

Some New Thorium (IV) Complexes of Azo-Ester Ligands

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Abstract

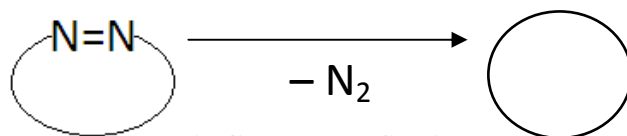
Some new complexes of thorium (IV) metal by varying anions (viz. Γ , NO_3^- and OAc^-) with azoester ligand have been synthesized. These complexes are characterized by conventional methods viz. melting point, conductance measurements as well as by spectral methods viz. IR including far IR spectral studies. Coordination number of the complexes on the basis of these studies were proposed to be 8- 12. The tentative structures of these complexes were also reported.

Keywords:- Thorium (IV) metal complexes / azoester / spectral / structures

Introduction

A number of complex forming compounds or ligands have been used to prepare the metal complexes of different metals including lanthanides and actinides¹⁻⁵. Schiff bases are one of these important class of compounds used as ligands. So far as the ligands are concerned, ligands which are capable of forming chelates are dominating in the area of higher polyhedra, in scope, in numbers and in kinetics as well as in thermodynamic stability. In fact more compact the ligands and the smaller the bite more effective is it in generating higher coordination structures.

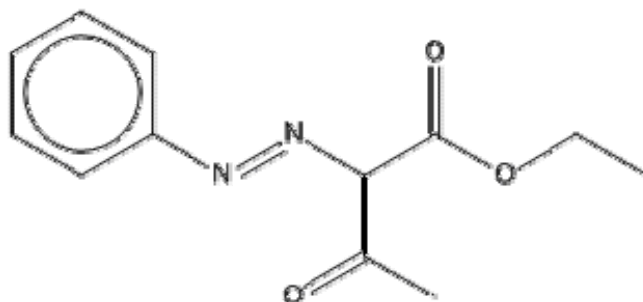
Reactions of azo compounds have been widely studied in which nitrogen molecule is eliminated either thermally or photo chemically and two reactive sites remain react to reform a ring (Fig. 1).



Cyclic Azo Compound **Cyclic Compound (Strained)**
(Fig. 1)

The main synthetic application of azo compound decomposition is in synthesis of strained ring systems. The required azo compounds can be prepared by dipolar cyclo-additions of diazo-compounds and the cyclic azo-esters so formed can be photochemically or thermally decomposed to strained ring system. Such reactions have been developed for pyridazine -3, 6 – dicarboxylate esters; 1,2,4-triazines and 1,2,4,5-tetrazines etc.

A very large number of metal complexes⁶⁻¹⁰ of Thorium (IV) and dioxo-uranium (VI) have been reported in literature but such complexes with azoester ligands are seldom found. In this present communication studies related to thorium (IV) metal complexes with azoester ligands viz. Ethyl- α -phenylazo acetoacetate and Ethyl- α -(2-chloro phenylazo) acetoacetate have been reported. Ligands used for formation of complexes are reported in figure 2 below



Chemical Formula: $C_{12}H_{14}N_2O_5$

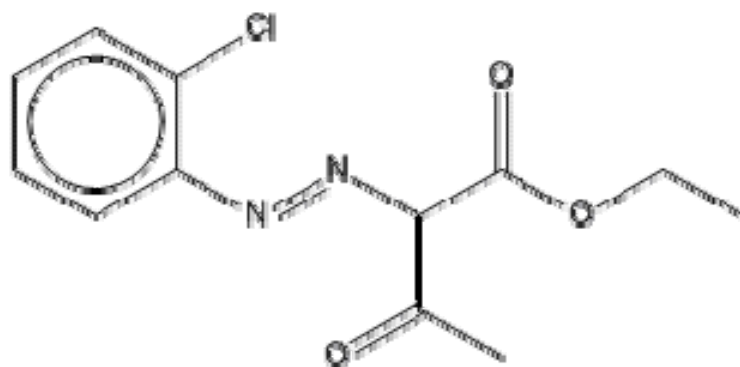
Exact Mass: 234.10

Molecular Weight: 234.25

m/z : 234.10 (100.0%), 235.10 (13.8%)

Elemental Analysis: C, 61.53; H, 6.02; N, 11.96; O, 20.49

Ethyl- α -phenylazo acetoacetate



Chemical Formula: $C_{12}H_{13}ClN_2O_5$

Exact Mass: 268.06

Molecular Weight: 268.70

m/z : 268.06 (100.0%), 270.06 (32.1%), 269.06 (13.7%), 271.06 (4.5%), 270.07 (1.4%)

Elemental Analysis: C, 53.64; H, 4.88; Cl, 13.19; N, 10.43; O, 17.86

Figure 2 Ethyl- α -(2-chloro phenylazo) acetoacetate

Experimental:

All the chemicals used for the preparation of new compounds were obtained in the sealed containers from standard companies e.g. Emerck, Aldrich, CDH and BDH. Thorium chloride, Thorium nitrate, Thorium acetate, Thorium iodide salts were obtained from the RJ (Robbert Johnson Company Ltd.) and the BDH (British Drug House), Poole, England. All the chemicals were of AR, AnalR grade. Thorium iodide was also prepared in laboratory by the reaction of Thorium nitrate with potassium iodide.

Formation of Azo-ester Ligands and their complexes

Jolly et al¹¹⁻¹² have reported synthesis of many new azo-esters and have explored their activity and reactions. The complex forming capabilities of some of the azo-esters have been explored in the present investigation with thorium(IV) and dioxouranium(VI) metal salts.

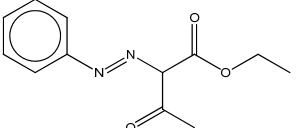
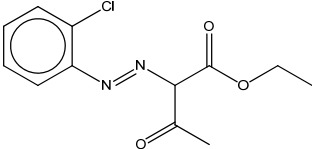
The azo-ester compounds [IUPAC Name: 2-Aceto-2-N (substituted phenyl) azoethylethanoates] were prepared by the methods reported in literature¹³⁻¹⁴. All the substituted azo-ester compounds obtained are deeply coloured reddish brown solids with low melting points and most of them became viscous in the hot summer season of this north central region of Madhya Pradesh where the temperature in this season reaches almost 44-45⁰C.

The new coordination compounds of Thorium were obtained by the reaction of the azoester ligand with suitable moiety at the pH ranging from 8 to 10 at the room temperature in water medium containing small amount of alcohol/butanol/mixture of two alcohols. All the analysis or studies done on the newly synthesized compounds were carried out as reported earlier in related literature⁶⁻¹⁰.

Results and Discussion:

Physical Data viz. yield, color, mol. Weight etc. of Azoester Ligands are reported in table 1

Table-1: Physical data of azoester ligands

S.No.	Azoester Ligands : Structure & Name	R	Yield	Color	Molecular Formula	Molecular Weight
1.	 Ethyl- α -phenylazo acetoacetate	H	70%	Dark Brown	C ₁₂ H ₁₄ N ₂ O ₃	234.25
2.	 Ethyl- α -(2-chloro phenylazo) acetoacetate	2 - Cl	60%	Dark Brown	C ₁₂ H ₁₃ ClN ₂ O ₃	268.70

Mass spectral data of the ligands are also reported in the tables 2,3. The prominent peaks are listed in these tables for these compounds. Base ion peak are marked and shown in the tables itself for these compounds. Though spectra of azoesters show the peaks related to fragments that may be formed after fragmentation but investigator was not able to record parent ion peak.

Despite of the semi solid physical state of the azo ester ligands during summer season the new coordination compounds obtained were all crystalline solid with generally high melting points and were packed in polythene tubes after filtration and re-crystallization. The purity of the new compounds was checked by the chromatographic methods.

Table 2 : Mass Spectral Details of Ethyl – α – phenylazo acetoacetate

m/z	Relative Abundance (%)
134	2
127	2
119	2
105	2
93	99
87	2
78	5
73	2
66	45
61	2

 Table 3 : Mass Spectral Details of Ethyl – α – (2 – chloro phenylazo) acetoacetate)

m/z	Relative Abundance (%)
112	98
97	2
85	2
77	60
70	5
61	5
51	30

The new complexes prepared are listed below along with their physical data in table 4.

- i. [Bis (ethyl– α – phenylazo acetoacetato) tetrakis iodo] Thorium (IV)
- ii. [Bis (ethyl– α – phenylazo acetoacetato) tetrakis nitrato] Thorium (IV)
- iii. [Bis (ethyl– α –(phenylazo acetoacetato) tetrakis acetato] Thorium (IV)
- iv. [Bis (ethyl– α –(2–chloro phenylazo) acetoacetato) tetrakis iodo] Thorium (IV)
- v. [Bis (ethyl– α –(2–chloro phenylazo) acetoacetato) tetrakis nitrato] Thorium (IV)
- vi. [Bis (ethyl– α –(2– chloro phenylazo) tetrakis acetato] Thorium (IV)

Table 4 :-Physical Data of the New Thorium (IV)metal Complexes

S. No.	Compound Name	Molecular Formula	Color	Molecular Weight Calculated (Observed)
1.	[Bis (ethyl– α –phenylazo acetoacetato) tetrakis iodo] Thorium (IV)	C ₂₄ H ₂₈ I ₄ N ₄ O ₆ Th	Yellow	1208.16 (1198)
2.	[Bis (ethyl – α – phenylazo acetoacetato) tetrakis nitrato] Thorium (IV)	C ₂₄ H ₂₈ N ₈ O ₁₈ Th	Deep Yellow	948.56 (940)
3.	[Bis (ethyl – α – phenylazo acetoacetato) tetrakis acetato] Thorium (IV)	C ₃₂ H ₄₀ N ₄ O ₁₄ Th	Deep Yellow	936.72 (929)
4.	[Bis (ethyl– α –(2–chloro phenylazo) acetoacetato] tetrakis iodo] Thorium (IV)	C ₂₄ H ₂₆ Cl ₂ I ₄ N ₄ O ₆ Th	Deep Yellow	1277.05 (1272)
5.	[Bis (ethyl– α –(2–chloro phenylazo) acetoacetato] tetrakis acetato] Thorium (IV)	C ₃₂ H ₃₈ Cl ₂ N ₄ O ₁₄ Th	Light Yellow	1005.61 (1001)
6.	[Bis (ethyl – α – (2–chloro phenylazo) acetoacetato) tetrakis nitrato] Thorium (IV)	C ₂₄ H ₂₆ Cl ₂ N ₈ O ₁₈ Th	Yellow	1017.45 (1011)

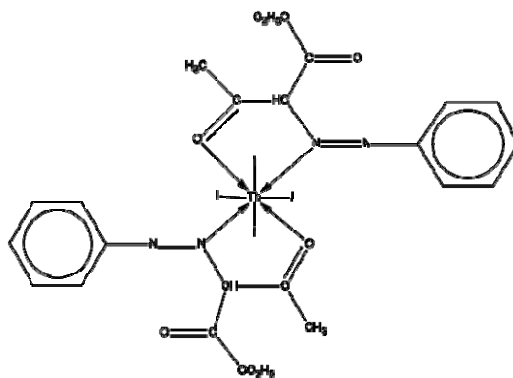
All the complexes are insoluble in common organic solvents. They are sparingly soluble in DMF and DMSO. Conductance measurement in DMF are too low account for disassociation of these complexes in DMF at the concentration of the 10^{-5} M. Hence the complexes may be regarded as non electrolytes.

IR spectral studies

The N=N stretching vibration¹⁵ of a symmetrical trans-azo compound is forbidden in the infra red spectrum but absorbs in the 1576 cm^{-1} region of the Raman spectrum. Unsymmetrical para-substituted azo-benzenes in which the substituent is an electron donating group absorb near 1429 cm^{-1} . The bonds are weak because of the non-polar nature of the bond. The bonds at 1570 cm^{-1} and 1590 cm^{-1} due to $\nu(\text{N}=\text{N})$ undergo bathochromic shift to 1550 cm^{-1} in metal complexes indicates that one of the azo nitrogen is bonded to the metal atom.¹⁶⁻¹⁷

Infrared (IR) spectroscopy has proved to be a tool to establish anions in the complexes. In this present report nitrate (NO_3^-); acetate (CH_3COO^-); and iodo (I) are chiefly used as counterpart to metal ions in these complexes.

Lever separation rule may be applied to distinguish between monodentate or bidentate nitrate ions. Lever et. Al¹⁸ showed that this to be true that the separation for monodentate nitrate in ($\nu_1 - \nu_4$) is appeared to be $5 - 26\text{ cm}^{-1}$ and that for bidentate nitrate group this may lies in $20-60\text{ cm}^{-1}$. This method has been tried in present case of complexes and a separation of $\underline{\text{Ca}}\ 250 - 200\text{ cm}^{-1}$ in the combination bands in the region $1550 - 1290\text{ cm}^{-1}$ suggest that nitrate ion is bidentate in nature in these complexes¹⁹⁻²¹. Similar to nitrate acetate ion in the present study of complexes also appears to be bidentate ligand. In case of halo complexes (M-X) vibrations could not be assigned because they are out of the range of studied region in the present investigations.



C.N. = 8

Chemical Formula: $\text{C}_{24}\text{H}_{24}\text{I}_4\text{N}_4\text{O}_6\text{Th}$

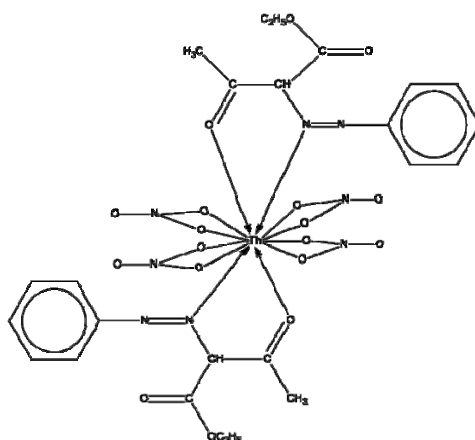
Exact Mass: 1207.86

Molecular Weight: 1208.16

m/z : 1207.86 (100.0%), 1208.86 (26.5%), 1209.86 (4.9%), 1208.85 (1.5%)

Elemental Analysis: C, 23.86; H, 2.34; I, 42.02; N, 4.64; O, 7.95; Th, 19.21

[Bis (Ethyl - α - phenylazo acetoacetato) tetrakis iodo] Thorium (IV)



C.N. = 12

Chemical Formula: $C_{24}H_{28}N_8O_{18}Th$

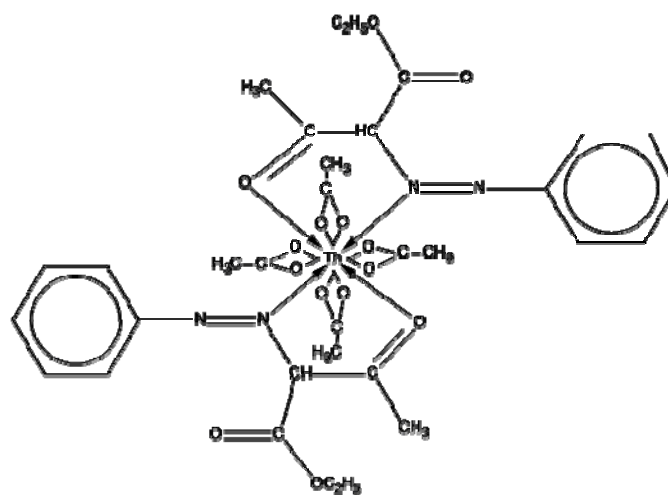
Exact Mass: 948.19

Molecular Weight: 948.56

m/z : 948.19 (100.0%), 949.19 (29.6%), 950.19 (4.5%), 950.20 (3.5%), 951.20 (1.3%)

Elemental Analysis: C, 30.39; H, 2.98; N, 11.81; O, 30.36; Th, 24.46

[Bis (Ethyl – α – phenylazo acetoacetato) tetrakis nitrate] Thorium (IV)



C.N. = 12

Chemical Formula: $C_{22}H_{40}N_4O_{14}Th$

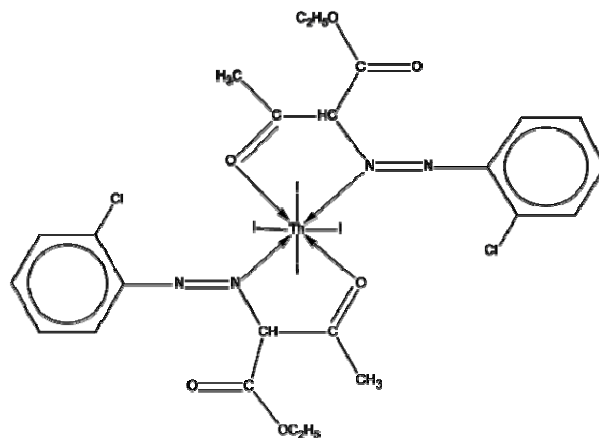
Exact Mass: 936.29

Molecular Weight: 936.72

m/z : 936.29 (100.0%), 937.30 (35.6%), 938.30 (9.0%), 939.30 (1.8%), 937.29 (1.5%)

Elemental Analysis: C, 41.03; H, 4.30; N, 5.98; O, 23.91; Th, 24.77

[Bis (Ethyl – α – phenylazo acetoacetato) tetrakis 24cetate] Thorium (IV)



C.N. = 8

Chemical Formula: $C_{24}H_{26}Cl_2I_4N_4O_6Th$

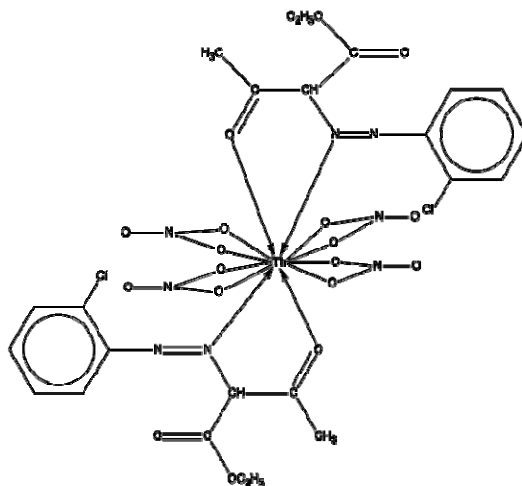
Exact Mass: 1275.78

Molecular Weight: 1277.05

m/z : 1275.78 (100.0%), 1277.78 (65.5%), 1276.78 (27.7%), 1278.78 (17.0%), 1279.77 (10.2%), 1277.79 (3.4%), 1279.78 (3.1%), 1280.78 (3.0%)

Elemental Analysis: C, 22.57; H, 2.05; Cl, 5.55; I, 39.75; N, 4.39; O, 7.52; Th, 18.17

[Bis (Ethyl – α – (2-chloro phenylazo acetoacetato) tetrakis iodo] Th(IV)



C.N. = 12

Chemical Formula: $C_{24}H_{26}Cl_2N_6O_{15}Th$

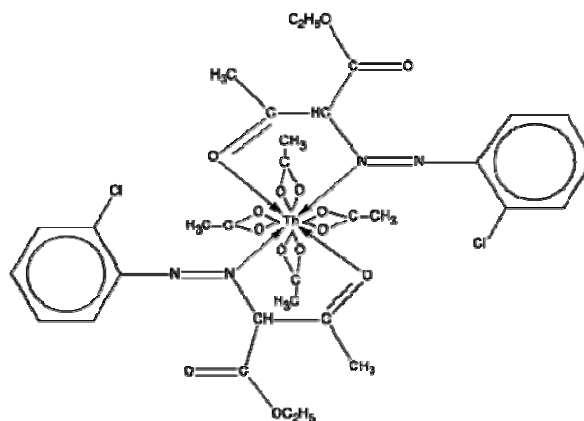
Exact Mass: 1016.11

Molecular Weight: 1017.45

m/z : 1016.11 (100.0%), 1018.11 (64.7%), 1017.12 (26.9%), 1019.11 (19.0%), 1020.11 (13.1%), 1018.12 (7.2%), 1017.11 (3.0%), 1021.11 (2.9%), 1020.12 (2.5%), 1019.12 (1.6%)

Elemental Analysis: C, 28.33; H, 2.58; Cl, 6.97; N, 11.01; O, 28.30; Th, 22.81

[Bis (Ethyl – α – (2-chloro phenylazo acetoacetato) tetrakis nitrate] Thorium (IV)



C.N. = 12

Chemical Formula: $C_{22}H_{28}Cl_2N_4O_{14}Th$

Exact Mass: 1004.21

Molecular Weight: 1005.61

m/z : 1004.21 (100.0%), 1006.21 (64.4%), 1005.22 (35.6%), 1007.21 (23.1%), 1008.21 (10.6%), 1006.22 (9.0%), 1008.22 (5.8%), 1009.21 (3.8%), 1007.22 (2.4%), 1005.21 (1.5%), 1009.22 (1.2%)

Elemental Analysis: C, 38.22; H, 3.81; Cl, 7.05; N, 5.57; O, 22.27; Th, 23.07

[Bis (Ethyl – α – (2-chloro phenylazo acetoacetato) tetrakis 26ceta] Thorium (IV)

Figure 3

Magnetic Behaviour of Complexes :

Complexes of Thorium (IV) metal salts are diamagnetic in nature depending upon the other ions present and the corresponding ligand field. The magnetic susceptibilities are independent of field strength and temperature. In the present studies complexes are weakly diamagnetic as observed²²⁻²⁴ as they contain no unpaired electrons.

Conclusions

Based on the studies done on newly synthesized complexes of thorium (IV) metal salts their structures were proposed along with their coordination numbers. The coordination numbers of these complexes were proposed to be 8-12, based upon these studies. The tentative structures for these complexes are given in figure 3 below.

References

- [1]. Kirby, H.W.; Morss, L.R. Actinium. In *The chemistry of the Actinide and Transactinide Elements*; Springer: Dordrecht, The Netherlands,; Volume I, pp. 18-51.(2006)
- [2]. Cotton S.C. Coordination chemistry of the actinides. In *Lanthanide and Actinide Chemistry*; John Wiley & Sons, Ltd.: Sussex, UK,(2006.)
- [3]. Jayarami, R.M.; Sudhavani, T.J.; Sivagangi, R. Synergistic extraction of uranium (VI) by complexation with CYANEX-272 and CYANEX-923 TPBD, TNBD, TOPO in presence of nitrate. *Int. j.; Res. Chem. Environ.*, 2, 158-163.(2012)
- [4]. Vercouter, T.; Vitorge, P.; Amekraz, B.; Giffaut, E.; Hubert, S.; Moulin, C. Stabilities of the Aqueous Complexes $Cm(CO_3)_3^{3-}$ and $Am(CO_3)_3^{3-}$ in the Temperature Range 10-70 °C *Inorg. Chem.*, 5833-5843.(2005)

- [5]. Polinski, M.J.; Wang, S.; Alekseev, E.V.; Depmeier, W.; Liu, G.; Haire, R.G.; Albrecht-schmitt, T.E. Curium(III) borate shows coordination environments of both plutonium(III) and Americium(III) borates. *Angew. Chem.Int.Ed*, 51, 1869-1872. (2012)
- [6]. K. Arora and Sonal Agnihotri, *Reviews in Inorganic Chemistry*, Vol. 26, No. 6, pp. 565-593, (2006).
- [7]. R.K. Agrawal, H. Agrawal and K. Arora, *Rev. Inorg. Chem.*, 20, 1 (2002).
- [8]. S. Agnihotri and Kishor Arora *E Journal of chemistry* 7 (3) 1045, (2010)
- [9]. Mallikarsin S. Yadawe and Sangamesh A. Patil, *Global J. Science Frontier Research Chemistry*, 12 (2002) ISSN 2249-4626.
- [10]. Vaibhav, Raut, S.P. Roy, M.K. Das, S. Jeya kumar. K.L. Ram Kumar, *Inter National Journal of analytical Mass Spectrometry and Chromatography*, 1, 61-71 (2013).
- [11]. V.S. Jolly, M.Y. Dalvi and A.K. Shrivastav, *J. Indian Chem. SOC.* Vol. 68, pp. 513-514 (1991).
- [12]. V.S. Jolly, A.K. Halve and A.K. Shrivastava, *Indian J. Chem.*, 12, 1117 (1978).
- [13]. K. Shrivastava and J.K. Malhotra, *Indian J. Appl. Chem.*, 32, 116 (1969).
- [14]. V.S. Jolly, A.K. Shrivastava, S.P. Sing and K.S. Tiwari, *Journal of Indian Chem SOC.* Volume 57 (LVII) Page 539-541 (1980).
- [15]. Robert M. Silverstein and Francis X. Webster, *Spectrometric Identification of Organic Compounds*, 6th Ed., John Wiley & Sons, Inc., New York, ISBN : 0-471-13457-0, , p. 104. (1997)
- [16]. R.B. King, *Inorg. Chem.*, 5, , p. 300. (1966)
- [17]. R.B. Agrawal and G.K. Agrawal, *J. Indian Chem. Soc.*, 55, , p. 681. (1978)
- [18]. A.B.P. Lever, E. Mautio Veni and B.S. Ramaswamy, *Canld. J. Chem.*, 49, 1957 (1971).
- [19]. R.K. Agrawal, K. Arora and Prashant Dutt, *Synth. React. Inorg. Met. Org. Chem.*, 24(2), 301, (1994).
- [20]. R.K. Agrawal and K. Arora, *Synth. React. Inorg. Met. Org. Chem.*, 23(10), 1671, (1993).
- [21]. R.K. Agrawal, K. Arora, Miss Priyanka and I. Chakravorti, *Polish J. Chem.*, 67, 1913 (1993).
- [22]. E.D. Eastman, L. Brown, L.A. Bromley, P.W. Gilles, N.L. Lofgern, *J. Am. Chem. Soc.*, 72, 4019, (1950).
- [23]. R.K. Agrawal, K. Arora and P. Dutt, *Polyhedron*, 13(6), 957, (1994).
- [24]. Sonal Agnihotri and Kishor Arora, *Asian J. Chem.*, 25(8), 4323, (2013).