

Synthesis and spectral studies of thorium(IV) and dioxouranium(V) metal complexes with Schiff base ligand^ψ

Kishor Arora^{a*}, R. C. Goyal^b, D. D. Agarwal^c and M. C. Pathak^d

^aDepartment of Chemistry, Government Autonomous K. R. G. College, Gwalior-474 001, India

E-mail : kishorarora@rediffmail.com

^bDepartment of Chemistry, Government P. G. College, Morena-476 001, India

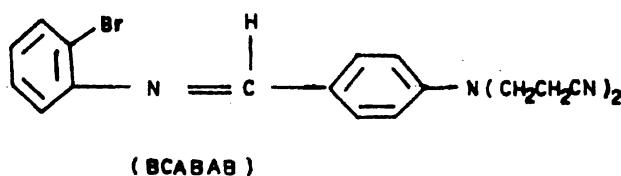
^cSchool of Studies in Chemistry, Jiwaji University, Gwalior-474 011, India

^dDepartment of Chemistry, Government Autonomous Science College, Gwalior, India

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A series of new complexes of Schiff base 2-bromo-1N-[4-N,N-bis(2'-cynoethylaminobenzalidene)]aminobenzene (BCABAB) have been prepared from thorium(IV) and dioxouranium(V) metal salts having composition $\text{UO}_2\text{X}_2.n\text{L}$ ($\text{X} = \text{CH}_3\text{COO}^-$, NO_3^- , I^- or NCS^- , $n = 2$; $\text{X} = \text{ClO}_4^-$, $n = 4$; $\text{L} = \text{BCABAB}$) and $\text{ThX}_4.n\text{L}$ ($\text{X} = \text{NO}_3^-$, NCS^- , $n = 2$, $\text{X} = \text{I}^-$; $n = 4$ and $\text{X} = \text{ClO}_4^-$; $n = 6$, $\text{L} = \text{BCABAB}$). BCABAB acts as neutral monodentate ligand and coordinate to the metal ion via azomethine nitrogen.

Complexing behavior of various neutral donor ligands involving Schiff bases derived from 4-aminoantipyrine, 2-aminopyridine and various other amines have been reported with transition metals and with thorium(IV) and dioxouranium(V)^{1,2}. In all these complexes ligands coordinate through the azomethine nitrogen. We now report the studies done on the complexes of a Schiff base, 2-bromo-1N-[4-N,N-bis(2'-cynoethylaminobenzalidene)]aminobenzene (BCABAB) with thorium(IV) and dioxouranium(V).



Results and Discussion

The interaction of BCABAB with Th^{IV} and UO_2^V salts resulted in the formation of $\text{UO}_2\text{X}_2.n\text{L}$ ($\text{X} = \text{CH}_3\text{COO}^-$, NO_3^- , I^- or NCS^- ; $n = 2$; $\text{X} = \text{ClO}_4^-$, $n = 4$; $\text{L} = \text{BCABAB}$) and $\text{ThX}_4.n\text{L}$ ($\text{X} = \text{NO}_3^-$, NCS^- , $n = 2$; $\text{X} = \text{I}^-$; $n = 4$ and $\text{X} = \text{ClO}_4^-$; $n = 6$, $\text{L} = \text{BCABAB}$). The complexes are quite stable and can be stored for a long period. All these complexes are essentially non-electrolyte with λ_m ranging from 3.7 and $4.2 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ except the iodo and perchlorato com-

plexes of Th^{IV} in PhNO_2 medium which dissociate in the solvent. The iodo complex appears to be 1 : 2 with λ_m equal to $51.9 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ while perchlorato complex appears to be 1 : 4 electrolytes with λ_m equal to $92.5 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. The uranyl complexes are essentially non-electrolytes in PhNO_2 medium with λ_m ranging from 3.6 to $4.3 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. The conductivity of the halo complexes is in general agreement with the stability of the U-halogen bond found earlier³. The conductance value for the perchlorato complex $[\text{UO}_2\text{L}_4](\text{ClO}_4)_2$ is $54.2 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ which suggests the ionic perchlorato groups in this complex.

Data on molecular weight of the complexes in nitrobenzene are contained in Table 1 along with the values calculated on the basis of established formula of the complexes. The ratio of molecular weight observed for $\text{ThX}_4.2\text{L}$ ($\text{X} = \text{NO}_3^-$ or NCS^-) and $\text{UO}_2\text{X}_2.2\text{L}$ ($\text{X} = \text{CH}_3\text{COO}^-$, NO_3^- , I^- or NCS^-) to the calculated is *ca* 0.98 which shows that the complexes are monomeric in solution⁴. In case of $\text{ThI}_4.4\text{L}$, $\text{UO}_2(\text{ClO}_4)_2.4\text{L}$ and $\text{Th}(\text{ClO}_4)_4.6\text{L}$ the ratios are 0.33, 0.33 and 0.30, respectively. These data further support the formation of more than one species in these complexes⁴. Analytical data for these complexes are given in Table 1.

Uranyl complexes are diamagnetic in nature depending on the diamagnetism of the ions and corresponding ligand field⁵. The magnetic susceptibilities are independent of

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field strength and temperature⁶. Thorium(IV) salts are diamagnetic⁷. The present complexes of these metals are weakly diamagnetic. The ground states of these metal compounds contain no unpaired electrons. The compounds are therefore expected to be weakly diamagnetic as observed by others^{7,8}.

Table 1. Analytical and physical data of the Th^{IV} and U^{VI} complexes⁹

Compd.	Colour/ M.p., °C	Metal % : Found (Calcd.)	Mol. wt. : Found (Calcd.)
Th(NO ₃) ₄ .2BCABAB	Brown, 230	17.6 (18.7)	1232 (1240)
Th(NCS) ₄ .2BCABAB	Yellow, 188	17.7 (18.9)	1215 (1224)
ThI ₄ .4BCABAB	Black, 220	9.8 (10.2)	652 (2260)
Th(ClO) ₄ .6BCABAB	Brown, 208	6.2 (7.9)	792 (2910)
UO ₂ (NO ₃) ₂ .2BCABAB	Brown, 223	19.5 (20.6)	1142 (1154)
UO ₂ I ₂ .2BCABAB	Black, 232	17.4 (18.5)	1264 (1284)
UO ₂ (NCS) ₂ .2BCABAB	Orange, 198	19.8 (20.7)	1132 (1146)
UO ₂ (CH ₃ COO) ₂ .2BCABAB	Yellow, 210	19.5 (20.7)	1132 (1148)
UO ₂ (ClO ₄) ₂ .4BCABAB	Yellow, 188	10.7 (11.9)	585 (1989)

* All compounds gave satisfactory N and anion analysis.

Spectral studies :

Infrared absorptions of the Schiff base have been assigned by the comparison of the spectral data of this Schiff base with other ligands⁴ which have been already reported with mono-substituted benzene ring system⁹. The ligand is expected to coordinate through azomethine nitrogen atom. An important band occurs at 1664 cm⁻¹ attributed to ν_{C=N} (azomethine) mode¹⁰. In the spectra of complexes this band is shifted to lower wave number and appears at 1640–1610 cm⁻¹ indicating the involvement of nitrogen of the azomethine group in coordination¹¹. The strong bands observed at 1596 and 1059 cm⁻¹ are assigned as ring breathing and deformation bands which remain almost unaffected on coordination and appear at ca 1595–1590 and 1050–1045 cm⁻¹, respectively, in case of the complexes.

The band assigned to benzene ring vibration compares well with those of mono-substituted derivatives of benzene¹². Several other absorptions associated with C–H out-of-plane deformation modes appear at 760–740 cm⁻¹. The other notable feature in the stretching frequency of U–O bond in uranyl(VI) compounds before and after complexation with the ligands is due to lowering of dπ–pπ interaction of U=O bond which is supported by the reported observation¹³.

In the far-IR region some new medium and weak intensity bands are observed in the range 450–410 cm⁻¹ in the complexes where the ligand have no absorptions. These new bands are tentatively assigned to ν_{M-N} modes observed for several Th^{IV} and U^{VI} complexes¹⁴.

Configuration of complexes :

Thorium(IV) complexes : The preferred coordination number of Th^{IV} is 6 or 8, higher coordination number have also been observed¹⁵. In isothiocyanato complex, the conductance and molecular weight data suggest that in this complex the coordination number of thorium(IV) is 6. In iodo complex, 1 : 2 electrolytic nature of the complex shows that two iodo ions are present outside the coordination sphere generating the coordination number of thorium(IV) equal to 6. Since nitro groups are functioning as bidentate ligand, the coordination number of thorium(IV) is ten in this complex. In perchlorato complex, conductance and molecular weight data reveal that the perchlorato ions are present outside the coordination sphere thereby producing coordination number six for thorium(IV)⁴ in this complex.

Dioxouranium(V) complexes : In dioxouranium(V) halo and thiocyanato complexes, both the anions are covalently bonded. In these cases it may be considered to have an six coordinated uranium atom. The infrared data of nitro complex suggest that nitro groups are bidentate in nature. Thus it may be considered that in this complex uranium is 8 coordinated. Similarly, eight coordinated uranium is considered in case of uranyl acetato complex¹⁶. In perchlorato complex both the perchlorato ions are ionic in nature, thereby generating 6 coordinated uranium atom in this complex¹⁷. This is in agreement with previous observations¹⁸.

Experimental

This ligand was prepared by treating the solution of bromoaniline (1 mmol) in absolute alcohol with the corresponding aldehyde (1.1 mmol) in the same solvent and refluxing the reaction mixture for 4–5 h. The reaction mixture was then cooled and excess solvent removed. The resulting solid was washed with the solvent and crystallized from the same solvent and dried under reduced pressure over CaCl₂ (Found : C, 59.82; H, 3.74; N, 13.47. Calcd. for : C, 60.02; H, 4.47; N, 14.74%).

The complexes of this ligand were synthesized by one of the following general methods. The respective metal salt solutions were treated with ligand solution in the required molar concentrations (i.e. 1 : 2, 1 : 4 or 1 : 6). In some cases, the complexes were isolated immediately in cold while in some cases in hot solutions. In some cases, resulting solutions were refluxed for 2–3 h at 65–75°. The solvents used were ethanol, isopropanol and acetone. The complexes were washed with solvent and then with anhydrous ether and dried under reduced pressure over CaCl₂.

All the physicochemical studies and analysis were performed as reported earlier².

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