

Thorium Nitrate Complexes of Some Schiff Bases Derived from Substituted Benzaldehydes & Amino Compounds

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A series of thorium nitrate complexes with some schiff bases derived from substituted benzaldehydes and amino compounds has been synthesised and characterised. The schiff bases employed are N-(3-methoxy-4-hydroxybenzylidene)isonicotinylhydrazone (MHBIH), N-(3-methoxy-4-hydroxybenzylidene)benzhydrazone (MHBBH), N-(3-methoxy-4-hydroxybenzylidene)salicyloylhydrazone (MHBSH), N-(3-methoxy-4-hydroxybenzylidene)anthranilic acid (MHBA A), 4-N-(3-methoxy-4-hydroxybenzylidene)aminoantipyrine (MHBAAP), 1,2-N,N-(3-methoxy-4-hydroxybenzylidene)phenylenediamine (MHBPDA), N-(3,4-dimethoxybenzylidene)isonicotinylhydrazone (DMBIH), N-(3,4-dimethoxybenzylidene)benzhydrazone (DMBBH), N-(3,4-dimethoxybenzylidene)salicyloylhydrazone (DMBSH), N-(3,4-dimethoxybenzylidene)anthranilic acid (DMBA A), 4-N-(3,4-dimethoxybenzylidene)aminoantipyrine (DMBAAP) and 1,2-N,N-(3,4-dimethoxybenzylidene)phenylenediamine (DMBPDA). Elemental analysis and molecular weight data of the complexes indicate that they have composition $\text{ThL}_2(\text{NO}_3)_4$ (L = MHBIH, MHBBH, MHBSH, MHBA A, MHBAAP, DMBIH, DMBBH, DMBSH, DMBA A and DMBAAP) and $\text{ThL}(\text{NO}_3)_4$ (L = MHBPDA and DMBPDA). IR spectral and conductance data show that all the ligands act as neutral bidentate ones and nitrate groups are coordinated to the metal ion in a monodentate fashion.

As a part of our programme on the synthesis and characterisation of solid actinide complexes^{1,2}, we report here some thorium(IV) nitrate complexes with schiff bases derived from substituted benzaldehydes and amino compounds.

Thorium(IV) nitrate was a BDH reagent (99.9% pure) and was used as such. The schiff bases were prepared by a known method³ and their purities were checked by TLC and IR spectral analyses.

The complexes were prepared as described. For the preparation of the complexes of MHBIH, MHBBH, MHBSH, MHBA A, MHBAAP, DMBIH, DMBBH, DMBSH, DMBA A and DMBAAP, solutions of thorium nitrate (2 mmol) and the ligand (4 mmol) in hot dry acetone were mixed and refluxed on a water bath for 3-4 h. The reaction mixture was concentrated and the precipitated complexes of DMBIH, DMBSH, DMBA A and DMBAAP were filtered and washed with acetone whereas the complexes of MHBIH, MHBBH, MHBSH, MHBA A, MHBAAP and DMBBH were separated by the addition of ben-

zene to the viscous mass obtained on concentration. These were filtered, washed several times with hot benzene to remove excess ligand, redissolved in minimum amount of hot dry acetone and precipitated by the addition of dry diethylether. For the preparation of the complexes of MHBPDA and DMBPDA, thorium nitrate (2 mmol) and the ligand (MHBPDA or DMBPDA, 2 mmol) in hot dry acetonitrile were mixed and refluxed on a water bath for 3 h. The complexes so precipitated were filtered and washed several times with hot acetonitrile. All the complexes were dried *in vacuo* over phosphorus(V) oxide. These complexes were analysed for the thorium content by the oxalate-oxide method⁴; C, H, N data were obtained from the Central Drug Research Institute, Lucknow. IR spectra of the ligands and the complexes in the 400-4000 cm^{-1} region were recorded on a Perkin-Elmer 397 double beam IR spectrophotometer using the KBr disc technique. Molar conductivities of the complexes in acetonitrile, methanol and nitrobenzene ($\sim 10^{-3}$ M solutions) were measured at room temperature ($28 \pm 2^\circ\text{C}$) using an ELICO conductivity bridge type CM82 with a dip-type cell (type CC-03) having platinum electrodes (cell constant, 1.30 cm^{-1}). Magnetic susceptibilities were also measured at room temperature using the Gouy method with $\text{Hg}[\text{Co}(\text{CNS})_4]$ as the calibrant. Molecular weights of the complexes ($\sim 10^{-3}$ M solutions) were determined by the cryoscopic method in nitrobenzene⁵.

Analytical data of the complexes (Table 1) indicate that they may be formulated as $\text{ThL}_2(\text{NO}_3)_4$ (L = MHBIH, MHBBH, MHBSH, MHBA A, MHBAAP, DMBIH, DMBBH, DMBSH, DMBA A and DMBAAP) and $\text{ThL}(\text{NO}_3)_4$ (L = MHBPDA and DMBPDA). All the complexes are intensely coloured non-hygroscopic solids which are soluble in acetone, acetonitrile, ethanol, methanol and nitrobenzene and insoluble in benzene, carbon tetrachloride, petroleum ether and diethylether. Molar conductance values indicate that all the complexes exhibit non-electrolytic behaviour in nitrobenzene⁶ ($\Lambda_{\text{M}} = 1.3-9.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) suggesting that the nitrate groups are coordinated to the metal ion. However, almost all the complexes show higher conductance values in acetonitrile (35.2-63.4 $\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) and methanol (45.6-108.3 $\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$). These higher values are approximately equal to those of 1:1 electrolytes and are probably due to partial displacement of the anionic nitrates with the polar acetonitrile or methanol molecules⁷. All the complexes show almost zero magnetic moments as expected for the Th^{4+} ion.

Table 1—Analytical and Molecular Weight Data of Thorium(IV) Nitrate Complexes of Some Schiff Bases

Complex	Found (Calc.)				
	Metal %	C %	H %	N %	Mol wt
[Th(MHBIH) ₂ (NO ₃) ₄]	22.5 (22.7)	30.9 (31.1)	2.5 (2.4)	12.9 (13.0)	1052 (1022)
[Th(MHBBH) ₂ (NO ₃) ₄]	22.6 (22.8)	35.4 (35.3)	2.8 (2.7)	10.9 (11.0)	1060 (1020)
[Th(MHBSH) ₂ (NO ₃) ₄]	22.0 (22.1)	34.3 (34.2)	2.9 (2.7)	10.8 (10.7)	1008 (1052)
[Th(MHBAA) ₂ (NO ₃) ₄]	22.5 (22.7)	35.0 (35.2)	2.3 (2.5)	8.0 (8.2)	1050 (1022)
[Th(MHBA-AP) ₂ (NO ₃) ₄]	20.0 (20.1)	39.1 (39.5)	3.5 (3.3)	12.1 (12.1)	1123 (1154)
[Th(MHBPDA)(NO ₃) ₄]	27.0 (27.1)	30.5 (30.8)	2.2 (2.3)	9.7 (9.8)	837 (856)
[Th(DMBIH) ₂ (NO ₃) ₄]	22.0 (22.1)	34.5 (34.2)	3.2 (2.9)	13.1 (13.3)	1018 (1050)
[Th(DMBBH) ₂ (NO ₃) ₄]	21.9 (22.1)	36.5 (36.6)	3.0 (3.1)	10.3 (10.7)	1010 (1048)
Th(DMBSH) ₂ (NO ₃) ₄]	21.3 (21.5)	35.7 (35.6)	2.9 (3.0)	10.2 (10.4)	1040 (1080)
Th(DMBAA) ₂ (NO ₃) ₄]	22.1 (22.1)	36.3 (36.6)	2.7 (2.9)	7.7 (8.0)	1032 (1050)
[Th(DMBA-AP) ₂ (NO ₃) ₄]	19.5 (19.6)	40.6 (40.6)	3.9 (3.6)	11.6 (11.8)	1210 (1182)
[Th(DMBPDA)(NO ₃) ₄]	26.1 (26.3)	32.3 (32.6)	2.6 (2.7)	9.2 (9.5)	856 (884)

All the twelve ligands show a strong or medium IR band in the region 1580-1610 cm⁻¹, which is assigned to $\nu\text{C} = \text{N}$. This band is shifted to lower frequency region by 30-40 cm⁻¹ in the spectra of all the complexes indicating that the nitrogen of the azomethine group is coordinated to the metal ion.

The IR spectra of MHBIH, MHBBH, MHBSH, DMBIH, DMBBH and DMBSH show a sharp band in the region 1630-1650 cm⁻¹ which is attributed to the side chain $\nu\text{C} = \text{O}$ mode. This band is shifted by ~ 30 cm⁻¹ to the lower frequency side in the spectra of the complexes indicating the coordination of side chain carbonyl group. The strong band at 1680 cm⁻¹ observed in the spectra of MHBA A and DMBA A is assigned to the stretching vibration of the side chain carbonyl group. This band is shifted to lower frequency side by ~ 55 cm⁻¹ in both the complexes indicating the coordinative participation of the side chain carbonyl group. The spectra of MHBAAP and DMBAAP exhibit a sharp band around 1640 cm⁻¹ assignable to

ring $\nu\text{C} = \text{O}$ mode. This band is shifted to 1610 cm⁻¹ indicating that the ring carbonyl group is coordinated to the metal ion. The ligands MHBIH, MHBSH, MHBBH, MHBA A, MHBAAP, MHBPDA and DMBSH show a broad medium intensity band in the region 3430-3450 cm⁻¹ and a rather weak one in the region 1320-1330 cm⁻¹, which may be assigned to $\nu\text{O} - \text{H}$ (phenolic) and $\nu\text{C} - \text{O}$, respectively. These bands occur in the same region without any shift showing that the phenolic oxygen is not involved in coordination^{8,9}.

In the spectra of all the complexes three additional bands, which are not present in the spectra of the ligands, are observed at 1390, 1280 and 1020 cm⁻¹. These are assigned to ν_4 , ν_1 and ν_2 vibrations, respectively of the nitrate group. The bands at 1390 cm⁻¹ (ν_4) and 1280 cm⁻¹ (ν_1) are the split bands of ν_3 mode of the free nitrate group and the difference $\nu_4 - \nu_1$ is ~ 110 cm⁻¹ indicating that the nitrate groups are coordinated to the metal ion monodentately¹⁰. The conductance values of the complexes confirm this evidence of nitrate coordination.

On the basis of the above observations the complexes are assigned the stoichiometries [ThL₂(NO₃)₄] (where L = MHBIH, MHBBH, MHBSH, MHBA A, MHBAAP, DMBIH, DMBBH, DMBSH, DMBA A and DMBAAP) and [ThL(NO₃)₄] (where L = MHBPDA and DMBPDA). All the ligands are bonded to the Th⁴⁺ ion in a neutral bidentate fashion and the nitrate ions in a monodentate fashion resulting in a coordination number of 8 in the first set of complexes and 6 in the second set of complexes.

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