Asian Journal of Chemistry Vol. 12, No. 3 (2000), 893–895

NOTE

Synthesis and Characterization of Thorium(IV) Metal Complexes with a Schiff Base

KISHOR ARORA†, D.D. AGRAWAL‡ and R.C. GOYAL*
Department of Chemistry
Government Post Graduate College, Morena-476 001, India

A series of new thorium(IV) complexes with a Schiff base derived from 2-amino pyridine, *i.e.*, 2N-(benzalidene) aminopyridine (BAPy) has been synthesized. Analytical, conductance, mol. wt. and spectral data reveal that the complexes have the general composition $ThX_4 \cdot nL$ ($X = NO_3^-$ or NCS^-, $n = 2$; $X = I^-$, $n = 4$ and $X = ClO_4^-$, $n = 6$; $L =$ BAPy) Thorium(IV) atom is either 6 or 10-coordinated depending upon the anions present in these complexes.

In the recent past studies on the thorium(IV) and dioxouranium(VI) metals and other oxocation metals with various oxygen and nitrogen donor ligands including Schiff bases have been reported[1–14]. In this present communication we wish to report some investigations done on the high coordination compounds of thorium(IV) metal ion with a Schiff base of 2-amino pyridine namely 2-N-(benzalidene) amino pyridine (BAPy).

The ligand was found to act as neutral monodentate (N) ligand which leads to the formation of high coordination compounds having the general composition $ThX_4 \cdot nL$ ($X = NO_3^-$ or NCS^-, $n = 2$; $X = I^-$, $n = 4$ and $X = ClO_4^-$, $n = 6$; $L =$ BAPy). These complexes are generally soluble in common organic solvents and are quite stable and can be stored at room temperature except the iodide complex which decomposes slowly at room temperature with evolution of iodine vapours.

All the reagents were used as supplied by BDH and Merck. Thorium nitrate was obtained commercially and all other salts were prepared by respective reported methods[15–18]. All the physio-chemical measurements were done according to the reported method[4] and the metal was estimated as ThO_2.[19]

A solution of distilled benzaldehyde (1 mmol) in absolute alcohol (50 mL) was mixed with 2-amino pyridine (1.1 mmol) in the same solvent and the mixture was refluxed for 3–4 h. On cooling a yellow product separated out which was filtered off and recrystallized in the same solvent and dried *in vacuo* over anhydrous $CaCl_2$.

---

†Department of Chemistry, K.R. Government (P.G.) College, Gwalior, India.

‡Department of Chemistry, Jiwaji University, Gwalior. India.

The respective metal salt solutions were treated with ligand solution in required molar concentrations. In some cases complexes were isolated in hot solutions while in some cases after refluxing the resulting solutions for 2–3 h at 60°–80°C. The solvents used were ethanol or isopropanol. The complexes were collected, washed with solvent and finally with anhydrous ether and dried *in vacuo* over $CaCl_2$.

The reaction of thorium(IV) metal salts with Schiff base ligand results in the formation of $ThX_4 \cdot nL$ ($X = NO_3^-$ or NCS^-, n = 2; $X = I^-$, n = 4 and $X = ClO_4^-$, n = 6; L = BAPy). Electrical conductance values for these complexes were determined in $PhNO_2$ medium and it was inferred that iodo complex behaves as 1 : 2 and perchlorato complex as 1 : 4 electrolyte while other complexes are essentially non-electrolytes. This is in general agreement with stability of metal-anion bond found earlier[9].

The IR spectral studies of the complexes, when compared with those of the ligand, show a considerable shift in ν(C=N) azomethine absorption to lower frequency indicating a decrease in the stretching force constant of C=N. As a consequence of the coordination, through azomethine nitrogen, the double bond character between carbon and nitrogen is reduced[20–23]. The strong bands observed at *ca.* 1570 and 1050 cm^{-1} are tentatively assigned to antisymmetric and symmetric ν(C=C) and ν(C—N) of pyridine ring which remain practically unchanged, revealing non-involvement of pyridine nitrogen and metal bonds. Some new medium and weak bands are observed in the range 425–420 cm^{-1} in the complexes where the ligand has no absorptions. These bands are tentatively assigned to ν(Th—N) stretching modes[24, 25]. The partial IR data is given in Table-1.

TABLE-1
PARTIAL IR DATA FOR THORIUM(IV) COMPLEXES OF (BAPy)

Complex	ν(C=N) str. azomethine	Pyridine ring breathing and deformation bands		ν(Th—N)
		ν(C=C)	ν(C—N)	
$Th(NO_3)_4 \cdot 2(BAPy)$	1620 s	1570 m	1055 sh	420 m
$Th(NCS)_4 \cdot 2(BAPy)$	1625 s	1575 m	1050 sh	420 m
$ThI_4 \cdot 4(BAPy)$	1614 s	1570 sh	1055 m	425 m
$Th(ClO_4)_4 \cdot 6(BAPy)$	1630 s	1570 sh	1050 sh	420 m
BAPy	1660 s	1578 m	1050 m	–

The preferred coordination number of Th(IV) is 6 or 10 in these complexes depending upon the anions present. In isothiocyanato complex conductance, mol. wt. data suggest that in this complex Th(IV) has coordination number six. Iodo complex which shows 1 : 2 electrolytic nature shows that two iodo ions are present outside the coordination sphere generating the coordination number six for Th(IV) metal ion. Similarly in perchlorato complex, perchlorato ions are present ouside the coordination sphere, so Th(IV) has coordination number six. Since nitrato groups are bidentate in nature, in $(Th(BAPy)_2(NO_3)_4)$, Th(IV) ion is surrounded by 8 oxygen (from 4 nitrato ions) and 2 nitrogen (from the ligands) atoms forming the coordinating number 10 for Th(IV) atom.[6]

ACKNOWLEDGEMENT

One of the authors (R.C.G.) sincerely acknowledges the financial support from UGC Central Regional Office, Bhopal in the form of minor research project for this work.

REFERENCES

1. R.K. Agarwal, K. Arora and P. Dutt, *Polyhedron*, **13**, 957 (1994).
2. R.K. Agarwal and K. Arora, *Synth. React. Inorg. Met-Org. Chem.*, **23**, 653 (1993).
3. ————, *Synth. React. Inorg. Met-Org, Chem.*, **23**, 1671 (1993).
4. ————, *Polish J. Chem.* **67**, 25 (1993).
5. R.K. Agarwal, K. Arora and P. Dutt, *Nat. Acad. Sc. Letters (India)*, **15**, 295 (1992).
6. R.K. Agarwal, K. Arora, Miss Priyanka and I. Chakravorti, *Polish J. Chem.*, **67**, 1913 (1993).
7. R.K. Agarwal, K. Aroora and P. Dutt, *Synth. React. Inorg. Met-Org. Chem.* **24**, 301 (1994).
8. K. Arora, *Asian J. Chem.*, **7**, 424 (1995).
9. K. Arora, J. Ambwani and M.C. Pathak, *Asian J. Chem.*, **9**, 309 (1997).
10. K. Arora, R.C. Goyal, Susheel Sharma and M.C. Pathak, *Asian J. Chem.*, **11**, 1005 (1999).
11. K. Arora, R.C. Goyal, D.P. Sharma and M.C. Pathak, *Asian J. Chem.*, **11**, 1329 (1999).
12. K. Arora, D.P. Sharma and Susheel Sharma, *Asian J. Chem.*, **11**, 1357 (1999).
13. K. Arora, D.P. Sharma and M.C. Pathak, *Oriental J. Chem.*, **15**, 331 (1999).
14. K. Arora, R.C. Goyal, and Susheel Sharma, *Oriental J. Chem.*, **15**, 367 (1999).
15. S.S. Sandhu and S.S. Sandhu (Jr.), *Indian J. Chem.*, **IIA** , 369 (1973).
16. P. Ramamurthy and C.C. Patel, *J. Inorg. Nucl. Chem.* **25**, 310 (1963).
17. N.V. Sidgewick The Chemical Elements and their Compounds, Oxford University Press, Oxford (1952).
18. V.V. Savant and C.C. Patel, *J. Inorg. Nucl. Chem.*, **35**, 1462 (1972).
19. K.W. Bagnall and M.W. Wakerley, *J. Less Common Metals*, **35**, 267 (1974).
20. P.S. Radhakrishnan and P. Indersenan, *J. Indian Chem. Soc.*, **67**, 243 (1990).
21. G. Shankar, R.R. Prem Kumar and S.K. Ramalingham, *Polyhedron*, **5**, 991 (1986),
22. G.R. Burns, *Inorg. Chem.*, **7**, 277 (1968).
23. K. Swaminathan and N.H. Irving, *J. Inorg. Nucl. Chem.*, **26**, 1291 (1964).
24. P.A. Vigato, U. Casellato and M. Vidali, *Gazz. Chem. (Ital.)*, **107**, 61 (1977).
25. A.K. Srivastava, S. Sharma and R.K. Agarwal, *Inorg. Chim. Acta*, **61**, 235 (1982).

(*Received*: 3 January 2000; *Accepted*: 29 April 2000) AJC-2021