



E-J.Chem
<http://www.e-journals.net>



ISSN: 0973-4945; CODEN ECJHAO
E-Journal of Chemistry
2010, 7(3), 1045-1054

Physicochemical Investigations of Th(IV) and UO₂(VI) Complexes with New Schiff Bases Along with their Toxic Effects

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Received 31 October 2009; Accepted 20 December 2009

Abstract: Schiff bases were obtained using *p*-trimethoxy benzaldehyde, *p*-hydroxyl benzaldehyde and 2-amino pyridine to prepare new complexes of thorium(IV) and dioxouranium(VI) metals by various anions. The synthesized ligands and complexes were analytically studied through spectral studies, elemental analysis conductance measurements along with semi empirical and thermogravimetric methods. The complexes were assigned various coordination numbers ranging from 6-10 on the basis of these studies.

Keywords: Synthesis, Analytical studies, Thorium(IV) and dioxouranium(VI) complexes, Schiff base, Coordination number.

Introduction

Th(IV) and UO₂(VI) metal complexes with variety of Schiff bases and exhibit high coordination numbers. Their enormous complex forming tendency is attributed to the vacant inner 5f sub shell which can expand greatly to accommodate a number of ligands. The greater spatial extension of 5f orbitals of actinides along with the fact that these orbitals are diffused at the periphery of atom make them suitable to form number of complexes because in such situation the orbitals are disturbed by ligands. Hence actinide complexes may be ionic in nature along with covalent characters¹. Also, the +4 oxidation state of Th and +6 of UO₂ have adequate sizes so that their complex forming tendency is further enhanced.

Nitrogen donor ligands particularly Schiff bases have been of great interest for various coordination chemist who used them as ligands against thorium(IV) and dioxouranium(VI) metal to form complexes. Schiff bases form a class of compounds with azomethine (-C=N-) group which can be obtained by condensation of primary amine and carbonyl compounds by elimination of water molecule. In this present work two Schiff base are reported which were derived from 2-amino pyridine and 3,4,5-trimethoxy benzaldehyde and *p*-hydroxy benzaldehyde.

Experimental

All the chemicals used were of AR grade and were used with further purification where ever required. Elemental analyses were carried on Elemental Vario EL III Carlo Erba 1108. Conductivity measurements for the complexes have been carried out on Elico 01/01 cell type Conductivity Bridge. Molecular weights were determined in freezing PhNO₂ using Beckmann Thermometer method cryoscopically in the laboratory. IR spectra were taken through Schimadzu 8201 PC (4000-400 cm⁻¹). Mass spectra were obtained through JEOL SX- 102 (FAB). PMR spectra of selected samples were recorded on τ scale through Bruker Avance IT 400 NMR spectrometer. TGA were carried on Mettler.

Synthesis of ligand

Solution of 3,4,5-trimethoxybenzaldehyde and 4-hydroxybenzaldehyde (1 mmole) in approx. 30 mL ethanol was mixed with solution of 2-amino pyridine (1 mmole) each in approx. 30 mL ethanol. The resultant solutions were refluxed in RB flask fitted with water condenser for six hours. On cooling Schiff bases crystallized out which were filtered and re-crystallized with solvent and then ether. The structures of ligands are given in Figure 1 & 2.

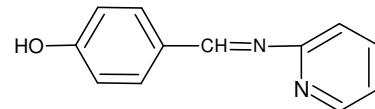
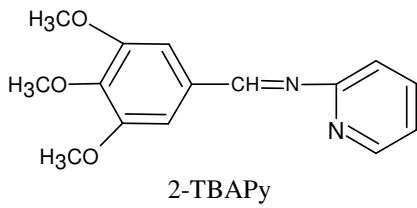


Figure 1. 2N-[3,4,5-Trimethoxybenzalidene] aminopyridine. **Figure 2.** 2N-[4-Hydroxybenzalidene] aminopyridine.

Preparation of complexes

Th⁴⁺ and UO₂²⁺ complexes of Schiff base were prepared by refluxing the nitrate, iodide, isothiocyanate, perchlorate salts of Th⁴⁺ and UO₂²⁺ in proper M:L ratio using ethanol solvent. Uranyl acetate was also complexed with in proper M:L ratio. The complexes were left in petri dish to obtain crystalline product and were recrystallised with ethanol.

Results and Discussion

The complexes are obtained in dry crystalline state and are quite stable for a long period of time except for that of iodide complexes in which evolution of iodine vapours through a slow gradual process at room temperature convert complexes gradually into sticky mass. The melting point of these complexes was examined on melting point apparatus of our laboratory. Conductivity experiments of the complexes were carried out in nitrobenzene and as only iodide and perchlorate complexes showed significant conductivity as these furnish more than one ion in solution. This is suggestive of the fact that anions of the complexes are ionisable, primary valencies of complex^{2,3}. The analytical results are discussed in Table 1 & 2.

Mass spectra

Mass spectra of both ligands were recorded. For 2-TBAPy the base peak at 273 is (M+) peak and loss of pyridine ($m=76$) causes significantly intense peak at 196 m/z. When pyridine moiety along with azomethine part fragments off then peak at 153 m/z is obtained. In case of 2-HBAPy the parent peak at 199 loses rings and at 154 m/z arises and the benzene ring along with hydroxyl moiety fragments off to produce peak at 95 m/z.

Table 1. Analytical results of 2-TBAPy and its complexes.

Base/Complex	Elemental Anal.			Mol.wt. obs/calcd	M.P. °C	Cond. $\Omega \text{cm}^{-1} \text{eq}^{-1}$
	% C Obs (calcd)	% H Obs (calcd)	% N Obs (calcd)			
2TBAPy	64.65(66.1)	5.79(5.8)	8.9(10.29)	273(272)	182-185	-
[Th(2TBAPy) ₂ (NO ₃) ₄]	46.1(45.9)	5.1(4.08)	11.2(10.7)	1536(1568)	272	2.3
[Th(2TBAPy) ₄ I ₂]I ₂	47.8(46.99)	5.0(4.17)	7.8(7.3)	359(1088)	196	112.5
[Th(2TBAPy) ₄ (NCS) ₄]	48.9(49.48)	4.1(4.12)	9.9(10.8)	1520.9(1552)	212	1.8
[Th(2TBAPy) ₆](ClO ₄) ₄	37.1(36.96)	3.19(3.28)	4.9(5.74)	389(1948)	232	212.8
[UO ₂ (2TBAPy) ₂ (NO ₃) ₂]	40.24(38.5)	3.46(3.42)	7.46(6.0)	915(934)	184	2.5
[UO ₂ (2TBAPy) ₂ (NCS) ₂]	72.17(77.75)	3.23(3.45)	5.8(6.04)	907(926)	203	3.1
[UO ₂ (2TBAPy) ₄](ClO ₄) ₂	45.18(46.34)	4.01(4.12)	6.89(7.21)	558(1552)	217	238.4
[UO ₂ (2TBAPy) ₂ (CH ₃ COO) ₂]	42.8(43.9)	3.9(4.09)	5.08(6.03)	909(928)	175	2.4
[UO ₂ (2TBAPy) ₂ I ₂]	37.6(39.3)	3.24(3.49)	5.79(6.11)	898(916)	131	1.8

Table 2. Analytical results of 2HBAPy and its complexes.

Base/Complex	Elemental Anal.			Mol.wt. obs/calcd	M.P. °C	Cond. $\Omega \text{cm}^{-1} \text{eq}^{-1}$
	% C Obs (Calcd)	% H Obs (Calcd)	% N Obs (Calcd)			
2HBAPy	64.29(72.7)	5.13(5.05)	17.18(14.14)	199(198)	170-175	-
[Th(2HBAPy) ₂ (NO ₃) ₄]	25.11(32.8)	2.08(2.28)	9.73(12.78)	858(876)	212	1.8
[Th(2HBAPy) ₄ I ₂]I ₂	41.04(46.60)	3.1(3.23)	8.4(9.06)	407(1236)	145	122.6
[Th(2HBAPy) ₄ (NCS) ₄]	40.9(49.48)	2.2(2.68)	10.4(11.29)	1458(1488)	195.3	2.3
[Th(2HBAPy) ₆](ClO ₄) ₄	39.8(40.56)	2.5(2.81)	6.8(7.88)	284(1420)	209	242.8
[UO ₂ (2HBAPy) ₂ (NO ₃) ₂]	41.87(36.64)	3.5(2.54)	7.86(10.54)	770(786)	164.2	1.8
[UO ₂ (2HBAPy) ₂ (NCS) ₂]	38.9(40.10)	2.3(2.57)	8.79(10.79)	762(778)	194	2.1
[UO ₂ (2HBAPy) ₄](ClO ₄) ₂	43.4(45.85)	3.0(3.18)	6.9(8.91)	452(1256)	207	236.4
[UO ₂ (2HBAPy) ₂ (CH ₃ COO) ₂]	31.42(43.07)	2.36(3.33)	4.48(3.58)	764(780)	141.8	3.1
[UO ₂ (2HBAPy) ₂ I ₂]	34.3(37.5)	1.98(2.6)	4.56(3.6)	753(768)	202.5	3.5

Semi empirical studies

With the help of AM1 Hamiltonian in the MOPAC package, bond length, bond energy, ionization potential, core -core repulsion *etc* details are obtained. Structures of amine and Schiff bases were drawn on Serena software, PCMODEL package and used further in MOPAC.

The binding site is located in Schiff base with the help of electron density. The data given in Table 3 reveal that the hetero atom of Schiff base has high electron density and N atom of azomethine, O of methoxy and chloro atom have high electron densities and these may act as binding sites. Another supporting fact is the ‘charge factor’ on these atoms as the value of charges is highly negative because of accumulation of electrons, thus rendering them as effective site for bonding. The hydroxy group, chlorine atom and oxygen of the methoxy group cannot serve as binding site for metals because they are present at *para* positions and bonding at these positions may develop strain in the ring or the meta and *para* methoxy group do not serve as bonding site because of steric hindrance. Thus, it becomes nearly established that N atom of azomethine group serves as binding site for the metal atom. Dipole moment values can also indicate the bonding site. From the values given in Table 3 it is clear that high dipole moment is because of charges and thus the site becomes reactive.

IR spectral studies

IR spectra were taken through Schimadzu 8201 PC for range 4000-400 cm⁻¹ using KBr pellets. When the IR spectra of ligands are compared with those of complexes then shift in the azomethine (-C=N-) peaks are observed through which the metal atom is believed to be bonded thus the azomethine bond is considered to be a part of coordination^{4,5}. For 2-TBAPy the significant peaks include one at 781-740 cm⁻¹ belonging to 2- substituted pyridine system and other at 1275-1200 cm⁻¹ peculiar to C-O-C stretching mode of aryl alkyl ether⁶. In the spectra of 2-HBAPy the typical peak of 1,4 di-substituted benzene ring around 800 cm⁻¹ and aromatic aldehydic system involved in conjugation around 1600 cm⁻¹ are clearly distinct. The -C=N- stretching frequency for 2-TBAPy is around 1593 cm⁻¹ while for its thorium iodide, thorium isothiocyanate and thorium perchlorate the absorption is around 1507 cm⁻¹, 1593 cm⁻¹ and 1590 cm⁻¹ respectively. For 2-HBAPy the same is around 1596 cm⁻¹ and for thorium iodide, thorium isothiocyanate and thorium perchlorate these are around 1593 cm⁻¹, 1514 cm⁻¹ and 1504 cm⁻¹ respectively. The dioxouranium complexes also show such type of shifts in their IR absorption frequencies. The details are discussed in Tables 4-7.

PMR spectra

PMR spectra of 2-TBAPy and its complex with uranyl acetate were recorded. The azomethine proton produces a multiplet around 6.5 ppm which remain persisted in the uranyl acetate complex as well. For methoxy protons singlet is observed around 9.8 ppm also found in the complex. The signal of amino pyridine protons is observed in the 6-8 ppm range. Other signal obtained for these complexes are at 7.1489-7.3980 and around 7.97 ppm value.

Antibacterial and antifungal studies

Antibacterial and antifungal activities of some of the representative complexes were done through paper disc method in our own laboratory. The bacterial strain *E.coli* and fungal strain *Aspergillus* and *Mucor* were grown on PDA medium. Paper disc of approx. 1.5 cm diameter were cut and dipped in different concentration of complexes (w/v) in DMF. Paper disc dipped in pure DMF solution was chosen as control. Later these plates were inoculated by bacteria or fungi and incubated in oven for 2-3 days in inverted position. Culture medium was chosen as NA solution.

The results were analyzed on two bases *viz* the radial distance of colony developed from the periphery of paper disc^{7,9} and diameter of largest colony developed around the paper disc.

Toxic effects of complexes with 2-TBAPy

Three representatives complexes were chosen for this purpose *viz.* [UO₂(2TBAPy)₂(CH₃COO)₂], [UO₂(2TBAPy)₄(NO₃)₂], [UO₂(2TBAPy)₂I₂]. The significant results are discussed in Table 8. For bacterial species the uranyl acetate complex showed negligible toxicity at minimum concentration while uranyl iodide was found to be maximum efficient amongst the complexes at moderate concentrations. Uranyl acetate proved to be potent antifungal agent in this series.

Toxic effects of complexes with 2-HBAPy

Two representative complexes of uranyl salts were chosen in this series of hydroxy benzalidene ligands *viz* [UO₂(2HBAPy)₂I₂], [UO₂(2HBAPy)₂(NCS)₂]. For bacterial toxicity the thiocyanate complex came out to be effective as bacterial colony developed far away from its sample disc and that too of small diameter; whereas for *Aspergillus* sp, iodide complex was more potent antifungal than thiocyanate and the same was proved for *Mucor* sp as well. The significant results are tabulated in Table 8.

Table 3. AM 1 calculation results.

Base/Complex	Net atomic charge/elec.density on -NH ₂ of amino pyridine	Net atomic charge/elec.density on -C=N-of Schiff base	Net atomic charge/elec.density on -OCH ₃ Of Schiff base	Net atomic charge/elec.density on -OH of Schiff base	Dipole moment value in Debye
2-Amino pyridine	-0.3230/5.3230	-	-	-	2.249
2-TBAPy	-	-1.1798/5.1798	-0.2065/6.2065	-	2.186
2-HBAPy	-	1.1742/5.1742	-	-0.2472/6.2472	1.138

Table 4. Infra red absorpton frequencies (cm⁻¹) for thorium(IV) complexes of 2-TBAPy.

Assignment	2-TBAPy	Th(NO ₃) ₄ . (2-TBAPY) ₂	ThI ₄ . (2-TBAPY) ₄	Th(NCS) ₄ . (2-TBAPY) ₄	Th(ClO ₄) ₄ . (2-TBAPY) ₆
C=N stretching azomethine	1593,1506	1593	1592,1507	1593	1590
Ring stretching N phenyl stretching	1389,1334	1384, 1352	1384,1351	1384,1351	1383
Ring bending of benzene	1235,1126	1237	1237	1326	1063
Ring bending and deformation	1465	1459	1459,1422	1460	1440
C-N-C bending	990	993,903	996	998	980
Out of plane ring deformation	768,729	768	770	770	750
Out of plane for mono substituted benzene	673	669	669, 626	670	672
v M-N metal ligand vibration	-	512	514	510	530

Table 5. Infra red absorpton frequencies (cm⁻¹) for dioxouranium(VI) complexes of 2-TBAPy.

Assignment	2-TBAPy	UO ₂ (CH ₃ COO) ₂ . (2- TBAPy) ₂	UO ₂ (NO ₃) ₂ . (2-TBAPy) ₂	UO ₂ I ₂ . (2- TBAPy) ₂	UO ₂ (NCS) ₂ . (2- TBAPy) ₂	UO ₂ (ClO ₄) ₄ . TBAPy) ₂
C=N stretching azomethine	1593,1506	1589,1542	1591,1507	1594	1590,1505	1585
Ring stretching Nphenyl stretching	1389,1334	1391,1330	1385,1352	1384,1351	1386,1330	1382
Ring bending of benzene	1235,1226	1236,1128	1236,1127	1123	1236,1126	1064
Ring bending and deformation	1465	1463,1425	1460	1460	1460	1428
C-N-C bending	990	993,932	993,911	993	900	980
Out of plane ring deformation	768,729	759,731	770,727	769	768,727	765
Out of plane for mono substituted benzene	673	677,628	669,626	669	669,627	670
v M-N metal ligand vibration	-	529	521	520	463	510

Table 6. Infra red absorpton frequencies (cm^{-1}) for dioxouranium(VI) complexes of 2-HBAPy.

Assignment	2-HBAPy	$\text{ThI}_4(2\text{-HBAPY})_4$	$\text{Th}(\text{NCS})_4$ (2-HBAPy) ₄	$\text{Th}(\text{ClO}_4)_4$ (2-HBAPy) ₆
C=N stretching azomethine	1596,1508	1593,1510	1514	1597,1504
Ring stretching N phenyl stretching	1384,1351	1384	1389	1375
Ring bending of benzene	1282,1154	1159	1154	1275
Ring bending and deformation	1440	1450	1490	1433
C-N-C bending	995	828	840	832
Out of plane ring deformation	769,736	762	750	763
Out of plane for mono substituted benzene	605	610	673	629
v M-N metal ligand vibration	-	550,490	495	505

Table 7. Infra red absorpton frequencies (cm^{-1}) for dioxouranium(VI) complexes of 2-HBAPy.

Assignment	2-HBAPy	$\text{UO}_2(\text{CH}_3\text{COO})_2$ (2- HBAPy) ₂	$\text{UO}_2(\text{NO}_3)_2$ (2- HBAPy) ₂	UO_2I_2 (2- HBAPy) ₂	$\text{UO}_2(\text{NCS})_2$ (2- HBAPy) ₂	$\text{UO}_2(\text{ClO}_4)_4$ HBAPy) ₂
C=N stretching azomethine	1596,1508	1594	1594,1504	1524	1520	1520
Ring stretching N phenyl stretching	1384,1351	1384,1350	1384	1384	1381	1379
Ring bending of benzene	1282,1154	1153	1153	1162,1117	1112	1090
Ring bending and deformation	1440	1470	1490	1459	1430	1429
C-N-C bending	995	931,901	993	910	910	920
Out of plane ring deformation	769,736	768	764	760	755	750
Out of plane for mono substituted benzene	605	676,612	669,612	672	674	672,628
v M-N metal ligand vibration	-	510	515	510,490	510	490

Table 8. Colony diameter/ Radial distance of colony around sample disc (cm).

Study organism	Complex	Pure	Complex	Conc.	DMF
		DMF	20%	40%	60%
Antifungal <i>Aspergillus</i>	[UO ₂ (2TBAPy) ₄ (NO ₃) ₂]	0.4 / 0.1	0.2 / 0.1	0.1 / 0.4	0.0 / 0.7
Antifungal <i>Mucor</i>	[UO ₂ (2TBAPy) ₂ I ₂] [UO ₂ (2HBAPy) ₂ I ₂]	1.0 / 0.1 1.2 / 0.4	0.3 / 1.0 0.3 / 0.5	0.5 / 0.3 0.2 / 0.5	0.3 / 1.0 0.2 / 0.5

Probable structure of thorium(IV) and dioxouranium(VI) complexes

Complexes of Th(IV) in this research work are suggested¹⁰ to have co-ordination numbers 6, 8 or 10. The conductance, molecular weight data suggest that the co-ordination no. is eight for isothiocyanate complexes and six for perchlorate complexes as these ions are present outside the co-ordination sphere. This co-ordination number is observed by earlier worked as well¹¹⁻¹³.

The iodo complexes of Th(IV) have electrolytic nature as established by conductance measurements and that these are present outside the co-ordination sphere so these should have co-ordination no. six. The nitro group in these complexes is found to be bidentate in nature as established by IR spectral data in this work and is present inside the co-ordination sphere so its co-ordination should be 10.

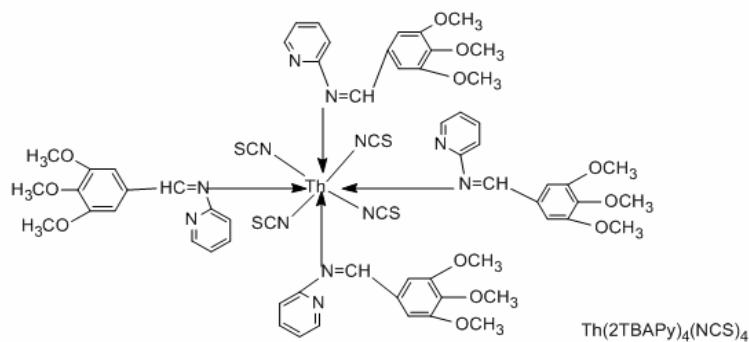
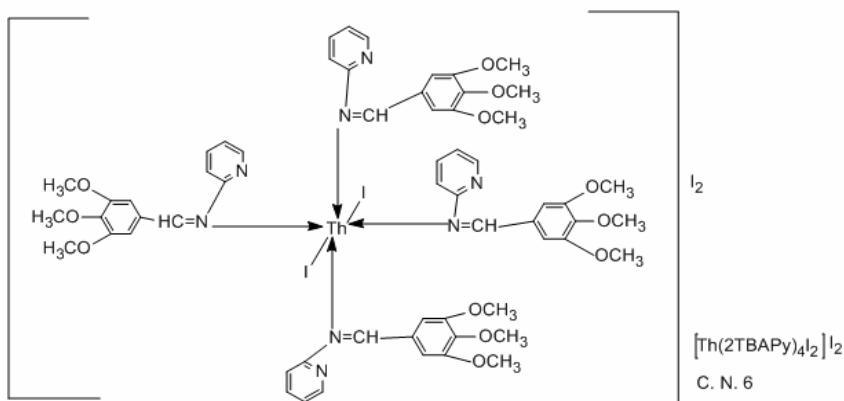
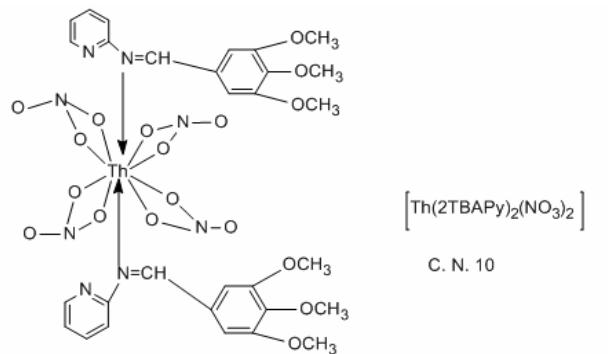
Like thorium complexes the dioxouranium(VI) complexes are believed to have 6,8 or 10 co-ordination number in these complexes. The nitro group is bidentate in nature as suggested by IR spectral studies and its presence inside the co-ordination no. eight likely the acetate complexes are also believed to have co-ordination no. eight¹⁴.

Table 9. Proposed coordination number of complexes.

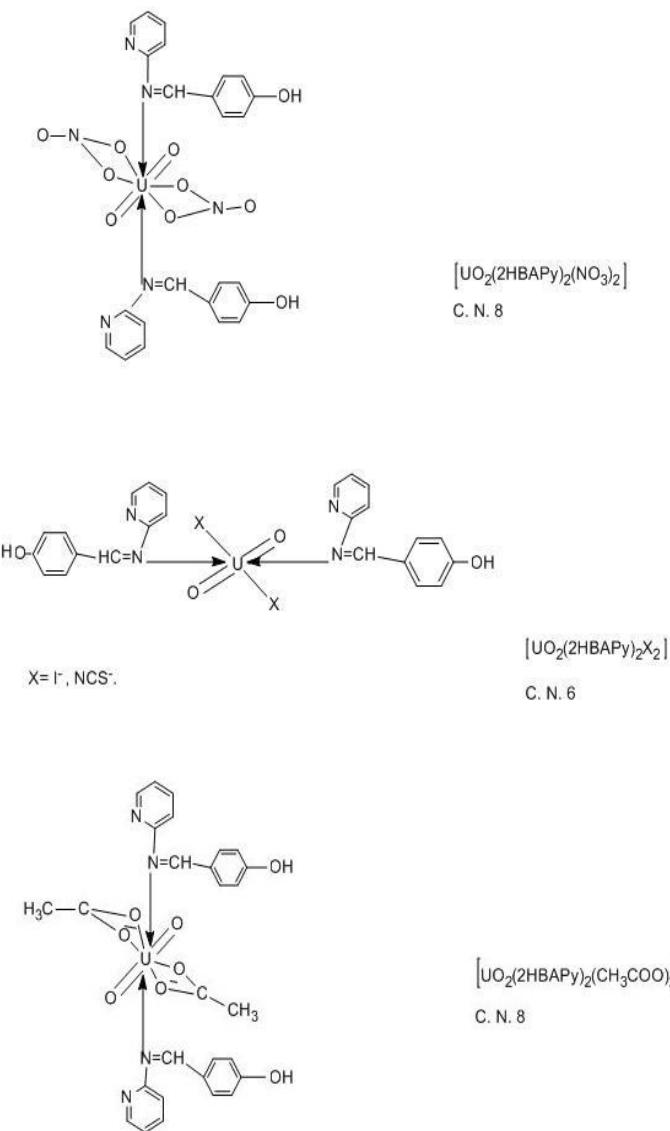
<u>Th⁴⁺ and UO₂²⁺ complexes of 2-TBAPy</u>		
Th(NO ₃) ₄ . 2(2-TBAPy)	[Th(2-TBAPy) ₂ (NO ₃) ₄]	10
Th(I) ₄ . 4(2-TBAPy)	[Th(2-TBAPy) ₄ I ₂]I ₂	6
Th(NCS) ₄ . 4(2-TBAPy)	[Th(2-TBAPy) ₄ (NCS) ₄]	8
Th(ClO ₄) ₄ . 6(2-TBAPy)	[Th(2-TBAPy) ₆](ClO ₄) ₄	6
UO ₂ (NO ₃) ₂ . 2(2-TBAPy)	[UO ₂ (2-TBAPy) ₂ (NO ₃) ₂]	8
UO ₂ (NCS) ₂ . 2(2-TBAPy)	[UO ₂ (2-TBAPy) ₂ (NCS) ₂]	6
UO ₂ (ClO ₄) ₂ . 4(2-TBAPy)	[UO ₂ (2-TBAPy) ₄](ClO ₄) ₂	6
UO ₂ (CH ₃ COO) ₂ . 2(2-TBAPy)	[UO ₂ (2-TBAPy) ₂ (CH ₃ COO) ₂]	8
UO ₂ (I) ₂ . 2(2-TBAPy)	[UO ₂ (2-TBAPy) ₂ I ₂]	6
<u>Th⁴⁺ and UO₂²⁺ complexes of 2-HBAPy</u>		
Th(NO ₃) ₄ . 2(2-HBAPy)	[Th(2-HBAPy) ₂ (NO ₃) ₄]	10
Th(I) ₄ . 4(2-HBAPy)	[Th(2-HBAPy) ₄ I ₂] I ₂	6
Th(NCS) ₄ . 4(2-HBAPy)	[Th(2-HBAPy) ₄ (NCS) ₄]	8
Th(ClO ₄) ₄ . 6(2-HBAPy)	[Th(2-HBAPy) ₆](ClO ₄) ₄	6
UO ₂ (NO ₃) ₂ . 2(2-HBAPy)	[UO ₂ (2-HBAPy) ₂ (NO ₃) ₂]	8
UO ₂ (NCS) ₂ . 2(2-HBAPy)	[UO ₂ (2-HBAPy) ₂ (NCS) ₂]	6
UO ₂ (ClO ₄) ₂ . 4(2-HBAPy)	[UO ₂ (2-HBAPy) ₄](ClO ₄) ₂	6
UO ₂ (CH ₃ COO) ₂ . 2(2-HBAPy)	[UO ₂ (2-HBAPy) ₂ (CH ₃ COO) ₂]	8
UO ₂ (I) ₂ . 2(2-HBAPy)	[UO ₂ (2-HBAPy) ₂ I ₂]	6

The iodo and thicyanato complexes of dioxouranium(VI) are believed to have co-ordination number six for uranyl atom as these establish covalent bonds with it. The perchlorato complexes of dioxouranium(VI) are known to be electrolytic in nature as

revealed by conductance data and that these ions must be present outside the co-ordination sphere is also inferred from this data so the preferred co-ordination must be six as also observed in earlier works¹⁵. The proposed coordination numbers and structures (Scheme 1 & 2) of for complexes of 2-TBAPy and 2-HBAPy are given in Table 9.



Scheme 1.

**Scheme 2.****References**

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