

Complexes of Uranium and Thorium with Pyrazine and Pyrazine Amides

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Reactions of uranium tetrachloride, uranyl nitrate and thorium nitrate with pyrazine (Pyz), pyrazine 2-carboxamide (Pyza) and pyrazine 2, 3-dicarboxamide (Pyzda) have been carried out to study their coordination behaviour. Structural aspects of the complexes formed are discussed from the results of molar conductance and infrared spectral studies.

It has been reported that pyrazine acts as a monodentate or a bridging ligand resulting in the formation of polymeric complexes¹⁻³. In the case of pyrazine 2-carboxamide and pyrazine 2,3-dicarboxamide, due to the presence of amide groups in the favourable position, these ligand molecules can act as chelating ligands through the pyrazine nitrogen and the amide groups. The presence of amide groups in 2 and 3 positions in the case of pyrazine 2,3-dicarboxamide can also result in the formation of a chelate through the amide carbonyl oxygens. The preparation of the complexes of group (IV) metal halides with these ligands and their structural aspects have already been reported by the authors¹. In view of the interesting results obtained in the above studies, this work has been extended to Th(IV), U(IV) and UO₂(II) Lewis acids.

Experimental

The chemicals UCl₄, UO₂(NO₃)₂·6H₂O and Th(NO₃)₄·5H₂O were prepared and purified by suitable methods. Pure ligands were obtained from commercial sources (K & K Laboratories, Inc., USA) and were used as such without further purification. The solvents tetrahydrofuran (THF), petroleum ether (40-60°), acetonitrile, N, N'-dimethylformamide and nitromethane were treated with appropriate drying agents and fractionally distilled before use.

Since UCl₄ and its complexes are highly sensitive to atmospheric moisture and oxygen, all experimental manipulations were carried out in a dry box continuously flushed with dry nitrogen. The experimental set-up and general methods of preparation of the complexes were similar to those reported earlier^{4,5}. The reactants, in 1:1 stoichiometry, were first dissolved separately in THF and then mixed under constant stirring to precipitate the product. The compound UCl₄·2 Pyzda was, however, obtained by the interaction of UCl₄ solution

in THF and suspension of the ligand in the same solvent in the excess of UCl₄. The reaction product was filtered, washed with the solvent after three days of stirring and finally dried *in vacuo* at room temperature.

The uranyl nitrate and thorium nitrate compounds with Pyz and Pyza were prepared by mixing and refluxing the reactants in THF for about 30 minutes. The compounds were isolated from the solution by adding petroleum ether after reducing the volume by evaporation. The analytical results of the complexes obtained in the study are given in Table 1. The metal and halogen contents in the compounds were determined by conventional analytical methods. Carbon, hydrogen and nitrogen contents were determined by microanalysis. Molar conductance of the complexes in acetonitrile (AN), N,N'-dimethyl formamide (DMF) and nitromethane (NM) were measured with 'Industrial Instrument Inc. Conductivity bridge Model RC-216-BI at 25°. Conductivity measurements were carried out with 10⁻³ M solutions of the compounds in these solvents. The molecular weights of the compounds were taken to be equal to the empirical formula for calculating the molar conductivities. The infrared spectra of the compounds were recorded on Perkin-Elmer Spectrophotometer Model 21, 577 and Perkin-Elmer Infracord in Nujol mull using sodium chloride and caesium iodide optics.

Results and Discussion

Pyrazine compounds : The reactions of pyrazine with uranium tetrachloride, uranyl nitrate and thorium nitrate have resulted in the formation of UCl₄·2.5 Pyz, 2UO₂(NO₃)₂·3 Pyz and Th(NO₃)₄·3Pyz (Table 1). Uranium(IV) is known to form 1:2.5 and 1:3 types of adducts with organic ligands⁶⁻⁸. Pyrazine is known⁹ to form compounds where it acts either as monodentate or a bidentate ligand bridging two metal atoms. The ir spectra

TABLE 1—ANALYTICAL RESULTS

Sl. No.	Compounds	Colour	Melting point °C	Metal%		Halide%		Carbon%		Hydrogen%		Nitrogen%		Nature of adduct
				Found	Cal.	Found	Cal.	Found	Cal.	Found	Cal.	Found	Cal.	
1.	UCl ₄ .2.5Pyz	Greenish gray	~140D	40.5	41.04	24.8	24.45	—	—	—	—	11.6	12.07	2 : 5
2.	UO ₂ (NO ₃) ₂ .1.5Pyz	Yellow	~275D	47.3	46.96	—	—	16.7	17.33	2.20	1.44	14.8	15.16	2 : 3
3.	Th(NO ₃) ₄ .3Pyz	Buff	85-87	32.2	32.22	—	—	18.7	20.01	2.92	1.67	19.0	19.44	1 : 3
4.	UCl ₄ .3Pyza	Light green	~130D	32.2	31.80	18.5	18.93	23.3	24.03	2.33	2.00	17.3	16.83	1 : 3
5.	UO ₂ (NO ₃) ₂ .4Pyza	Bright yellow	~170D	25.8	26.87	—	—	—	—	—	—	21.6	22.12	1 : 4
6.	Th(NO ₃) ₄ .2Pyza	Light brown	105-107°	32.8	31.96	—	—	16.50	16.53	1.47	1.38	—	—	1 : 2
7.	UCl ₄ .2Pyzda	Brown	~140D	33.2	33.43	19.7	19.91	—	—	—	—	14.4	15.7	1 : 2

D=Decomposed by turning black without melting.

Pyz=Pyrazine

Pyza=Pyrazine 2-carboxamide

Pyzda=Pyrazine 2,3-dicarboxamide.

of the compounds UCl₄.2.5 Pyz, 2UO₂(NO₃)₂.3Pyz and Th(NO₃)₄.3Pyz in the present study display additional bands in 1170 and 940 cm⁻¹ region, indicating that the Pyz molecules in these complexes act as monodentate^{2,3,9}. In the uranyl and thorium compounds, the NO₃ groups would also play an important role in determining the structure of the complex molecules. Nitrate groups can either be in ionic sphere or in coordination sphere. It has been found¹⁰ that D_{3h} symmetry of the free NO₃ ion is lowered to C_{2v} symmetry on coordination to the metal atom. A comparison of the observed ir bands for 2UO₂(NO₃)₂.3Pyz and Th(NO₃)₄.3Pyz with those reported in literature¹⁰⁻¹³ for C_{2v} symmetry is given in Table 2.

TABLE 2—Ir SPECTRA RESULTS (cm⁻¹)

10, 11, 12* C _{2v} NO ₃ modes	2UO ₂ (NO ₃) ₂ .3Pyz	Th(NO ₃) ₄ .3Pyz
ν_1 1485vs	1530vs, 1490sh	1527s
ν_2 1030vs	1038s	1036m
ν_3 748m	747ms	740sh
ν_4 1288s	1300vs	1300ms
ν_5 723w	720m	720m
ν_6 812msh	812m	810ms
$\nu_3 + \nu_2$ 1773vw	1785w	1770w
$\nu_2 + \nu_4$ 1730vw	1745w	1740w
$\nu_3 + \nu_1$ 2540vw	2560w	2550w
$\nu_3 + \nu_4$ 2296vw	2330w	2330w
v=very, w=weak,	s=strong, sh=shoulder	m=medium, * References.

The ir spectra of the complexes (Table 2) contain all the six fundamental and combination modes of coordinated nitrates. The separation of ν_1 and ν_4 by about 230 cm⁻¹ in the present case is of the same order as reported by Kim *et al*¹¹ for the bidentate nitrate groups. The energy separation of combination frequencies (Table 2) also support the bidentate nature of the nitrate groups^{11,13}. Similar coordination of all the four nitrate groups in the

case of Th(NO₃)₄.3DMSO (DMSO=dimethylsulphoxide) has been reported by Alvey and Bagnall¹⁴ on the basis of X-ray single crystal studies where the thorium atom exhibits a coordination number 11.

The molar conductance measurements of 10⁻³M solutions of 2UO₂(NO₃)₂.3Pyz and Th(NO₃)₄.3Pyz in acetonitrile (AN), N, N'-dimethylformamide (DMF) and nitromethane (NM) are reported in Table 3. It is interesting to note that while molar conductance of 10⁻³M solutions of uranyl compounds in AN(200 ohm⁻¹cm²mole⁻¹) and NM (76 ohm⁻¹cm²mole⁻¹) corresponds to 1:1 electrolyte, the same compounds in DMF(150 ohm⁻¹cm²mole⁻¹) seems to be 2:1 electrolyte^{15,16}. Similarly, the thorium compounds in AN(300 ohm⁻¹cm²mole⁻¹) and NM(154 ohm⁻¹cm²mole⁻¹) corresponds to 2:1 electrolyte nature, but in DMF (288 ohm⁻¹cm²mole⁻¹) the same compound seems to be

TABLE 3—MOLAR CONDUCTANCE MEASUREMENTS (ohm⁻¹cm²mole⁻¹)

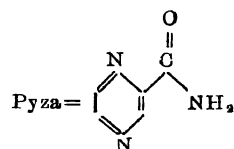
Compound	Solvent		
	CH ₃ CN	HCON(CH ₃) ₂	CH ₃ NO ₂
2UCl ₄ .5Pyz	200	100	105
2UO ₂ (NO ₃) ₂ .3Pyz	200	150	76
Th(NO ₃) ₄ .3Pyz	300	288	154
UCl ₄ .3Pyza	115	92	100
UO ₂ (NO ₃) ₂ .4Pyza	Insoluble	140	Insoluble
Th(NO ₃) ₄ .2Pyza	270	177	110

4:1 electrolyte¹⁶. This difference in DMF may be arising from the strong donor ability of DMF molecules which displace the coordinated nitrate groups into ionic sphere resulting in the change of electrolyte type¹⁶. The molar conductance measurements of 10⁻³M solutions of UCl₄.2.5 Pyz in AN, DMF and NM gave the value of 200, 100 and 105 ohm⁻¹cm²mole⁻¹ respectively (Table 3). These

TABLE 4—INFRARED SPECTRA (cm^{-1}) OF Pyza AND ITS COMPOUNDS

Pyza	$\text{UCl}_4 \cdot 3\text{Pyza}$	$\text{UO}_2(\text{NO}_3)_2 \cdot 4\text{Pyza}$	$\text{Th}(\text{NO}_3)_4 \cdot 2\text{Pyza}$	Band assignments
3520s	—	—	3430sb	} $\nu(\text{N}-\text{H})$
3360ms	3333vs	3390m	3355s	
3244s	3125vs	3175mb	3315sb	
1738vs	1695vs	1660s	1685s, 1655s	} $\nu(\text{C}=\text{O})$
1632s	1618s	1595ms	1610sh	
1601s	1582s	1568sh	1585s	
—	—	—	1520vsb	} $\delta(\text{NH}_2)$
—	—	1300ms	1300vsb	
1195m	1245s	1260s	1250sh	
1172s	1188s	1180m	1180m	} $\nu(\text{C}-\text{N})$
—	1160sh	1158sh	1160sh	
1105m	1130s	1134sh	1115sh	
1058s	1065s	1075m	1080sh	} Ring vib.
—	925w	1052m	1035vs	
—	—	956sh	935sh	
—	—	940m, 915m	—	} $\nu_{\text{as}}(\text{UO}_2)$
874s	880m	878m	875sh	
810sh	820m	812m	812sh	
—	—	—	818vsh	} $\text{C}-\text{H}$ out of plane
790s	785m	785m	782mw	
—	—	758s	752s	
—	—	712m	—	} $\text{C}-\text{H}$ out of plane
—	—	—	—	

s=strong, m=medium, w=weak, sh=shoulder b=broad, v=very,



values correspond to the 1:1 electrolyte. Therefore, the possible formulation of $\text{UCl}_4 \cdot 2.5\text{Pyz}$ compound can be the ionic species of the type $[\text{UCl}_6]^{2-}[\text{UCl}_2 \cdot 5\text{Pyz}]^{2+}$. Such a possibility has been established by Bombieri *et al.*^{17,18} for the actinide complexes of stoichiometries $\text{MCl}_4 \cdot 3\text{L}$ and $\text{MCl}_4 \cdot 2.5\text{L}$. However, the appearance of a strong band at 255 cm^{-1} with shoulders at 245 and 235 cm^{-1} in the $\nu(\text{U}-\text{Cl})$ region could be attributed due to terminal and bridging chlorine atoms in $\text{UCl}_4 \cdot 2.5\text{Pyz}$. Thus, the possibility of the compound being a dimer in the solid state with halogen bridging cannot be ruled out.

Pyrazine 2-carboxamide compounds :

Pyza is an amide derivative of pyrazine where it can conveniently coordinate to a metal through one of the heterocyclic nitrogens and one of the side chain donor atoms of the amide group forming a five membered chelate. The reaction of ligand with UCl_4 , $\text{UO}_2(\text{NO}_3)_2$ and $\text{Th}(\text{NO}_3)_4$ gave $\text{UCl}_4 \cdot 3\text{Pyza}$, $\text{UO}_2(\text{NO}_3)_2 \cdot 4\text{Pyza}$ and $\text{Th}(\text{NO}_3)_4 \cdot 2\text{Pyza}$ respectively.

The ir spectra of the compounds, Table 4, show negative shifts in the range of $40\text{--}80\text{ cm}^{-1}$ in the $\nu(\text{C}=\text{O})$ as compared to the corresponding value of the uncoordinated ligand. In the $\nu(\text{C}-\text{N})$ region of the amide group, two bands at 1195 and 1172 cm^{-1} for the free ligand appear in the higher frequency region for the complexes. These results

are in conformity with the coordination of the amide group through the $\text{C}=\text{O}$ oxygen¹⁸⁻²⁰. It is interesting to note that similar to the ir spectra of the Pyza compounds with group (IV) halides¹, in the present study also new bands at 1160 and 940 cm^{-1} , characteristic of the involvement of one of the hetero nitrogens of pyrazine ring in bonding have been observed. Thus, it suggests that in the Pyza compounds under discussion, the ligand molecule is bonded to the metal atom through the $\text{C}=\text{O}$ group and through one of the heterocyclic nitrogens.

It is further interesting to note that while the ir spectrum of $\text{Th}(\text{NO}_3)_4 \cdot 2\text{Pyza}$ displays bands at 1520 , 1300 , 990 , 818 and 752 cm^{-1} for the nitrate groups, the spectrum of $\text{UO}_2(\text{NO}_3)_2 \cdot 4\text{Pyza}$ shows only three bands at 1300 , 758 and 712 cm^{-1} . This difference in spectra can be interpreted^{10,21} due to the covalent nature of the NO_3 groups in the thorium compound and ionic nature in the uranyl compound.

Molar conductance measurements of 10^{-3}M solutions of $\text{UCl}_4 \cdot 3\text{Pyza}$, $\text{Th}(\text{NO}_3)_4 \cdot 2\text{Pyza}$ and $\text{UO}_2(\text{NO}_3)_2 \cdot 4\text{Pyza}$ in AN, DMF and NM (Table 3) suggest that while $\text{UCl}_4 \cdot 3\text{Pyza}$ is 1:1 electrolyte in nature, $\text{Th}(\text{NO}_3)_4 \cdot 2\text{Pyza}$ and $\text{UO}_2(\text{NO}_3)_2 \cdot 4\text{Pyza}$ compounds in solution behave as 2:1 electrolytes¹⁶. The formulation of the compounds can be explained on the basis of ionic species $[\text{UCl}_6][\text{UCl}_2 \cdot 3\text{Pyza}]$, $[\text{Th}(\text{NO}_3)_2 \cdot 2\text{Pyza}][2\text{NO}_3]$ and $[\text{UO}_2 \cdot 4\text{Pyza}][2\text{NO}_3]$ respectively.

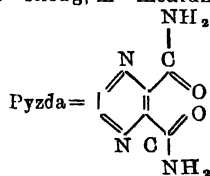
Pyrazine 2, 3-dicarboxamide compound :

Unlike the formation of 2 : 1 adduct¹ in the case of $TiCl_4$ and Pyzda, the reaction with UCl_4 gave 1 : 2 adduct, $UCl_4 \cdot 2Pyzda$. The compound is insoluble in common organic solvents. Our attempts to prepare Pyzda compounds with thorium nitrate and uranyl nitrate have not been successful. The infrared spectral results (Table 5) of the compound as compared to the ligand show a lowering of $\nu(N-H)$, $\nu(C=O)$ and $\delta(NH_2)$ by 115, 40 and 30 cm^{-1} respectively. This indicates the bonding of the ligand to the metal atom through the carbonyl groups.

TABLE 5—INFRARED SPECTRA (cm^{-1}) OF Pyzda AND ITS COMPOUNDS

Pyzda	$UCl_4 \cdot 2Pyzda$	Band assignments
3550s	3435sh	} $\nu(N-H)$
3390s	3315s	
3283s	3265s	
1710sb	1670s	$\nu(C=O)$
1632s	1600sh	$\delta(NH_2)$
1586ms	1570s	Ring vib $\nu(C-O)$, $\nu(C-N)$
1409s	1415sh	
1360s	1350sh	} $\nu(C-N)$
1201m	1215m	
1172m	1185m	
1105s	1103s	} Ring vib.
1075m	1050m	
1066s	1065m	
—	925s	} C-H out of plane
882s	880sh	
860s	862s	
800w	795s	
760s	765s	

s=strong, m=medium, w=weak, sh=shoulder, b=broad,



interest in this work. Thanks are also due to the Bio-Organic Division, B.A.R.C. for carrying out microanalysis.

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