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Synthesis and Spectral Properties of Dioxouranium(VI) Complexes of N-isonicotinamidio-*p*-anisalaldimine and N-isonicotinamido-*p*-dimethylaminobenzalaldimine†

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In the present work, the ligational behaviour of N-isonicotinamido-*p*-anisalaldimine (INH-ANSL) and N-isonicotinamido-*p*-dimethylaminobenzalaldimine (INH-PDAB) toward dioxouranium (VI) salts were studied. The isolated complexes have the general composition $UO_2X_2 \cdot nL$ ($X = Br^-$, I^-, NCS^-, NO_3^- or CH_3COO^-, $n = 2$, $X = ClO_4^-$, $n = 3$ and L = INH-ANSL or INH-PDAB). All these complexes were characterized by infrared, conductance, magnetic moment, molecular weight data and elemental analyses. In these complexes both the ligands behave as neutral bidentate ligand coordinating through amido-oxygen and azomethinic-nitrogen atoms. The electrical conductance indicates that except $UO_2(ClO_4)_2$ complexes all the complexes are non-electrolytes, while $UO_2(ClO_4)_2 \cdot 3L$ are 1 : 2 electrolytes. The probable coordination number of U(VI) is either 8 or 10 depending on the nature of anions. Thermal properties of the complexes are also discussed.

INTRODUCTION

Actinide ions generally present high coordination number and the type of polyhedron obtained is influenced by the nature of the coordinating ligands.[1] A number of workers have investigated the high coordination compounds of uranium(VI) with different coordinating agents.[2–5] In the present work, we are presenting some eight and ten coordinated dioxouranium(VI) complexes of N-isonicotinamido-*p*-anisalaldimine (INH-ANSL) and N-isonicotinamido-*p*-dimethylaminobenzalaldimine (INH-PDAB).

EXPERIMENTAL

Uranyl nitrate and uranyl acetate were used as received from BDH and were dehydrated by keeping it over concentrated sulphuric acid.[6] Dioxouranium(VI) halides were prepared from uranyl nitrate[7–9], while perchlorate was prepared by the known method.[10] The hydrazones of isonicotinic acid were prepared by

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mixing the solution of isonicotinic acid hydrazide (isoniazid) (aqueous methanol) and respective aromatic aldehyde (*p*-anisaldehyde or *p*-dimethylamino-benzalaldehyde) (in methanol) in equimolar ratio and refluxed on water bath for *ca.* 3 h. The reaction mixture was cooled, filtered under suction and washed with water, methanol and-solvent ether. The end product was recrystallized from ethanol (95%) and dried under vacuum over fused calcium chloride.

All the complexes of dioxouranium(VI) were isolated as follow. To a solution of metal salt (1 mmol) in isopropanol (25 mL) was added a hot solution of ligand (2 mmol/3 mmol) in the same solvent (30 mL). In some cases the desired complex was obtained immediately. But in others, the reaction mixture was refluxed for 1–2 h. On cooling at room temperature the desired complex was obtained. The solid product was filtered off, washed with isopropanol and dried in vacuum over P_4O_{10}.

All the physical measurements and analyses were performed as reported earlier.[11]

RESULTS AND DISCUSSION

The interaction of dioxouranium(VI) salts with INH-ANSL and INH-PDAB results in the formation of complexes with the general composition $UO_2X_2 \cdot nL$ ($X = Br^-, I^-, NO_3^-$, NCS^- or CH_3COO^-, $n = 2$; $X = ClO_4^-$, $n = 3$). The analytical data for these complexes are recorded in Table-1. All the complexes are quite stable and can be stored for a long period. They are soluble in common organic solvents like acetone, nitrobenzene and dimethyl formamide. The molar conductivities of UO_2(VI) complexes in nitrobenzene suggest that the bromo, iodo, nitrato, thiocyanato and acetato complexes are non-electrolytes, while the perchlorato complexes are 1 : 2 electrolytes, which shows that both the perchlorato groups are present outside the coordination sphere. Molecular weight data of the complexes (Table-1) show that the complexes are monomeric in nature as the ratio of the observed molecular weight and the formula weight for $UO_2X_2 \cdot 2L$ ($X = Br^-$, I^-, NO_3^-, NCS^- or CH_3COO^-) is *ca.* 0.98; while in case of $UO_2(ClO_4)_2 \cdot 3L$ the ratio is 0.33, which supports that 3 species are formed in this complex in nitrobenzene.

The ground state of uranyl complexes contains no unpaired electrons, the compounds are therefore expected to be weakly diamagnetic as observed.[12, 13]

Infrared

The comparison of the infrared spectra of the ligands and their UO_2^{2+} complexes suggests that the ligands are bidentate in nature with the carbonyl-oxygen and azomethinic nitrogen as two coordinating sites. The partial IR data are presented in Table-2. (i) The IR spectra of these ligands exhibit a very strong band at *ca.* 1590 cm^{-1} assigned to $\nu(C{=}N)$ (azomethine) group. (i) In the spectra of all these complexes this band is shifted to lower wavenumber in 1558–1537 cm^{-1} region. The shift in this mode clearly indicates that azomethine group is participating in the coordination[14, 15]. (ii) The amide bands, the CO stretching (amide-I) and out-of-plane bending (amide-VI) modes can be used to diagnose

TABLE-1
ANALYTICAL, CONDUCTIVITY AND MOLECULAR WEIGHT DATA OF DIOXOURANIUM(VI) COMPLEXES OF INH-ANSL AND INH-PDAB

Complex	Yield (%)	Analysis: Found (calcd.) %			Mol. wt. found (calcd.)	Ω_m ohm^{-1} cm^2 mole^{-1}
		U	N	Anion		
$UO_2(NO_3)_2\cdot 2$(INH—ANSL)	76	26.21 (26.32)	12.29 (12.38)	—	897 (904)	3.5
$UO_2(OAc)_2\cdot 2$(INH—ANSL)	72	26.35 (26.50)	9.28 (9.35)	—	890 (898)	2.9
$UO_2Br_2\cdot 2$(INH—ANSL)	75	25.17 (25.31)	8.86 (8,.93)	16.90 (17.02)	931 (940)	3.6
$UO_2I_2\cdot 2$(INH—ANSL)	70	22.82 (23.01)	8.07 (8.12)	24.40 (24.56)	1025 (1034)	2.7
$UO_2(NCS)_2\cdot 2$(INH—ANSL)	75	26.42 (26.56)	12.39 (12.50)	12.83 (12.94)	892 (896)	3.2
$UO_2(ClO_4)_2\cdot 3$(INH—ANSL)	70	19.14 (19.28)	10.13 (10.21)	15.90 (16.12)	408 (1234)	52.9
$UO_2(NO_3)_2\cdot 2$(INH—PDAB)	75	25.40 (25.59)	14.96 (15.05)	—	925 (930)	3.2
$UO_2(OAC)_2\cdot 2$(INH—PDAB)	75	25.62 (25.75)	12.06 (12.12)	—	919 (924)	3.7
$UO_2Br_2\cdot 2$(INH—PDAB)	70	24.51 (24.63)	11.51 (11.59)	16.47 (16.56)	960 (966)	4.1
$UO_2I_2\cdot 2$(INH—PDAB)	68	22.33 (22.45)	10.49 (10.56)	23.82 (23.96)	1055 (1060)	3.3
$UO_2(NCS)_2\cdot 2$(INH—PDAB)	72	25.69 25.81	15.08 (15.18)	12.49 (12.58)	917 (922)	3.6
$UO_2(ClO_4)_2\cdot 3$(INH—PDAB)	70	18.47 (18.69)	13.10 (13.19)	15.55 (15.63)	423 (1273)	53.6

O or N-coordination.[16, 17] The decrease in frequency of band-I and the increase in frequency of band-VI on complex formation confirm that the amide group is O-bonded in all the complexes. (iii) The pyridine ring stretching and out-of-plane modes appearing at 1472 and 710 cm^{-1} respectively in the infrared spectra of the ligands do not undergo any shift in the spectra of the complexes indicating that the pyridinic nitrogen is not participating in coordination.[14] The overall IR spectral evidence suggests that both the ligands act as a neutral bidentate N,O-ligands and forming a five-membered chelate ring with central metal ion. In far IR region ν(U—N)/ν(U—O) are assigned in 490–380 cm^{-1} region.

In the IR-spectra of $[UO_2(L)_3](ClO_4)_2$ the presence of a very strong ν_3 band at *ca.* 1085 cm^{-1} and strong narrow band at *ca.* 620 cm^{-1} is indicative of tetrahedral symmetry of perchlorato ions which are not bonded to uranium

TABLE-2

KEY IR BANDS (cm^{-1}) OF UO_2 (VI) COMPLEXES OF INH-ANSL AND INH-PDAB

Compound	ν(NH) (asym and sym)	Amide-I	ν(C=N) (azomethine)	Amide-II + δ (NH)	ν(U—N) ν(U—O)
INH-ANSL	3290 m 3200 sh 3198 m	1698 s 1640 s	1590 vs	1570 sh 1540 m	—
$UO_2(NO_3)_2\cdot 2$(INH-ANSL)	3292 m 3227 m	1620 s 1610 s	1542 m	1550 sh	482 m 390 w
$UO_2(OAc)_2\cdot 2$(INH-ANSL)	3292 m 3220 m 3200 w	1622 s 1612 s	1545 m	1555 sh	475 m 385 w
$UO_2Br_2\cdot 2$(INH-ANSL)	3292 m 3218 m	1630 m 1612 m	1558 m	1556 sh	490 m 390 w
$UO_2I_2\cdot 2$(INH-ANSL)	3292 m 3245 m	1625 s 1610 m	1542 s	1555 sh	485 m 392 w
$UO_2(NCS)_2\cdot 2$(INH-ANSL)	3287 m 3220 m	1620 s 1612 s	1555 m	1555 sh	492 m 385 w
$UO_2(ClO_4)_2\cdot 3$(INH-ANSL)	3292 m 3205 w	1622 s 1612 s	1540 m	1560 sh	480 m 390 w
INH-PDAB	3300 m 3200 m	1655 s	1588 vs	1540 sh 1520 s	—
$UO_2(NO_2)_2\cdot 2$(INH-PDAB)	3298 m 3202 m	1620 s	1550s	1542 sh 1522 s	482 m 392 w
$UO_2(OAc)_2\cdot 2$(INH-PDAB)	3295 m 3200 m	1630 vs	1548 s	1540 sh 1522 m	470 m 385 w
$UO_2Br_2\cdot 2$(INH-PDAB)	3300 m 3205 m	1639 s 1610 s	1540 s	1550 sh 1522 m	475 m 380 w
$UO_2I_2\cdot 2$(INH-PDAB)	3298 m 3200 m	1635 s 1610 s	1543 s	1535 sh 1520 m	475 m 382 w
$UO_2(NCS)_2\cdot 2$(INH-PDAB)	3295 m 3200 m	1615 s	1537 s	1530 m	482 m 390 w
$UO_2(ClO_4)_2\cdot 3$(INH-PDAB)	3300 m 3202 m	1618 s	1538 s	1525 m	492 m 388 w

ion.[18] In $UO_2(NO_3)_2\cdot 2L$ The bands appearing at 1510 (ν_1), 1300–1280 (ν_4), 1030 (ν_2), 810 (ν_6), 750 (ν_3) and 725 (ν_5) cm^{-1} due to NO_3^- are almost in the same frequency ranges as in $UO_2(NO_3)_2\cdot 2H_2O$[19] in which the bidentate nature of NO_3^- ions were already established. In the thiocyanato complexes the bands in the regions 2050–2040 and 840 cm^{-1} correspond to ν(C≡N) and ν(C—S) vibrations respectively in the NCS group suggesting N-coordination of this ambidentate anion.[20] Similar to nitrato, the acetato ions are also a potential bidentate ligand towards uranyl group. A number of complexes of uranyl acetate with neutral monodentate ligands like. TPPO, TPAsO or DPSO are reported in literature[21] in which the acetate ion behaves as covalent bidentate ion with coordination number seven or eight depending upon whether the complexes are monomeric or dimeric in nature. In the present complexes which are monomeric in nature, infrared spectra of these complexes show two bands at 1540 cm^{-1} and 1470 cm^{-1} attributed to antisymmetric and symmetric stretching vibrations of COO^- respectively.

In all dioxouranium(VI) complexes, the ν_1 and ν_3 modes are assigned in the range 840–825 cm^{-1} and 930–920 cm^{-1} respectively.[18] (Table-3). Wilson's G–F matrix method[22] was used to determine the stretching and interaction force constants from which the U—O bond distances were calculated using Badger's formula.[23] It is apparent from the calculated data that U—O bond length decreases with increase in the value of symmetric stretching frequency (ν_1).[24] A plot of ($\nu_1 + \nu_3$) *vs.* force constants gave a straight line. The U—O bond distances in dioxouranium salts generally range from 1.60 to 1.92 Å depending upon the nature of equatorial ligands.[25] The calculated values of the U—O bond distances in the present complexes are close to 1.73–1.74 Å (Table 3).

TABLE-3
VARIOUS FORCE-CONSTANTS (mdynes/Å), U—O BOND DISTANCES (Å) AND FREQUENCIES (cm^{-1}) OF ν_1 AND ν_3 OF DIOXOURANIUM(VI) COMPLEXES OF INH-ANSL AND INH-PDAB

Complex	U—O force constant	Force constant due to interaction between bonds	U—O bond distance	ν_1	ν_3
$UO_2(NO_3)_2 \cdot 2$(INH-ANSL)	6.8796	–0.2759	1.7378	837 w	928 m
$UO_2(OAc)_2 \cdot 2$(INH-ANSL)	6.8016	–0.3078	1.7405	830 m	925 m
$UO_2Br_2 \cdot$ 2(INH-ANSL)	6.9188	–0.2676	1.7369	840 m	930 m
$UO_2I_2 \cdot 2$(INH-ANSL)	6.8793	–0.3071	1.7378	835 m	930 m
$UO_2(NCS)_2 \cdot$ 2(INH-ANSL)	6.8172	–0.2921	1.7399	832 w	925 m
$UO_2(ClO_4)_2 \cdot 3$(INH-ANSL)	6.8796	–0.2759	1.7378	837 w	928 m
$UO_2(NO_3)_2 \cdot 2$(INH-PDAB)	6.7632	–0.2695	1.7411	830 m	920 m
$UO_2(OAc)_2 \cdot 2$(INH-PDAB)	6.8025	–0.2302	1.7402	835 w	920 m
$UO_2Br_2 \cdot 2$(INH-PDAB)	6.8166	–0.3698	1.7399	827 m	930 m
$UO_2I_2 \cdot 2$(INH-PDAB)	6.7779	–0.3622	1.7408	825 m	927 m
$UO_2(NCS)_2 \cdot 2$(INH-PADB)	6.8090	–0.3465	1.7399	828 w	928 m
$UO_2(ClO_4)_2 \cdot 3$(INH-PDAB)	6.7242	–0.3085	1.7423	825 w	920 m

Thermal studies

Thermal results of UO_2 (VI) complexes of INH-ANSL and INH-PDAB are presented on Tables 4 and 5. Except perchlorato complexes all of them behave similarly on heating. The decomposition of the complexes starts from 215°C and is completed at *ca.* 460°C. The break at *ca.* 320°C in these complexes indicates that at this temperature only one molecule of organic ligand has been lost and at 460°C, there is an additional decrease in weight due to total loss of the organic molecules. The oxide U_3O_8 is formed around 760°C via the formation of UO_3, following which there is no appreciable change in weight.[26] The low temperature decomposition of iodo complexes probably indicates the presence of loosely held iodo ligands. In brief, these changes can be shown as follows:

$$UO_2X_2\cdot 2L \rightarrow UO_2X_2\cdot L \rightarrow UO_2X_2 \rightarrow [UO_3] \rightarrow U_3O_8$$

($X = Br^-, NO_3^-, NCS^-$ or OAc^-)

$$UO_2(ClO_4)_2\cdot 3L \rightarrow UO_2(ClO_4)_2\cdot 2L \rightarrow UO_2(ClO_4)_2 \rightarrow [UO_3] \rightarrow U_3O_8.$$

TABLE-4

THERMOANALYTICAL RESULTS OF UO_2(VI) COMPLEXES OF INH-ANSL

Complex	Sample wt. (mg.)	Residual wt. (mg.)	Ligand mass loss (%)				Residual (%) *ca.* 765°C	
			215–320°C		360–450°C			
			Theor.[a]	Exp.	Theor.[b]	Exp.	Theor.[c]	Exp.
$UO_2Br_2\cdot 2$(INH-ANSL)	24.20	7.10	27.12	27.86	54.25	55.16	29.85	29.34
$UO_2(NO_3)_2\cdot 2$(INH-ANSL)	26.10	8.03	28.20	28.88	56.41	57.29	31.04	30.79
$UO_2(NCS)_2\cdot 2$(INH-ANSL)	22.80	7.06	28.45	29.22	56.91	57.82	31.32	30.98
$UO_2(OAc)_2\cdot 2$(INH-ANSL)	20.90	6.45	28.39	28.92	56.79	57.62	31.25	30.89
$UO_2(ClO_4)_2\cdot 3$(INH-ANSL)	27.40	6.09	20.66	21.24	61.99	63.06	22.74	22.25

a—Calculated for loss of 1 mole of organic ligand.

b—Calculated for total loss of organic ligand.

c—Calculated as U_3O_8

TABLE-5

THERMOANALYTICAL RESULTS OF UO_2 (VI) COMPLEXES OF INH-PDAB

Complex	Sample wt. (mg.)	Residual wt. (mg.)	Ligand mass loss (%)				Residual (%) *ca.* 760°C	
			225–325°C		355–460°C			
			Theor.[a]	Exp.	Theor.[b]	Exp.	Theor.[c]	Exp.
$UO_2Br_2\cdot 2$(INH-PDAB)	26.20	7.54	27.74	28.29	44.51	45.41	29.05	28.80
$UO_2(NO_3)_2\cdot 2$(INH-PDAB)	22.80	6.80	28.81	29.32	57.63	58.42	30.17	29.86
$UO_2(NCS)_2\cdot 2$(INH-PDAB)	24.80	7.43	29.06	29.50	58.13	58.89	30.44	29.96
$UO_2(OAc)_2\cdot 2$(INH-PDAB)	20.90	6.23	29.00	29.46	58.00	58.76	30.37	29.84
$UO_2(ClO_4)_2\cdot 3$(INH-PDAB)	25.00	5.44	21.05	21.49	63.15	63.89	22.04	21.79

a—Calculated for loss of 1 mole of organic ligand.

b—Calculated for total loss of organic ligand.

c—Calculated as U_3O_8

In conclusion, the coordination number of U(VI) in these complexes is either 8 or 10 depending upon the nature of coordinating anionic ligands.

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