IJNRD.ORG ISSN : 2456-4184
INTERNATIONAL JOURNAL OF NOVEL RESEARCH AND DEVELOPMENT (IJNRD) | IJNRD.ORG
An International Open Access, Peer-reviewed, Refereed Journal

A Study on Synthesis of derivatives of organoheterotrimetallic dibutyl [Al(III);Sn(IV);Ti(IV)]-µ-oxo-*iso*propoxide with salicylates

JASHMER SINGH*[1],ATTIMUKAT[2],JOGINDER[3]
[1,2]DAV College (Lahore) Ambala City-134003, Haryana, India
[3]S.D College (Lahore) Ambala Cantt-134003, Haryana, India
Email: jasmerdav70@gmail.com

Abstract:The reaction of organoheterotrimetallic dibutyl [Al(III);Sn(IV);Ti(IV)]-µ-oxo-*iso*propoxide with salicylates (HRSal) such as methyl salicylate (HMeSal), ethyl salicylate (HEtSal) and phenyl salicylate (HPhSal) in the molar ratios 1:1 and 1:2 carried out in refluxing benzene yielded derivatives of the type [$Bu_2SnO_2TiAl(O\text{-}i\text{-}Pr)_4(RSal)$] and [$Bu_2SnO_2TiAl(O\text{-}i\text{-}Pr)_3(RSal)_2$] respectively. The salicylate derivatives have been characterized by elemental, liberated isopropanol and spectral analysis (IR, ^1H , ^{13}C NMR).

Keywords: Aluminium,Metal alkoxide, Salicylates, Tin, Titanium**.**

1.Introduction

Metal derivatives of the alkoxide and β-diketonate ligands have become the predominant single-source precursors for oxide-based ceramic materials, mainly through sol-gel processing and MOCVD respectively, because of their commercial availability,high solubility in routinely used organic solvents and easy tunability of their hydrolytic characteristics and mass-transport properties.[1-4] Another important axis of the molecular engineering is the synthesis of bi- and higher metallic derivatives with appropriate properties.[5-12] These single-source precursors simultaneously provide two or more metals in an accurate stoichiometry allowing complex ceramic materials to be generated in one step by eliminating the prerequisite of matching the reaction rates in a multicomponent precursor mixture.[13-17] Among the various properties desired in MOCVD precursors, the most important ones are the high volatility and good thermal stability for efficient transport as well as high reactivity to easily obtain the desired material.[18-20]

A large number of heterometallic alkoxides which can be used as single-source precursors for the synthesis of oxide ceramics are known in the literature.[21] In addition to homoleptic {MM′(OR)x}, heteroleptic {MM′(OR)x(X)y where X = OAc, OR′, halide) and oxo alkoxide species {MM′O(OR)x} or {MM′(OR)x(X)y}, alkoxide derivatives with different metal combinations and up to three different metals[22] in a single molecule show the rich synthetic and structural chemistry of metal alkoxides.[23]

The heterobimettalic-µ-oxo-alkoxides are found to be associated in organic solvent like the simple metal alkoxides.[24,25] The association results from the tendency of metals to fulfill their coordination number by forming inter and intra molecular oxygen-metal bonds. The mean degrees of association of these compounds have been obtained from cryoscopic measurement and other spectroscopic studies. The chemical reactivity, solubility and molecular association of the bimetallic-µ-oxo-alkoxides are largerly affected by the nature of alkoxy groups (steric factors).

The above features underline the importance and utility of µ-oxo compounds, it was therefore considered worthwhile to synthesize salicylate derivatives of organoheterotrimetallic dibutyl [Al(III); Sn(IV); Ti(IV)] -µ-oxoisopropoxide.

2.Experimental Methodology

Due to highly hygroscopic nature of metal alkoxides, stringent precautions were taken to exclude moisture throughout the study using glasswares with interchangeble joints, solvents and the reagents used were of analytical grade and purified by recommended methods.[26] The general techniques and physical measurements were carried out as described elsewhere.[27-29,] [$Bu_2SnO_2TiAl(O\text{-}i\text{-}Pr)_5$] was prepared in the laboratory by reported method.[30] Methyl salicylate, ethyl salicylate were distilled under reduced pressure before use. Phenyl salicylate (Hi-media) was used as received. The estimation of isopropyl alcohol liberated in synthesis of salicylate derivatives were carried out oxidimetrically[31]. Tin, titanium and aluminium in the derivatives were analyzed gravimetrically[29]. Infrared spectra were recorded on a Perkin-Elmer 1710 FTIR spectrometer over the range of 4000-400 cm^{-1}. The ^1H and $^{13}CNMR$ spectra were recorded in $CDCl_3$ on Bruker Avance II 400 NMR spectrometer. Elemental analysis was carried on Perkin Elmer 2400 CHN Elemental Analyser.

2.1 Synthesis of 1:1 methyl salicylate derivative of organoheterotrimetallic dibutyl [Al(III);Sn(IV);Ti(IV)]-µ-oxo-isopropoxide

$[Bu_2SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ (0.623 g,(0.981) mmol) and methyl salicylate (0.210g, 1.38 mmol) were refluxed in benzene (~60 ml) for 3 hrs, on an oil bath (temp. ~100 °C). The reaction can be represented by the following equation:

$$[Bu_2SnO_2TiAl(O\text{-}i\text{-}Pr)_5] + HRSal \xrightarrow[\text{Reflux}]{\text{Benzene}} [Bu_2SnO_2TiAl(O\text{-}i\text{-}Pr)_{5-n}(RSal)_n] + nHO\text{-}i\text{-}Pr \quad (77)$$

(n=1; Rsal=deprotonated methyl salicylate)

The freed isopropanol was gathered constantly at 72-78^{0}C as a double azeotrope of isoproponol-benzene. The isopropanol in azeotrope was assessed oxidimetrically to check the consummation of the reaction.[30,32,] The excess of solvent was removed at 40 °C/1 mm pressure. A pale yellow solid product was obtained. Similar reaction was carried in 1:2 molar ratio resulting in $[Bu_2SnO_2TiAl(O\text{-}i\text{-}Pr)_3(MeSal)_2]$.

The preparation of other salicylate derivatives of $[Bu_2SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ in 1:1 and 1:2 molar ratios were carried out by similar procedure and their analytical data along with metal and liberated *iso*propanol estimation have been summarized in the **(Table 1).** All the derivatives were found to be pale yellow in color soluble in common organic solvents (benzene, chloroform benzene, hexane), susceptible to hydrolysis and decompose on heating above ~ 180 ^{o}C.

3. Result and discussion

The reaction of organoheterotrimetallic dibutyl [Al(III);Sn(IV);Ti(IV)]-µ-oxo-*iso*propoxide with salicylates (HRSal) such as methyl salicylate (HMeSal), ethyl salicylate (HEtSal) and phenyl salicylate (HPhSal) in the molar ratios 1:1 and 1:2 carried out in refluxing benzene yielded derivatives of the type $[Bu_2SnO_2TiAl(O\text{-}i\text{-}Pr)_4(RSal)]$ and $[Bu_2SnO_2TiAl(O\text{-}i\text{-}Pr)_3(RSal)_2]$ respectively according to the following general reaction :

$$[Bu_2SnO_2TiAl(O\text{-}i\text{-}Pr)_5] + HRSal \xrightarrow[\text{Reflux}]{\text{Benzene}} [Bu_2SnO_2TiAl(O\text{-}i\text{-}Pr)_{5-n}(RSal)_n] + nHO\text{-}i\text{-}Pr \quad (77)$$

(n=1-2; Rsal=deprotonated methyl/ethyl/phenyl salicylate)

The *iso*propanol liberated during the reaction was collected as binary azeotrope of *iso*propanol-benzene. The azeotrope was estimated oxidimetrically to check the progress of reaction.

The salicylates derivatives of organoheterotrimetallic dibutyl [Al(III);Sn(IV);Ti(IV)]-µ-oxo-*iso*propoxide obtained were pale yellow solids, soluble in common organic solvents (benzene, chloroforms, carbon tetrachloride etc.), susceptible to hydrolysis and decompose on heating above 180 °C.

3.1 Infrared Spectral Studies

1:1 salicylate derivatives show absorption bands in the region 1360-1340 cm^{-1}, 1165-1150 cm^{-1} and 1125-1090 cm^{-1} are characteristics of *gem*-dimethyl portion and combination band ν(C-O + O-*i*-Pr) of the terminal and bridging *iso*propoxy groups respectively.[33,34] The absence of band at ~ 1165-1150 cm^{-1} in 1:2 salicylate derivatives indicating complete replacement of terminal *iso*propoxy groups. A broad band in the region ~3100cm^{-1} due to ν(O-H) in salicylates is found absent in derivatives of $[Bu_2SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ indicates the deprotonation of these ligands. The ν(C=O) band appearing in salicylates at ~1650 cm^{-1} shows a downward shift of 15-25 cm^{-1} in the derivatives, indicating the coordination of the carbonyl oxygen of the salicylate to the metal atom. A strong band observed at 1245 cm^{-1} in salicylates due to phenolic ν(C-O)) vibration is shifted 15-20 cm^{-1} higher in the derivatives indicating bond formation of phenolic oxygen of salicylates to the metal atom. Some bands observed in salicylate derivatives at 765 cm^{-1} and lower are due to M-O stretching vibrations.[35] The bands related to phenyl groups in the derivatives are observed at their usual positions in the IR spectra. The IR spectra of the derivatives indicate that salicylates behave as monobasic bidentate ligands.

Table-1: Analytical data

S.No	Compound g(mmol)	Ligand g(mmol)	Molar Ratio	Refluxing time	Product g(%)	Anal. Calcd. (found)			
						HO-*i*-Pr g	Sn (%)	Ti (%)	Al (%)
1	$[Bu_2SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ 0.623 (0.981)	HMeSal 0.210 (1.38)	1:1	3	$[Bu_2SnO_2TiAl(O\text{-}i\text{-}Pr)_4(MeSal)]$ 0.585 (82.0)	0.059 (0.055)	16.33 (16.05)	6.59 (6.17)	3.72 (3.50)
2	$[Bu_2SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ 0.588 (0.927)	HMeSal 0.396 (2.61)	1:2	$5^{1/2}$	$[Bu_2SnO_2TiAl(O\text{-}i\text{-}Pr)_3(MeSal)_2]$ 0.635 (83.7)	0.111 (0.101)	14.48 (14.20)	5.85 (5.65)	3.30 (2.95)
3	$[Bu_2SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ 0.612 (0.964)	HEtSal 0.225 (1.36)	1:1	$3^{1/2}$	$[Bu_2SnO_2TiAl(O\text{-}i\text{-}Pr)_4(EtSal)]$ 0.591 (82.8)	0.058 (0.052)	16.03 (15.86)	6.46 (6.06)	3.65 (3.40)
4	$[Bu_2SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ 0.427 (0.673)	HEtSal 0.314 (1.89)	1:2	6	$[Bu_2SnO_2TiAl(O\text{-}i\text{-}Pr)_3(EtSal)_2]$ 0.479 (84.1)	0.080 (0.076)	14.02 (13.81)	5.65 (5.07)	3.25 (3.05)
5	$[Bu_2SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ 0.590 (0.930)	HPhSal 0.260 (1.31)	1:1	$3^{1/2}$	$[Bu_2SnO_2TiAl(O\text{-}i\text{-}Pr)_4(PhSal)]$ 0.621 (84.8)	0.056 (0.050)	15.05 (14.87)	6.07 (5.86)	3.43 (3.10)
6	$[Bu_2SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ 0.379 (0.597)	HPhSal 0.360 (1.68)	1:2	6	$[Bu_2SnO_2TiAl(O\text{-}i\text{-}Pr)_3(PhSal)_2]$ 0.480 (85.4)	0.072 (0.067)	12.59 (12.31)	5.08 (4.76)	2.87 (2.60)

3.2 NMR Spectral Studies

3.2.1 ^{1}H NMR spectra

The ^{1}H NMR spectrum of 1:1 derivative show number of peaks in the regions δ 0.7-1.2 ppm are due to intermixing of methyl protons of the *iso*propoxy groups and protons of the butyl groups bonded to tin atom.[36] A multiplet centered at δ 4.1 ppm in [$Bu_2SnO_2TiAl(O$-*i*-$Pr)_5$] due to methine proton of the *iso*propoxy groups[30] is found to overlap with the peak observed at ~ δ 3.8 ppm and a quartet centered at ~ δ 3.6 ppm are assigned to methyl and methylene protons in 1:2 derivative of [$Bu_2SnO_2TiAl(O$-*i*-$Pr)_5$] with methyl and ethyl salicylates respectively. A broad singlet at ~δ 12.8 ppm due to phenolic proton in the salicylate is found absent in the derivatives confirms their deprotonation. The signals due to phenyl ring protons of salicylate moiety are observed at their usual positions (δ 6.8 –δ 7.8 ppm) in all the derivatives.

3.2.2 ^{13}C NMR spectra

The ^{13}C NMR spectra of 1:1 salicylate derivatives of organoheterotrimetallic dibutyl [Al(III);Sn(IV);Ti(IV)]-μ-oxo-*iso*propoxide shows two prominent peaks at δ ~ 26.6 ppm and δ ~ 28.8 ppm assignable to the methyl carbon of terminal and bridged *iso*propoxy groups. Two different type of methine carbons of *iso*propoxy groups[37] is confirmed by the two signals observed at δ ~ 64.1 ppm and δ ~ 64.5 ppm. The other peaks at δ 26.1 ppm, δ 25.6 ppm, δ 15.5 ppm and δ 14.0 ppm are assignable to C-1, C-2, C-3 and C-4 respectively of the butyl group.[30] The 1:2 salicylate derivatives of μ-oxo-*iso*propoxide show the absence of terminal *iso*propoxy groups. The peaks observed in the region δ125.2-136.7 ppm are due to carbon atoms on benzene ring; however, the peak observed at about δ168.2 ppm is due to ring carbon linked to the ester group and a peak observed at about δ186.4 ppm is due to carbon of the ester group (-COOR).[38]

On the basis of above spectral studies following tentative structures **(Fig.1 & 2)** are assigned to 1:1 and 1:2 methyl salicylate derivatives of [$Bu_2SnO_2TiAl(O$-*i*-$Pr)_5$]:

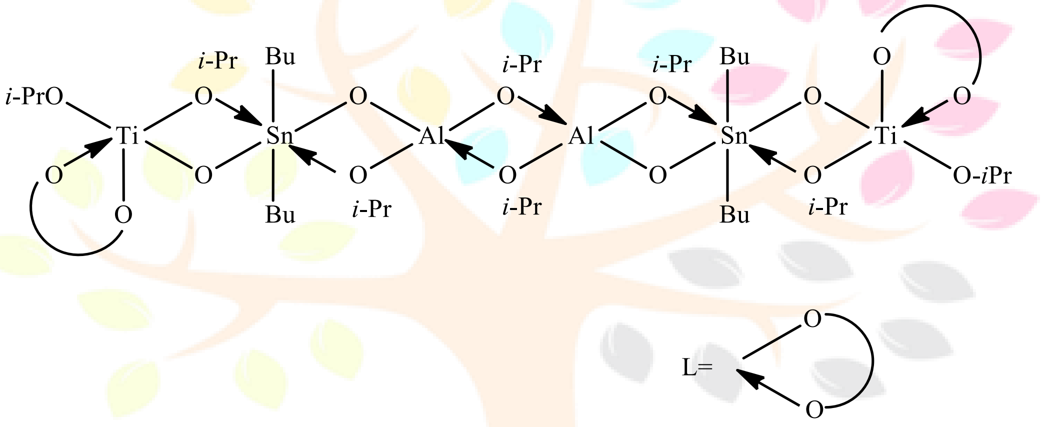

Fig. 1 [$Bu_2SnO_2TiAl(O$-*i*-$Pr)_4(MeSal)$]

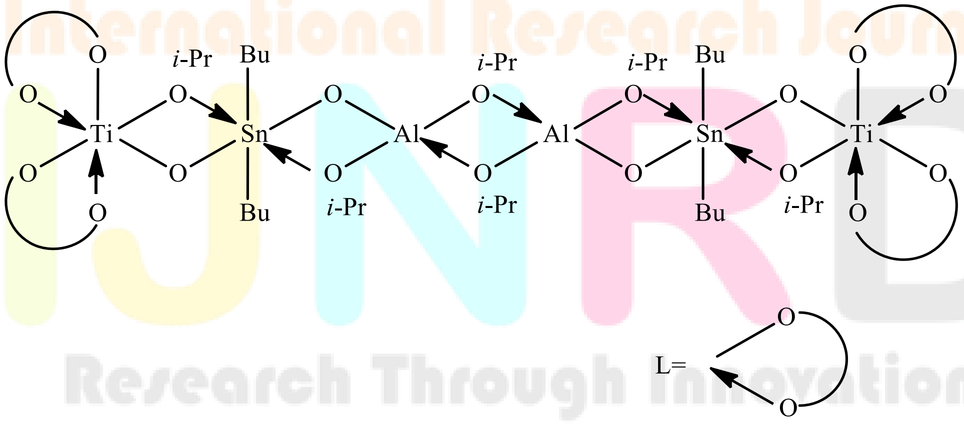

Fig. 2: [$Bu_2SnO_2TiAl(O$-*i*-$Pr)_3(MeSal)_2$]

ACKNOWLEDGEMENTS: The authors gratefully acknowledge to DAV College(Lahore), Ambala City, S.D. College(Lahore) Ambala Cantt and Kurukshetra University, Kurukshetra for providing the necessary facilities, SAIF PU for spectral and elemental analysis.

CONCLUSION : The study concluded that all the salicylate derivatives exhibited pale yellow solids . They were soluble in organic solvents but prone to hydrolysis.

References

1. Bradley, D. C.; Mehrotra, R. C.; Rothwell, I. P.; Singh, A. *Alkoxo and Aryloxo derivatives of Metals*, Academic Press, New York, 2001.

2. Turova, N. Ya.; Turevskaya, E. P.; Kessler, V. G.; Yanovskaya, M. I. *The Chemistry of Metal Alkoxide*, Kluwer Academic Publishers, Boston, 2002.

3. Condorelli, G. G.; Malandrino, G.; Fragalà, I. L. Engineering of molecular architectures of β-diketonate precursors toward new advanced materials. *Coord. Chem. Rev.* **2007**, *251*, 1931-1950.

4. Tiitta, M.; Niinisto, L. Volatile Metal β-Diketonates: ALE and CVD Precursors forElectroluminescent Device Thin Films. *Chem. Vap. Deposition* **1997**, *3*, 167-182.

5. Gahlot, S.; Jeanneau, E.; Singh, D.; Panda, P. K.; Mishra, Y. K.; Ahuja, R.; Ledoux, G.;Mishra, S. Molecules versus nanoparticles: Identifying a reactive molecular intermediate in thesynthesis of ternary coinage metal chalcogenides. *Inorg. Chem*. **2020**, *59*, 7727-7738.

6. John, L.; Sobota, P. Synthesis of Heterometallic Compounds with Uncommon Combinationsof Elements for Oxide Nanomaterials Using Organometallics. *Acc. Chem. Res.* **2014**, *47*, 470-481.

7. Chen, Y.; Mishra, S.; Ledoux, G.; Jeanneau, E.; Daniel, M.; Zhang, J.; Daniele, S. Directsynthesis of hexagonal $NaGdF_4$ nanocrystals from a single-source precursor: Upconverting$NaGdF_4$:Yb^{3+},Tm^{3+} and its composites with TiO_2 for near-IR-driven photocatalysis. *Chem. Asian J.* **2014**, *9*, 2415-2421.8. Wei, Z.; Filatov, A. S.; Dikarev, E. V. Volatile Heterometallic Precursors for the Low-Temperature Synthesis of Prospective Sodium Ion Battery Cathode Materials. *J. Am. Chem. Soc.***2013**, *135*, 12216-12219.

9. Mishra, S.; Mendez, V.; Jeanneau, E.; Caps, V.; Daniele, S. A single source precursor routeto group 13 homo- and heterometal oxides as highly active supports for gold catalyzed aerobic epoxidation of *t*-stilbene. *Eur. J. Inorg. Chem.* **2013**, 500-510.

10. Mishra, S.; Ledoux, G.; Jeanneau, E.; Daniele, S.; Joubert, M.-F. Novel heterometal-organic complexes as first single source precursors for up-converting $NaYF_4$:Yb^{3+}, Er^{3+}/Tm^{3+} nanomaterials. *Dalton Trans.* **2012**, *41*, 1490-1502.

11. Mishra, S.; Jeanneau, E.; Daniele, S.; Mendez, V. Aminoalkoxo-supported heteroleptic hexanuclear gallium(III) wheel as a synthon for group 13 heterometallics: A rare sol-gel precursor for mixed Al-Ga oxide as a support for gold catalysts. *Dalton Trans.* **2010**, *39*, 7440-7443.

12. Mishra, S.; Daniele, S.; Ledoux, G.; Jeanneau, E.; Joubert, M. F. Heterometallic Na-Y(Ln)trifluoroacetate diglyme complexes as novel single source precursors for upconverting $NaYF_4$nanocrystals co-doped with Yb and Er/Tm ions. *Chem. Commun.* **2010**, *46*, 3756-3758.

13. Lu, H.; Wright, D. S.; Pike, S. D. The use of mixed-metal single source precursors for thesynthesis of complex metal oxides. *Chem. Commun.* **2020**, *56*, 854-871.

14. Schubert, U. Heterobimetallic sol–gel precursors and intermediates. *J. Sol-Gel Sci. Technol.***2016**, *79*, 249-261.

15. John, L.; Sobota, P. Synthesis of Heterometallic Compounds with Uncommon Combinationsof Elements for Oxide Nanomaterials Using Organometallics. *Acc. Chem. Res.* **2014**, *47*, 470-481.

16. Matthews, P. D.; King, T. C.; Wright, D. S. Structure, photochemistry and applications ofmetal-doped polyoxotitanium alkoxide cages. *Chem. Commun.* **2014**, *50*, 12815-12823.

17. Szafert, S.; John, L.; Sobota, P. Well-defined polynuclear heterobimetallic complexes asprecursors for ceramic and magnetic materials. *Dalton Trans.* **2008**, 6509–6520.

18. Hatanpää, T.; Ritala, M.; Leskelä, M. Precursors as enablers of ALD technology:Contributions from University of Helsinki. *Coord. Chem. Rev*. **2013**, *257*, 3297-3322.

19. Emslie, D. J. H.; Chadha, P.; Price, J. S. Metal ALD and pulsed CVD: Fundamental reactionsand links with solution chemistry. *Coord. Chem. Rev*. **2013**, *257*, 3282-3296.

20. Potts, S. E.; Carmalt, C. J.; Blackman, C. S.; Abou-Chahine, F.; Leick, N.; Kessels, V. M. M.; Davies, H. O.; Heys, P. N. Bis(cyclopentadienyl) zirconium(IV) amides as possible precursors for low pressure CVD and plasma-enhanced ALD. *Inorg. Chim. Acta* **2010**, *363*,1077-1083.

21. (a) L. G. Hubert-Pfalzgraf, *Coord. Chem. Rev.*, **178−180,** 967 (1998), (b) L. G. Hubert- Pfalzgraf, *Polyhedron*, **13,** 1181 (1994), (c) W. A. Herrmann, N. W.Huber, O.Runte, *Angew. Chem.* **107,** 2371 (1995), (d) W. A.Herrmann, N. W.Huber, O.Runte, *Angew. Chem., Int. Ed. Engl.* **34,** 2187 (1995), (e) M.Veith, S.Faber, R.Hempelmann, S.Janssen, J.Prewo, H.Eckerlebe, *J. Mater. Sci.* **31,** 2009 (1996).

22. M. Veith, S. Mathur, V. Huch, *J. Am. Chem. Soc.* **118,** 903 (1996).

23. M. Veith, S. Mathur, C. Mathur, *Polyhedron* , **17,** 1005 (1998).

24.R. C. Mehrotra, *Chemtracts,* **2,** 389, 1990.

25.R. C. Mehrotra, *Inorg. Chem. Acta Rev.,* **99,** 1967.

26. R.S. Ghadwal, M. Sharma, A. Singh and R.C. Mehrotra, *Transition Met. Chem*., **29**, 419 (2004)

27. H.K. Sharma and R. Kumar, *Indian J. Chem*., **47A**, 854 (2008).

28. R. Ramachandran, B. Singh, A.K. Narula, P.N. Kapoor, P.K. Gupta and R.N. Kapoor, *Polyhedron*, **4**, 1007 (1985).

29. A.I. Vogel, A Text Book of Quantitative analysis, Longman, London, (1989).

30. Harish K. Sharma and Jashmer Singh, *Asian Journal of Chemistry;*. **26(18),** 6151 (2014).

31. D.C. Bradley, F.M. Abd-El Halim and W. Wardlaw, *J. Chem. Soc*., 3450, (1950).

32. H.K. Sharma, Jashmer Singh, Rajesh Kumar and Amardeep, *J. Indian Chem. Soc.* **90,** 669 (2013)

33. C. T. Lynch, K.S. Masdiyanni, J. S. Smith and W. J. Grawford, *Anal. Chem.*, **36,** 2332 (1964).

34. V. A. Koznov, N. I. Kuzlova, N. Y. Turova and Y.S. Nekrasov, *Zh. Neorg. Khim.*, **24,** 1526 (1979).

35. K. Nakamoto, “Infrared and Raman Spectra of Inorganic and Coordination Compounds”, John Wiley and Sons, New York, (1986).

36. Sonika, A.K. Narula, O.P. Vermani, H.K. Sharma and A.S. Sarpal, *J. Organomet. Chem*., **470**, 67 (1994).

37. T. Ouhadi, A. Hamitou, R. Jerome and Ph. Teyssie, *Macromol*., **9**, 927 (1976).

38. V. J. Shiner, Jr. D. Whittaker and V. F. Fernandes, *J. Am. Chem. Soc.*, **85,** 2318 (1963).