Thorium(IV) and Dioxouranium(VI) Chelates of Aromatic Amine N-Oxides

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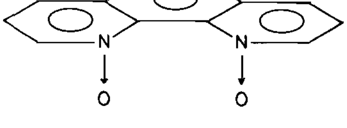
Received November 23, 1981

Thorium(IV) and dioxouranium(VI) chelates of 1,10-phenanthroline N–N′-dioxide (phenO_2) and dioxouranium(VI) chelates of mono N-oxides of 2,2′-bipyridine (bipyNO) and 1,10-phenanthroline (phenNO) of the general composition $ThX_4 \cdot 2phenO_2$ (X = Cl, Br, NO_3 or NCS); $ThX_4 \cdot 3phenO_2$ ($X = ClO_4$ or I); $UO_2X_2 \cdot 2L$ (X = Cl, Br, and L = bipyNO, phenNO or phen$_2$); $UO_2(NO_3)_2 \cdot L$; $UO_2X_2 \cdot 3L$ ($X = ClO_4$ or I) and $UO_2(NCS)_2 \cdot 1.5L$ have been synthesised and characterized employing i.r. spectral, molar conductance, molecular weights, d.t.a. and t.g.a. data. phenO_2 acts as O,O-bidentate ligand while bipyNO and phenNO act as N,O-bidentate ligands. The coordination number of thorium in these complexes is either 6, 8 or 12; in uranium the coordination number is either 7 or 8 depending on the nature of the anions.

Introduction

In continuation of our work [1] on mono N-oxides of 2,2′-bipyridine and 1,10-phenanthroline chelates of thorium(IV), we report herein on thorium(IV) and dioxouranium(VI) chelates of 1,10-phenanthroline N-N′-dioxide (phenO_2) (I) and dioxouranium(VI) chelates of mono N-oxides of 2,2′-bipyridine (bipyNO) and 1,10-phenanthroline (phenNO). The donor properties of phenO_2 have been studied to a limited extent [2, 3], whereas dioxouranium(VI) complexes of pyridine N-oxides [4], 2,2′-bipyridine N-N′-dioxide [5–7] have already been reported.



(1)

Experimental

Materials

Thorium(IV) salts, the ligands bipyNO and phenNO were prepared as reported earlier [1]. AnalaR-grade uranyl nitrate was obtained from B.D.H. Uranyl halides were prepared from nitrate while perchlorate was prepared as reported earlier [8]. The ligand phenO_2 was prepared by the method described for 2,2′-bipyridine N-N′-dioxide [9, 10]. 2,2′-dimethoxypropane (Aldrich Chemical Company, Inc. U.S.A.) and other reagent grade organic solvents were used throughout.

Preparation of the Complexes

Dioxouranium(VI) complexes of bipyNO and phenNO were prepared by a similar method as that used for thorium(IV) complexes [1]. Thorium(IV) and dioxouranium(VI) complexes of phenO_2 were prepared by the following general method. Metal salt was dissolved in a mixture of absolute EtOH and a dehydrating agent 2,2′-dimethoxypropane and warmed on a water bath for 1 h; phenO_2 was dissolved in hot absolute EtOH. The two solutions were mixed and refluxed for 1 h. The complexes were generally isolated as fine crystals. These were filtered, washed with EtOH and finally with anhydrous Et_2O and dried *in vacuo* over P_4O_{10}.

All the physical measurements and analyses were performed as reported earlier [1]. Uranium was estimated as U_3O_8 [11]. The analytical results are presented in Table I.

Results and Discussion

The molar conductances of the complexes in $MeNO_2$ and $PhNO_2$ (*ca.* 10^{-3} *M*) determined at room temperature are given in Table I. The chloro, bromo, nitrato and thiocyanato complexes are non-electrolytes in both solvents. The iodo and perchlorato complexes dissociate in these solvents and behave as uni–bivalent, only thorium(IV) perchlorate complex being uni–tetravalent electrolyte. The molecular weight

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0020-1693/82/0000-0000/$02.75

TABLE I. Analytical Data of Thorium(IV) and Uranyl(VI) Complexes.

Complex	Found (Calc.) %					Λ_m ohm^{-1} cm^2 mol^{-1}	Electrolytic nature	M.W. Found (Calc.)
	M	G	H	N	Anion			
ThCl$_2$2phenO$_2$	28.9	36.35	1.9	6.83	17.45	4.9[a]	Non-electrolyte	769
	(29.1)	(36.1)	(2.0)	(7.0)	(17.8)	9.7[b]		(798)
ThBr$_4$2phenO$_2$	23.9	29.75	1.5	5.5	32.05	6.8[b]	Non-electrolyte	–
	(23.8)	(29.5)	(1.6)	(5.7)	(32.8)			(976)
ThI$_4$3phenO$_2$	16.8	31.55	1.6	5.85	35.7	59.9[a]	1:2	432
	(16.9)	(31.4)	(1.7)	(6.1)	(36.9)	156.9		(1376)
Th(ClO$_4$)$_4$3phenO$_2$	18.15	34.3	1.85	6.45	30.65	96.9[a]	1:4	237
	(18.3)	(34.1)	(1.9)	(6.6)	(31.4)	290.6[b]		(1266)
Th(NO$_3$)$_4$2phenO$_2$	25.2	31.95	1.7	12.2	–	4.5[a]	Non-electrolyte	852
	(25.6)	(31.85)	(1.8)	(12.4)		20.9[b]		(904)
Th(NCS)$_4$2phenO$_2$	26.35	37.6	1.65	12.43	25.3	5.6[a]	Non-electrolyte	838
	(26.1)	(37.8)	(1.8)	(12.6)	(26.1)	15.8[b]		(888)
UO$_2$Cl$_2$2phenO$_2$	31.4	37.9	2.0	7.2	9.1	3.8[a]	Non-electrolyte	730
	(31.1)	(37.6)	(2.1)	(7.3)	(9.3)	9.3[b]		(765)
UO$_2$Br$_2$2phenO$_2$	27.45	33.95	1.75	6.4	18.3	4.0[a]	Non-electrolyte	829
	(27.9)	(33.7)	(1.9)	(6.55)	(18.7)	8.7[b]		
UO$_2$I$_2$3phenO$_2$	20.7	37.35	2.15	7.1	20.83	57.6[a]	1:2	370
	(20.5)	(37.2)	(2.1)	(7.2)	(21.9)	168.7[b]		(1160)
UO$_2$(ClO$_4$)$_2$3phenO$_2$	21.35	39.4	2.2	7.75	16.95	59.3[a]	1:2	332
	(21.5)	(39.1)	(2.2)	(7.6)	(18.0)	172.3[b]		(1105)
UO$_2$(NO$_3$)$_2$phenO$_2$	39.7	24.2	1.2	9.1	–	2.8[a]	Non-electrolyte	573
	(39.3)	(23.8)	(1.3)	(9.2)		14.9[b]		(606)
UO$_2$(NCS)$_2$1.5phenO$_2$	33.95	34.35	1.65	9.65	15.95	3.8[a]	Non-electrolyte	670
	(33.8)	(34.1)	(1.7)	(9.9)	(16.5)	19.6[b]		(704)
UO$_2$Cl$_2$2phenNO$_2$	32.25	39.7	2.15	7.45	9.25	3.7[a]	Non-electrolyte	702
	(32.5)	(39.3)	(2.2)	(7.6)	(9.7)	21.3[b]		(733)
UO$_2$Br$_2$2phenNO	28.7	33.25	1.8	6.6	19.0	4.9[a]	Non-electrolyte	790
	(28.95)	(33.0)	(1.9)	(6.8)	(19.5)			(822)
UO$_2$I$_2$3phenNO	21.25	38.6	2.1	7.35	21.95	[c]	1:2	339
	(21.4)	(38.8)	(2.15)	(7.55)	(22.8)	178.9[b]		(1112)
UO$_2$(ClO$_4$)$_2$3phenNO	22.3	40.7	2.2	7.7	17.15	58.9[a]	1:2	326
	(22.5)	(40.9)	(2.3)	(7.9)	(18.8)	172.6[b]		(1057)
UO$_2$(NO$_3$)$_2$phenNO	40.55	24.6	1.2	9.35	–	3.7[a]	Non-electrolyte	542
	(40.3)	(24.4)	(1.33)	(9.5)		17.4[b]		(590)
UO$_2$(NCS)$_2$1.5phenNO	35.25	35.7	1.7	10.15	16.35	3.8[a]	Non-electrolyte	625
	(35.0)	(35.3)	(1.8)	(10.3)	(17.05)	14.9[b]		(680)
UO$_2$Cl$_2$2bipyNO	34.25	35.25	2.2	8.1	10.1	4.2[a]	Non-electrolyte	650
	(34.7)	(35.0)	(2.3)	(8.2)	(10.4)	16.7[b]		(685)
UO$_2$Br$_2$2bipyNO	30.5	30.9	2.0	7.1	20.95	4.8[a]	Non-electrolyte	732
	(30.7)	(31.0)	(2.1)	(7.2)	(20.7)	[c]		(774)
UO$_2$I$_2$3bipyNO	23.15	34.8	2.0	7.9	23.7	[c]	1:2	–
	(22.9)	(34.6)	(2.3)	(8.1)	(24.4)	167.3[b]		(1040)
UO$_2$(ClO$_4$)$_2$3bipyNO	24.7	36.9	2.2	8.3	19.4	58.7[a]	1:2	298
	(24.2)	(36.5)	(2.4)	(8.5)	(20.2)	179.6[b]		(285)
UO$_2$(NO$_3$)$_2$bipyNO	42.15	21.7	1.25	9.7	–	4.3[a]	Non-electrolyte	542
	(42.0)	(21.2)	(1.4)	(9.9)	–	14.6[b]		(566)
UO$_2$(NCS)$_2$1.5bipyNO	37.15	31.5	1.85	10.6	18.3	3.8[a]	Non-electrolyte	610
	(36.95)	(31.7)	(1.9)	(10.9)	(18.0)	19.3[b]		(644)

[a] In PhNO$_2$. [b] In MeNO$_2$. [c] Partially soluble.

data (Table I) also support the above mentioned electrolytic behaviour of the complexes. The magnetic moments of thorium(IV) and dioxouranium(VI) complexes indicate them (as expected) to be diamagnetic [1, 12, 13].

I.R. Spectra

Table II records important i.r. bands for the ligands and the complexes. The assignments are largely based on the previous work on these ligands [1, 2] and i.r. studies of thorium(IV) and uranyl(VI)

TABLE II. Partial[a] I.R. Spectral Data[b] of $\mathrm{phenO_2}$, phenNO and bipyNO and their Metal Chelates.

Compound	ν(N–O)	ν(M–O)	ν(M–N)	ν(M–X)
$\mathrm{phenO_2}$	1312s 1282s	–	–	–
$\mathrm{ThCl_4 \cdot 2phenO_2}$	1280s 1265m	410m 402sh	–	250m,br
$\mathrm{ThBr_4 \cdot 2phenO_2}$	1290s 1270m	405m	–	175m 170m,sh 165w
$\mathrm{ThI_4 \cdot 3phenO_2}$	1290m 1280m	402m	–	135m 120w
$\mathrm{Th(ClO_4)_4 \cdot 3phenO_2}$	1270s 1260m	398m	–	–
$\mathrm{Th(NO_3)_4 \cdot 2phenO_2}$	1272s 1262m	405m	–	–
$\mathrm{Th(NCS)_4 \cdot 2phenO_2}$	1280s 1270m	395m	–	–
$\mathrm{UO_2Cl_2 \cdot 2phenO_2}$	1272s 1260m	330m	–	260m,br
$\mathrm{UO_2Br_2 \cdot 2phenO_2}$	1280s 1265m	325m	–	165m
$\mathrm{UO_2I_2 \cdot 3phenO_2}$	1290m 1282m	320m	–	–
$\mathrm{UO_2(ClO_4)_2 \cdot 3phenO_2}$	1270s 1260m	332m	–	–
$\mathrm{UO_2(NO_3)_2 \cdot phenO_2}$	1270s 1262m	335m	–	–
$\mathrm{UO_2(NCS)_2 \cdot 1.5phenO_2}$	1280s 1265m	325m	–	–
phenNO	1270s 1250s	–	–	–
$\mathrm{UO_2Cl_2 \cdot 2phenNO}$	1220s 1205m	325m	255m	258m,br
$\mathrm{UO_2Br_2 \cdot 2phenNO}$	1230s 1210s	320m	250m	160m
$\mathrm{UO_2I_2 \cdot 3phenNO}$	1235m 1210s	318m	250m	–
$\mathrm{UO_2(ClO_4)_2 \cdot 3phenNO}$	1230s 1205m	330m	255m	–
$\mathrm{UO_2(NO_3)_2 \cdot phenNO}$	1233m 1210m	332m	260m	–
$\mathrm{UO_2(NCS)_2 \cdot 1.5phenNO}$	1220m 1210s	320m	250m	–
bipyNO	1250s 1230s	–	–	–
$\mathrm{UO_2Cl_2 \cdot 2bipyNO}$	1235s 1210s	320m	250m	264m
$\mathrm{UO_2Br_2 \cdot 2bipyNO}$	1240s 1210m	318m	252m	162m
$\mathrm{UO_2I_2 \cdot 3bipyNO}$	1240s 1205m	315m	245m	–
$\mathrm{UO_2(ClO_4)_2 \cdot 3bipyNO}$	1215s 1205m	330m	255m	–
$\mathrm{UO_2(NO_3)_2 \cdot bipyNO}$	1220s 1207m	335m	255m	–
$\mathrm{UO_2(NCS)_2 \cdot 1.5bipyNO}$	1230s 1210m	320m	252m	–

[a] Detailed i.r. data on the complexes can be obtained from the author. [b] In cm^{-1}. [c] X = Cl, Br, or I.

chelates with 2,2′-bipyridine [5, 14], 1,10-phenanthroline [14, 15] and 2,2′-bipyridine N–N′-dioxide [6, 7, 16].

In the i.r. spectra of the free ligands two (N–O) bands have been observed at 1250 and 1230 cm^{-1} in the case of bipyNO [1]; 1270 and 1250 cm^{-1} for phenNO [1] and 1312 and 1282 cm^{-1} for phenO_2 [2, 3]. These bands have been observed to shift to lower frequencies upon complex formation. The decrease in the frequency of the ν(N–O) vibration is attributed to O,O chelation in phenO_2 and oxygen coordination of phenO and bipyNO. Absorptions of strong intensities in the 880–800 cm^{-1} region have been assigned to NO bending mode, and from the tabulated data it appears that these absorptions change only slightly on complexation [17]. This further supports oxygen linkage between metal and the ligands. Coordination through the nitrogen atom of the pyridine fragment of bipyNO and phenNO is suggested by frequency shifts and splittings of the several i.r. bands associated with vibration of this fragment [1, 18–20]. In the far infrared region metal–ligand vibrations are tentatively assigned to ν(M–O) and ν(M–N) modes. The overall i.r. spectral evidence suggests that phenO_2 acts as O,O-bidentate chelating agent forming seven-membered chelate; while bipyNO and phenNO act as bidentate O,N-chelating agents forming six-membered rings.

The ν(U=O) in all dioxouranium(VI) complexes has been assigned at *ca.* 960 and 920 cm^{-1} as asymmetric and symmetric frequencies [5, 6, 21].

The metal–halogen [1, 22] modes in the spectra of the complexes (Table II) have also been assigned tentatively in the present study. The strong ν_3 and ν_4 bands in the spectra of perchlorato complexes occur unsplit at *ca.* 1090 and 625 cm^{-1} respectively, showing the ionic character of the perchlorato groups [6, 8, 11]. The ν(C–N) frequency in the actinide thiocyanate complexes lie in 2080–2060 cm^{-1} region and ν(C–S) frequency at *ca.* 820 cm^{-1} strongly suggesting N-bonded NCS [23, 24]. The i.r. spectra of the nitrato complexes show the absence of ν_3 bands at *ca.* 1360 cm^{-1} due to ionic nitrate [25]. The bidentate nature of covalent nitrato groups in $Th(NO_3)_4 \cdot 2phenO_2$ has been established by comparing the i.r. bands at *ca.* 1505 (ν_4), 1285 (ν_1), 1035 (ν_2), 800 (ν_6) and 730 (ν_3/ν_5) cm^{-1} with the spectral bands of $Th(NO_3)_4 \cdot 5H_2O$ at 1520, 1290, 1030, 808, 745 and 715 cm^{-1} respectively [26, 27]. in $UO_2(NO_3)_2 \cdot L$ (L = bipyNO, phenNO or phenO_2) the nitrate groups also seem to be bidentate since the i.r. frequencies at *ca.* 1520, 1280, 1032, 800 and 740 cm^{-1} in these complexes due to this group occur almost at the same frequencies as reported earlier [25, 28, 29].

Thermal Behaviour

The differential thermal behaviour of thorium(IV) complexes of phenO_2 is almost similar to that of other aromatic amine N-oxide complexes [1, 16, 30]. All the complexes decompose below *ca.* 280 °C. A final exothermic peak below 700 °C in all the complexes is due to the formation of ThO_2. The t.g.a. of the complexes is more or less similar to that of phenNO complexes [1].

The thermal behaviour of uranyl complexes of amine N-oxides has been studied to a limited extent [5, 8]. The d.t.a. of the uranyl(VI) complexes of amine N-oxides reveal that halo and nitrato complexes decompose endothermically, while perchlorato complexes decompose exothermically with evolution of smoke. In iodo complexes the peak at *ca.* 150 °C may be due to loosely-bonded iodide present in the complexes. All the complexes decompose below *ca.* 320 °C. A final exothermic peak at *ca.* 550 °C in all the complexes is due to the formation of U_3O_8. The thermogravimetric experiments show that in uranyl(VI) complexes all the attached ligand molecules are lost between 270–320 °C. At *ca.* 550 °C the decomposition is complete. In all the cases U_3O_8 is obtained as end product. On the basis of thermal studies, the thermal stability of uranyl(VI) complexes of bipyNO, phenNO and phenO_2 is in the order:

Nitrate > Chloride > Perchlorate > Bromide >

> Thiocyanate

Acknowledgements

The authors are grateful to Prof. T. N. Srivastava, Lucknow University, for taking keen interest in the work. Thanks are also due to University Grants Commission, New Delhi, and C.S.I.R., New Delhi for financial support.

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