SYNTHESIS AND STRUCTURAL INVESTIGATIONS OF
DIOXOURANIUM(VI) COORDINATION COMPOUNDS OF
4-[N-(p-DIMETHYLANIMINOBENZALIDENE)AMINO]
ANTIPYRINE THIOSEMICARBAZONE

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ABSTRACT. This paper reports the isolation of some solid coordination compounds of dioxouraniun(VI) with a 4-[N-(p-dimethylaminobenzalidene)amino]antipyrine thiosemicarbazone (DABAAPT). The analytical data indicate that the complexes have the general composition UO₂X₂ₙ(DABAAPT) (X = Br⁻, I⁻, NCS⁻ or Cl⁻, n = 2; X = NO₃⁻ or CH₃COO⁻, 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: Dioxouraniun(VI) coordination compounds, 4-[N-(p-Dimethylaminobenzalidene)amino]antipyrine thiosemicarbazone, Tridentate N,N,S-donor

INTRODUCTION

Dioxouraniun ion, UO₂⁻², 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 dioxouraniun(VI) complexes of various Schiff bases [1-4]. To our knowledge no report has been published on UO₂⁻² 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 dioxouraniun(VI) with this ligand.

EXPERIMENTAL

Reagents. Dioxouraniun(VI) nitrate was used as received from B.D.H. Dioxouraniun(VI) nitrate was dehydrated by keeping it over concentrated sulphuric acid [5]. UO₂Br₃ was prepared from UO₂(CHO₂COO)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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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-Dimethylaminobenzaldehyde)amino]antipyrine thiosemicarbazone (DABAAPT).](image)

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-aminoantipyrine (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-aminoantipyrine was dissolved in hot ethanol and refluxed with an equimolar ratio of thiosemicarbazide for $\sim$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 $\sim$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 $\sim$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 $\sim$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 $\text{U}_2\text{O}_8$.

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 $\text{Hg}[\text{Co(SCN)}_4]$ 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 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 dioxoaurium(VI) salts with DABAAAPT gave complexes of the general composition \( \text{UO}_x(\text{DABAAAPT})_y \) \( n = 2, x = Br, I, \text{NCS}^-, \text{ClO}_4^-; n = 1, x = \text{NO}_3^- \) or \( \text{CH}_2\text{COO}^- \). 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 acetato complexes are essentially non-electrolytes while the perchlorate complex dissociates in nitrobenzene and behaves as a 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 dioxoaurium(VI) complexes are independent of field strength and temperature [13]. The ground states of dioxoaurium(VI) compounds contain no unpaired electrons and the compounds are weakly diamagnetic, as observed by previous workers [14, 15].

<table>
<thead>
<tr>
<th>Complex</th>
<th>Yield %</th>
<th>Found (calc.) %</th>
<th>Mol. wt. (calc.)</th>
<th>Ω M ( (\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{UO}_2\text{Br}_2(\text{DABAAAPT}) )</td>
<td>75</td>
<td>18.99 (19.13) 40.03 (40.51) 3.97 (4.01) 15.62 (15.75) 5.08 (5.14)</td>
<td>1236 (1244)</td>
<td>3.1</td>
</tr>
<tr>
<td>( \text{UO}_2\text{I}_2(\text{DABAAAPT}) )</td>
<td>70</td>
<td>17.65 (17.78) 37.46 (37.66) 3.69 (3.73) 14.45 (14.64) 4.72 (4.78)</td>
<td>1330 (1338)</td>
<td>3.4</td>
</tr>
<tr>
<td>( \text{UO}_2(\text{NO}_3)_2(\text{DABAAAPT}) )</td>
<td>75</td>
<td>29.59 (29.71) 31.28 (31.46) 3.08 (3.12) 15.57 (15.73) 3.92 (3.99)</td>
<td>792 (801)</td>
<td>3.3</td>
</tr>
<tr>
<td>( \text{UO}_2(\text{NCS})_2(\text{DABAAAPT}) )</td>
<td>75</td>
<td>19.70 (19.83) 43.88 (44.00) 4.11 (4.16) 18.53 (18.66) 10.60 (10.66)</td>
<td>1187 (1200)</td>
<td>3.7</td>
</tr>
<tr>
<td>( \text{UO}_2(\text{CH}_2\text{COO})_2(\text{DABAAAPT}) )</td>
<td>81</td>
<td>32.19 (32.33) 40.53 (40.76) 4.16 (4.21) 13.18 (13.31) 4.30 (4.34)</td>
<td>727 (736)</td>
<td>3.9</td>
</tr>
<tr>
<td>( \text{UO}_2(\text{ClO}_4)_2(\text{DABAAAPT}) )</td>
<td>75</td>
<td>18.42 (18.55) 39.13 (39.28) 3.84 (3.89) 15.15 (15.27) 4.95 (4.98)</td>
<td>419 (1283)</td>
<td>54.6</td>
</tr>
</tbody>
</table>

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 thiketo group.

The strong bands observed at 3440-3270 cm\(^{-1}\) in the free ligand have been assigned to \( v(\text{NH}) \) vibrations. Practically no effect on these frequencies after complexation precludes the possibility of complexation at this group. The absorptions at \( \sim 1600 \text{ cm}^{-1} \) in the free ligand can be attributed to (C=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 (C=S) stretching bonds vibration are strong with other vibrations such as (CN) stretching and bending as well as (N-C-S) bending modes [18]. In the spectra of present ligand, the bands observed in 1300-1125 cm\(^{-1}\) region, 1120-1095 cm\(^{-1}\) and 840-730 cm\(^{-1}\) region are assigned to \( v(\text{C=S}) + v(\text{C=N}) + v(\text{C-N}) \), \( δ(\text{N-C-S}) + δ(\text{C=S}) \) bending and \( v(\text{C=S}) \) 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, C- and 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 1300-1125 cm\(^{-1}\) increased by nearly 50-60 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 840-730 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 (H-N-C=S \( \rightleftharpoons \) C=N-SH) in this ligand can be ruled out because no bands around 2700-2500 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 350-315 cm\(^{-1}\) region in all the complexes tentatively are assigned to \( v(U-N) \) and \( v(U-S) \) in accordance with other reports [25, 26].

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

<table>
<thead>
<tr>
<th>Complex</th>
<th>( v(NH) )</th>
<th>( v(C=N) )</th>
<th>( v(C=S) + \delta(CN) )</th>
<th>( \delta(NCS) + \delta(C=S) )</th>
<th>( v(C=S) )</th>
<th>( v(U-N)/v(U-S) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>DABAAPT</td>
<td>3360 s</td>
<td>1600 vs</td>
<td>1310 m</td>
<td>1115 m</td>
<td>830 s</td>
<td>~</td>
</tr>
<tr>
<td></td>
<td>3330 s</td>
<td></td>
<td>1290 m</td>
<td>1095 w</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{UO}_2\text{Br}_2 ) ( (\text{DABAAPT}) )</td>
<td>3362 s</td>
<td>1572 m</td>
<td>1365 m</td>
<td>1165 m</td>
<td>782 m</td>
<td>342 m</td>
</tr>
<tr>
<td></td>
<td>3320 m</td>
<td></td>
<td>1340 m</td>
<td>1132 m</td>
<td>710 m</td>
<td>310 w</td>
</tr>
<tr>
<td>( \text{UO}_2\text{Cl}_2 ) ( (\text{DABAAPT}) )</td>
<td>3360 m</td>
<td>1570 m</td>
<td>1370 m</td>
<td>1172 m</td>
<td>775 m</td>
<td>350 m</td>
</tr>
<tr>
<td></td>
<td>3335 m</td>
<td></td>
<td>1350 m</td>
<td>1138 m</td>
<td>710 m</td>
<td>315 w</td>
</tr>
<tr>
<td>( \text{UO}_2\text{NO}_3 ) ( (\text{DABAAPT}) )</td>
<td>3360 s</td>
<td>1575 m</td>
<td>1365 m</td>
<td>1160 m</td>
<td>770 s</td>
<td>337 m</td>
</tr>
<tr>
<td></td>
<td>3332 m</td>
<td></td>
<td>1342 m</td>
<td>1142 m</td>
<td>705 m</td>
<td>320 w</td>
</tr>
<tr>
<td>( \text{UO}_2\text{NCS}_2 ) ( (\text{DABAAPT}) )</td>
<td>3362 s</td>
<td>1565 m</td>
<td>1372 m</td>
<td>1165 m</td>
<td>775 m</td>
<td>345 m</td>
</tr>
<tr>
<td></td>
<td>3330 m</td>
<td></td>
<td>1345 m</td>
<td>1130 m</td>
<td>722 m</td>
<td>325 w</td>
</tr>
<tr>
<td>( \text{UO}_2\text{CH}_2\text{COO}_2 ) ( (\text{DABAAPT}) )</td>
<td>3365 s</td>
<td>1565 m</td>
<td>1370 m</td>
<td>1162 m</td>
<td>770 m</td>
<td>350 m</td>
</tr>
<tr>
<td></td>
<td>3335 m</td>
<td></td>
<td>1340 m</td>
<td>1135 m</td>
<td>715 m</td>
<td>320 w</td>
</tr>
<tr>
<td>( \text{UO}_2\text{ClO}_4 ) ( (\text{DABAAPT}) )</td>
<td>3360 s</td>
<td>1570 m</td>
<td>1372 m</td>
<td>1170 m</td>
<td>775 m</td>
<td>345 m</td>
</tr>
<tr>
<td></td>
<td>3340 m</td>
<td></td>
<td>1335 m</td>
<td>1130 m</td>
<td>710 m</td>
<td>322 w</td>
</tr>
</tbody>
</table>

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 \( (v_1) \) occurs in the range 900-800 cm\(^{-1}\). (ii) Non-degenerate asymmetric stretching \( (v_2) \) occurs at \~1000-900 cm\(^{-1}\) region. (iii) Doubly degenerate O-U-O bending vibration \( (v_3) \) appears at \~250 cm\(^{-1}\). In the present investigation the \( v(U=O) \) in all the complexes has been assigned in the range 930-920 cm\(^{-1}\) and in the 840-825 cm\(^{-1}\) region as \( v_1 \) and \( v_3 \), 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$_{nm}$ and bent (C$_2$) 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 $v_1$, asymmetric stretching, $v_2$ bending and $v_3$ anti-symmetry stretching vibrations. From X-ray studies Zachariasen [29] has predicted that the U-O bond distance varies from 1.60 Å in Na[UO$_2$(CH$_3$COO)$_2$] to 1.92 Å in MgU$_2$O$_4$. 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 UO$_2$$^{2+}$ complexes of DABAAPT, it has been observed that the $v_1$ mode of uranyl ion appears with weak intensity and the $v_2$ mode with strong intensity in the IR spectra (Table 3). A group theoretical consideration [37] shows that a linear and symmetrical triatomic UO$_2$$^{2+}$ ion possessing D$_{nm}$ 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 dyne/Å), U-O bond distance (Å) and frequencies (cm$^{-1}$) of $v_1$ and $v_3$ of UO$_2$$^{2+}$ complexes of DABAAPT.

<table>
<thead>
<tr>
<th>Complex</th>
<th>U-O force constant</th>
<th>Force constant due to interaction between bonds</th>
<th>U-O bond distance</th>
<th>$v_1$</th>
<th>$v_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[UO$_2$(DABAAPT)$_2$]Br$_2$</td>
<td>6.80</td>
<td>-0.230</td>
<td>1.74</td>
<td>835 m</td>
<td>920 m</td>
</tr>
<tr>
<td>[UO$_2$(DABAAPT)$_2$I$_4$]</td>
<td>6.82</td>
<td>-0.292</td>
<td>1.74</td>
<td>835 w</td>
<td>925 m</td>
</tr>
<tr>
<td>[UO$_2$(DABAAPT)$_2$(NO$_3$)$_2$]</td>
<td>6.92</td>
<td>-0.268</td>
<td>1.74</td>
<td>840 m</td>
<td>930 m</td>
</tr>
<tr>
<td>[UO$_2$(DABAAPT)$_2$(NCS)$_2$]</td>
<td>6.88</td>
<td>-0.276</td>
<td>1.74</td>
<td>837 w</td>
<td>928 m</td>
</tr>
<tr>
<td>[UO$_2$(DABAAPT)$_2$(CH$_3$COO)$_2$]</td>
<td>6.76</td>
<td>-0.270</td>
<td>1.74</td>
<td>830 m</td>
<td>920 m</td>
</tr>
<tr>
<td>[UO$_2$(DABAAPT)$_2$(ClO$_4$)$_2$]</td>
<td>6.88</td>
<td>-0.307</td>
<td>1.74</td>
<td>835 m</td>
<td>930 m</td>
</tr>
</tbody>
</table>

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 ($v_1$) [38]. Another observation is that a plot of ($v_1$ + $v_3$) 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 [UO$_2$(DABAAPT)$_2$(ClO$_4$)$_2$] the presence of the $v_3$ (1090 cm$^{-1}$) and $v_4$ (620 cm$^{-1}$) bands indicate that the T$_2$ symmetry of ClO$_4^-$ is maintained in this complex and suggests the presence of ClO$_4^-$ outside the coordination sphere [39, 40]. In the [UO$_2$(DABAAPT)$_2$(NCS)$_2$] complex, the three fundamental absorption C-N stretch ($v_1$ at 2070 cm$^{-1}$), C-S stretch ($v_3$ at 855 cm$^{-1}$) and N-C-S bending ($v_2$ at 475 cm$^{-1}$) are identified. These frequencies are associated with terminal N-bonded isothiocyanate ions [41, 42].

The infrared studied of dioxouranium(VI) nitrato 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 nitrato complexes. However, Curtis et al. [44] showed that the overtone and combination bands of the nitrato group sometimes might be used to distinguish monodentate and bidentate nitrato 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 nitrato groups. The fundamental vibrational modes of the nitrato group in [UO₂(DABAAAPT)(NO₃)₂] complex occur at 1520 (ν₄), 1295 (ν₅), 1030 (ν₆), 805 (ν₇), 740 (ν₈) and 710 cm⁻¹ (ν₉). The nitrato 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 UO₂(NO₃)₂.2H₂O, UO₂(NO₃)₂.2Apy and UO₂(NO₃)₂.AcyPy [46, 47].

Similar to nitrato, the acetato 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 [UO₂(DABAAAPT)(CH₃COO)] is monomeric and the infrared spectra of this complex shows two bands at 1550 and 1460 cm⁻¹ attributed to asymmetric and the symmetric stretching vibrations of COO⁻, respectively [49, 50]. A difference, Δν(COO⁻), of ~ 90 cm⁻¹ suggests bidentate 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 °C and is completed at ~ 480 °C. The break in the curves in the 340 °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 °C there is an additional decrease in weight due to loss of second organic ligand molecule. For nitrat and acetato complexes the loss at ~ 340 °C is found to be 51.22-55.59%. At this stage only the organic ligand molecule is lost. The oxide U₃O₈ is formed around 750 °C via the formation of UO₃, following which is no measurable change in weight [51]. In summary, these changes can be written as:

\[
\begin{align*}
\text{UO}_2\text{X}_2\cdot 2\text{(DABAAAPT)} & \rightarrow \text{UO}_2\text{X}_2\cdot \text{(DABAAAPT)} & \rightarrow & \text{UO}_2\text{X}_2 & \rightarrow & [\text{UO}_3] \\
& \rightarrow & \text{U}_3\text{O}_8 & (X = \text{Br}^-, \text{NCS}^- \text{or ClO}_4^-)
\end{align*}
\]

\[
\begin{align*}
\text{UO}_2\text{X}_2\cdot \text{(DABAAAPT)} & \rightarrow \text{UO}_2\text{X}_2 & \rightarrow & [\text{UO}_3] & \rightarrow & \text{U}_3\text{O}_8 \\
& (X = \text{NO}_3^- \text{or CH}_3\text{COO}^-)
\end{align*}
\]

**Stereochemistry.** In the complex UO₂(H₂O)₃(NO₃)₃, Glueckauf and Mckay [52] suggested that dioxouranium(VI) nitrate forms a covalent complex possibly involving the 5f-orbitals. The IR data of the [UO₂(DABAAAPT)(NO₃)₂] complex suggest bicovalent NO₃⁻ 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 [UO₂(DABAAAPT)(CH₃COO)_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 [UO$_4$(DABAAPT)(ClO$_4$)$_2$] complex, both perchlorate groups are ionic. Thus this complex, the uranium atom has a coordination number of eight [15].

Table 4. Thermoanalytical results of UO$_2$ complexes of DABAAPT.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Sample weight (mg)</th>
<th>Residual weight (mg)</th>
<th>Ligand mass loss (%)</th>
<th>Residual (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>240-340 °C</td>
<td>390-480 °C</td>
</tr>
<tr>
<td>UO$_4$Br$_2$.2(DABAAPT)</td>
<td>20.2</td>
<td>4.50</td>
<td>Theor. $^a$ 32.71</td>
<td>Exp. 33.16</td>
</tr>
<tr>
<td>UO$_4$(NO$_3$)$_2$.2(DABAAPT)</td>
<td>19.1</td>
<td>6.60</td>
<td>Theor. $^a$ 50.81</td>
<td>Exp. 51.22</td>
</tr>
<tr>
<td>UO$_4$(NCS)$_2$.2(DABAAPT)</td>
<td>17.9</td>
<td>4.00</td>
<td>Theor. $^a$ 33.91</td>
<td>Exp. 34.27</td>
</tr>
<tr>
<td>UO$_4$(CH$_3$COO)$_2$.2(DABAAPT)</td>
<td>16.8</td>
<td>6.30</td>
<td>Theor. $^a$ 55.29</td>
<td>Exp. 55.59</td>
</tr>
<tr>
<td>UO$_4$(ClO$_4$)$_2$.2(DABAAPT)</td>
<td>15.2</td>
<td>3.25</td>
<td>Theor. $^a$ 31.72</td>
<td>Exp. 32.16</td>
</tr>
</tbody>
</table>

$^a$Calculated for loss of 1 mole of DABAAPT, $^b$calculated for total loss of DABAAPT. $^c$calculated as UO$_4$.

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REFERENCES
