This article was downloaded by: [York University Libraries]
On: 27 December 2014, At: 21:42
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt19

Studies on Some Thorium(IV) Complexes with High Coordination Numbers Derived from Semicarbazones of 4-Aminoantipyrine

Ram K. Agarwal [a] , Indranil Chakraborti [b] & Himanshu Agarwal [b]

[a] Department of Chemistry, School of Pure and Applied Sciences , The University of the South Pacific , P.O. Box 1168, Suva, Fiji Islands

[b] Department of Chemistry , Lajpat Rai Postgraduate College , Sahibabad, Ghaziabad, India

Published online: 16 Nov 2010.

To cite this article: Ram K. Agarwal , Indranil Chakraborti & Himanshu Agarwal (2004) Studies on Some Thorium(IV) Complexes with High Coordination Numbers Derived from Semicarbazones of 4-Aminoantipyrine, Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 34:8, 1431-1452, DOI: 10.1081/SIM-200026274

To link to this article: http://dx.doi.org/10.1081/SIM-200026274

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Downloaded by [York University Libraries] at 21:42 27 December 2014

SYNTHESIS AND REACTIVITY IN INORGANIC AND METAL-ORGANIC CHEMISTRY
Vol. 34, No. 8, pp. 1431–1452, 2004

Downloaded by [York University Libraries] at 21:42 27 December 2014

Studies on Some Thorium(IV) Complexes with High Coordination Numbers Derived from Semicarbazones of 4-Aminoantipyrine

Ram K. Agarwal,[1,*] Indranil Chakraborti,[2] and Himanshu Agarwal[2]

[1]Department of Chemistry, School of Pure and Applied Sciences, The University of the South Pacific, Suva, Fiji Islands
[2]Department of Chemistry, Lajpat Rai Postgraduate College, Sahibabad, Ghaziabad, India

ABSTRACT

The interaction of thorium(IV) salts with 4[*N*-(benzylidene)amino]antipyrine semicarbazone (BAAPS), 4[*N*-(4′-methoxybenzylidene)amino]antipyrine semicarbazone (MBAAPS), 4[*N*-(4′-dimethoxyaminobenzylidene)amino]antipyrine semicarbazone (DABAAPS), 4[*N*-(2′-nitrobenzylidene)amino]antipyrine semicarbazone (2′-NO_2BAAPS), and 4[*N*-(3′-nitrobenzylidene)amino]antipyrine semicarbazone (3′-NO_2BAAPS) in non-aqueous solvents resulted in the formation of $[ThL_2X_4]$ (X = Cl, Br, or NCS), $[ThL_2I_2]I_2$, $[ThL_2](ClO_4)_2$ or $[ThL(NO_3)_4]$ (L = BAAPS,

*Correspondence: Ram K. Agarwal, Department of Chemistry, School of Pure and Applied Sciences, The University of the South Pacific, P.O. Box 1168, Suva, Fiji Islands; E-mail: agarwal_r@usp.ac.fj.

DOI: 10.1081/SIM-200026274 0094-5714 (Print); 1532-2440 (Online)
Copyright © 2004 by Marcel Dekker, Inc. www.dekker.com

Request Permissions / Order Reprints
powered by RIGHTSLINK

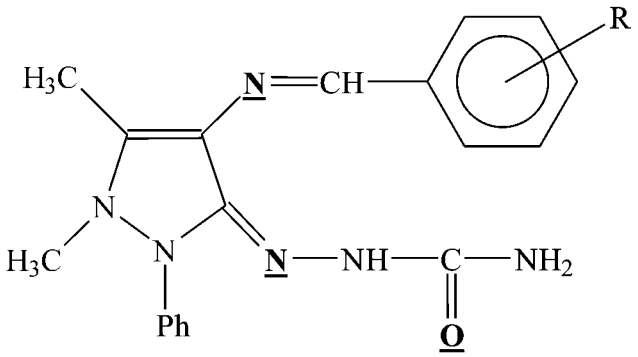
MBAAPS, DABAAPS, 2-NO_2BAAPS, or 3-NO_2BAAPS). All of these compounds were characterized by elemental analyses, electrical conductivity, IR, and thermal methods. X-ray powder diffraction studies of a representative complex were also undertaken. Th(IV) displays the coordination numbers 6, 8, 10, and 11 in these compounds depending on the nature of the coordinated anion and the stoichiometry.

Key Words: Thorium(IV); Semicarbazones; Complexes; Coordination number.

Downloaded by [York University Libraries] at 21:42 27 December 2014

INTRODUCTION

The coordination polyhedra of actinide ions have been extensively investigated and sufficiently well characterized in the solid state especially by x-ray investigations. The contraction of the ionic radius with increasing atomic number is related to the maximum obtainable coordination number with tropolonato and 8-hydroxyquinolinato ligands. It is possible to prepare Th(IV) and U(IV) 10-coordinated complexes and only eight coordinated complexes of Np(IV) and Pu(IV) with these ligands. Thorium(IV) with an atomic radius of 1.65 Å and a high charge fulfills the optimum conditions for high coordination.[1] Thorium(IV) is an example of a typical hard Lewis acid, as compared to the tendency to coordination of oxygen and sulfur donors and also of nitrogen and phosphorus donors.[2,3] Both oxygen and nitrogen have an appreciable tendency to coordinate to thorium(IV) although complexes containing O-donors are more common than those containing N-donors. In thorium(IV) complexes, the coordination number of thorium(IV) varies from 6 to 12. The coordination numbers 6, 8, 10, 11, and 12 are usually found in thorium(IV) complexes, while the coordination numbers 7 and 9 are rather uncommon for thorium(IV) complexes.[4,5] In the literature a good number of thorium(IV) complexes of Schiff bases are reported,[6,7] but comparatively less is known about thorium(IV) complexes of semicarbazones. In view of this, the present studies are devoted to the preparation and characterization of 30 coordination compounds of thorium(IV) with 4[4-(benzylidene)amino] antipyrine semicarbazone (BAAPS), 4[*N*-(4′-methoxybenzylidene)amino] antipyrine semicarbazone (MBAAPS), 4[*N*-(4′-dimethoxyaminobenzylidene) amino]antipyrine semicarbazone (DABAAPS), 4[*N*-(2′-nitrobenzylidene) amino]antipyrine semicarbazone (2′-NO_2BAAPS), and 4[*N*-(3′-nitrobenzylidene)amino]antipyrine semicarbazone (3′-NO_2BAAPS) (Fig. 1). In these compounds thorium(IV) displays the coordination numbers 6, 8, 10, or 11 depending on the nature of the coordination anion and the stoichiometry.



R = H; L = BAAPS
R = 4'-OCH_3; L = MBAAPS
R = 4'-$N(CH_3)_2$; L = DABAAPS
R = 2'-NO_2; L = 2'-NO_2BAPAAS
R = 3'-NO_2; L = 3'-NO_2BAPAAS

Figure 1. Structure of ligands.

EXPERIMENTAL

Materials

Thorium(IV) nitrate was obtained from BDH. Thorium(IV) perchlorate was prepared as reported.[8] Crystals of ThX_4 (X = Cl, Br, I, or NCS) were prepared by known methods.[9] All the thorium(IV) salts are hygroscopic and were stored in a desiccator over concentrated sulfuric acid. 4-Aminoantipyrine (Koch & Light), benzaldehyde, 4-methoxybenzaldehyde, 4-dimethylaminobenzaldehyde, 2/3-nitrobenzaldehyde, and semicarbazide hydrochloride (CDH) were obtained commercially and used as received. The following semicarbazones (Fig. 1) were prepared in the laboratory.

1. 4[4-(benzylidene)amino]antipyrine semicarbazone (BAAPS), ($C_{19}H_{20}N_6O$).
2. 4[*N*-(4′-methoxybenzylidene)amino]antipyrine semicarbazone (MBAAPS), ($C_{19}H_{22}N_6O_2$).
3. 4[*N*-(4′-dimethoxyaminobenzylidene)amino]antipyrine semicarbazone (DABAAPS), ($C_{21}H_{25}N_7O$).

Downloaded by [York University Libraries] at 21:42 27 December 2014

4. 4[*N*-(2′-nitrobenzylidene)amino]antipyrine semicarbazone (2′-NO_2BAAPS) ($C_{19}H_{19}N_7O_3$).
5. 4[*N*-(3′-nitrobenzylidene)amino]antipyrine semicarbazone (3′-NO_2BAAPS) ($C_{19}H_{19}N_7O_3$).

Synthesis of Semicarbazones

All five derivatives were synthesized in two steps.[10]

1. A solution of an aromatic aldehyde (1 mmol) in absolute ethanol (20 mL) was mixed with 4-aminoantipyrine (1.1 mmol, 0.2234 g) in the same solvent (20 mL) and the reaction mixture was refluxed for 2–3 hr. On cooling, a yellow crystalline product separated, which was filtered and recrystallized in the same solvent.
2. Semicarbazones were prepared by the following method. Semicarbazide hydrochloride ($H_2NNHCONH_2 \cdot HCl$) (15 g, 0.134 mol) and sodium acetate (CH_3COONa) (13 g, 0.15 mol) were dissolved in 60 mL distilled water and mixed with the corresponding Schiff base (0.1 mol) [prepared in (1)] in ethanol (25 mL). The mixture was refluxed on a water bath for 1 hr. On cooling the contents, the semicarbazones crystallized out. They were filtered, washed with 50% ethanol, and recrystallized from ethanol. The obtained light yellow crystals were filtered and dried at $\sim$60 °C in an electric oven.

Synthesis of the Complexes

$[ThL_2X_4]$ (X = Cl, Br, or NCS) (L = BAAPS, MBAAPS, DABAAPS, 2′-NO_2BAAPS, or 3′-NO_2BAAPS)

A methanolic solution (10 mL) of ThX_4 (X = Cl, Br, and NCS) (1 mmol) was added to the respective ligand solution (2.1 mmol, 20 mL of methanol) dropwise. The reaction mixture was refluxed for 2 hr on a water bath. Solid compounds were obtained after reducing the volume of the reaction mixture to 1/2 under a fan. The precipitate was filtered by suction, washed with methanol, and dried under *vacuo* over P_4O_{10}.

$[ThL_2I_2]I_2$ (L = BAAPS, MBAAPS, DABAAPS, 2′-NO_2BAAPS, or 3′-NO_2BAAPS)

A methanolic solution (10 mL) of ThI_4 (1 mmol, 0.74 g) was added to the respective ligand solution (2.1 mmol, 20 mL of methanol) dropwise.

Downloaded by [York University Libraries] at 21:42 27 December 2014

The reaction mixture was refluxed for 2 hr on a water bath. The reaction mixture was left overnight for complete precipitation. The precipitate was filtered by suction, washed with methanol, and dried under *vacuo* over P_4O_{10}.

$[ThL_2](ClO_4)_4$ (L = BAAPS, MBAAPS, DABAAPS, 2′-NO_2BAAPS, or 3′-NO_2BAAPS)

To a solution of $Th(ClO_4)_4$ (1 mmol, 0.63 g) in isopropyl alcohol (10 mL) was added a hot solution of the respective ligand (2 mmol) in the same solvent (10 mL). In case of BAAPS, MBAAPS, and DABAAPS, the desired complex was obtained immediately. But in case of 2′-NO_2BAAPS and 3′-NO_2BAAPS the reaction mixture was refluxed for 1–2 hr. On cooling to room temperature the desired complexes were obtained. The solid products were filtered, washed with isopropyl alcohol, and dried *in vacuo* over P_4O_{10}.

$[ThL(NO_3)_4]$ (L = BAAPS, MBAAPS, DABAAPS, 2′-NO_2BAAPS, or 3′-NO_2BAAPS)

To a solution of $Th(NO_3)_4$ (1 mmol, 0.56 g) in ethyl acetate (15 mL) was added the respective ligand (1.1 mmol) in the same solvent (10 mL) and the reaction mixture was refluxed for about 1 hr and then left for overnight at room temperature. Fine crystalline products were obtained which were filtered by suction, washed with ethyl acetate, and finally dried *in vacuo* over P_4O_{10}.

All of the physico-chemical measurements and analyses were performed as reported previously.[4,5] Infrared spectra in the range of 4000–200 cm^{-1} were measured on a Perkin–Elmer Infracord Spectrophotometer model 521 in Nujol mulls at the Department of Chemistry, University of Delhi. We have not tried NMR studies of present studies. Thermogravimetric analyses were carried with a Santon Redcraft Thermobalance Model TG-750 thermobalance in open air. We did not succeed in obtaining single crystals.

RESULTS AND DISCUSSION

The physical characteristics and chemical analysis of all of the five semicarbazones are summarized in Table 1. The interaction of thorium(IV) salts with BAAPS, MBAAPS, DABAAPS, 2′-NO_2BAAPS, or 3′-NO_2BAAPS results in the formation of ThL_2X_4 (X = Cl, Br, or NCS] (L = BAAPS, MBAAPS, DABAAPS, 2′-NO_2BAAPS, or 3′-NO_2BAAPS); $[ThL_2I_2]I_2$,

Downloaded by [York University Libraries] at 21:42 27 December 2014

Downloaded by [York University Libraries] at 21:42 27 December 2014

Table 1. Characteristic properties of semicarbazones of 4-aminoantipyrine.

Semicarbazone (color)	Molecular formula (MW)	Mp (°C)	Yield (%)	Analysis: found (calcd.) (%)		
				C	H	N
BAAPS (yellow)	$C_{19}H_{20}N_6O$ (348)	216	76	65.26 (65.51)	5.68 (5.74)	23.89 (24.13)
MBAAPS (yellow)	$C_{20}H_{22}N_6O_2$ (378)	230	76	63.24 (63.49)	5.75 (5.82)	22.01 (22.22)
DABAAPS (yellow)	$C_{21}H_{25}N_7O$ (391)	232	75	64.22 (64.45)	6.32 (6.39)	24.92 (25.06)
2′-NO_2BAAPS (bright yellow)	$C_{19}H_{19}N_7O_3$ (393)	216	75.6	57.87 (58.01)	4.77 (4.83)	24.70 (24.93)
3′-NO_2BAAPS (deep yellow)	$C_{19}H_{19}N_7O_3$ (393)	220	75	57.85 (58.01)	4.76 (4.83)	24.71 (24.93)

$[ThL_2](ClO_4)_4$ and $[ThL(NO_3)_4]$ according to the following general equations.

$$\underset{(X = Cl, Br \text{ or } NCS)}{ThX_4} + 2L \xrightarrow[\text{Reflux for 2 hr and cool}]{\text{Methanol}} [ThL_2X_4] \quad (1)$$

$$ThI_4 + 2L \xrightarrow[\text{Reflux for 2 hr and cool}]{\text{Methanol}} [ThL_2I_2]I_2 \quad (2)$$

$$Th(ClO_4)_4 + 2L \xrightarrow[\text{Reflux for 1–2 hr}]{\text{Isopropyl alcohol}} [ThL_2](ClO_4)_4 \quad (3)$$

$$Th(NO_3)_4 + L \xrightarrow[\text{Reflux for 1 hr and left stand overnight}]{\text{Ethyl acetate}} [ThL(NO_3)_4] \quad (4)$$

The analytical data of these complexes are given in Table 2. The complexes are anhydrous, which is evident from the analytical, infrared, and thermal studies. All of the complexes are quite stable and can be stored for long periods except the thorium(IV) iodide complexes, which decompose slowly at room temperature with the evolution of iodine vapours. All of the complexes are generally soluble in common organic solvents. Among the thorium(IV) complexes, the chloro, bromo, nitrato, and thiocyanato complexes are non-electrolytes (Table 2) in $PhNO_2$, whereas the iodo and perchlorato complexes dissociate in this solvent. The iodo complexes appear to be a 1 : 2, while the perchlorato complexes are 1 : 4 electrolytes. Data on the molecular weight of the complexes in freezing $PhNO_2$ are contained in Table 2, along with values calculated on the basis of the established formula of the complexes. The ratio of molecular weight observed for $[ThL_2X_4]$ (X = Cl, Br, or NCS; L = BAAPS, MBAAPS, DABAAPS, 2′-NO_2BAAPS, or 3′-NO_2BAAPS) and $[ThL(NO_3)_4]$ to that calculated is ~0.98 which shows that the complexes are monomeric in solution. In the cases of $[ThL_2I_2]I_2$ and $[ThL_2](ClO_4)_4$, the ratios are ~0.33 and ~0.20, respectively. These data further support that three species are formed in the former complexes and five species are formed in the latter set of complexes.

Infrared Spectra

The infrared spectra of all of the five semicarbazones derived from 4-aminoantipyrine are too complex to make definite band assignments. Empirical assignments by referring to the group frequencies may not be effective since coupling between various modes of vibration are expected as a result of resonance in the pyrazolone ring. Infrared absorption of the five semicarbazones of 4-aminoantipyrine have been assigned by a comparison of their

Downloaded by [York University Libraries] at 21:42 27 December 2014

Downloaded by [York University Libraries] at 21:42 27 December 2014

Table 2. Analytical, conductivity, and molecular weight data of thorium(VI) coordination compounds of semicarbazones.

Complex (empirical formula)	Yield (%)	Color	Mp (°C)	Analysis: found (calcd.) (%)			MW found (calcd.)	Λ_m ($ohm^{-1}\,cm^2\,mol^{-1}$)
				Th	N	Anion		
$[Th(BAAPS)_2Cl_4]$ ($C_{38}H_{40}Cl_4N_{12}O_2Th$)	85	Bright yellow	210	21.44 (21.68)	15.58 (15.70)	13.17 (13.27)	1063 (1070)	4.9
$[Th(BAAPS)_2Br_4]$ ($C_{38}H_{40}Br_4N_{12}O_2Th$)	80	Dark yellow	220	18.40 (18.58)	13.34 (13.46)	25.32 (25.64)	1239 (1248)	5.1
$[Th(BAAPS)_2I_2]I_2$ ($C_{38}H_{40}I_4N_{12}O_2Th$)	78	Brown yellow	250	15.98 (16.15)	11.56 (11.69)	35.19 (35.37)	480 (1436)	50.9
$[Th(BAAPS)_2(NCS)_4]$ ($C_{42}H_{40}N_{16}O_2S_4Th$)	82	Light yellow	193	19.82 (20.00)	19.17 (19.31)	19.82 (20.00)	1154 (1160)	3.2
$[Th(BAAPS)(NO_3)_4]$ ($C_{19}H_{20}N_{10}O_{13}Th$)	90	Yellow	205 d	27.80 (28.01)	16.78 (16.90)	—	824 (828)	4.1
$[Th(BAAPS)_2](ClO_4)_4$ ($C_{38}H_{40}Cl_4N_{12}O_{18}Th$)	75	Pale yellow	180	17.38 (17.52)	12.54 (12.68)	29.73 (29.90)	266 (1324)	98.6
$[Th(MBAAPS)_2Cl_4]$ ($C_{40}H_{44}Cl_4N_{12}O_4Th$)	82	Yellow	210	20.39 (20.53)	14.74 (14.86)	12.39 (12.56)	1125 (1130)	3.9
$[Th(MBAAPS)_2Br_4]$ ($C_{40}H_{44}Br_4N_{12}O_4Th$)	78	Yellow	220 d	17.61 (17.73)	12.69 (12.84)	24.28 (24.46)	1303 (1308)	4.3
$[Th(MBAAPS)_2I_2]I_2$ ($C_{40}H_{44}I_4N_{12}O_4Th$)	70	Brownish yellow	225 d	15.38 (15.50)	11.17 (11.22)	33.45 (33.95)	501 (1496)	52.6
$[Th(MBAAPS)_2(NCS)_4]$ ($C_{44}H_{44}N_{16}O_4S_4Th$)	75	Yellow	198	18.79 (19.01)	18.27 (18.36)	18.82 (19.01)	1217 (1220)	3.8
$[Th(MBAAPS)(NO_3)_4]$ ($C_{20}H_{22}N_{10}O_{14}Th$)	85	Yellow	202	26.82 (27.03)	16.20 (16.31)	—	853 (858)	4.7
$[Th(MBAAPS)_2](ClO_4)_4$ ($C_{40}H_{44}Cl_4N_{12}O_{20}Th$)	72	Yellow	185	16.68 (16.76)	12.04 (12.13)	28.20 (28.61)	279 (1384)	99.6

Downloaded by [York University Libraries] at 21:42 27 December 2014

$[Th(DABAAPS)_2Cl_4]$ $(C_{42}H_{50}Cl_4N_{14}O_2Th)$	80	Yellow	212	19.92 (20.06)	16.85 (16.95)	12.09 (12.28)	1151 (1156)	4.6
$[Th(DABAAPS)_2Br_4]$ $(C_{42}H_{50}Br_4N_{14}O_2Th)$	80	Yellow	220 d	17.21 (17.39)	14.59 (14.69)	23.68 (23.98)	1330 (1334)	5.1
$[Th(DABAAPS)_2I_2]I_2$ $(C_{42}H_{50}I_4N_{14}O_2Th)$	75	Yellow brown	230 d	14.83 (14.94)	12.54 (12.62)	32.50 (32.73)	520 (1552)	50.4
$[Th(DABAAPS)_2(NCS)_4]$ $(C_{46}H_{50}N_{18}O_2S_4Th)$	83	Yellow	199	18.50 (18.61)	20.11 (20.22)	18.49 (18.61)	1243 (1246)	3.7
$[Th(DABAAPS)(NO_3)_4]$ $(C_{21}H_{25}N_{11}O_{13}Th)$	85	Yellow	200	25.52 (26.63)	17.57 (17.68)	—	867 (871)	4.1
$[Th(DABAAPS)_2](ClO_4)_4$ $(C_{42}H_{50}Cl_4N_{14}O_{18}Th)$	72	Pale yellow	182 d	16.32 (16.45)	13.78 (13.90)	27.98 (28.08)	284 (1410)	99.2
$[Th(2'\text{-}NO_2BAAPS)_2Cl_4]$ $(C_{38}H_{38}Cl_4N_{14}O_6Th)$	80	Yellow	210	19.89 (20.00)	16.78 (16.89)	12.08 (12.24)	1156 (1160)	4.9
$[Th(2'\text{-}NO_2BAAPS)_2Br_4]$ $(C_{38}H_{38}Br_4N_{14}O_6Th)$	80	Yellow	215 d	17.21 (17.33)	14.55 (14.64)	23.69 (23.91)	1335 (1338)	5.3
$[Th(2'\text{-}NO_2BAAPS)_2I_2]I_2$ $(C_{38}H_{38}I_4N_{14}O_6Th)$	75	Yellow	215 d	15.10 (15.20)	12.73 (12.84)	33.02 (33.28)	511 (1526)	50.9
$[Th(2'\text{-}NO_2BAAPS)_2(NCS)_4]$ $(C_{42}H_{38}N_{18}O_6S_4Th)$	82	Pinkish yellow	205	18.49 (18.56)	20.05 (20.16)	18.30 (18.56)	1246 (1250)	3.8
$[Th(2'\text{-}NO_2BAAPS)(NO_3)_4]$ $(C_{19}H_{19}N_{11}O_{15}Th)$	85	Yellow	210	26.46 (26.57)	17.55 (17.64)	—	869 (873)	4.3
$[Th(2'\text{-}NO_2BAAPS)_2](ClO_4)_4$ $(C_{38}H_{38}Cl_4N_{14}O_{22}Th)$	78	Yellow	200 d	16.31 (16.40)	13.77 (13.86)	27.82 (28.00)	284 (1414)	96.3
$[Th(3'\text{-}NO_2BAAPS)_2Cl_4]$ $(C_{38}H_{38}Cl_4N_{14}O_6Th)$	80	Yellow	208	19.88 (20.00)	16.77 (16.89)	12.06 (12.24)	1155 (1160)	4.5
$[Th(3'\text{-}NO_2BAAPS)_2Br_4]$ $(C_{38}H_{38}Br_4N_{14}O_6Th)$	81	Dark yellow	220 d	17.20 (17.33)	14.55 (14.64)	23.68 (23.91)	1334 (1338)	5.3

(*continued*)

Downloaded by [York University Libraries] at 21:42 27 December 2014

Table 2. Continued.

Complex (empirical formula)	Yield (%)	Color	Mp (°C)	Analysis: found (calcd.) (%)			MW found (calcd.)	Λ_m ($ohm^{-1}\,cm^2\,mol^{-1}$)
				Th	N	Anion		
$[Th(3'\text{-}NO_2BAAPS)_2I_2]I_2$ ($C_{38}H_{38}I_4N_{14}O_6Th$)	78	Brown	220 d	15.12 (15.20)	12.72 (12.84)	33.04 (33.28)	510 (1526)	51.8
$[Th(3'\text{-}NO_2BAAPS)_2(NCS)_4]$ ($C_{42}H_{38}N_{18}O_6S_4Th$)	75	Yellow	205	18.49 (18.56)	20.04 (20.16)	18.29 (18.56)	1245 (1250)	3.7
$[Th(3'\text{-}NO_2BAAPS)(NO_3)_4]$ ($C_{19}H_{19}N_{11}O_{15}Th$)	83	Yellow	208	26.44 (26.57)	17.54 (17.64)	—	868 (873)	4.6
$[Th(3'\text{-}NO_2BAAPS)_2](ClO_4)_4$ ($C_{38}H_{38}Cl_4N_{14}O_{22}Th$)	75	Light yellow	205 d	16.29 (16.40)	13.76 (13.86)	27.83 (28.00)	285 (1414)	98.3

Downloaded by [York University Libraries] at 21:42 27 December 2014

spectra with those of antipyrine, 4-aminoantipyrine[11–13] and some previous works on semicarbazones.[10,14,15]

In these complexes, as expected, $\nu(NH_2)$ of the hydrazinic nitrogen of semicarbazide ($\sim$1622 cm^{-1}) is absent in the infrared spectra of BAAPS, MBAAPS, DABAAPS, 2′-NO_2BAAPS, and 3′-NO_2BAAPS.[16] It has also been observed that the amide-II band in the complexes is shifted towards the lower energy side compared to that of the semicarbazone. The effect is due to the electron density drift from the hydrazinic nitrogen to metal ion.[17] The characteristic absorption of the carbonyl group in BAAPS, MBAAPS, DABAAPS, 2′-NO_2BAAPS, or 3′-NO_2BAAPS is observed in the 1700–1680 cm^{-1} region.[18]. In the complexes, these bands are shifted toward lower energy in the 1650–1640 cm^{-1} region (Table 3). The amide-II band in the free ligands has been observed at $\sim$1565 cm^{-1}. In all the present complexes, this band is also shifted towards lower wave numbers by $\sim$30 cm^{-1}. This observation suggests coordination through the carbonyl oxygen atom. The strong bands at $\sim$1600 cm^{-1} in these semicarbazones apparently have a large contribution from the ν(C=N) mode of the semicarbazone moiety.[19] This has been observed as a blue-shift in the position of the C=N band in all complexes as compared to the free ligands. Another strong band was observed at $\sim$1610 cm^{-1} due to azomethine C=N absorption. On complexation this band is shifted towards the lower frequency region, clearly indicating the coordination through the azomethine N atom.[20–22] In the far-infrared region the bands due to ν(Th–N)/ν(Th–O) are also observed[23,24] (Table 3). From these facts, it is clearly indicated that these ligands serve as tridentate ligands, coordinating through the carbonyl O; hydrazone N and azomethine N atoms.

The occurrence of two strong bands at $\sim$1070 and 620 cm^{-1} in the spectra of the $[ThL_2](ClO_4)_4$ complexes attributed to ν_3 and ν_4 vibrations of ionic perchlorate suggests[25–27] the presence of a perchlorate group outside the coordination sphere in the complex[4,26] (Table 4).

For thorium(IV) nitrate complexes, the occurrence of two strong absorptions in the 1540–1514 and 1295–1270 cm^{-1} regions is attributed to ν_4 and ν_1 modes of vibration of the covalently bonded nitrate group, respectively, suggesting that the nitrate groups are inside the coordination sphere.[28,29] Other absorption bands associated with the covalent nitrate groups are also observed in the spectra of the complexes. The spectral bands of $[ThL(NO_3)_4]$ (L = semicarbazones) were compared with the known bands of $Th(NO_3)_4 \cdot 5H_2O$[30] i.e. 150 (ν_4), 1290 (ν_1), 1030 (ν_2), 808(ν_6), 745 (ν_3) and 715 cm^{-1}(ν_5), in which the bidentate character of the nitrato groups has been established by x-ray[31] and neutron diffraction studies.[32,33] It is inferred that the nitrate groups in these complexes also behave as bidentate ligands[33–35] (Table 5).

Downloaded by [York University Libraries] at 21:42 27 December 2014

Table 3. Selected infrared bands (cm^{-1}) of thorium(IV) complexes of semicarbazones.

	Assignments					
			ν(C=O)			
Compounds	ν(C=N) (azomethinic)	ν(C=N) (hydrazinic)	I	II	III	ν(Th–O)/ ν(Th–N)
BAAPS	1610 s	1600 s	1700 s	1565 m	1350 m	—
$[Th(BAAPS)_2Cl_4]$	1592 s	1620 s	1645 s	1535 m	1335 m	480 m 390 w
$[Th(BAAPS)_2Br_4]$	1585 s	1625 s	1652 s	1530 m	1332 m	482 m 392 w
$[Th(BAAPS)_2I_2]I_2$	1582 s	1628 s	1645 s	1530 m	1330 m	482 m 385 w
$[Th(BAAPS)_2(NCS)_4]$	1585s	1630 s	1640 s	1535 m	1332 m	475 m 390 w
$[Th(BAAPS)(NO_3)_4]$	1590 s	1628 s	1645 s	1535 m	1330 m	470 m 385 w
$[Th(BAAPS)_2](ClO_4)_4$	1588 s	1625 s	1650 s	1530 m	1332 m	465 m 380 w
MBAAPS	1620 s	1605 s	1702 s	1560 m	1355 m	—
$[Th(MBAAPS)_2Cl_4]$	1582 s	1630 s	1640 s	1532 m	1342 m	482 m 390 w
$[Th(MBAAPS)_2Br_4]$	1600 m	1625 s	1652 s	1540 m	1338 m	475 m 382 w
$[Th(MBAAPS)_2I_2]I_2$	1598 s	1628 s	1650 s	1535 m	1340 m	480 m 378 w

Downloaded by [York University Libraries] at 21:42 27 December 2014

$[Th(MBAAPS)_2(NCS)_4]$	1590 s	1635 s	1645 s	1538 m	1337 m	482 m 380 w
$[Th(MBAAPS)(NO_3)_4]$	1595 s	1625 s	1648 s	1535 m	1340 m	485 m 375 w
$[Th(MBAAPS)_2](ClO_4)_4$	1588 s	1630 s	1650 s	1537 m	1335 m	470 m 370 w
DABAAPS	1620 s	1605 s	1705 s	1570 s	1350 m	—
$[Th(DABAAPS)_2Cl_4]$	1600 s	1630 s	1645 s	1535 m	1342 m	470 m 392 w
$[Th(DABAAPS)_2Br_4]$	1598 s	1635 s	1640 s	1540 m	1340 m	472 m 390 w
$[Th(DABAAPS)_2I_2]I_2$	1595 s	1638 s	1645 s	1542 m	1335 m	470 m 385 m
$[Th(DABAAPS)_2(NCS)_4]$	1602 s	1635 s	1650 s	1545 m	1333 m	465 m 390 w
$[Th(DABAAPS)(NO_3)_4]$	1600 s	1632 s	1642 s	1540 m	1342 m	472 m 380 w
$[Th(DABAAPS)_2](ClO_4)_4$	1595 m	1635 s	1648 s	1542 m	1340 m	470 m 378 w
2′-NO_2BAAPS	1612 m	1602 m	1700 s	1565 s	1340 m	—
$[Th(2'\text{-}NO_2BAAPS)_2Cl_4]$	1595 s	1625 s	1642 s	1532 m	1335 s	482 m 380 w
$[Th(2'\text{-}NO_2BAAPS)_2Br_4]$	1592 s	1630 s	1640 s	1540 m	1333 s	485 m 382 w
$[Th(2'\text{-}NO_2BAAPS)_2I_2]I_2$	1590 s	1628 s	1650 s	1542 m	1330 s	490 m 378 w

(*continued*)

Downloaded by [York University Libraries] at 21:42 27 December 2014

Table 3. Continued.

Compounds	Assignments					
	ν(C=N) (azomethinic)	ν(C=N) (hydrazinic)	ν(C=O) I	ν(C=O) II	ν(C=O) III	ν(Th–O)/ ν(Th–N)
[Th(2′-NO_2BAAPS)$_2$(NCS)$_4$]	1593 s	1630 s	1642 s	1545 m	1328 s	485 m 375 w
[Th(2′-NO_2BAAPS)(NO_3)$_4$]	1595 s	1625 s	1648 s	1540 m	1332 m	480 m 380 w
[Th(2′-NO_2BAAPS)$_2$](ClO_4)$_4$	1590 s	1627 s	1645 s	1542 m	1325 s	482 m 382 w
3′-NO_2BAAPS	1608 m	1600 m	1702 s	1565 s	1340 s	—
[Th(3′-NO_2BAAPS)$_2$$Cl_4$]	1582 m	1630 m	1650 s	1530 m	1325 m	482 m 390 w
[Th(3′-NO_2BAAPS)$_2$$Br_4$]	1580 m	1625 s	1642 m	1528 m	1330 m	465 m 372 w
[Th(3′-NO_2BAAPS)$_2$$I_2$]$I_2$	1585 m	1628 m	1645 s	1535 m	1327 m	468 m 372 w
[Th(3′-NO_2BAAPS)$_2$(NCS)$_4$]	1588 m	1630 m	1642 m	1537 m	1325 m	460 m 370 w
[Th(3′-NO_2BAAPS)(NO_3)$_4$]	1580 m	1628 s	1648 m	1535 m	1326 m	465 m 372 w
[Th(3′-NO_2BAAPS)$_2$](ClO_4)$_4$	1588 m	1625 s	1645 m	1538 m	1325 m	470 m 378 w

Table 4. Infrared absorption frequencies (cm^{-1}) of the perchlorato group in thorium(IV) perchlorato complexes of semicarbazones.

Complexes	ν_3	ν_4
$[Th(BAAPS)_2](ClO_4)_4$	1080 vs	620 s
$[Th(MBAAPS)_2](ClO_4)_4$	1085 s	622 s
$[Th(DABAAPS)_2](ClO_4)_4$	1100 s	625 s
$[Th(2'\text{-}NO_2BAAPS)_2](ClO_4)_4$	1080 s, br	620 s
$[Th(3'\text{-}NO_2BAAPS)_2](ClO_4)_4$	1096 vs, br	622 vs

The C–N stretching frequency in the thiocyanato complexes of thorium appears in the 2070–2040 cm^{-1} region, which lies on the borderline for distinguishing,[36–38] although the high relative intensity of the band in these cases suggests that the thiocyanate groups are N-bonded.[37,38] The frequency of the C–S stretching vibration has also been used to diagnose the bonding mode in thiocyanates.[37,38] The C–S band identified in the 840–780 cm^{-1} region, further confirms that the thiocyanate group is almost certainly N-bonded,[39] the N–C–S bending (ν_2) is also identified in these complexes (Table 6).

In the halide complexes the ν(Th–Cl) vibration has been assigned at the 290–250 cm^{-1} region[40] while the ν(Th–Br) and ν(Th–I) frequencies could not be assigned because they are out of the region studied here.

X-Ray Powder Diffraction Studies

X-ray powder diffraction studies of $[Th(BAAPS)(NO_3)_4]$ have been done on a model PW 1140 Phillips x-ray diffractometer with $CuK_\alpha = 1.54178$ Å. It was found that this complex belongs to the monoclinic crystal system with $a = 8.910(1)$ Å, $b = 11.134(6)$ Å; $c = 11.652(3)$ Å, and $\beta = 84.766(7)^o$

Thermal Studies

The thermal studies results of the Th(IV) complexes of BAAPS, MBAAPS, DABAAPS, and 2′-NO_2BAAPS are presented in Table 7. The TG curves of the Th(IV) complexes do not show the presence of water molecules, either in or out of the coordination sphere. The thermogravimetric curves of the chloro, bromo, and thiocyanato complexes indicate that in step 1 only one molecule of ligand molecule is lost, while at ~430 °C, the remaining ligand molecule has also been lost. Finally, at ~605 ± 5 °C,

Downloaded by [York University Libraries] at 21:42 27 December 2014

Downloaded by [York University Libraries] at 21:42 27 December 2014

Table 5. Infrared absorption frequencies (cm^{-1}) of the nitrato group in thorium(IV) nitrate complexes of semicarbazone.

Complexes	ν_4	ν_1	ν_2	ν_6	ν_3	ν_5
$[Th(NO_3)_4 \cdot 5H_2O$	1520 s	1290 s	1030 m	808 m	745 w	715 w
$[Th(BAAPS)(NO_3)_4]$	1530 s	1280 s	1025 m	800 m	735 w	710 w
$[Th(MBAAPS)(NO_3)_4]$	1514 vs	1294 vs	1025 m	810 w	755 m	697 m
$[Th(DABAAPS)(NO_3)_4]$	1540 s	1270 s	1037 s	815 s	770 m	710 w
$[Th(2'\text{-}NO_2BAAPS)(NO_3)_4]$	1530 s	1270 s	1037 s	815 s	770 m	710 w
$[Th(3'\text{-}NO_2BAAPS)(NO_3)_4]$	1525 s	1280 m	1028 m	812 s	750 m	705 w

Table 6. Infrared absorption frequencies (cm^{-1}) of the isothiocyanato group in thorium(IV) isothiocyanato complexes of semicarbazones.

Complexes	ν_1	ν_3	ν_2
$[Th(BAAPS)_2(NCS)_4]$	2051 vs	757 m	480 m
$[Th(MBAAPS)_2(NCS)_4]$	2050 vs	760 m	475 m
$[Th(DABAAPS)_2(NCS)_4]$	2055 vs	755 m	482 m
$[Th(2'\text{-}NO_2BAAPS)_2(NCS)_4]$	2045 vs	820 m	475 m
$[Th(3'\text{-}NO_2BAAPS)_2(NCS)_4]$	2065 vs	832 m	480 w

oxohalide and oxothiocyanato formation takes place. The thorium(IV) nitrate complexes decompose in the 280–425 °C temperature region, losing the ligand molecule. Finally, ThO_2 is obtained as residual mass at ~610 °C. The thermogravimetric curve of $[Th(DABAAPS)_2](ClO_4)_4$ shows that the complex starts to decompose at 215 °C and decomposition continues up to 605 °C, after which ThO_2 remains as residue (Table 7). From the pyrolysis curve, it is clear that no stable intermediate perchlorate complex has been formed in this species. For the iodo complexes, which form a sticky mass, we have not studied the thermal analyses. The analyses of the thermograms indicate the following decomposition schemes:

$$[ThL_2X_4] \longrightarrow [ThLX_4] \longrightarrow ThX_4 \longrightarrow ThOX_2$$

(X = Cl, Br, or NCS)(L = BAAPS, MBAAPS, DABAAPS, or 2′-NO_2BAAPS)

$$[ThL(NO_3)_4] \longrightarrow Th(NO_3)_4 \longrightarrow ThO_2$$

(L = BAAPS, MBAAPS , DABAAPS, or 2′-NO_2BAAPS)

$$[Th(DABAAPS)_2](ClO_4)_4 \longrightarrow ThO_2$$

In general, if the minimum TG decomposition temperature is taken as a rough criterion of thermal stability then the order of stability of the Th(IV) complexes is: $NO_3 > Cl > Br > NCS > ClO_4$.

Stereochemistry

The preferred coordination number of Th(IV) is 6 or 8, but higher coordination numbers have also been observed.[41,42] In the chloro, bromo, and thiocyanato complexes, conductance and molecular weight determinations suggest that the complexes are non-ionic in nature and do not dissociate in nitrobenzene solvent. Thus, in the case of the BAAPS, MBAAPS,

Downloaded by [York University Libraries] at 21:42 27 December 2014

Downloaded by [York University Libraries] at 21:42 27 December 2014

Table 7. Thermal data of thorium(IV) complexes of semicarbazones.

Complex	Decomposition temperature (°C)		Decomposition product	Weight loss (%)	
	Initial	Final		Found	Calcd.
$[Th(BAAPS)_2Cl_4]$	230	280	$Th(BAAPS)Cl_4$	32.89	32.52
	330	415	$ThCl_4$	65.39	65.04
	550	605	$ThOCl_2$	70.59	70.18
$[Th(BAAPS)_2Br_4]$	220	275	$Th(BAAPS)Br_4$	28.11	27.88
	320	420	$ThBr_4$	55.99	55.76
	500	600	$ThOBr_2$	67.76	67.30
$[Th(BAAPS)(NO_3)_4]$	280	420	$Th(NO_3)_4$	42.49	42.02
	460	610	ThO_2	68.39	68.11
$[Th(BAAPS)_2(NCS)_4]$	230	290	$Th(BAAPS)(NCS)_4$	30.33	30.00
	340	430	$Th(NCS)_4$	60.76	60.00
	500	595	$ThO(NCS)_2$	69.32	68.62
$[Th(DABAAPS)_2Cl_4]$	240	295	$Th(DABAAPS)Cl_4$	34.11	33.82
	345	425	$ThCl_4$	68.29	67.64
	510	605	$ThOCl_2$	72.90	72.40
$[Th(DABAAPS)_2Br_4]$	225	280	$Th(DABAAPS)Br_4$	28.89	29.31
	320	430	$ThBr_4$	59.22	58.62
	505	610	$ThOBr_2$	70.10	69.41
$[Th(DABAAPS)(NO_3)_4]$	290	425	$Th(NO_3)_4$	45.23	44.89
	465	610	ThO_2	70.21	69.69
$[Th(DABAAPS)_2(NCS)_4]$	230	300	$Th(DABAAPS)(NCS)_4$	31.69	31.38
	345	435	$Th(NCS)_4$	63.11	62.76
	500	600	$ThO(NCS)_2$	71.12	70.78
$[Th(DABAAPS)_2](ClO_4)_4$	215	605	ThO_2	83.02	81.27

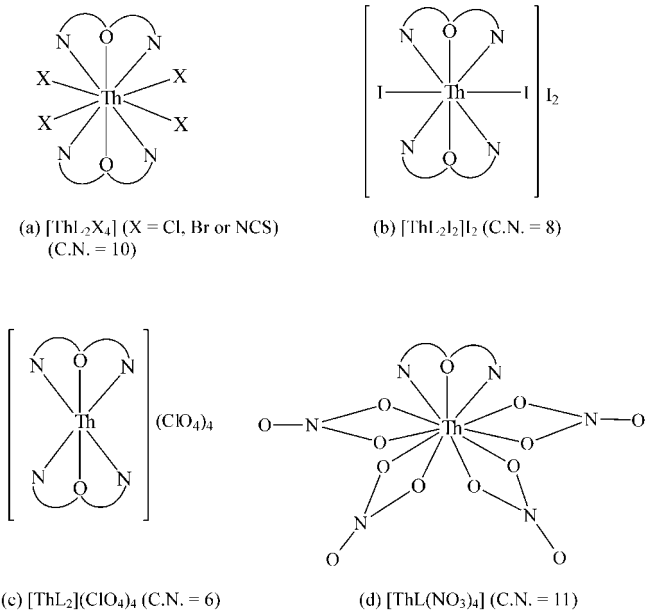


Figure 2. Suggested structures of thorium(IV) complexes of semicarbazones.

DABAAPS, 2′-NO_2BAAPS, and 3′-NO_2BAAPS complexes of ThX_4 (X = Cl, Br, or NCS) the coordination number of Th(IV) is found to be 10. In case of iodo complexes the 1 : 2 electrolytic nature suggests that two iodine atoms are present outside the coordination sphere and, hence, the coordination number of Th(IV) in $[Th(L_2)I_2]I_2$ [L = BAAPS, MBAAPS, DABAAPS, 2′-NO_2BAAPS, or 3′-NO_2BAAPS] is found to be eight.

It has been found from a single crystal x-ray structure determination of $Th(NO_3)_4 \cdot 5H_2O$ that the nitrato groups are linked to thorium through two oxygen atoms, each nitrato group thus functioning as a bidentate ligands. In the $[Th(L)(NO_3)_4]$ [L = BAAPS, MBAAPS, DABAAPS, 2′-NO_2BAAPS, or 3′-NO_2BAAPS] complexes, the Th(IV) atom is surrounded by nine oxygens (eight oxygens from four nitrato groups and one oxygen from the amide group) and two nitrogen atoms of azomethine groups and thus the products have a coordination number of 11 for the thorium atom. In $[ThL_2](ClO_4)_4$ (L = BAAPS, MBAAPS, DABAAPS, 2′-NO_2BAAPS, and 3′-NO_2BAAPS) the conductance, molecular weight, and IR studies reveal that all four perchlorato groups are present outside the coordination sphere, hence suggesting the presence of six-coordinated Th(IV) in these complexes. The proposed structures of the present thorium(IV) complexes are given in Fig. 2.

Downloaded by [York University Libraries] at 21:42 27 December 2014

ACKNOWLEDGMENTS

One of the authors (R.K.A.) is thankful to the University Grants Commission, New Delhi, for financial assistance and Mr. Steven Sutcliffe, Chief Technician, Chemistry Department, The University of the South Pacific for his assistance in finalizing the paper.

Downloaded by [York University Libraries] at 21:42 27 December 2014

REFERENCES

1. Lippard, S.J. Eight coordination chemistry. Prog. Inorg. Chem. **1967**, *8*, 109.
2. Bagnall, K.W. The coordination chemistry of the actinide halides. Coord. Chem. Rev. **1967**, *2*, 145.
3. Agarwal, R.K.; Agarwal, H.; Arora, K. Thorium(IV) metal complexes with neutral oxygen donor—A Review. Rev. Inorg. Chem. **2000**, *20*, 1.
4. Savant, V.V.; Ramamurthy, P.; Patel, C.C. Antipyrine complexes of titanium(IV), zirconium(IV) and thorium(IV) and uranium(VI) perchlorates. J. Less Common Metals **1970**, *22*, 479.
5. Agarwal, R.K.; Srivastava, A.K.; Srivastava, T.N. Thorium(IV) complexes of 2,6-lutidine N-oxide and tetramethylene sulphoxide. Transit. Met. Chem. **1980**, *5*, 95.
6. Agarwal, R.K.; Arora, K.; Dutt, P. Studies on thorium(IV) and dioxouranium(VI) complexes of Schiff bases derived from 4-aminoantipyrine. Synth. React. Inorg. Met.—Org. Chem. **1994**, *24*, 301.
7. Agarwal, R.K.; Arora, K.; Dutt, P. Some high coordination compounds of thorium(IV) and dioxouranium(VI) derived from hydrazones of isonicotinic acid hydrazide. Polyhedron **1994**, *13*, 957.
8. Savant, V.V.; Patel, C.C. Diphenyl sulphoxide complexes of thorium(IV). J. Less Common Metals **1971**, *24*, 459.
9. Ramamurthy, P.; Patel, C.C. Crystal structure of thorium perchlorate tetrahydrate by x-ray method. J. Inorg. Nucl. Chem. **1963**, *25*, 310.
10. Agarwal, R.K.; Agarwal, H.; Manglik, A.K. Chelating behaviour of 4[*N*-(benzylidene)amino]antipyrine semicarbazone towards lanthanide ions. Synth. React. Inorg. Met.—Org. Chem. **1996**, *26*, 1163.
11. Agarwal, R.K.; Srivastava, A.K.; Srivastava, T.N. Thorium(IV) complexes of pyrazolone ligands. Proc. Natl. Acad. Sci. (India) **1981**, *51A*, 79.
12. Agarwal, R.K.; Rastogi, S.C. Infrared and thermal studies of uranyl(VI) complexes of antipyrine. Thermochim. Acta **1985**, *95*, 279.
13. Agarwal, R.K.; Prakash, J. Synthesis and characterization of thorium(IV) and dioxouranium (VI) complexes of 4[*N*(2-hydroxy-1-naphthalidene)] amino antipyrine. Polyhedron **1991**, *10*, 2399.

14. Usha. Synthesis and Characterization of Transition Metal Complexes of Semicarbazones and Thiosemicarbazones; Ch. Charan Singh University: Meerut, 1996; Ph.D. Thesis.
15. Garg, P. A Comparative Studies of the Ligational Behavior of Various Azomethines, viz., Hydrazones of Isoniazid, Semicarbazones, Thiosemicarbazones and Oximes Derived from 4-Aminoantipyrine Towards Bio-Metals Ions; Ch. Charan Singh University: Meerut, 1995; Ph.D. Thesis.
16. Marykutty, P.V.; Parameswaran, G. Synthesis and characterization of Mn(II), Fe(II), Co(II) and Ni(II) complexes of anthracene carboxaldehyde semicarbazone. Asian J. Chem. **2001**, *13*, 905.
17. Lavanon, H.; Luz, Z. ESR and NMR of Mn(II) complexes in methanol. J. Chem. Phys. **1969**, *49*, 2031.
18. Campbell, M.J.; Grzeskowiak, R. Some copper(II) complexes of semicarbazide. J. Inorg. Nucl. Chem. **1968**, *30*, 1865.
19. Dyer, J.R. *Applications of Absorption Spectroscopy of Organic Compounds*; Prentice-Hall: New Delhi, 1984.
20. Agarwal, R.K.; Sarin, R.K. Synthesis and characterization of lanthanide(III) perchlorate complexes of 4[*N*-(4-dimethylaminobenzalidene) amino]antipyrine. Synth. React. Inorg. Met.—Org. Chem. **1994**, *24*, 185.
21. Agarwal, R.K. Spectral and thermal studies of dioxouranium(VI)sulphato complexes of some Schiff bases of 4-aminoantipyrine. J. Indian Chem. Soc. **1995**, *72*, 263.
22. Agarwal, R.K.; Garg, P.; Agarwal, H.; Agarwal, S.K. Synthesis, magneto-spectral and thermal studies of cobalt(II) and nickel(II) complexes of 4[*N*(4-dimethylaminobenzalidene)amino]antipyrine. Synth. React. Inorg. Met.—Org. Chem. **1997**, *27*, 251.
23. Radhakrishnan, P.S.; Indrasenan, P.; Nair, C.G.R. Complexes of lanthanide nitrates with 4-*N*-(2′-Hydroxybenzylidene)aminoantipyrine. Polyhedron **1984**, *3*, 67.
24. Radhakrishnan, P.K.; Indrasenan, P. Synthesis and characterization of some lanthanide nitrate and perchlorate complex of 4-(pyridine-2′-carboxalidene)amino-antipyrine. J. Indian Chem. Soc. **1990**, *67*, 243.
25. Bellamy, L.S. *The Infrared Spectra of Complex Molecules*; Methuen: London, 1958.
26. Van Leumann, P.W.N.M. Inorganic Complexes of Ligands Containing the Thionyl Group; Leiden, 1967; Ph.D. Thesis.
27. Ramamurthy, P.; Patel, C.C. Pyridine N-oxide complexes of zirconyl, thorium and uranyl perchlorate. Can. J. Chem. **1964**, *42*, 856.
28. Agarwal, R.K.; Agarwal, H. The Synthesis, structure and bonding in some lanthanide(III) coordination compounds of 4[(*N*-furfural)amino]antipyrine. Synth. React. Inorg. Met.—Org. Chem. **2001**, *31*, 263.

Downloaded by [York University Libraries] at 21:42 27 December 2014

29. Hester, R.E.; Grossman, W.E.L. Vibrational analysis of bidentate nitrate and carbonate complexes. Inorg. Chem. **1966**, *5*, 1308.
30. Ferraro, J.R.; Walker, A. Comparison of the infrared spectra of the hydrates and anhydrous salt in the systems $UO_2(NO_3)_2$ and $Th(NO_3)_4$. J. Chem. Phys. **1966**, *45*, 550.
31. Ueki, T.; Zalkin, A.; Templeton, D.H. Crystal structure of thorium nitrate pentahydrate by X-ray diffraction. Acta Crystallogr. **1966**, *20*, 836.
32. Taylor, J.C.; Mueller, M.H.; Hittermann, R.L. Crystal structure of thorium nitrate pentahydrate by neutron diffraction. Acta Crystallogr. **1966**, *20*, 842.
33. Rawat, H.K. A Study of Complexing Behavior of Oxygen Donor Ligands Towards Some Group(IV) Metal Ions; Meerut University: Meerut, 1987; Ph.D. Thesis.
34. Agarwal, R.K.; Rawat, H.K.; Srivastava, A.K. Synthesis and characterization of thorium(IV) and dioxouranium(IV) complexes of 4[(*N*-benzoyl) amine]antipyrine. Indian J. Chem. **1988**, *27A*, 1105.
35. Agarwal, R.K.; Prakash, J. Synthesis and characterization of thorium(IV) and dioxouranium(VI) complexes of pentamethylene sulphoxide. Polyhedron **1991**, *10*, 2567.
36. Al-Kazzaz, Z.M.S.; Bagnall, K.W.; Brown, D. Phosphine oxide complexes of the actinide(IV) thiocyanates. J. Inorg. Nucl. Chem. **1973**, *35*, 1501.
37. Burmeister, J.L. Recent developments in the coordination chemistry of ambidentate ligands. Coord. Chem. Rev. **1966**, *1*, 205.
38. Burmeister, J.L. Linkage isomerism in metal complexes. Coord. Chem. Rev. **1968**, *3*, 225.
39. Bailey, R.A.; Kozak, S.L.; Michelsen, T.W.; Mills, W.N. Infrared spectra of complexes of the thiocyanate and related ions. Coord. Chem. Rev. **1971**, *6*, 407.
40. Al-Kazzaz, Z.M.S.; Bagnall, K.W.; Brown, D. Some phosphine oxide complexes of the actinide tetrachlorides. J. Inorg. Nucl. Chem. **1973**, *35*, 1493.
41. Rastogi, S.C. Studies of the Stereochemistry of High Coordination Compounds of ZrO(IV), UO_2(VI) and Th(IV) Involving Some Oxygen and Nitrogen Donor Ligands; Meerut University: Meerut, 1985; Ph.D. Thesis.
42. Smith, B.C.; Wassef, M.A. Some complex compounds of thorium(IV). J. Chem. Soc.(A) **1968**, 1817.

Received April 30, 2001
Accepted April 6, 2004

Downloaded by [York University Libraries] at 21:42 27 December 2014