

Complexes of Dioxouranium(VI) and Thorium(IV) with Potential Bidentate Schiff Base

K.L. SAHOO and H.N. MOHANTA*

Department of Chemistry
Government College, Angul-759 122, India

A series of complexes of dioxouranium(VI) and thorium(IV) have been prepared using 2-amino benzoic furfuraldeneimine. The complexes have been isolated in solid state and characterised on the basis of elemental analysis, IR, UV, TGA, molecular weight determination and conductivity measurements. The complexes formed are of the type $[\text{UO}_2(\text{HL})_3]\text{X}_2$ ($\text{X} = \text{NO}_3^-, \text{Cl}^-, \text{I}^-, \text{SCN}^-, \text{CH}_3\text{COO}^-, \frac{1}{2}\text{SO}_4^{2-}$), $[\text{UO}_2\text{-HL-L}_2]$; $[\text{Th}(\text{HL})_2\text{X}_4]$ ($\text{X} = \text{Cl}^-, \text{I}^-, \text{SCN}^-$) $[\text{Th}(\text{HL})_2(\text{NO}_3)_2]$ $(\text{NO}_3)_2$.

INTRODUCTION

The coordination compounds of f-block elements are less extensively studied^{1, 2} even though they present an excellent area of research because of the possibility of forming compounds with coordination number greater than 6 and hence attracted wide attention in recent years.^{3, 4} The Schiff base complexes for the transition metals were well documented; those for uranium and other f-block elements are not so frequent. Some recent reports show the formation of Schiff base complexes with dioxouranium(VI) and thorium(IV)^{5, 6}. This paper reports the results of investigation of a series of uranyl(II), thorium(IV) complexes with a bidentate Schiff base (HL), 2-amino benzoic furfuraldeneimine (ABFF). The complexes reported are characterised by elemental analysis, IR, UV, TGA and conductivity measurements.

EXPERIMENTAL

Preparation of the ligand

1.38 g (10^{-2} M) 2-amino-benzoic acid was dissolved in 10 mL ethanol and 1 mL (10^{-2} M) furfural was mixed with constant stirring. The colour of the solution was changed immediately to violet. On refluxing the above solution for about $\frac{1}{2}$ h, an amorphous light yellow compound was formed which was cooled, suction filtered, washed with ethanol and dried in vacuum.

Preparation of complexes

$\text{UO}_2(\text{NO}_3)_2$, $\text{UO}_2(\text{CH}_3\text{COO})_2$, UO_2Cl_2 , UO_2SO_4 , $\text{Th}(\text{NO}_3)_4$ and ThCl_4 salts

† G.M. College, Sambalpur-768 004, india.

were either BDH or Fluka reagent grade. Thiocyanate and iodide salts were prepared by the metathetic reactions of nitrate salts in absolute ethanol and ethanolic solution of KSCN and KI respectively in stoichiometric proportions. The KNO₃ precipitate was filtered off with a Whatmann No. 41 filter paper. The filtrate containing the metal salt solution was used as such for complex preparation. In all cases the metal salt (1 mmol) solution in absolute ethanol was mixed with 50 mL boiling ethanolic solution of the ligand (2 mmol) with constant stirring. In case of UO₂²⁺ complexes the colour of the solution immediately turned deep violet which on refluxing for about 2 h a violet solid was separated out and in case of Th⁴⁺ complexes immediately after the addition of ligand solution a red solid was separated out. The solid compounds formed were suction filtered washed in ethanol and dried in vacuum. The neutral UO₂²⁺ complex was prepared by adding (1 mmol) uranyl acetate to (2 mmol) ethanolic ligand solution in presence of 1 g sodium acetate. In all cases the yield is about 40%.

Metal ions and anions are analysed by standard methods⁷. Carbon, hydrogen and nitrogen analysis were done in CDRI, Lucknow. Conductance measurements in MeOH and PhNO₂ were carried out at 25°C using an ELICO conductivity bridge with a deep type cell having cell constant 0.50. IR. spectrum was measured by Perkin-Elmer-781 instrument in KBr and UV was measured in Varian Carry-2390 instrument. Molecular weights of the compounds were determined by Rast's camphor method.

RESULTS AND DISCUSSION

All the complexes prepared are given in Table-1 along with their analytical and conductance data. The IR data is given in Table-2. All the complexes are very much stable and have high m.p. and are sparingly soluble in common organic solvents. The molar conductance in PhNO₂ and MeOH shows that the complexes are ionic in nature.

In the IR spectra of the ligand, bands in the range 1660–1570 cm⁻¹ for $\nu(\text{C}=\text{N})$ at 1300, 1255 cm⁻¹ for $\nu(\text{C}-\text{O})$ and at about 1210, 1165 cm⁻¹ for $\nu(\text{C}-\text{N})$ and the phenyl ring vibrations multiplet around 1600–1400 cm⁻¹ are obtained. The $\nu(\text{O}-\text{H})$ vibration appears as a band at 2780–2720 cm⁻¹ suggesting the coordination of a neutral ligand and not the anion of the ligand.⁸ The neutral —COOH group is involved in bonding is evident from the presence of IR bands at 1725, 1600, 1560, 1410, 1130, 864, 605 cm⁻¹ corresponding to $\nu\text{C}=\text{O}$, $\nu_{\text{asym}}(\text{COO}^-)$, $\nu_{\text{sym}}(\text{COO}^-)$, $\nu_{\text{asym}}(\text{C}-\text{C}=\text{O})$, $\nu_{\text{sym}}(\text{C}-\text{C}=\text{N})$ and $\delta(\text{COO}^-)$ absorptions respectively.^{9, 10} The $\nu(\text{C}=\text{N})$ in the ligand at 1575 cm⁻¹ is shifted to near 1560 cm⁻¹ indicating that the imino nitrogen is involved in bonding. The oxygen present in the ring is not involved in bonding due to resonance. Thus the ligand behaves as a bidentate ligand.

The conductivity measurement indicates that all the uranyl complexes are 1:2 electrolyte in nature except [UO₂HL·L₂] which is non-electrolyte. Thus the general formula of the compounds is [UO₂(HL)₃]X₂ where X=Cl⁻, I⁻, SCN⁻, NO₃⁻, $\frac{1}{2}\text{SO}_4^{2-}$, CH₃COO⁻. Thus the coordination number around UO₂²⁺ is 8 in all cases with 6 (ligand N, O) in the equatorial plane and two oxygen (UO₂) in the

axial position. All the thorium complexes are non-electrolyte excepting $\text{Th}(\text{NO}_3)_4$ complex which is found to be 1:2 electrolyte. The IR bands for different anions indicate that thorium has a coordination number 8.

TABLE-1
ANALYTICAL AND CONDUCTANCE DATA ON COMPLEXES OF UO_2^{2+} AND Th^{4+}
WITH 2-AMINO BENZOIC FURFURALDENEIMINE (HL)

Compound	m.p. (°C) Colour	Analyses % Found (Calcd.)				λ_M	
		M	C	H	N	MeOH	PhNO ₂
HL	190 Light yellow	—	66.58 (66.98)	4.61 (4.19)	7.01 (6.51)	—	—
$[\text{UO}_2(\text{HL})_3](\text{NO}_3)_2$	>260 Violet	23.01 (22.91)	41.05 (41.58)	2.49 (2.60)	6.35 (6.74)	158	i
$[\text{UO}_2(\text{HL})_3]\text{SO}_4$	>260 Violet	24.05 (23.54)	42.52 (42.73)	2.39 (2.67)	4.03 (4.15)	14.2	i
$[\text{UO}_2(\text{HL})_3]\text{Cl}_2$	>260 Violet	24.06 (24.14)	42.93 (43.81)	2.35 (2.74)	4.01 (4.26)	148	6
$[\text{UO}_2(\text{HL})_3]\text{I}_2$	>260 Violet	20.58 (20.36)	36.48 (36.95)	2.33 (2.31)	3.01 (3.59)	162	42
$[\text{UO}_2(\text{HL})_3](\text{SCN})_2$	>260 Violet	23.15 (23.08)	43.94 (44.23)	2.31 (2.62)	6.52 (6.79)	120	35
$[\text{UO}_2(\text{HL})_3](\text{CH}_3\text{COO})_2$	>260 Violet	22.85 (23.04)	46.12 (46.47)	3.01 (3.19)	4.13 (4.07)	—	—
$[\text{UO}_2(\text{HL})\text{L}_2]$	>260 Violet	25.89 (26.10)	46.82 (47.31)	2.45 (2.73)	4.21 (4.60)	12.5	i
$[\text{Th}(\text{HL})_2(\text{NO}_3)_2](\text{NO}_3)_2$	>260 Red	25.01 (25.49)	31.15 (31.65)	1.81 (1.98)	9.01 (9.23)	162	51
$[\text{Th}(\text{HL})_2(\text{SCN})_4]$	>260 Red	25.55 (25.95)	37.01 (37.58)	2.05 (2.01)	9.11 (9.40)	22.5	12.5
$[\text{Th}(\text{HL})_2\text{Cl}_4]$	>260 Red	28.25 (28.86)	35.53 (35.82)	2.09 (2.24)	3.07 (3.48)	15.4	11.2
$[\text{Th}(\text{HL})_2\text{I}_4]$	>260 Red	19.42 (19.83)	24.01 (24.62)	1.04 (1.54)	2.02 (2.39)	25.2	i

i—insoluble

The ν_3 bands at 1160, 1120, 1080, 1050 cm^{-1} and ν_4 at 670, 640 cm^{-1} are observed for ionic sulphate group, in uranyl sulphato complex.¹² In the thorium thiocyanato complex the IR bands at 2045, 810 cm^{-1} corresponding to $\nu_{\text{sym}}(\text{C}=\text{N})$ and $\nu_{\text{sym}}(\text{C}-\text{S})$ respectively of isothiocyanate group confirm coordination through nitrogen atom¹³ and in uranyl thiocyanato complex IR bands corresponding to ionic thiocyanate group are observed. The nitrate group in $\text{UO}_2(\text{NO}_3)_2$ complex is found to be ionic as bands are observed at 1380, 1275, 830 cm^{-1} where the ionic nitrate vibrations were observed. Thus the coordination number of uranium is 8 in this complex. For the thorium nitrate complex $[\text{Th}(\text{HL})_2(\text{NO}_3)_2](\text{NO}_3)_2$, it is clear that two different types of nitrate anions are present, a set of 2 NO_3^- ions are coordinated in a bidentate manner and the other

TABLE-2
INFRARED SPECTRA (cm⁻¹) OF UO₂²⁺ AND Th⁴⁺ COMPLEXES WITH SCHIFF BASE

Sl. No.	Compound	Anion vibrations	Ligand vibrations				Uranyl modes	
			v(OH) and v(C—H)	v(C=N)	v(C—O)	v(C—N)	v(C=O)	v _{sym} (UO ₂) v _{asym} (UO ₂)
1.	Ligand HL	—	3320 m, 2960 s, 2850 s, 2720 s	1660s 1575 s	1300 s, 1255 br 1165 m, 1160m	1205 s	1730 s	—
2.	[UO ₂ (HL) ₃](NO ₃) ₂	1455 m, 1380 s, 1275s, 890 w, 830 s, 720 s	2900 br 2740 s	1455 s	1300 w 1290 s 1280 s	1170 w 1160 s 1150 w	1710 w 1690 s 1600 s	820 s 890 s
3.	[UO ₂ (HL) ₃]SO ₄	1190 s, 1160 s, 1155 s, 1120 s, 750 br, 715 s, 710 s	2900 br 2820 s	1615 s 1600 s 1590 s	1270 s 1220 s	1190 s	1715 s	850 s 920 s
4.	[UO ₂ (HL) ₃]Cl ₂	—	2800 br 2720 s	1618 s 1592 s	1310s 1295s	1200 s 1185 s	—	840 s 910 s
5.	[UO ₂ (HL) ₃]I ₂	—	2810 s 2760 s	1610 s 1590 s	1315 s 1290 s	1205 s 1185 s 1165 s	—	850 s 930 s
6.	[UO ₂ (HL) ₃](SCN) ₂	—	2860 s 2940 br	1690 s, 1680 s, 1635 s, 1595 s, 1455 m	1375 s 1270 s 1230 m	1165 s 1160 m	1700 s	820 s 920 s

Sl. No.	Compound	Anion vibrations	Ligand vibrations				Uranyl modes		
			v(OH) and v(C—H)	v(C≡N)	v(C—O)	v(C—N)	v(C=O)	v _{sym} (UO ₂)	v _{asym} (UO ₂)
7.	[UO ₂ (HL) ₃](CH ₃ COO) ₂	1610 s, 1590 s, 1580 s, 1510 w, 1500 w, 780 m, 720 s	2900 br 2820 br	1695 s, 1665 w, 1640 s, 1620 s, 1590 s	1380 s 1280 s 1275 m	1220 m 1190 s 1120 w	1700 s 1695 s	810 s	940 br
8.	[UO ₂ HLL ₂]	—	—	—	—	—	—	—	—
9.	[Th(HL) ₂ (NO ₃) ₂](NO ₃) ₂	1510 s, 1450 s, 1380 vs, 1280 m, 1045 s, 1020 s, 820 s, 790 s, 755 s	2960 br 2820 s	1690 s, 1645 s, 1605 m, 1580 w, 1530 s, 1450 s	1380 s 1290 s	1165 s 1160 s 1090 s 1060 s	1730 s	—	—
10.	[Th(HL) ₂ (SCN) ₄]	2045s, 810s	2920s 2820br	1690s, 1610 s, 1600 s, 1580 w	1370 s	1160 s	1700 s	—	—
11.	[Th(HL) ₂ Cl ₄]	—	2900 s 2810 br	1680 s, 1610 s, 1590 m	1350 s 1280 s	1170 s 1155 s	1710 s	—	—
12.	[Th(HL) ₂] ₄	—	2910 s 2820 br	1680 s, 1620 m 1580 s	1360 s 1295 s	1190 s 1165 m	1720 s	—	—

set of 2 NO₃⁻ ions are present as ionic nitrate. Bands at 1510, 1280, 1020, 820, 790 and 755 cm⁻¹ corresponding to bidentate nitrate groups^{11, 14} are observed. Ionic nitrate vibrations are observed at 1380, 1270, 1045 and 830 cm⁻¹. Thus the coordination number of thorium is 8 is suggested for Th(HL)₂(NO₃)₂(NO₃)₂ complex. A similar observation for thorium nitrate complex was observed earlier by Molodkin *et al.*¹⁵

It is interesting to note that in the ligand the carboxylic group gets deprotonated while reacting with uranyl acetate in presence of sodium acetate. This fact has also been confirmed from the absence of IR band at 2720 cm⁻¹ in the neutral complex. In the acetate complex IR bands at 1610, 1545, 1570, 1420, 955, 720, 665 cm⁻¹ indicate the presence of ionic acetate group.¹⁶ In all the complexes the bands observed around 920 and 810 cm⁻¹ are due to $\nu_{\text{asym}}(\text{U}=\text{O})$, $\nu_{\text{sym}}(\text{U}=\text{O})$ respectively of a linear O=U=O moiety¹⁷.

The electronic spectra of the ligand and the complexes exhibit bands at 330–440 nm due to the vibronic structure of the O=U=O group which seem to be overlapped by the fairly strong ligand-to-metal charge transfer bands.¹⁸ The bands obtained below 330 nm corresponding to the ligand π - π^* region and provide no assistance in determining the environment of the metal atom in the complexes.

The TGA analyses of the ligands and their complexes were carried out to get information about the decomposition trend and relative volatility of the complexes. It is found that the ligand is stable up to 200°C and then starts losing weight and completely volatilises at about 500–550°C. It indicates that there is no water molecule present as coordinated or as water of crystallisation. U₃O₈ is the final product for uranyl complexes and ThO₂ is the final product for the thorium complexes. The complexes lose the ligands earlier than the anion and finally form the stable oxides.

ACKNOWLEDGEMENTS

The authors thank the authority of the College for providing research facilities; we are also thankful to the Director, RSIC, IIT Madras for IR, UV/VIS spectrum, Director, CDRI, Lucknow for CHN analysis and Director, RRL for TGA/DTA analysis.

REFERENCES

1. S.M. Crawford, *Spectrochim. Acta*, **19**, 255 (1963); A. Bigotto, V. Glasso and G. Dealty, *Spectrochim. Acta*, **28A**, 1581 (1972); S.V. Sheat and T.N. Waters, *J. Inorg. Nucl. Chem.*, **26**, 1221 (1964); S.M. Abu-El-Wafa, R.M. Issa and C.A. McAuliffe, *Inorg. Chim. Acta*, **99**, 103 (1985); R.E. Hester and E.M. Nour, *J. Raman Spectrosc.*, **11**, 49 (1981).
2. R.A. Bailey, S.L. Kozak, T.W. Michelsen and W.N. Mills, *Coord. Chem. Rev.*, **6**, 407 (1971).
3. E.L. Muettterties and C.M. Wright, *Quart. Rev.*, **21**, 109 (1967).
4. R.H. Holm and M.J.O. Cornor, *Progr. Inorg. Chem.*, **14**, 241 (1971).
5. D. Brown, *Halides of Lanthanides and Actinides*, Wiley, London (1968).
6. K.C. Dash and H.N. Mohanta, *J. Inorg. Nucl. Chem.*, **39**, 1345 (1977).
7. A.I. Vogel, *Quantitative Inorganic Analysis*, ELBS (1965).

8. K. Nakamoto, in E.A. Martel (ed.), *Coordination Chemistry*, Van Nostrand, New York (1971); Y.R. Sharma, *Elementary Organic Spectroscopy*, S. Chand and Co., New Delhi (1989).
9. H.N. Mohanta and Kailash C. Dash., *J. Indian Chem. Soc.*, **57**, 26 (1980).
10. K. Biemann (ed.), *Spectral Data for Structure Determination of Organic Compounds*, Springer-Verlag, Berlin -New York (1983).
11. J.R. Ferraro and A.J. Walker, *J. Chem. Phys.*, **45**, 550 (1966).
12. E.P. Herzberg and J.C. Bailer (Jr.), *Inorg. Chem.*, **10**, 2371 (1971); Ross, *Inorganic Infrared and Raman Spectrum*, McGraw-Hill, p. 210 (1977).
13. (a) H.N. Mohanta and K.C. Dash, *Russian J. Inorg. Chem.*, **25** (1980); (b) R.A. Bailey, S.L. Kozak, T.W. Michelsen and W.N. Mills, *Coord. Chem. Rev.*, **6**, 407 (1971).
14. C.C. Addison, N. Logan, S.C. Wallwork and C.D. Garner, *Quart. Rev.*, **35**, 289 (1971).
15. A.D. Moloduin, O.M. Ivanov and L.E. Kozina, *Russ. J. Inorg. Chem.*, **13**, 1192 (1968).
16. L.H. Jones and E. Melaren, *J. Chem. Phys.*, **26**, 1796 (1954).
17. L. Cattalini, U. Croatto, S. Degetto and E. Tendello, *Inorg. Chem. Acta Rev.*, **5**, 19 (1971).
18. C.G. Wallrand and L.G. Vanquichenbern, *J. Chem. Phys.*, **54**, 4178 (1971).

(Received: 6 September 1995; Accepted: 30 October 1995)

AJC-1041