Asian Journal of Chemistry Vol. 13, No. 4 (2001), 1618–1624

Synthesis, Spectral and Thermal Studies of Some Dioxouranium(VI) Coordination Compounds of 4[N-(4-Hydroxy-3-Methoxybenzalidene) Amino] Antipyrine Semicarbazone and 4[N-(3,4,5-Trimethoxybenzalidene) Amino] Antipyrine Semicarbazone†

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In view of high coordination compounds formed by actinide metal ions, the present work describes the 8, 9 and 10-coordinated compounds of dioxouranium(IV) with 4[N-(4-hydroxy-3-methoxybenzalidene) amino] antipyrine semicarbazone (HMBAAPS) and 4[N-(3,4,5-trimethoxybenzalidene) amino] antipyrine semicarbazone (TMBAAPS) with the general composition $UO_2X_2 \cdot 2L$ ($X = Br^-$, I^-, NCS^- or ClO_4^-) and $UO_2X_2 \cdot L$ ($X = NO_3^-$ or CH_3COO^- and L = HMBAAPS or TMBAAPS). All these complexes were characterized through elemental, spectral and thermal studies.

INTRODUCTION

In recent years Agarwal *et al.*[1–4] and Maurya *et al.*[5] have reported a large number of dioxouranium(VI) coordination compounds of Schiff hases. But less is known about the ligational behaviour of semicarbazones having pyrazolone ring. In view of formation of high coordination compounds by actinide metal ions, the present work is devoted to synthesis and characterization of dioxouranium(VI) complexes of 4[N-(4-hydroxy-3-methoxybenzalidene) amino] antipyrine semicarbazone (HMBAAPS) and 4[N-(3,4,5-trimethoxybenzalidene) amino] antipyrine semicarbazone (TMBAAPS).

EXPERIMENTAL

The ligands HMBAAPS/TMBAAPS wre synthesized by refluxing an ethanolic solution of 1 : 1 : 1 molar ratio of 4-aminoantipyrine, aromatic aldehyde (4-hydroxy-3-methoxybenzaldehyde or 3,4,5-trimethoxybenzaldehyde) and neutralized semicarbazone for *ca.* 2 h. On cooling the corresponding ligand precipitated

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†Presented at 37th Annual Convention of Chemists-2002, Gurukula Kangri University, Hardwar, 15–18 Nov. 2000 and XIX Annual Conference of Indian Council of Chemists, Kuvempu University, Shimoga, 27–29 Nov. 2000.

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out. It was filtered, washed with ethanol, ether and finally dried in vacuum desiccator over P_4O_{10}. Uranyl nitrate and uranyl acetate were used as received from BDH. Uranyl nitrate was dehydrated by keeping it over concentrated sulphuric acid[6]. Uranyl bromide was prepared from uranyl acetate by treating it with HBr. After evaporating most of the solvent, the solution was kept over sulphuric acid till yellow crystals separated out[7] and uranyl iodide was obtained by treating uranyl nitrate with barium iodide in dry ether[8]. Uranyl thiocyanate was prepared by mixing alcoholic solution of anhydrous uranyl nitrate and potassium thiocyanate[9]. Uranyl perchlorate was prepared by digesting uranyl nitrate with calculated amount of perchloric acid and evaporating the mixture to dryness. Uranyl perchlorate was crystallized until free from the nitrate ions[10].

Synthesis of the Complexes

The solid metal complexes were prepared by the following general method. The corresponding metal salt and the respective ligand were taken in the required molar ratios in isopropanol and refluxing the reaction mixture for *ca.* 2 h. Complexes were collected after cooling and were washed with solvent and finally with ether and then dried *in vacuo* over P_4O_{10}.

The analyses and physical measurements were performed as reported earlier[4].

RESULTS AND DISCUSSION

The analytical data of the synthesized complexes are shown in Table-1. The electrical conductances measured in nitrobenzene are inconsistent with the non-electrolytic nature of nitrato, halo, acetato and thiocyanato complexes while the perchlorato complexes are 1 : 2 electrolytes. Molecular weight data of these complexes in freezing $PhNO_2$ given in Table-1 agree with conductance data.

The dioxouranium(VI) complexes are either diamagnetic or weakly paramagnetic depending upon the diamagnetism of other ions and the surrounding ligand field. Since the ground state of dioxouranium(VI) compounds contains no unpaired electron, all these complexes are weakly diamagnetic as observed by earlier workers[11, 12].

Infrared spectra

The key infrared bands of the free ligands and their UO_2^{2+} complexes are given in Table-2. The characteristic absorption of the carbonyl group in free semicarbazones is observed[13] at *ca.* 1700 cm^{-1} (amide-I band). In all the complexes this band is shifted toward lower energy in 1652 –1642 cm^{-1} region. The amide-II band in these ligands is observed in 1565–1560 cm^{-1} region. In all the present complexes, this band is also shifted towards lower wave numbers by 25–30 cm^{-1}. This observation suggests coordination through the carbonyl oxygen atom. The strong band at *ca.* 1600 cm^{-1} apparently has a large contribution from the $\nu(C{=}N)$ band of the semicarbazone moiety. 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 ligand. Another strong band was observed at *ca.* 1620 cm^{-1} due to azomethinic (C═N) absorption. On complexation, this band is shifted towards the lower frequency region which is suggestive of coordination through the azomethinic N-atom[14]. ν(U—N)[ν(U—O) (metal-ligand) stretching bands occur at 460–390 cm^{-1} region[1-3].

TABLE-1
ANALYTICAL, CONDUCTIVITY AND MOLECULAR WEIGHT DATA OF DIOXOURANIUM(VI) COMPLEXES OF HMBAAPS AND TMBAAPS

Complex and colour	Yield (%)	% Analysis, Found (Calcd.)			m.w. exp. (calcd.)	Λ_m (ohm^{-1} cm^2 $mole^{-1}$)
		U	N	Anion		
$UO_2Br_2 \cdot 2(HMBAAPS)$	78	19.39	13.64	13.01	1210	4.3
(Dark yellow)		(19.54)	(13.79)	(13.13)	(1218)	
$UO_2I_2 \cdot 2(HMBAAPS)$	75	17.89	12.68	19.15	1308	4.9
(Brown yellow)		(18.14)	(12.80)	(19.35)	(1312)	
$UO_2(NCS)_2 \cdot 2(HMBAAPS)$	80	20.05	16.50	9.79	1169	3.8
(Yellow)		(20.27)	(16.69)	(9.88)	(1174)	
$UO_2(ClO_4)_2 \cdot 2(HMBAAPS)$	75	18.72	13.22	15.43	413	51.9
(Yellow)		(18.93)	(13.36)	(15.83)	(1257)	
$UO_2(NO_3)_2(HMBAAPS)$	82	30.03	14.07	–	783	3.9
(Dark yellow)		(30.20)	(14.21)	–	(788)	
$UO_2(CH_3COO)_2(HMBAAPS)$	78	30.20	10.59	–	777	3.6
(Yellow)		(30.43)	(10.74)	–	(782)	
$UO_2Br_2 \cdot 2(TMBAAPS)$	75	18.09	12.79	12.13	1299	4.1
(Dark yellow)		(18.22)	(12.86)	(12.25)	(1306)	
$UO_2I_2 \cdot 2(TMBAAPS)$	70	16.87	11.89	18.03	1393	4.7
(Brown yellow)		(17.00)	(12.00)	(18.14)	(1400)	
$UO_2(NCS)_2 \cdot 2(TMBAAPS)$	72	18.69	15.42	9.11	1258	3.7
(Yellow)		(18.85)	(15.53)	(9.19)	(1262)	
$UO_2(ClO_4)_2 \cdot 2(TMBAAPS)$	70	17.54	12.37	14.62	446	52.3
(Yellow)		(17.69)	(12.49)	(14.79)	(1345)	
$UO_2(NO_3)_2(TMBAAPS)$	75	28.42	13.34	–	828	3.9
(Dark yellow)		(28.60)	(13.46)	–	(832)	
$UO_2(CH_3COO)_2(TMBAAPS)$	75	28.69	10.04	–	823	3.8
(Yellow)		(28.81)	(10.16)	–	(826)	

The above discussion clearly indicates that HMBAAPS/TMBAAPS serves as a tridentate ligand coordinating through the carbonyl-O, hydrazinic-N and azomethinic-N atoms.

In $UO_2(NCS)_2 \cdot 2L$, three main frequencies ν(C—N)(ν_1), ν(C═S)(ν_2) and δ(NCS)(ν_3) fall at *ca.* 2060, 840 and 430 cm^{-1} respectively suggesting the N-bonding of NCS anion[15]. For $UO_2(ClO_4)_2 \cdot 2L$, the occurrence of two strong

TABLE-2

KEY IR BANDS (cm^{-1}) OF DIOXOURANIUM(VI) COMPLEXES OF HMBAAPS AND TMBAAPS

Complex	ν(C=N) azomethinic	ν(C=N) hydrazinic	ν(C=O)			ν(U—O)/ ν(U—N)
			I	II	III	
HMBAAPS	1620 s	1605 s	1702 s	1560 m	1355 m	– –
$UO_2Br_2\cdot2$(HMBAAPS)	1595 s	1625 s	1645 s	1535 m	1335 m	450 m, 390 w
$UO_2I_2\cdot2$(HMBAAPS)	1590 s	1630 s	1650 s	1530 m	1332 m	458 m, 395 w
$UO_2(NCS)_2\cdot2$(HMBAAPS)	1598 s	1632 s	1652 s	1532 m	1335 m	465 m, 398 w
$UO_2(ClO_4)_2\cdot2$(HMBAAPS)	1590 s	1628 s	1645 s	1530 m	1330 m	462 m, 385 w
$UO_2(NO_3)_2$(HMBAAPS)	1599 s	1635 s	1640 s	1537 s	1332 m	455 m, 385 w
$UO_2(CH_3COO)_2$(HMBAAPS)	1595 s	1632 s	1645 s	1532 m	1330 m	452 m, 382 w
TMBAAPS	1615 s	1600 s	1700 s	1565 m	1350 m	– –
$UO_2Br_2\cdot2$(TMBAAPS)	1585 s	1630 s	1645 s	1535 m	1330 m	460 m, 395 w
$UO_2I_2\cdot2$(TMBAAPS)	1590 s	1622 s	1652 s	1532 m	1332 m	465 m, 390 w
$UO_2(NCS)_2\cdot2$(TMBAAPS)	1592 s	1632 s	1645 s	1528 m	1335 m	458 m, 395 w
$UO_2(ClO_4)_2\cdot2$(TMBAAPS)	1587 m	1625 s	1640 s	1533 m	1332 m	455 m, 385 w
$UO_2(NO_3)_2$(TMBAAPS)	1580 m	1630 s	1642 s	1530 m	1335 m	452 m, 380 w
$UO_2(CH_3COO)_2$(TMBAAPS)	1580 s	1632 s	1650 s	1530 m	1330 m	455 m, 385 w

bands at *ca.* 1080 and 625 cm^{-1} attributed to ν_3 and ν_4 vibrations of ionic perchlorate suggest the presence of perchlorato groups outside the coordination sphere[16]. In $UO_2(NO_3)_2\cdot L$, the nitrato groups coordinate in a bidentate fashion, since the infrared frequencies due to this group are almost in the same frequency ranges (1510, 1285, 1025, 1015, 830, 740 and 720 cm^{-1} as ν_1, ν_4, ν_2, ν_6, ν_3 and ν_5 respectively) as in $UO_2(NO_3)_2\cdot2H_2O$[17]. Ueki[18] and Taylor[19] established the bidentate character of the NO_3^- groups in $UO_2(NO_3)_2\cdot2H_2O$ by X-ray and neutron diffraction studies. Similar to nitrato ion, the acetato ion is also a potentially bidentate ligand towards uranyl group. The present complexes

$UO_2(CH_3COO)_2 \cdot L$ are monomeric in nature and the infrared spectra of these complexes show two bands at 1550 and 1465 cm^{-1} region attributed to the asymmetric and symmetric stretching vibrations of COO^- respectively[20].

In the present investigation, the ν(U=O) in all the complexes has been assigned to 930–925 cm^{-1} region and 837–825 cm^{-1} region as ν_3 and ν_1 frequency respectively[1-3] (Table-3).

Complexation Effects on Uranyl Ion Spectra

In the present studies, it has been observed that ν_1 mode of the uranyl ion appears as the weak intensity and ν_3 mode as the strong intensity in the infrared spectra (Table-3). A group theoretical consideration[21] 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 GF matrix method[22] has been used to determine the stretching and interaction force constants. By using Badger's formula[23] (U—O) bond distances were calculated and summarised in Table-3.

TABLE-3
VARIOUS FORCE CONSTANTS (mdynes/Å), U-O BOND DISTANCE (Å) AND FREQUENCIES OF ν_1 and ν_3 OF UO_2(VI) COMPLEXES OF HMBAAPS AND TMBAAPS

Complex	ν_1	ν_3	U—O force constant	Force constant due to interaction between bonds	U—O bond distance
$UO_2Br_2 \cdot 2$(HMBAAPS)	835	930	6.8793	–0.3071	1.7378
$UO_2I_2 \cdot 2$(HMBAAPS)	837	928	6.8796	–0.2759	1.7378
$UO_2(NCS)_2 \cdot 2$(HMBAAPS)	825	927	6.7779	–0.3622	1.7408
$UO_2(ClO_4)_2 \cdot 2$(HMBAAPS)	827	930	6.8166	–0.3698	1.7390
$UO_2(NO_3)_2$(HMBAAPS)	837	930	6.8951	–0.2914	1.7375
$UO_2(CH_3COO)_2$(HMBAAPS)	832	925	6.8172	–0.2921	1.7399
$UO_2Br_2 \cdot 2$(TMBAAPS)	835	930	6.8793	–0.2302	1.7402
$UO_2I_2 \cdot 2$(TMBAAPS)	833	930	6.8557	–0.3307	1.7384
$UO_2(NCS)_2 \cdot 2$(TMBAAPS)	837	928	6.8796	–0.2759	1.7378
$UO_2(ClO_4)_2 \cdot 2$(TMBAAPS)	830	925	6.8016	–0.3078	1.7405
$UO_2(NO_3)_2$(TMBAAPS)	825	927	6.7779	–0.3622	1.7408
$UO_2(CH_3COO)_2$(TMBAAPS)	837	928	6.8796	–0.2759	1.7378

Thermal Studies

Thermal results are presented in Table-4. T.G. curves of all the six complexes clearly indicate the absence of water molecules in the complexes. The decomposition of these complexes has started at 250–355°C and completed in 405–475°C region. Finally at 650°C, U_3O_8 is formed as the final product, TABLE-4

THERMAL DATA ON UO_2(VI) COMPLEXES OF HMBAAPS AND TMBAAPS

Complex	Sample wt. (mg)	Residual mass (mg)	Ligand mass loss (%)				Residual (%) *ca.* 640°C	
			250–355°C		405–475°C			
			Theor.[a]	Exp.	Theor.[b]	Exp.	Theor.[c]	Exp.
$UO_2Br_2 \cdot 2$(HMBAAPS)	22.40	5.30	32.50	32.21	65.01	64.33	23.15	23.69
$UO_2(NCS)_2 \cdot 2$(HMBAAPS)	24.60	6.02	33.73	33.36	67.46	66.98	24.02	24.50
$UO_2(ClO_4)_2 \cdot 2$(HMBAAPS)	28.10	6.42	31.49	31.12	62.98	62.12	22.43	22.87
$UO_2Br_2 \cdot 2$(TMBAAPS)	23.10	5.05	33.53	33.39	67.07	66.93	21.49	21.87
$UO_2(NCS)_2 \cdot 2$(TMBAAPS)	25.20	5.70	34.70	34.54	69.41	69.30	22.23	22.63
$UO_2(ClO_4)_2$(TMBAAPS)	28.30	5.98	32.56	32.40	65.13	65.00	20.86	21.16

[a] Calculated for loss of 1 mole of organic ligand; [b] Calculated for total loss of organic ligand; [c] Calculated as U_3O_8.

following which there is no measurable change in weight. In brief these thermal changes are shown as

$$UO_2X_2\cdot 2L \rightarrow UO_2X_2\cdot L \rightarrow UO_2X_2 \rightarrow U_3O_8$$

Stereochemistry of the Complexes

In halo and thiocyanato complexes, both the anions are covalently bonded and the ligand is tridentate (N, N, O) in nature; thus in these complexes, it may be considered to have a ten-coordinated U(VI) atom. In $[UO_2(L)_2](ClO_4)_2$ both the perchlorato groups are ionic in nature; thus in this complex, a coordination number eight is suggested for U(VI). In $UO_2(NO_3)_2\cdot L$ and $UO_2(CH_3COO)_2\cdot L$, U(VI) displays a coordination number nine.

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(*Received*: 11 July 2001; *Accepted*: 5 September 2001) AJC-2424