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Synthesis, Structural, and Thermal Aspects of Dioxouranium(VI) Coordination Compounds of Semicarbazones Derived from 4-Aminoantipyrine

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ABSTRACT

A series of 18 new coordination compounds of dioxouranium(VI) with semicarbazones of 4-aminoantipyrine, viz., 4[*N*-(*p*-dimethylaminobenzylidene)amino]antipyrine semicarbazone (DABAAPS), 4[*N*-(2′-nitrobenzylidene)amino]antipyrine semicarbazone (2′-NO_2BAAPS), and 4[*N*-(3′-nitrobenzylidene)amino]antipyrine semicarbazone (3′-NO_2BAAPS) of the general composition $[UO_2L_2X_2]$ ($X = Br$, I, or NCS), $[UO_2L_2](ClO_4)_2$, $[UO_2L(NO_3)_2]$, and $[UO_2L(OOCCH_3)_2]$ ($L =$ DABAAPS, 2′-NO_2BAAPS, and 3′-NO_2BAAPS) were synthesized in non-aqueous solution and

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characterized on the basis of elemental analyses, electrical conductivity, magnetic moments, and IR spectral studies. In all of the complexes, these ligands act as neutral tridentate (N, N, O) ligands. In all dioxouranium(VI) complexes, the ν_1 and ν_3 modes are assigned to $845-825\,cm^{-1}$ and $930-910\,cm^{-1}$, respectively. 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 using Badger's formula. The probable coordination number of U(VI) varies from 8–10 in these complexes. The thermal properties of these compounds are also discussed.

Key Words: Dioxouranium(IV); Semicarbazones; Coordination compounds.

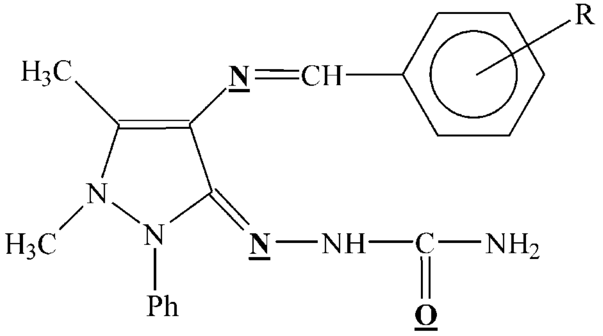
INTRODUCTION

The uranyl ion is quite peculiar both in its own structure and in its coordination chemistry. The U–O bond distances in the linear O–U–O ion are very short compared with the L–U distances in the equatorial coordination plane and also to the size of the uranium atom. This means that the UO_2^{2+} group roughly can be considered, from the geometric point of view, as a single particle. Since coordination occurs in a plane normal to the O–U–O axis and the number 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-group metal ions. This peculiarity could be of great interest not only from the speculative point of view, but also because of the various possible applications involving the technology and the uses of uranium derivatives. Uranyl(VI) is a typical hard Lewis acid, as shown by comparing the tendency to coordination of oxygen and sulfur donors and also of nitrogen and phosphorus donors.[1,2] Both oxygen and nitrogen have an appreciable tendency to coordinate to uranyl(VI). In view of this, in the present work, we report a new series of 18 coordination compounds of dioxouranium(VI) with the semicarbazones of 4-aminoantipyrines *viz.*, [*N*-(*p*-dimethylaminobenzylidene)amino]-antipyrine semicarbazone (DABAAPS), 4[*N*-(2′-nitrobenzylidene)amino]antipyrine semicarbazone (2′-NO_2BAAPS), and 4[*N*-(3′-nitrobenzylidene)amino]antipyrine semicarbazone (3′-NO_2BAAPS), as shown in Fig. 1.

EXPERIMENTAL

Materials and Methods

Uranyl nitrate and uranyl acetate were used as received from B.D.H. Uranyl nitrate was dehydrated by keeping it over concentrated sulfuric



R = 4'-N(CH$_3$)$_2$; L = DABAAPS
R = 2'-NO$_2$; L = 2'-NO$_2$BAPAAS
R = 3'-NO$_2$; L = 3'-NO$_2$BAPAAS

Figure 1. Structure of the ligands L.

acid.[3] Uranyl bromide was prepared from uranyl acetate by treating it with aqueous HBr. After evaporating most of the solvent, the solution was kept over concentrated sulfuric acid until yellow crystals were separated out,[4] and uranyl iodide was obtained by treating uranyl nitrate with barium iodide in dry ether.[5] Uranyl thiocyanate was prepared by mixing an alcoholic solution of anhydrous uranyl nitrate and potassium thiocyanate.[6] Uranyl perchlorate was prepared by digesting uranyl nitrate with the calculated amount of perchloric acid and evaporating the mixture to dryness.[7]

The chemical analyses and physico-chemical measurements were performed as reported earlier.[8,9] Infrared spectra in the range of 4000–200 cm^{-1} were measured on a Perkin Elmer Infracord Spectrophotometer model 521 in Nujol mulls at Department of Chemistry, Delhi University. Thermogravimetric analyses were carried out at Santon Red Craft Thermobalance Model T-750 in open air.

Synthesis of Ligands DABAAPS, 2′-NO$_2$BAAPS, and 3′-NO$_2$BAAPS

These were synthesized in two steps by reported methods.[10,11]

(1) A solution of aromatic aldehyde (1 mmol) in absolute ethanol (20 mL) was mixed with 4-aminoantipyrine (2.2234 g, 1.1 mmol) in the same solvent

(20 mL) and the reaction mixture was refluxed for 2–3 hr. On cooling, a yellow crystalline product separated, which was filtered and recrystallized in the same solvent.

(2) The semicarbazones were prepared by the following method. A 15 g (0.134 mol) of semicarbazide hydrochloride ($H_2NNHCONH_2 \cdot HCl$) and 13 g (0.15 mol) of sodium acetate (CH_3COONa) were dissolved in 60 mL of distilled water and mixed with the corresponding Schiff base (0.1 mol) [prepared in step (1) in ethanol (25 mL)]. The mixture was refluxed on a water bath for 1 hr. On cooling, the semicarbazone crystallized out. It was filtered and washed with 50% ethanol. The product was recrystallized from ethanol. The light yellow crystals were filtered and dried at ~60 °C in an electric oven.

Synthesis of the Complexes

$[UO_2L_2X_2]$ (X = Br, I, and NCS) (L = DABAAPS, 2′-NO_2BAAPS, or 3′-NO_2BAAPS)

A methanolic solution (10 mL) of UO_2X_2 (X = Br, I, or NCS) (1 mmol) was added drop-wise to the respective ligand solution (2.1 mmol in 20 mL of methanol). The reaction mixture was refluxed for 2 hr on a water bath. A solid compound was obtained after partial evaporation under a fan. This was filtered by suction, washed with methanol, and dried under vacuum over P_4O_{10}.

$[UO_2L_2](ClO_4)_2$ (L = DABAAPS, 2′-NO_2BAAPS, or 3′-NO_2BAAPS)

To a solution of $UO_2(ClO_4)_2$ (1 mmol, 0.63 g) in isopropyl alcohol (10 mL) was added a hot solution of the corresponding ligand (2 mmol) in the same solvent (20 mL). In case of DABAAPS, the desired complex was obtained immediately. However, in the case of 2′-NO_2BAAPS and 3′-NO_2BAAPS, refluxing of the reaction mixture for 1–2 hr was required. On cooling to room temperature, the desired complex was obtained. The solid product was filtered, washed with isopropyl alcohol, and dried *in vacuo* over P_4O_{10}.

$[UO_2L(NO_3)_2]$ (L = DABAAPS, 2′-NO_2BAAPS, or 3′-NO_2BAAPS)

To a solution of $UO_2(NO_3)_2$ (1 mmol, 0.56 g) in ethyl acetate (10 mL) was added the corresponding ligand (1.1 mmol, 10 mL) in the same solvent and the reaction mixture was refluxed for about 1 hr and then the solution was left overnight at room temperature. A fine-crystalline product was thus obtained;

it was filtered by suction, washed with ethyl acetate, and finally dried in vacuum over P_4O_{10}.

$[UO_2L(OOCCH_3)_2]$ (L = DABAAPS, 2′-NO_2BAAPS, or 3′-NO_2BAAPS)

To a solution of $UO_2(OOCCH_3)_2$ (1 mmol, 0.66 g) in acetone (10 mL) was added a hot (*ca.* 50 °C) acetonic solution of the corresponding ligand (1.1 mmol in 10 mL of acetone) with constant stirring. Stirring was continued for 2 hr to complete the reaction. The solid product was filtered in a sintered crucible, washed with acetone and diethyl ether, and finally dried in vacuum over P_4O_{10}.

RESULTS AND DISCUSSION

The interaction of dioxouranium(VI) salts with DABAAPS, 2′-NO_2BAAPS, or 3′-NO_2BAAPS results in the formation of $[UO_2L_2X_2]$ (X = Br, I, or NCS), $[UO_2L_2](ClO_4)_2$, $[UO_2L(NO_3)_2]$, or $[UO_2L(OOCCH_3)_2]$ (L = DABAAPS, 2′-NO_2BAAPS, or 3′-NO_2BAAPS) according to the following general equations.

$$\underset{(X = Br,\ I,\ \text{or NCS})}{UO_2X_2} + 2L \xrightarrow[\text{Reflux for 2 hr and cool}]{\text{Methanol}} [UO_2L_2X_2] \quad (1)$$

$$UO_2(ClO_4)_2 + 2L \xrightarrow[\text{Reflux for 1–2 hr}]{\text{Isopropyl alcohol}} [UO_2L_2](ClO_4)_2 \quad (2)$$

$$UO_2(NO_3)_2 + L \xrightarrow[\substack{\text{Reflux for 1 hr and left}\\ \text{stand over night}}]{\text{Ethyl acetate}} [UO_2L(NO_3)_2] \quad (3)$$

$$UO_2(OOCCH_3)_2 + L \xrightarrow[\text{Stirring for 1 hr}]{\text{acetone}} [UO_2L(OOCCH_3)_2] \quad (4)$$

$$(L = \text{DABAAPS},\ 2'\text{-}NO_2\text{BAAPS},\ \text{or}\ 3'\text{-}NO_2\text{BAAPS})$$

The analytical data of these complexes are recorded in Table 1. The complexes are anhydrous, which is evident from the analytical, infrared, and thermal studies. All of the complexes are quite stable and can be stored for long periods. The complexes are generally soluble in common organic solvents. All the complexes except $[UO_2L_2](ClO_4)_2$ are non-electrolytes in $PhNO_2$. For the perchlorate complexes, $[UO_2L_2](ClO_4)_2$, we suggest ionic perchlorate groups, the presence of which was further confirmed by the infrared spectra. Data on the molecular weight of the complexes in freezing $PhNO_2$ are also shown in Table 1 along with values calculated on the basis of the established formula of the complexes. The ratio of molecular weight

Table 1. Analytical, conductivity and molecular weight data of dioxouranium(VI) complexes of semicarbazones.

Complex (empirical formula)	Yield (%)	Color	M.p./ decomp. (°C)	Analysis: found (calcd) (%)					M.W. found (calcd)	Λ_m ($ohm^{-1} cm^2 mol^{-1}$)
				C	H	N	U	Anion		
$[UO_2(DABAAPS)_2Br_2]$ $(C_{42}H_{50}Br_2N_{14}O_4U)$	80	Dark yellow	215 d	41.38 (41.58)	4.07 (4.13)	16.09 (16.17)	19.53 (19.63)	12.98 (13.20)	1208 (1212)	4.7
$[UO_2(DABAAPS)_2I_2]$ $(C_{42}H_{50}I_2N_{14}O_4U)$	78	Yellow brown	215 d	38.39 (38.59)	3.76 (3.83)	14.92 (15.00)	18.13 (18.22)	19.20 (19.44)	1301 (1306)	5.1
$[UO_2(DABAAPS)_2(NCS)_2]$ $(C_{44}H_{50}N_{16}O_4S_2U)$	80	Pinkish yellow	210 d	45.03 (45.20)	4.24 (4.28)	19.06 (19.17)	20.23 (20.37)	9.82 (9.93)	1162 (1168)	3.9
$[UO_2(DABAAPS)_2](ClO_4)_2$ $(C_{42}H_{50}Cl_2N_{14}O_{12}U)$	75	Yellow	192 d	40.06 (40.28)	3.89 (3.99)	15.55 (15.56)	18.93 (19.02)	15.49 (15.90)	420 (1251)	51.9
$[UO_2(DABAAPS)(NO_3)_2]$ $(C_{21}H_{25}N_9O_9U)$	82	Yellow	210	31.96 (32.10)	3.14 (3.18)	15.98 (16.05)	30.19 (30.31)	—	782 (785)	4.1
$[UO_2(DABAAPS)(OOCCH_3)_2]$ $(C_{25}H_{31}N_7O_7U)$	78	Yellow	210 d	38.39 (38.51)	3.92 (3.98)	12.49 (12.58)	30.42 (30.55)	—	775 (779)	3.8
$[UO_2(2'\text{-}NO_2BAAPS)_2Br_2]$ $(C_{38}H_{38}Br_2N_{14}O_8U)$	78	Dark yellow	215 d	37.37 (37.50)	3.08 (3.13)	15.99 (16.11)	19.43 (19.57)	13.03 (13.15)	1209 (1216)	4.3
$[UO_2(2'\text{-}NO_2BAAPS)_2I_2]$ $(C_{38}H_{38}I_2N_{14}O_8U)$	75	Brown yellow	215 d	34.62 (34.81)	2.86 (2.90)	14.87 (14.96)	18.05 (18.16)	19.19 (19.38)	1304 (1310)	4.9

$[UO_2(2'\text{-}NO_2BAAPS)_2(NCS)_2]$	80	Yellow	215 d	40.77	3.19	18.99	20.20	9.79	1165	3.8
($C_{40}H_{38}N_{16}O_8S_2U$)				(40.96)	(3.24)	(19.11)	(20.30)	(9.89)	(1172)	
$[UO_2(2'\text{-}NO_2BAAPS)_2](ClO_4)_2$	75	Yellow	190 d	36.17	2.99	15.49	18.85	15.73	421	52.3
($C_{38}H_{38}Cl_2N_{14}O_{16}U$)				(36.33)	(3.03)	(15.61)	(18.96)	(15.85)	(1255)	
$[UO_2(2'\text{-}NO_2BAAPS)(NO_3)_2]$	82	Yellow	210	28.74	2.37	15.93	30.11	—	783	4.1
($C_{19}H_{19}N_7O_{11}U$)				(28.97)	(2.41)	(16.01)	(30.24)		(787)	
$[UO_2(2'\text{-}NO_2BAAPS)(OOCCH_3)_2]$	78	Yellow	215 d	35.23	3.16	12.43	30.29	—	777	3.9
($C_{23}H_{25}N_7O_9U$)				(35.34)	(3.20)	(12.54)	(30.47)		(781)	
$[UO_2(3'\text{-}NO_2BAAPS)_2Br_2]$	80	Dark yellow	215 d	37.36	3.08	16.00	19.44	13.03	1210	4.2
($C_{38}H_{38}Br_2N_{14}O_8U$)				(37.50)	(3.13)	(16.11)	(19.57)	(13.15)	(1216)	
$[UO_2(3'\text{-}NO_2BAAPS)_2I_2]$	70	Brownish yellow	215 d	34.67	2.86	14.87	18.06	19.20	1304	4.8
($C_{38}H_{38}I_2N_{14}O_8U$)				(34.81)	(2.90)	(14.96)	(18.16)	(19.38)	(1310)	
$[UO_2(3'\text{-}NO_2BAAPS)_2(NCS)_2]$	80	Yellow	220 d	40.82	3.19	19.00	20.20	9.78	1165	3.7
($C_{40}H_{38}N_{16}O_8S_2U$)				(40.96)	(3.24)	(19.11)	(20.30)	(9.89)	(1172)	
$[UO_2(3'\text{-}NO_2BAAPS)_2](ClO_4)_2$	72	Yellow	190 d	36.18	2.99	15.49	18.84	15.74	422	52.9
($C_{38}H_{38}Cl_2N_{14}O_{16}U$)				(36.33)	(3.03)	(15.61)	(18.96)	(15.85)	(1255)	
$[UO_2(3'\text{-}NO_2BAAPS)(NO_3)_2]$	82	Yellow	210 d	28.79	2.37	15.92	30.12	—	782	4.1
($C_{19}H_{19}N_7O_{11}U$)				(28.97)	(2.41)	(16.01)	(30.24)		(787)	
$[UO_2(3'\text{-}NO_2BAAPS)(OOCCH_3)_2]$	80	Yellow	210 d	35.19	3.16	12.43	30.30	—	776	3.7
($C_{23}H_{25}N_7O_9U$)				(35.34)	(3.20)	(12.54)	(30.47)		(781)	

observed for $[UO_2L_2X_2]$ (X = Br, I, or NCS) and $[UO_2LX_2]$ (X = NO_3 or CH_3COO) to that calculated is ~0.98, which shows that the complexes are monomeric in solution. In case of $[UO_2L_2](ClO_4)_2$, the ratios are ~0.33, which indicates that three species are present in solution and the compound is a 1 : 2 electrolyte. The dioxouranium(VI) compounds are diamagnetic depending upon the diamagnetism of the other ions and the surrounding ligand field. The magnetic susceptibilities are independent of field strength and temperature.[12] The ground states of dioxouranium(VI) salts contain no unpaired electrons; the compounds, therefore, are weakly diamagnetic as observed by others.[13]

Infrared Spectra

The infrared spectra of the three semicarbazone ligands derived from 4-aminoantipyrine are too complex to allow definite band assignments. Empirical assignments by referring to group frequencies may not be effective as coupling between various modes of vibration are expected as a result of resonance in the pyrazolone ring. Infrared absorptions of all three semicarbazones of 4-aminoantipyrine have been assigned by comparison of their spectra with those of antipyrine, 4-aminoantipyrine,[14–16] and some previous communications on semicarbazones.[17–19]

In the complexes, as expected, the $\nu(NH_2)$ band of the hydrazinic nitrogen of semicarbazide (~1622 cm^{-1}) is absent in the infrared spectra of DABAAPS, 2′-NO_2BAAPS, and 3′-NO_2BAAPS.[19] It has also been observed that the amide-II band in the complexes is shifted towards the lower energy side compared to that of the semicarbazones. This effect is due to the electron density drift from the hydrazinic nitrogen[20] to metal ion. The characteristic absorption of the carbonyl group in DABAAPS, 2′-NO_2BAAPS or 3′-NO_2BAAPS is observed in the 1700–1680 cm^{-1} region.[21] In the complexes, these bands are shifted towards lower energy in the 1650–1640 cm^{-1} region (Table 2). The amide-II band in the free ligands has been observed at ~1565 cm^{-1}. In all of the present complexes, this band is also shifted towards lower wave numbers by ~30 cm^{-1}. This observation suggests coordination through the carbonyl oxygen atom. The strong bands at ~1600 cm^{-1} in the semicarbazones apparently have a large contribution from the $\nu(C{=}N)$ mode of the semicarbazone moiety.[22] This has been observed as a blue-shift in the position of the (C=N) band in all the complexes as compared to the free ligands. Another strong band was observed at ~1610 cm^{-1} due to the azomethine (C=N) absorption. On complexation, this band is shifted towards the lower frequency region, clearly indicating the coordination through the azomethine N atom.[23,24] In the far-infrared region the bands

Table 2. Key infrared bands (cm^{-1}) of the ligands and their dioxouranium(IV) complexes of semicarbazones.

Compounds	ν(C=N) (azomethinic)	ν(C=N) (hydrazinic)	ν(C=O)			ν(U–O), ν(U–N)
			I	II	III	
DABAAPS	1620 s	1605 s	1705 s	1570 s	1350 m	—
[UO_2(DABAAPS)$_2$$Br_2$]	1595 s	1630 s	1645 s	1540 m	1335 m	482 m, 385 w
[UO_2(DABAAPS)$_2$$I_2$]	1600 s	1635 s	1650 s	1542 m	1333 m	480 m, 382 w
[UO_2(DABAAPS)$_2$(NCS)$_2$]	1598 s	1638 s	1642 s	1545 m	1342 m	478 m, 378 w
[UO_2(DABAAPS)$_2$](ClO_4)$_2$	1595 s	1635 s	1648 s	1540 m	1340 m	482 m, 390 w
[UO_2(DABAAPS)(NO_3)$_2$]	1590 s	1632 s	1640 s	1545 m	1342 m	485 m, 382 w
[UO_2(DABAAPS)($OOCCH_3$)$_2$]	1595 s	1635 s	1642 s	1539 m	1340 m	480 m, 382 w
2′-NO_2BAAPS	1612 s	1602 s	1700 s	1565 s	1340 m	—
[UO_2(2′-NO_2BAAPS)$_2$$Br_2$]	1585 s	1630 s	1640 s	1530 m	1330 m	480 m, 390 w
[UO_2(2′-NO_2BAAPS)$_2$$I_2$]	1582 s	1635 s	1635 s	1535 m	1328 m	482 m, 385 w
[UO_2(2′-NO_2BAAPS)$_2$(NCS)$_2$]	1585 s	1638 s	1643 s	1538 m	1325 m	478 m, 382 w
[UO_2(2′-NO_2BAAPS)$_2$](ClO_4)$_2$	1580 s	1635 s	1645 s	1536 m	1330 m	475 m, 380 w
[UO_2(2′-NO_2BAAPS)(NO_3)$_2$]	1578 s	1632 s	1640 s	1535 m	1328 m	485 m, 382 w
[UO_2(2′-NO_2BAAPS)($OOCCH_3$)$_2$]	1582 s	1630 m	1642 s	1537 m	1326 m	480 m, 385 w
3′-NO_2BAAPS	1608 s	1600 s	1702 s	1565 s	1340 s	—
[UO_2(3′-NO_2BAAPS)$_2$$Br_2$]	1590 s	1628 s	1650 s	1530 m	1325 m	460 m, 382 w
[UO_2(3′-NO_2BAAPS)$_2$$I_2$]	1580 m	1630 m	1642 m	1528 m	1330 m	472 m, 380 w
[UO_2(3′-NO_2BAAPS)$_2$(NCS)$_2$]	1585 m	1625 s	1645 s	1535 m	1327 m	472 m, 385 w
[UO_2(3′-NO_2BAAPS)$_2$](ClO_4)$_2$	1585 m	1628 m	1645 s	1530 m	1322 m	465 m, 375 w
[UO_2(3′-NO_2BAAPS)(NO_3)$_2$]	1590 m	1630 m	1642 m	1537 m	1325 m	475 w, 382 w
[UO_2(3′-NO_2BAAPS)($OOCCH_3$)$_2$]	1582 m	1628 m	1642 m	1535 m	1322m	470 m, 380 w

due to $\nu(\mathrm{U{-}M})/\nu(\mathrm{U{-}O})$ are also observed[11,25] (Table 2). From these facts, it is clearly indicated that the ligands serve as tridentate ligands, coordinating through the carbonyl-O; hydrazone-N and azomethine-N atoms.

Oxocation (O═U═O) Vibrations

The uranyl ion UO_2^{2+} is quite peculiar both in its own structure and its coordination compounds.[26–28] The ion retains its identity over a wide range of vibrations under the experimental conditions and may be considered, from the geometric point of view, as a single particle. It has four fundamental vibrations.[28] The non-degenerate symmetric stretching vibration, ν_1, normally IR-forbidden, occurs in the range 900–800 cm^{-1}. The non-degenerate asymmetric stretching vibration, ν_3, which is IR-active, occurs at ~1000–900 cm^{-1}. The doubly degenerate O–U–O bending vibration, ν_2, which is IR-active, appears at ~250 cm^{-1}.

In the present investigation, $\nu(\mathrm{U{=}O})$ in all the complexes (Table 3) has been assigned in the 930–920 and 840–825 cm^{-1} region as ν_3 and ν_1 frequencies, respectively (Table 3). The infrared absorption spectra of dioxouranium(VI) compounds give valuable information regarding the various vibrations due to the uranyl ions, anions, and crystal lattice. The available structural data indicate that the uranyl bond length is not constant in the various uranyl compounds. In general, single crystal x-ray or neutron diffraction studies are required to determine accurate bond lengths. Because of 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 is generally conceded that in the ground state the uranyl ion has a linear structure in the solid phase and probably in the solution phase.[29,30]

In the present studies of Schiff base complexes of uranyl ions, it has been observed that the ν_1 mode of the uranyl ion is of weak intensity and the ν_3 mode is of strong intensity in the IR spectra (Table 3). A group theoretical consideration[29,30] shows that a linear and symmetrical triatomic UO_2^{2+} ion possessing $D_{\infty h}$ symmetry gives rise to three fundamental modes of vibrations. Wilson's GF matrix method[31,32] has been used to determine the stretching and interaction force constants. The results were in turn used to evaluate U–O bond distances following Badger's formula.[33] The force constants, bond distances, and spectral data used herein are summarized in Table 3.

It is apparent from Table 3 that the bond length decreases with the increase in the value of the symmetric stretching frequency (ν_1).[29] Another observation is that a plot of $(\nu_1 + \nu_3)$ vs. the force constant gives a straight

Table 3. Various force constants (mdynes Å^{-1}), U–O bond distances (Å) and frequencies (cm^{-1}) of ν_1 and ν_3 of the UO_2(VI) complexes of the semicarbazone ligands.

Complex	U–O force constant	Force constant due to interaction between bonds	U–O bond distance	ν_1	ν_3
$[UO_2(DABAAPS)_2Br_2]$	6.80	−0.34	1.73	828	928
$[UO_2(DABAAPS)_2I_2]$	6.91	−0.26	1.73	840	930
$[UO_2(DABAAPS)_2(NCS)_2]$	6.80	−0.30	1.74	830	925
$[UO_2(DABAAPS)_2](ClO_4)_2$	6.87	−0.27	1.73	837	928
$[UO_2(DABAAPS)(NO_3)_2]$	6.87	−0.30	1.73	835	925
$[UO_2(DABAAPS)(OOCCH_3)_2]$	6.76	−0.26	1.74	830	920
$[UO_2(2'\text{-}NO_2BAAPS)_2Br_2]$	6.72	−0.30	1.74	825	920
$[UO_2(2'\text{-}NO_2BAAPS)_2I_2]$	6.80	−0.23	1.74	835	920
$[UO_2(2'\text{-}NO_2BAAPS)_2(NCS)_2]$	6.72	−0.30	1.74	825	920
$[UO_2(2'\text{-}NO_2BAAPS)_2](ClO_4)_2$	6.81	−0.36	1.73	827	930
$[UO_2(2'\text{-}NO_2BAAPS)(NO_3)_2]$	6.87	−0.23	1.74	835	930
$[UO_2(2'\text{-}NO_2BAAPS)(OOCCH_3)_2]$	6.85	−0.33	1.73	832	930
$[UO_2(3'\text{-}NO_2BAAPS)_2Br_2]$	6.87	−0.27	1.73	837	928
$[UO_2(3'\text{-}NO_2BAAPS)_2I_2]$	6.80	−0.30	1.74	830	925
$[UO_2(3'\text{-}NO_2BAAPS)_2(NCS)_2]$	6.77	−0.36	1.74	825	927
$[UO_2(3'\text{-}NO_2BAAPS)_2](ClO_4)_2$	6.87	−0.27	1.73	837	928
$[UO_2(3'\text{-}NO_2BAAPS)(NO_3)_2]$	6.91	−0.26	1.73	840	930
$[UO_2(3'\text{-}NO_2BAAPS)(OOCCH_3)_2]$	6.85	−0.36	1.73	830	932

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.[28] The calculated values of the U–O bond distances of the present complexes are well[29,30] within the range of 1.736–1.7423 Å.

Anions

The detailed proposals for the assignment of infrared bands of uranyl nitrato complexes were first reported in 1958 by Gatehouse and Comyns.[3] Although several authors[27,34,35] reported the IR of a series of complexes of uranyl nitrate, no satisfactory explanations have been given for deciding between monodentate and bidentate nitrate complexes. Many infrared data on uranyl complexes can be found in the work of Bullock;[36] they are consistent with the presence of bidentate nitrato groups. The fundamental vibrational modes of the nitrato group for the complexes studied in the present work have been identified. It is clear that a weak band at ~710 cm^{-1} may be assigned to ν_5 while ν_3 occurs near 745 cm^{-1}. The separation of these two frequencies is of the order ~35 cm^{-1} and similar values were reported previously.[36] Other frequencies such as ν_1, ν_2, ν_4, and ν_6 are comparable to these reported bidentate complexes. Thus, it can be said that in the present complexes the nitrato group behaves as a bidentate ligands.

The C–N stretching frequency in the present thiocyanato complexes of dioxouranium appears in the 2070–2040 cm^{-1} range, which lies on the borderline for distinguishing between sulfur and nitrogen bonding in the thiocyanate,[37–39] although the high relative intensity of the band in these cases suggests that the thiocyanate groups are N-bonded.[40] The frequency of the C–S stretching vibration has also been used to diagnose the bonding mode in thiocyanates.[38,39] The C–S band, identified in the 840–780 cm^{-1} region, further confirms that the thiocyanate group is almost certainly N-bonded,[40] the N–C–S bending (ν_2) has also been identified in these complexes.

The occurrence of two strong bands at ~1070 and 620 cm^{-1} in the spectra of the $[UO_2L_2](ClO_4)_2$ complexes and attributed to ν_3 and ν_4 vibrations of ionic perchlorate confirms[41,42] the presence of perchlorate groups outside the coordination sphere of the complex.[41,42]

Similar to the nitrato ion, the acetato ion is also potentially a bidentate ligand towards the uranyl group. In these complexes, the acetato ion behaves as a covalent bidentate and the coordination number is found to be seven or eight depending on whether the complexes are monomeric or dimeric.[43] In the present case, all of the uranyl acetato complexes of the semicarbazones are monomeric and the infrared spectra of these complexes show two bands in the 1560–1545 and 1475–1460 cm^{-1} regions attributed, respectively, to the antisymmetric and symmetric stretching vibrations of COO$^-$.[42,44]

Thermal Studies

The thermal results of UO_2(VI) complexes of DABAAPS and 2′-NO_2BAAPS are summarized in Table 4. The TG curves of the complexes clearly indicate the absence of water molecules in the complexes. The entire pyrolysis curves of both complexes behave similarly and show that decomposition of the complexes starts at ~230 °C and ends at ~490 °C. The break in the curves in the 325–340 °C region indicates that at this stage only one molecule of organic ligand molecule has been lost. In the temperature range of 410–470 °C, there is an additional decrease in weight due to loss of both organic ligand molecules. The oxide U_3O_8 is formed at 625 °C via the formation of UO_3, following which there is no measurable change in weight.[45] In brief, these changes can be summarized as follows:

$$[UO_2L_2X_2] \longrightarrow [UO_2LX_2] \longrightarrow UO_2X_2 \longrightarrow [UO_3] \longrightarrow U_3O_8$$

(X = Br or NCS; L = DABAAPS or 2′-NO_2BAAPS)

$$[UO_2L_2](ClO_4)_2 \longrightarrow [UO_2L](ClO_4)_2 \longrightarrow UO_2(ClO_4)_2 \longrightarrow [UO_3] \longrightarrow U_3O_8$$

(L = DABAAPS or 2′-NO_2BAAPS)

Stereochemistry

In the halo and thiocyanato complexes, both anions are covalently bonded. The $[UO_2L_2X_2]$ complexes (X = Br, I, or NCS; L = DABAAPS, 2′-NO_2BAAPS, or 3′-NO_2BAAPS) may be considered to have a 10-coordinate uranium atom. In the complex $[UO_2(NO_3)_2(H_2O)_4]$, Glueckauf and McKay[46] suggested that dioxouranium(VI) nitrate forms covalent complexes possibly involving the 5f-orbitals. The IR data of all the dioxouranium(IV) nitrate complexes of semicarbazone also suggest a bidentate nature of the nitrato groups in theses complexes. Thus, tridentate organic ligand (DABAAPS, 2′-NO_2BAAPS, or 3′-NO_2BAAPS) complexes of dioxouranium(VI) nitrate may be considered to have a nine-coordinate uranium atom with five oxygen atoms (four oxygen from the two bidentate nitrato groups and one oxygen from amide) and two nitrogen atoms of azomethine groups in a plane perpendicular to the linear O–U–O group. Similar to the nitrato complexes, the dioxouranium(VI) acetato complexes with tridentate organic ligands and bidentate chelating acetato groups

Table 4. Thermal data of dioxouranium(VI) complexes of semicarbazones.

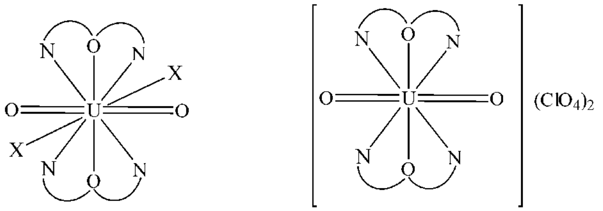
Complex	Sample weight (mg)	Residual mass (mg)	Ligand mass loss (%)				Residual (%) ($\sim$630 °C)	
			$t_1 - t_2$ (°C)		$t_3 - t_4$ (°C)			
			Calcd[a]	Found	Calcd[b]	Found	Calcd[c]	Found
[UO_2(DABAAPS)$_2$$Br_2$]	30.89	7.09	32.26	32.59	64.52	64.96	23.15	22.98
[UO_2(DABAAPS)$_2$(NCS)$_2$]	33.10	7.90	33.47	33.87	66.95	67.30	24.02	23.89
[UO_2(DABAAPS)$_2$](ClO_4)$_2$	28.62	6.37	31.25	31.49	62.51	63.08	22.43	22.27
[UO_2(2′-NO_2BAAPS)$_2$$Br_2$]	31.42	7.20	32.31	32.86	64.63	65.12	23.08	22.94
[UO_2(2′-NO_2BAAPS)$_2$(NCS)$_2$]	29.36	6.98	33.53	33.91	67.06	67.90	23.94	23.79
[UO_2(2′-NO_2BAAPS)$_2$](ClO_4)$_2$	27.62	6.23	31.31	31.89	62.62	63.26	22.36	22.56

Note: $t_1 = 250$ °C for DABAAPS/240 °C for 2′-NO_2BAAPS; $t_2 = 355$ °C for DABAAPS/340 °C for 2′-NO_2BAAPS; $t_3 = 390$ °C for DABAAPS/410 °C for 2′-NO_2BAAPS; $t_4 = 460$ °C for DABAAPS/470 °C for 2′-NO_2BAAPS.

[a] Calculated for loss of 1 mol of DABAAPS/2′-NO_2BAAPS.

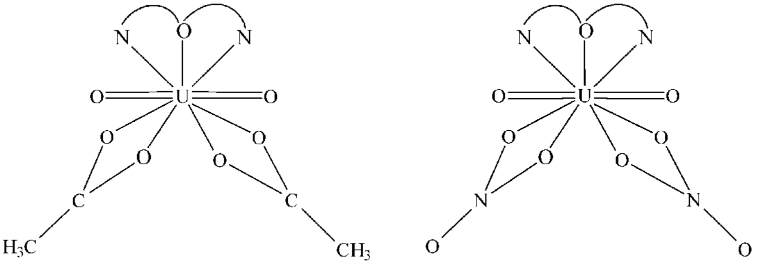
[b] Calculated for total loss of DABAAPS/2′-NO_2BAAPS.

[c] Calculated as U_3O_8.



(a) $[UO_2L_2X_2]$ (X = Br, I or NCS) (C.N. = 10)

(b) $[UO_2L_2](ClO_4)_2$ (C.N. = 8)



(c) $[UO_2L(OOCCH_3)_2]$ (C.N. = 9)

(d) $[UO_2L(NO_3)_2]$ (C.N. = 9)

Figure 2. Suggested structures of dioxouranium complexes of semicarbazones.

have a nine-coordinate structure. In $[UO_2L_2](ClO_4)_2$ (L = DABAAPS, 2′-NO_2BAAPS, or 3′-NO_2BAAPS), both perchlorato groups are ionic in nature and uranium has a coordination number of 8. The probable structures of these compounds are represented in Fig. 2.

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REFERENCES

1. Cattalini, L.; Croatto, U.; Degetto, S.; Tondello, E. Uranyl chelate complexes. Inorg. Chim. Acta Rev. **1971**, *5*, 19.

2. Arora, K.; Goyal, R.C.; Agarwal, D.D.; Agarwal, R.K. Dioxouranium(VI) metal complexes with neutral oxygen donor ligands. Rev. Inorg. Chem. **1998**, *18*, 283.
3. Gatehouse, B.M.; Comyns, A.E. Infrared spectra of uranyl nitrate hydrates and rubidium uranyl nitrate. J. Chem. Soc. **1958**, 3965.
4. Sandhu, S.S.; Sandhu, S.S., Jr. Complexes of ditertiary phosphines and arsine oxides with metal ions. Part IV. complexes of uranyl halides with oxides of 1,2-ethylene-*bis*-diphenylphosphine/arsine and 1,4-butylene *bis*-diphenyl phosphine/arsine. Indian J. Chem. **1973**, *11A*, 369.
5. Sidgwick, N.V. *The Chemical Elements and Their Compounds*; Oxford Press, U.K., 1952.
6. Savant, V.V.; Patel, C.C. Diphenyl sulphoxide complexes of oxovanadium(IV) and dioxouranium(VI). J. Inorg. Nucl. Chem. **1972**, *34*, 1462.
7. Ramamurthy, P.; Patel, C.C. Pyridine N-oxide complexes of zirconium, thorium, and uranyl perchlorates. Can. J. Chem. **1964**, *42*, 856.
8. Agarwal, R.K.; Srivastava, A.K.; Srivastava, T.N. Thorium(IV) complexes of 2,6-lutidine N-oxide and tetramethylene sulphoxide. Transition Met. Chem. **1980**, *5*, 95.
9. Srivastava, A.K.; Sharma, S.; Agarwal, R.K. Thorium(IV) and dioxouranium(VI) chelates of aromatic amine N-oxides. Inorg. Chim. Acta **1982**, *61*, 235.
10. Agarwal, R.K.; Agarwal, H.; Manglik, A.K. Chelating behaviour of 4[*N*-(benzylidene)amino]antipyrine semicarbazone towards lanthanide ions. Synth. React. Inorg. Met.-Org. Chem. **1996**, *26*, 1163.
11. Agarwal, R.K.; Agarwal, H.; Chakraborti, I. Studies on some thorium(IV) complexes with high coordination numbers derived from semicarbazones of 4-aminoantipyrine. Synth. React. Inorg. Met.-Org. Chem. **2004**, *34*, 1431–1452.
12. Day, J.P.; Venanzi, L.M. Some six coordinates of uranium(VI). J. Chem. Soc. (A) **1966**, 1363.
13. Misra, B.B.; Mohanty, S.R.; Murti, N.V.V.S.; Raychaudhuri, S. Sulphoxide complexes of thorium(IV) and uranyl(VI) chlorides and nitrates. Inorg. Chim. Acta **1979**, *28*, 275.
14. Agarwal, R.K.; Srivastava, A.K.; Srivastava, T.N. Thorium(IV) complexes of pyrazolone ligands. Proc. Natl. Acad. Sci. (India) **1981**, *51A*, 79 (Chem. Abstr. **1983**, *98*, 190594j).
15. Agarwal, R.K.; Rastogi, S.C. Infrared and thermal studies of uranyl(VI) complexes of antipyrine. Thermochim. Acta **1985**, *95*, 279.
16. Agarwal, R.K.; Prakash, J. Synthesis and characterization of thorium(IV) and dioxouranium(VI) complexes of 4-[*N*(2-hydroxy-1-naphthalidene)] amino antipyrine. Polyhedron **1991**, *10*, 2399.

17. Usha. Synthesis and Characterization of Transition Metal Complexes of Semicarbazones and Thiosemicarbazones; Ch. Charan Singh University: Meerut, 1996; Ph.D. Thesis.
18. Priyanka. A Comparative Studies of the Ligational Behaviour of Various Azomethines, viz., Hydrazones of Isoniazid, Semicarbazones, Thiosemicarbazones and Oximes Derived from 4-Aminoantipyrine Towards Biometal Ions; Ch. Charan Singh University: Meerut, 1995; Ph.D. Thesis.
19. Marykutty, P.V.; Parameswaran, G. Synthesis and characterization of Mn(II), Fe(II), Co(II), and Ni(II) complexes of anthracene carboxaldehyde semicarbazone. Asian J. Chem. **2001**, *13*, 905.
20. Lavanon, H.; Luz, Z. ESR and NMR of Mn(II) complexes in methanol. J. Chem. Phys. **1969**, *49*, 2031.
21. Campbell, M.J.; Grzeskowiak, R. Some copper(II) complexes of semicarbazide. J. Inorg. Nucl. Chem. **1968**, *30*, 1865.
22. Dyer, J.R. *Applications of Absorption Spectroscopy of Organic Compounds*; Prentice-Hall: New Delhi, 1984.
23. Radhakrishnan, P.S.; Indrasenan, P.; Nair, C.G.R. Complexes of lanthanide nitrates with 4-*N*-(2′-hydroxybenzylidene)aminoantipyrine. Polyhedron **1984**, *3*, 67.
24. Radhakrishnan, P.K.; Indrasenan, P. Synthesis and characterization of some lanthanide nitrate and perchlorate complex of 4-(pyridine-2′-carboxalidene)amino antipyrine. J. Indian Chem. Soc. **1990**, *67*, 243.
25. Agarwal, R.K.; Arora, K.; Dutt, P. Studies on thorium(IV) and dioxouranium(VI) complexes of Schiff bases derived from 4-aminoantipyrine. Synth. React. Inorg. Met.-Org. Chem. **1994**, *24*, 301.
26. Jones, L.H. Systematics in the vibrational spectra of uranyl complexes. Spectrochim. Acta **1958**, *10*, 395 (Chem. Abstr. **1958**, *52*, 9759d).
27. McGlynn, S.P.; Smith, J.K.; Neely, W.C. Electronic, structure, spectral and magnetic properties of oxycations. III. Ligational effects on IR spectrum of uranyl ion. J. Chem. Phys. **1961**, *35*, 105.
28. Zacharisen, W.H. UCl_3 type of crystal structure. Acta Cryst. **1954**, *8*, 743.
29. Rastogi, V.K.; Pandey, A.N.; Gupta, S.L.; Sharma, R.C. Spectral studies of some uranyl complexes. Indian J. Pure Appl. Phys. **1980**, *18*, 379.
30. Garga, C.L.; Gupta, S.D.; Narasimhan, K.V. Force constants and bond distances for the U–O bond or uranyl salts. Indian J. Pure Appl. Phys. **1970**, *8*, 108.
31. Wilson, L.B. A method of obtaining the expand secular equation for the vibrational frequencies of a molecule. J. Chem. Phys. **1939**, *7*, 1047.
32. Wilson, L.B. Some mathematical methods for the study of molecular vibrations. J. Chem. Phys. **1941**, *9*, 76.

33. Badger, R.M. The relation between the intermediate distance and force constants of molecules and its application to polyatomic molecules. J. Chem. Phys. **1935**, *3*, 710.
34. Devi, G.S.; Indrasenan, P. Uranyl nitrate complexes of some Schiff bases of 4-aminoantipyrine and certain carbonyl compounds. Inorg. Chim. Acta **1987**, *133*, 157.
35. Topping, G. Infrared assignments and force constants in metal–nitro complexes. Spectrochim. Acta **1965**, *21*, 1743.
36. Bullock, J.I. Infrared spectra of some uranyl nitrate complexes. J. Inorg. Nucl. Chem. **1967**, *29*, 2267.
37. Al-Kazzaz, Z.M.S.; Bagnall, K.W.; Brown, D. Phosphine oxide complexes of the actinide(IV) thiocyanates. J. Inorg. Nucl. Chem. **1973**, *35*, 1501.
38. Burmeister, J.L. Recent developments in the coordination chemistry of ambidentate ligands. Coord. Chem. Rev. **1966**, *1*, 205.
39. Burmeister, J.L. Linkage isomerism in metal complexes. Coord. Chem. Rev. **1968**, *3*, 225.
40. Bailey, R.A.; Kozak, S.L.; Michelsen, T.W.; Mills, W.N. Infrared spectra of complexes of the thiocyanate and related ions. Coord. Chem. Rev. **1971**, *6*, 407.
41. Savant, V.V.; Ramamurthy, P.; Patel, C.C. Antipyrine complexes of titanium(IV), zirconium(IV), thorium(IV), and uranium(VI) perchlorates. J. Less-Common Metals **1970**, *22*, 479.
42. Krishnamurthy, S.S.; Soundararajan, S. Dimethyl and diphenyl formamide complexes of lanthanide perchlorates. Can. J. Chem. **1969**, *47*, 995.
43. Agarwal, R.K.; Arora, K.; Dutt, P. Some high coordination compounds of thorium(IV) and dioxouranium(VI) derived from hydrazones of isonicotinic acid hydrazide. Polyhedron **1994**, *13*, 957.
44. Ahuja, I.S.; Yadava, C.L.; Tripathi, S. Coordination polymers of some uranyl salts involving 4,4′-bipridyl, 4,4′-bipyridyl *N*,*N*′-dioxide, 1,3-*bis*(4-pyridyl)propane and hexamethylenetetramine. Asian J. Chem. **1989**, *1*, 195.
45. Wendlandt, W.W. The thermal decomposition on the heavier rare earth metal chloride hydrates. J. Inorg. Nucl. Chem. **1959**, *9*, 136.
46. Glueckauf, E.; McKay, H.A.C. Possible f-shell covalency in the actinide elements. Nature **1950**, *165*, 594.

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