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Synthesis and Physico-Chemical Characteristics of Some Dioxouranium(VI) Complexes of N-isonicotinamido-3-Methoxy-4-Hydroxy Benzalaldimine and N-isonicotinamidocinnamalaldimine†

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A series of 12 new complexes of dioxouranium(VI) with hydrazones of isonicotinic acid hydrazide, *viz.*, N-isonicotinamido- cinnamalaldimine(INH–CIN) and N-isonicotinamido-3-methoxy-4-hydroxy benzalaldimine (INH-VAN) having the general composition $UO_2X_2 \cdot nL$ ($X = Br^-$, I^-, CH_3COO^-, NO_3^-, NCS^-, n = 2; $X = ClO_4^-$, n = 3; L = INH-VAN or INH-CIN) were prepared in non-aqueous media and characterized on the basis of elemental analyses, electrical conductivity, magnetic moment and IR spectral studies. In all the complexes these ligands act as neutral bidentate (N, O) ligands. In all dioxouranium(VI) complexes, the ν_1 and ν_3 modes are assigned in the 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 calculated data shows that U—O bond length decreases with increase in the value of symmetric stretching frequency (ν_1). A plot of ($\nu_1 + \nu_3$) *vs.* force constants gave a straight line. The calculated values of the U—O bond distances in the present complexes are close to 1.73–1.74 Å. The probable coordination number of U(VI) is 8 or 10, depending on the nature of anions. Thermal properties are also discussed.

INTRODUCTION

As an extension of previous work,[1] here we report some eight and ten coordinated complexes of dioxouranium(VI) with N-isonicotinamido-3-methoxy-4-hydroxy benzalaldimine (INH-VAN) and N-isonicotinamidocinnamalaldimine (INH-CIN).

EXPERIMENTAL

All the dioxouranium(VI) salts were prepared as reported earlier.[2] The hydrazones of isonicotnic acid were prepared by mixing the solution of isonicotinic acid hydrazide (isoniazid) (aqueous methanol) (aqueous methanol) and respective aromatic aldehyde (3-hydroxy-4-methoxybenzaldehyde or cinnamaldehyde) (in methanol) in equimolar ratio and refluxed on water bath for *ca.* 2–2.5 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 P_4O_{10}.

All the complexes of dioxouranium(VI) with INH-VAN/INH-CIN were isolated in microcrystalline state as follows: To a solution of respective metal salt

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(1 mmol) in dry isopropanol (20 mL) was mixed a hot solution of ligand (INH-VAN/INH-CIN) in required molar ratio (2 mmol/3 mmol) in the same solvent (25 mL). The reaction mixture was refluxed for 2–3 h. On cooling at room temperature (30°C), 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.[3]

RESULTS AND DISCUSSION

The interaction of dioxouranium(VI) salts with INH–VAN/INH–CIN results in the formation of adducts $UO_2X_2 \cdot 2L$ ($X = NO_3^-$, OAc^-, Br^-, I^- or NCS^-) and $UO_2(ClO_4)_2 \cdot 3L$ (L = INH-VAN or INH-CIN). The complexes are quite stable and can be stored for a long period at room temperature (*ca.* 30°C) except the iodide complexes which decomposed to a sticky mass after a few weeks. The complexes are sufficiently soluble in common organic solvents.

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

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-VAN)	80	25.31 (25.42)	11.89 (11.96)	—	932 (936)	3.5
$UO_2(OAc)_2 \cdot 2$(INH-VAN)	75	25.43 (25.59)	8.97 (9.03)	—	925 (930)	4.2
$UO_2Br_2 \cdot 2$(INH-VAN)	72	24.30 (24.48)	8.53 (8.64)	16.21 (16.46)	963 (972)	3.9
$UO_2I_2 \cdot 2$(INH-VAN)	70	22.20 (22.32)	7.79 (7.87)	23.59 (23.82)	1061 (1066)	2.6
$UO_2(NCS)_2 \cdot 2$(INH-VAN)	75	25.46 (25.64)	11.92 (12.06)	12.36 (12.50)	924 (928)	3.3
$UO_2(ClO_4)_2 \cdot 3$(INH-VAN)	70	18.38 (18.56)	9.69 (9.82)	15.39 (15.52)	419 (1282)	52.9
$UO_2(NO_3)_2 \cdot 2$(INH-CIN)	80	26.37 (26.56)	12.41 (12.50)	—	892 (896)	3.3
$UO_2(OAc)_2 \cdot 2$(INH-CIN)	76	26.53 (26.74)	9.36 (9.43)	—	883 (890)	2.9
$UO_2Br_2 \cdot 2$(INH-CIN)	74	25.41 (25.53)	8.92 (9.01)	17.09 (17.16)	927 (932)	3.6
$UO_2I_2 \cdot 2$(INH-CIN)	70	23.07 (23.19)	8.13 (8.18)	24.59 (24.75)	1021 (1026)	3.2
$UO_2(NCS)_2 \cdot 2$(INH-CIN)	75	26.62 (26.80)	12.50 (12.61)	12.91 (13.06)	884 (888)	3.5
$UO_2(ClO_4)_2 \cdot 3$(INH-CIN)	72	19.33 (19.47)	10.23 (10.31)	16.19 (16.28)	405 (1222)	53.6

In order to understand the nature of complexes in solution their molecular conductivities were determined in nitrobenzene medium. All the complexes are essentially non-electrolytes in nitrobenzene, as the conductivity of the halo, nitrato, acetato or thiocyanato complexes are too low to account for any dissociation as it is revealed by the molar conductance value, but perchlorato complexes behave like 1 : 2 electrolytes (Table-1). The analytical, electrical conductivity and molecular weight data for these complexes are given in Table-1. These complexes are found to be diamagnetic in nature.[4,5] Their magnetic susceptibilities are independent of field strength and temperature.[6] The ground states of dioxouranium(VI) complexes contain no unpaired electrons, the compounds are therefore expected to be weakly diamagnetic as observed.[5,7,8]

The important infrared data for these complexes are given in Table-2. In INH-VAN, the —OH group does not take part in the coordination, revealed the fact that ν(OH), which appears at *ca.* 3400 cm^{-1} is seen in the same region in the complexes, clearly indicating that the —OH group is not taking part in the coordination. The ligands are expected to coordiante through the C=O of the amide group. The amide-I band in the INH derivatives appears in 1700–1630 cm^{-1} region and in the IR spectra of complexes a considerable negative shift in ν(C=O) is observed, indicating a decrease in the stretching force constant of C=O as a consequence of coordination through the carbonyl oxygen atom of the free base. The amide-II band appears at the normal position of the NH-deformation rather than C—N link. In INH-derivatives, the absorption in the 1560–1530 cm^{-1} region has been assigned to amide-II. The NH stretching absorption in the free ligands occurs in 3300–3220 cm^{-1} and remains unaffected after complexation.[9,10] This precludes the possibility of coordination through the imine-nitrogen atom. Another important band occurring in 1600–1585 cm^{-1} region is attributed to the ν(C=N) (azomethine) mode.[9,10] In the spectra of all the complexes this band is shifted to a lower wavenumber and appears in the 1565–1525 cm^{-1} region, indicating the involvement of the nitrogen atom of the azomethine group in coordination.[11,12] The strong bands observed at 1575–1520 and 1080–1000 cm^{-1} are tentatively assigned[11–14] to antisymmetric and symmetric ν(C=C) and ν(C=N) of the pyridine ring and pyridine ring breathing and deformation remain practically unchanged in frequency and band intensities, revealing non-involvement of the pyridinic-nitrogen and metal bond. The overall IR-spectral evidence suggests that the ligands are bidentate, coordinating through the amide-oxygen and azomethinic-nitrogen atoms to form a five-membered chelate ring. In far IR region the bands appearing in 485–385 cm^{-1} are assigned to ν(U—N)/(U—O) mode.[15]

TABLE-2
KEY IR BANDS (cm^{-1}) OF UO_2(VI) COMPLEXES OF INH-VAN AND INH-CIN

Compound	ν(NH) (asym. and sym)	Amide-I	ν(C=N) (azomethine)	Amide-II + δ(NH)	ν(U—N)/ ν(U—O)
INA-VAN	3300 m 3220 w	1700 vs 1630 us	1585 s	1540 m 1530 m	—
$UO_2(NO_3)_2$·2(INH-VAN)	3305 m 3220 w	1670 vs 1605 vs	1525 m	1510 s	480 m 395 w
$UO_2(OAc)_2$·2(INH-VAN)	3302 m 3220 w	1670 s 1610 vs 1580 m	1530 vs	1530 vs	475 m 392 w
UO_2Br_2·2(INH-VAN)	3300 m 3220 w	1680 s 1620 s	1555 s	1525 m 1510 m	492 m 390 w
UO_2I_2·2(INH-VAN)	3302 m 3220 w	1670 vs 1600 vs, br	1525 m	1510 sh 1500 s	485 m 395 w
$UO_2(NCS)_2$·2(INH-VAN)	3300 m 3220 w	1670 s 1600 vs, br	1530 sh	1510 sh 1505 s	490 m 385 w
$UO_2(ClO_4)_2$·3(INH-VAN)	3300 m 3225 w	1660 s 1605 s	1525 m	1510 s, br	485 m 390 w
INH-CIN	3290 m 3220 m	1660 vs	1602 vs	1560 s 1550 s	—
$UO_2(NO_3)_2$·2(INH-CIN)	3292 m 3222 m	1635 s	1565 s	1550 w 1530 sh	485 m 392 w
$UO_2(OAc)_2$·2(INH-CIN)	3290 m 3220 m	1630 s	1562 s	1555 w 1530 sh	490 m 385 w
UO_2Br_2·2(INH-CIN)	3920 m 3220 w	1625 s	1560 s	1545 w 1525 sh	482 m 390 w
UO_2I_2·2(INH-CIN)	3292 m 3220 w	1622 m	1562 s	1550 m 1532 w	485 m 392 w
$UO_2(NCS)_2$·2(INH-CIN)	3290 m 3222 m	1625 s	1565 s	1550 m 1530 w	485 m 390 w
$UO_2(ClO_4)_2$·3(INH-CIN)	3290 m 3220 w	1630 s	1560 m	1545 m 1525 sh	485 m 392 w

The occurrence of two strong bands at *ca.* 1080 and 620 cm^{-1} in the spectra of the perchlorato complexes, attributed to ν_3 and ν_4 vibrations of ionic perchlorate, suggests[16] the presence of perchlorato groups outside the coordination sphere in the complexes. The spectral bands in the case of nitrato complexes studied here were comparable with the known bands of $UO_2(NO_3)_2·H_2O$, *i.e.*, 1520 (ν_4), 1290 (ν_1), 1030 (ν_2), 808 (ν_6), 745 (ν_3) and 715 cm^{-1} (ν_5), in which the bidentate character of the nitrato groups has been established by X-ray and neutron diffraction studies. It is inferred that the nitrate groups in these complexes also behave as bidentate ligands.[17,18] The C—N stretching band at *ca.* 2120 cm^{-1} suggests that the thiocyanato groups in the present complexes are nitrogen bonded.[19] The frequency of the (C—S) stretching vibration at 825 cm^{-1} is also

in agreement with a nitrogen bonded isothiocyanate. A medium intensity band at *ca.* 480 cm^{-1} may be assigned as δ(NCS) absorption. In the present case, all the uranyl acetato complexes of hydrazones are monomeric in nature and the IR 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[20] of COO^-.

In all dioxouranium(VI) complexes, the ν_1 and ν_3 modes of O=U=O are assigned in the 840–825 and 930–920 cm^{-1} respectively[21] (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 following 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 ($\nu_1 + \nu_3$) versus force-constants gave a straight line. The U—O bond distances in dioxouranium salts generally range from 1.60–1.92 Å depending upon the nature of equatorial ligands. 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 (IN DYNES/Å), U—O BOND DISTANCES (Å) AND FREQUENCIES (cm^{-1}) OF ν_1 AND ν_3 OF DIOXOURANIUM(VI) COMPLEXES OF INH-VAN AND INH-CIN

Complex	U—O force constant	Force constant due to interaction between bonds	U—O bond distances	ν_1	ν_3
$UO_2(NO_3)_2 \cdot 2$(INH-VAN)	6.9188	–0.2676	1.7369	840 m	930 m
$UO_2(OAC)_2 \cdot 2$(INH-VAN)	6.7632	–0.2695	1.7411	830 m	920 m
$UO_2Br_2 \cdot 2$(INH-VAN)	6.7242	–0.3085	1.7423	825 w	920 m
$UO_2I_2 \cdot 2$(INH-VAN)	6.8016	–0.3078	1.7405	830 m	925 m
$UO_2(NCS)_2 \cdot 2$(INH-VAN)	6.8793	–0.3071	1.7378	835 m	930 m
$UO_2(ClO_4)_2 \cdot 2$(INH-VAN)	6.8025	–0.2302	1.7402	835 m	920 m
$UO_2(NO_3)_2 \cdot 2$(INH-CIN)	6.8172	–0.2921	1.7399	832 w	925 m
$UO_2(OAC)_2 \cdot 2$(INH-CIN)	6.8796	–0.2759	1.7378	837 w	928 m
$UO_2Br_2 \cdot 2$(INH-CIN)	6.8090	–0.3465	1.7399	828 w	928 m
$UO_2I_2 \cdot 2$(INH-CIN)	6.8556	–0.3618	1.7384	830 m	932 m
$UO_2(NCS)_2 \cdot 2$(INH-CIN)	6.7779	–0.3622	1.7408	825 m	927 m
$UO_2(ClO_4)_2 \cdot 3$(INH-CIN)	6.8166	–0.3698	1.7399	827 m	930 m

TABLE-4
THERMOANALYTICAL RESULTS OF UO_2(VI) COMPLEXES OF INH-VAN

Complex	Sample wt. (mg)	Residual wt. (mg)	Ligand mass loss (%) 230–320°C		390–480°C		Residual (%) *ca.* 760°C	
			Theor.[a]	Exp.	Theor.[b]	Exp.	Theor.[c]	Exp.
$UO_2Br_2 \cdot 2$(INH·VAN)	23.20	6.57	27.88	28.20	55.76	56.69	28.87	28.34
$UO_2(NO_3)_2 \cdot 2$(INH·VAN)	26.40	7.81	28.95	29.62	57.90	58.79	29.98	29.59
$UO_2(NCS)_2 \cdot 2$(INH·VAN)	28.60	8.81	29.20	29.89	58.40	59.26	31.09	30.83
$UO_2(OAc)_2 \cdot 2$(INH·VAN)	21.60	6.45	29.13	29.96	58.27	59.06	30.17	29.87
$UO_2(ClO_4)_2 \cdot 3$(INH·VAN)	22.20	4.71	21.13	21.89	63.41	64.32	21.89	21.26

[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-VAN

Complex	Sample wt. (mg)	Residual wt. (mg)	Ligand mass loss (%) 210–305°C		375–460°C		Residual (%) *ca.* 755°C	
			Theor.[a]	Exp.	Theor.[b]	Exp.	Theor.[c]	Exp.
$UO_2Br_2 \cdot 2$(INH·VAN)	20.50	6.11	26.93	27.32	53.86	54.58	30.11	29.80
$UO_2(NO_3)_2 \cdot 2$(INH·VAN)	27.60	8.57	28.01	28.84	56.02	57.86	31.32	31.05
$UO_2(NCS)_2 \cdot 2$(INH·VAN)	24.80	7.77	28.26	28.93	56.53	57.36	31.60	31.33
$UO_2(OAc)_2 \cdot 2$(INH·VAN)	23.20	7.24	28.20	29.06	56.40	57.58	31.53	31.20
$UO_2(ClO_4)_2 \cdot 3$(INH·VAN)	21.20	4.80	20.54	21.24	61.62	62.79	22.96	22.68

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

Thermogravimetric analyses

The thermal analyses of present complexes show that there is no water molecule present either in or outside the coordination sphere. The thermal results are summarized in Tables 4 and 5. The thermal changes are summarized as follows:

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

($X = Br^-, NO_3^-, OAC^-$ or NCS^-; L = INH-VAN or INH-CIN)

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

In conclusion, the works presented on INH-VAN and INH-CIN complexes show that uranium(VI) has a tendency to form complexes having high coordination eight or ten depending on the nature of coordinated anions.

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