $\text{COO}^-$  groups in this complex.

**Thermal Studies.** The thermal behavior of these complexes is summarized in Table 4. The thermogravimetric curves of bromo, thiocyanate and perchlorato complexes are similar and show that the decomposition of these complexes starts at 240  $^\circ\text{C}$  and is completed at  $\sim 480 \text{ }^\circ\text{C}$ . The break in the curves in the 340  $^\circ\text{C}$  temperature region indicates that at this stage only one molecule of organic ligand has been lost (32.16-34.27%). In the temperature range 390-480  $^\circ\text{C}$  there is an additional decrease in weight due to loss of second organic ligand molecule. For nitrate and acetate complexes the loss at  $\sim 340 \text{ }^\circ\text{C}$  is found to be 51.22-55.59%. At this stage only the organic ligand molecule is lost. The oxide  $\text{U}_3\text{O}_8$  is formed around 750  $^\circ\text{C}$  via the formation of  $\text{UO}_3$ , following which is no measurable change in weight [51]. In summary, these changes can be written as:



**Stereochemistry.** In the complex  $\text{UO}_2(\text{H}_2\text{O})_4(\text{NO}_3)_2$ , Glueckauf and McKay [52] suggested that dioxouranium(VI) nitrate forms a covalent complex possibly involving the 5f-orbitals. The IR data of the  $[\text{UO}_2(\text{DABAAPT})(\text{NO}_3)_2]$  complex suggest bicovalent  $\text{NO}_3^-$  in this complex [48]. Thus, in this complex, the central metal ion has coordination number nine (surrounded by six-oxygen atoms, two nitrogen atoms and one sulphur atom). In  $[\text{UO}_2(\text{DABAAPT})(\text{CH}_3\text{COO})_2]$ , a nine-coordinated structure is suggested as a result of the tridentate (N,N,S) nature of the organic



ligand and bidentate chelating acetato groups. In the bromo and thiocyanate complexes, both the anions are covalently bonded. In both cases it appears there is a ten-coordinated uranium atom. In the  $[\text{UO}_2(\text{DABAAPT})(\text{ClO}_4)_2]$  complex, both perchlorato groups are ionic. Thus this complex, the uranium atom has a coordination number of eight [15].

Table 4. Thermoanalytical results of  $\text{UO}_2^{2+}$  complexes of DABAAPT.

Complex	Sample weight (mg)	Residual weight (mg)	Ligand mass loss (%)				Residual (%)	
			240-340 °C		390-480 °C		~ 750 °C	
			Theor. <sup>a</sup>	Exp.	Theor. <sup>b</sup>	Exp.	Theor. <sup>c</sup>	Exp.
$\text{UO}_2\text{Br}_2 \cdot 2(\text{DABAAPT})$	20.2	4.50	32.71	33.16	65.43	66.12	22.56	22.27
$\text{UO}_2(\text{NO}_3)_2 \cdot (\text{DABAAPT})$	19.1	6.60	50.81	51.22	-	-	35.03	34.55
$\text{UO}_2(\text{NCS})_2 \cdot 2(\text{DABAAPT})$	17.9	4.00	33.91	34.27	67.83	68.19	23.38	22.34
$\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot (\text{DABAAPT})$	16.8	6.30	55.29	55.59	-	-	38.13	37.50
$\text{UO}_2(\text{ClO}_4)_2 \cdot 2(\text{DABAAPT})$	15.2	3.25	31.72	32.16	63.44	63.87	21.87	21.38

<sup>a</sup>Calculated for loss of 1 mole of DABAAPT, <sup>b</sup>calculated for total loss of DABAAPT, <sup>c</sup>calculated as  $\text{U}_2\text{O}_7$ .

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