

## Physico-chemical Investigation of Th(IV) and UO<sub>2</sub>(VI) Complexes of Schiff Bases

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Schiff bases were obtained using *p*-methoxy benzaldehyde and *p*-chloro 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.

**Key Words:** Synthesis, Analytical studies, Thorium(IV) and dioxouranium complexes, Schiff base, Coordination number.

### INTRODUCTION

Th(IV) and UO<sub>2</sub>(VI) metal complexes with variety of Schiff bases and exhibit high coordination numbers. Their enormous complex forming tendency is attributed to the vacant inner 5*f* sub shell which can expand greatly to accommodate a number of ligands. The greater spatial extension of 5*f* 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 are ionic in nature along with covalent characters<sup>1</sup>.

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 were derived from 2-amino pyridine and *p*-methoxy benzaldehyde and *p*-chloro benzaldehyde.

### EXPERIMENTAL

All the chemicals used were of AR grade and were used with further purification where ever required. Elemental analysis were carried on Elemental Vario EL III Carlo Erba 1108 CDRI Lucknow. Conductivity measurements for the complexes have been carried out on Elico 01/01 cell type conductivity bridge. Molecular weights were determined in freezing PhNO<sub>2</sub> using Beckmann thermometer method cryoscopically in the laboratory.

IR spectra were taken through Shimadzu 8201 PC (4000-400 cm<sup>-1</sup>) from CDRI Lucknow. Mass spectra were obtained through JEOL SX-102 (FAB), CDRI Lucknow. PMR spectra of selected samples were recorded on t scale through Bruker Avance IT 400 NMR spectrometer SAIF Punjab University Chandigarh. TGA were carried on Mettler from Central instrumentation Laboratory from NIPER Mohali.

**Synthesis of ligand:** Solution of 4-methoxybenzaldehyde and 4-chlorobenzaldehyde (1 mmol) in *ca.* 30 mL ethanol was mixed with solution of 2-amino pyridine (1 mmol) each in *ca.* 30 mL ethanol. The resultant solutions were refluxed in RB flask fitted with water condenser for 6 h. On cooling Schiff bases crystallized out which were filtered and re-crystallized with proper solvent. The structure of ligands are given in Figs. 1 and 2.

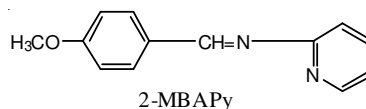


Fig. 1. 2N-[4-Methoxybenzaldiene]aminopyridine

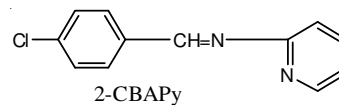


Fig. 2. 2N-[4-Chlorobenzaldiene]aminopyridine

**Preparation of complexes:** Th<sup>4+</sup> and UO<sub>2</sub><sup>2+</sup> complexes of Schiff base were prepared by refluxing the nitrate, iodide, isothiocyanate, perchlorate salts of Th<sup>4+</sup> and UO<sub>2</sub><sup>2+</sup> 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<sup>2</sup>. The analytical data are given in Tables 1 and 2.

**Mass spectra:** Mass spectra of both ligands were recorded. In case of 2-MBAPy the parent peak at 199 loses rings; benzene and pyridine to give rise to *m/z* 154 peak of 100 % intensity

and when the benzene ring along with hydroxyl moiety fragments off a peak is produced at *m/z* 95. For 2-CBAPy similar to earlier fragmentation pattern is observed and the rings are lost and *m/z* at 154 arises.

**IR spectral studies:** In the spectra of 2-MBAPy and 2-CBAPy the typical peak of 1,4-di-substituted benzene ring around 800  $\text{cm}^{-1}$  and aromatic aldehydic system involved in conjugation around 1600  $\text{cm}^{-1}$  are clearly distinct. The ligand 2-MBAPy show -C=N- stretching frequency at 1596  $\text{cm}^{-1}$  while its thorium isothiocyanate complex shows it at 1594  $\text{cm}^{-1}$ . The IR spectra of 2-CBAPy shows -C=N- stretching frequency at 1596  $\text{cm}^{-1}$  and its thorium isothiocyanate complex exhibit it at 1593  $\text{cm}^{-1}$ . The characteristic absorption frequencies for the two ligands and the Thorium complex are exhibited in the narrow range, but the striking difference in absorption frequency appears in terms of ring bending of benzene. The 2-MBAPy ligand and its thorium isothiocyanate complex show ring bending of benzene around 1288 and 1257  $\text{cm}^{-1}$ , respectively while 2-CBAPy ligand and the complex counterpart exhibit this around 1118 and 1158  $\text{cm}^{-1}$ , respectively (Tables 3-6).

TABLE-1  
ANALYTICAL RESULTS OF 2-MBAPy AND ITS COMPLEXES

Base/complex	Elemental analysis (%) data			m.w. (obs/calcd.)	m.p. (°C)	Cond. ( $\Omega \text{ cm}^{-1} \text{ eq}^{-1}$ )
	C obs/(calcd.)	H obs/(calcd.)	N obs/(calcd)			
2-MBAPy	70.56 (73.5)	5.99 (5.6)	14.14 (13.2)	213 (212)	179-182	–
[Th(2-MBAPy) <sub>2</sub> (NO <sub>3</sub> ) <sub>4</sub> ]	25.48 (34.5)	2.56 (2.65)	17.66 (12.38)	1301 (1328)	192.6	2.4
[Th(2-MBAPy) <sub>4</sub> I <sub>2</sub> ]	46.71 (48.29)	3.84 (3.71)	7.91 (8.66)	426 (1292)	154	136
[Th(2-MBAPy) <sub>4</sub> (NCS) <sub>4</sub> ]	45.73 (51.2)	3.0 (3.6)	18.02 (12.8)	1285 (1312)	183.7	2.4
[Th(2-MBAPy) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>4</sub>	32.91 (38.97)	3.41 (2.45)	11.07 (7.57)	295 (1476)	201.8	232.8
[UO <sub>2</sub> (2-MBAPy) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	32.61 (38.32)	2.7 (2.9)	5.42 (6.87)	8.5 (814)	169.7	3.1
[UO <sub>2</sub> (2-MBAPy) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	41.64 (47.56)	3.2 (3.65)	6.81 (8.53)	472 (1312)	236.4	2.8
[UO <sub>2</sub> (2-MBAPy) <sub>4</sub> (NCS) <sub>2</sub> ]	36.4 (38.7)	2.8 (2.97)	5.92 (6.94)	790 (806)	182	2.1
[UO <sub>2</sub> (2-MBAPy) <sub>2</sub> (CH <sub>3</sub> COO) <sub>2</sub> ]	41.34 (44.55)	3.5 (3.71)	5.9 (6.93)	791 (808)	184	2.4
[UO <sub>2</sub> (2-MBAPy) <sub>2</sub> I <sub>2</sub> ]	35.45 (39.19)	2.99 (3.01)	10.75 (7.03)	780 (796)	136.2	1.96

TABLE-2  
ANALYTICAL RESULTS OF 2-CBAPy AND ITS COMPLEXES

Base/complex	Elemental analysis (%) data			m.w. (obs/calcd.)	m.p. (°C)	Cond. ( $\Omega \text{ cm}^{-1} \text{ eq}^{-1}$ )
	C obs/(calcd.)	H obs/(calcd.)	N obs/(calcd)			
2-CBAPy	66.85 (66.5)	4.59 (4.15)	16.55 (16.39)	217 (216.5)	185-189	–
[Th(2-CBAPy) <sub>2</sub> (NO <sub>3</sub> ) <sub>4</sub> ]	27.73 (31.54)	1.08 (1.97)	13.76 (12.26)	895 (913)	186.4	1.4
[Th(2-CBAPy) <sub>4</sub> I <sub>2</sub> ]	40.12 (43.96)	2.3 (2.74)	9.46 (8.54)	432 (1310)	139	1.4
[Th(2-CBAPy) <sub>4</sub> (NCS) <sub>4</sub> ]	35.48 (39.94)	2.12 (2.3)	9.18 (10.75)	1530 (1562)	176.7	1.8
[Th(2-CBAPy) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>4</sub>	40.77 (38.55)	1.53 (2.40)	6.9 (7.49)	298.8 (1494)	202.8	200.9
[UO <sub>2</sub> (2-CBAPy) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	35.72 (34.99)	2.24 (2.18)	12.34 (10.20)	806 (823)	173.5	2.1
[UO <sub>2</sub> (2-CBAPy) <sub>2</sub> (NCS) <sub>2</sub> ]	38.67 (38.28)	2.79 (2.20)	13.69 (10.30)	799 (815)	178.8	2.1
[UO <sub>2</sub> (2CBAPy) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	41.4 (43.30)	2.1 (2.7)	9.6 (8.42)	479 (1330)	215.7	211.8
[UO <sub>2</sub> (2-CBAPy) <sub>2</sub> (CH <sub>3</sub> COO) <sub>2</sub> ]	40.74 (41.12)	2.75 (2.93)	9.82 (9.54)	800 (817)	179.1	3.6
[UO <sub>2</sub> (2-CBAPy) <sub>2</sub> I <sub>2</sub> ]	33.4 (35.77)	2.1 (2.23)	4.48 (3.47)	789 (805)	132.9	2.17

TABLE-3  
INFRA RED ABSORPTION FREQUENCIES ( $\text{cm}^{-1}$ ) FOR THORIUM (IV) COMPLEXES OF 2-MBAPy

Assignment	2-MBAPy	Th(NO <sub>3</sub> ) <sub>4</sub> ·(2-MBAPy) <sub>2</sub>	ThI <sub>4</sub> (2-MBAPy) <sub>4</sub>	Th(NCS) <sub>4</sub> (2-MBAPy) <sub>4</sub>	Th(ClO <sub>4</sub> ) <sub>4</sub> (2-MBAPy) <sub>6</sub>
C=N stretching azomethine	1596, 1512	1668, 1626	1593	1594	1593
Ring stretching Nphenyl stretching	1385, 1322	1384	1383	1383, 1351	1383, 1351
Ring bending of benzene	1288, 1247	1244, 1166	1121	1257	1119
Ring bending and deformation	1460, 1435	1479	1480	1423	1460
C-N-C bending	988	997	990	1029, 894	1119
Out of plane ring deformation	768, 718	770, 722	768	770	769
Out of plane for mono substituted benzene	646, 580	626	670	669, 611	669, 628
$\nu$ M-N metal ligand vibration	–	512	510	511	509

TABLE-4  
INFRA RED ABSORPTION FREQUENCIES (cm<sup>-1</sup>) FOR DIOXOURANIUM(VI) COMPLEXES OF 2-MBAPy

Assignment	2-MBAPy	UO <sub>2</sub> (CH <sub>3</sub> COO) <sub>2</sub> (2-MBAPy) <sub>2</sub>	UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> (2- MBAPy) <sub>2</sub>	UO <sub>2</sub> I <sub>2</sub> (2- MBAPy) <sub>2</sub>	UO <sub>2</sub> (NCS) <sub>2</sub> (2- MBAPy) <sub>2</sub>	UO <sub>2</sub> (ClO <sub>4</sub> ) <sub>4</sub> (2- MBAPy) <sub>2</sub>
C=N stretching azomethine	1596, 1512	1599, 1540	1600	1595	1599	1657, 1607, 1507
Ring stretching Nphenyl stretching	1385, 1322	1322	1383	1384, 1351	1382, 1352	1383, 1312
Ring bending of benzene	1288, 1247	1248, 1164	1261, 1163	1250	1254	1250
Ring bending and deformation	1460, 1435	1466, 1437	1480	1459, 1423	1465	1461
C-N-C bending	988	990, 932	902	899	994, 909	838
Out of plane ring deformation	768, 718	768, 717	770	769	768	765
Out of plane for mono substituted benzene	646, 580	678, 622	669, 622	670	623	672, 629
v(M-N) metal ligand vibration	–	535, 457	510	510	533, 490	530

**PMR Spectra:** PMR spectra of 2-CBAPy and its complex with thorium isothiocyanate was recorded where ligand shows significant peaks around 6.5-9.0 ppm values the complex showed signals in the range of 6.5-8.5 ppm values. The azomethine protons produce signal in the form of multiplet 6.5 ppm which faces chemical shift in the complex and a multiplet is observed 6.7 ppm value in the complex. Protons involved in the chloro-benzaldehyde ring produces a signal around 8.4 ppm values which becomes further deshielded<sup>3</sup> in the complex because of the azomethine linkage and signal is shifted downfield to 7.8-7.9 ppm values.

**Semi empirical studies:** Semi empirical AM1 and PM3 methods are helpful to obtain heat of formation and structures of organic compounds.

With the help of AM1 Hamiltonian in the MOPAC<sup>4</sup> 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<sup>5</sup>, PCMODEL package and used further in MOPAC. AM1 results are tabulated in Table-7.

The binding site is located in Schiff base with the help of electron density. The data given in Table-7 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 are highly negative because of accumulation of electrons, as a result these are effective site for bonding. The chlorine atom and O 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<sup>6</sup>.

TABLE-5  
INFRA RED ABSORPTION FREQUENCIES (cm<sup>-1</sup>)  
FOR THORIUM (IV) COMPLEXES OF 2-CBAPy

Assignment	2-CBAPy	Th(NCS) <sub>4</sub> (2- CBAPy) <sub>4</sub>
C=N stretching azomethine	1596	1593
Ring stretching N-phenyl stretching	1351	1383, 1551
Ring bending of benzene	118	1158
Ring bending and deformation	1471	1490
C-N-C bending	950	925
Out of plane ring deformation	770	768
Out of plane for mono substituted benzene	671	669
v(M-N) metal ligand vibration	–	520

TABLE-6  
INFRA RED ABSORPTION FREQUENCIES (cm<sup>-1</sup>) FOR DIOXOURANIUM (VI) COMPLEXES OF 2-CBAPy

Assignment	2-CBAPy	UO <sub>2</sub> (CH <sub>3</sub> COO) <sub>2</sub> (2- CBAPy) <sub>2</sub>	UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> (2- CBAPy) <sub>2</sub>	UO <sub>2</sub> I <sub>2</sub> (2- CBAPy) <sub>2</sub>	UO <sub>2</sub> (NCS) <sub>2</sub> (2- CBAPy) <sub>2</sub>	UO <sub>2</sub> (ClO <sub>4</sub> ) <sub>4</sub> (2- CBAPy) <sub>2</sub>
C=N stretching azomethine	1596	1601, 1590	1601, 1524	1520	1, 520	1518
Ring stretching Nphenyl stretching	1351	1535	1384	1384, 1326	1329	1383
Ring bending of benzene	1118	1155	1203, 1158	1158, 1119	1294, 1153	1250
Ring bending and deformation	1471	1473	1460	1485	1451	1420
C-N-C bending	950	931	992, 902	950	911	910
Out of plane ring deformation	770	771, 737	771	771	771	750
Out of plane for mono substituted benzene	671	677, 619	670	670	690, 618	670
v(M-N) metal ligand vibration	–	523, 505	543, 520	523	520, 428	520, 500

TABLE-7  
AM 1 CALCULATION RESULTS

	Net atomic charge/elec.density on -NH <sub>2</sub> of amino pyridine	Net atomic charge/elec.density on -C=N- of Schiff base	Net atomic charge/elec.density on -Cl of <i>p</i> -chloro benzaldehyde	Net atomic charge/elec.density on -OCH <sub>3</sub> of Schiff base
2-Amino pyridine	-0.3230/5.3230	–	–	–
4-Chloro benzaldehyde	–	–	-0.0047/7.0047	–
2-CBAPy	–	-0.1592/5.1692	-0.112/7.012	–
2-MBAPy	–	-1.1798/5.1798	–	-0.2065/6.2065

TABLE-8  
 THERMAL STUDIES OF COMPLEXES

Complex	Decomposition step	Proposed reaction scheme	Peak temp. (°C)	Temp. range (°C)
[UO <sub>2</sub> (2-MBAPy) <sub>2</sub> I <sub>2</sub> ]	I	[UO <sub>2</sub> (2-MBAPy) <sub>2</sub> I <sub>2</sub> ] → [UO <sub>2</sub> (2-MBAPy) <sub>0.9</sub> I <sub>2</sub> ]	130	120-220
	II	[UO <sub>2</sub> (2-MBAPy) <sub>0.9</sub> I <sub>2</sub> ] → U <sub>2</sub> O <sub>3</sub>	230	220-290

 TABLE-9  
 THERMAL STUDIES OF COMPLEXES

Complex	Decomposition step	Proposed reaction scheme	Peak temp. (°C)	Temp. range (°C)
[UO <sub>2</sub> (2-CBAPy) <sub>2</sub> (CH <sub>3</sub> COO) <sub>2</sub> ]	I	[UO <sub>2</sub> (2-CBAPy) <sub>2</sub> (CH <sub>3</sub> COO) <sub>2</sub> ] → [UO <sub>2</sub> (2-CBAPy)(CH <sub>3</sub> COO)]	90	50-240
	II	[UO <sub>2</sub> (2-CBAPy)(CH <sub>3</sub> COO)] → U <sub>2</sub> O <sub>3</sub>	250	240-360

**Thermogravimetric studies:** Thermogravimetric studies were done for [UO<sub>2</sub>(2-CBAPy)<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub>] and [Th(2-MBAPy)<sub>2</sub>(NO<sub>3</sub>)<sub>4</sub>]. The complexes were heated at 10 °C/min rate and graphs were plotted as rate of loss of mass *versus* temperature. The details are plotted in Tables 8 and 9. The data discussed in tables are based on information discussed by Freemann-Caroll, Coats -Redfern and Horowitz-Metzer<sup>7-9</sup>. Out of the three methods the Coats -Redfern method is found to be most accurate. According to this method.

For reaction aA → bB + cC the rate of disappearance of A is given as

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \quad (1)$$

where  $\alpha$  = fraction of A decomposed at time t, n = order of reaction and k is rate constant. When linear heating rate is considered then the following equations were deduced against 1/T.

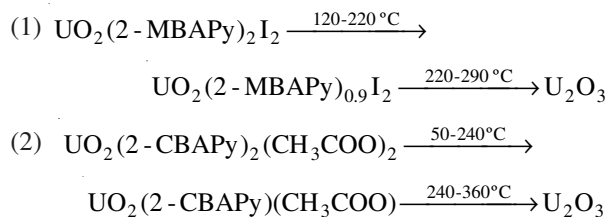
The plot of  $\frac{\log[1-(1-\alpha)^{1-n}]}{T^2(1-n)}$  against 1/t for n ≠ 1 and

$\frac{\log[-\log(1-\alpha)]}{T^2}$  for n = 1 should give a straight line whose slope is -E/2.3 R and A as intercep. The calculations were done for the complexes based on equation-

$$\alpha = \frac{W_o - W}{W_o - W_y}$$

where W<sub>o</sub> is initial weight W = weight at time t and W<sub>y</sub> is final weight.

Thus a general scheme can be proposed for the thermal decomposition of complexes as



Thus various methods used for analysis of thermal decomposition kinetics provide fairly acceptable facts. The analyzed result suggest the fact that since metal oxide are formed in the later stages of decomposition hence M-L bond must be breaking at prior stage of formation of oxide. This suggest the fact that M-L bond must be weaker in nature. This fact can well be accepted if we consider coordinate nature of M-L bond and that metal-anion bond is ionic in nature<sup>10</sup>.

Thus on the bases of these studies the complexes can be assigned coordination numbers as high as 10 and as low as 6 for this present work.

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