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

# Synthesis and Characterization of salicylate derivatives of heterotrimetallic [Al(III);Sn(II);Ti(IV)]-μ-oxo-*iso*propoxide

**JASHMER SINGH**

DAV College (Lahore) Ambala City-134003, Haryana, India

**Abstract**

The reaction of heterotrimetallic [Al(III);Sn(II);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 $[SnO_2TiAl(O\text{-}i\text{-}Pr)_4(RSal)]$ and $[SnO_2TiAl(O\text{-}i\text{-}Pr)_3(RSal)_2]$ respectively. The salicylate derivatives have been characterized by elemental, liberated isopropanol and spectral analysis (IR, $^1H$ , $^{13}C$ NMR).

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

## Introduction

The development of materials by soft chemical methods like sol-gel, Metal Organic Chemical Vapour Deposition (MOCVD), Atomic Layer Deposition (ALD), Metal-Organic Decomposition (MOD), etc. has always been closely associated with the chemistry of molecular precursors.[1-6] The molecular engineering to optimize the required properties in the precursors is usually achieved through judicious choice of ligands. 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.[7-10] Another important axis of the molecular engineering is the synthesis of bi- and higher metallic derivatives with appropriate properties.[11-18]

Metal oxide nanomaterials are attractive for a variety of applications including catalysis,[19,20] drug delivery,[21,22] photochemistry,[23] sensing[24] and optoelectronics.[25,26] In additional to potentially enhanced properties, structurally well-defined nano-sized oxides can offer a platform to precisely interrogate structure-activity relationships. Therefore, scientists have systematically investigated the properties/activities including conductivity, thermal stability, magnetic behavior, and catalytic

performance of the metal oxides with varied surface and/or interface-tuning approaches through regulating the exposed facets, chemical composition, morphology, size, and surface functional groups.[27-32]

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

**Experimental**

All manipulations have been carried out under anhydrous conditions, solvents and the reagents used were of analytical grade and purified by recommended methods.[33] The general techniques and physical measurements were carried out as described elsewhere.[34-36] $[SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ was prepared in the laboratory by reported method.[37] 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[38]. Tin, titanium and aluminium in the derivatives were analyzed gravimetrically[36]. Infrared spectra were recorded on a Perkin-Elmer 1710 FTIR spectrometer over the range of 4000-400 $cm^{-1}$. The $^{1}H$ and $^{13}C$NMR spectra were recorded in $CDCl_3$ on Bruker Avance II 400 NMR spectrometer. Elemental analysis was carried on Perkin Elmer 2400 CHN Elemental Analyser.

**Synthesis of 1:1 methyl salicylate derivative of heterotrimetallic [Al(III);Sn(II);Ti(IV)]-μ-oxo-isopropoxide**

$[SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ (0.623g,1.200) mmol) and methyl salicylate (0.182g,1.200) 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:

$$[SnO_2TiAl(O\text{-}i\text{-}Pr)_5] + HRSal \xrightarrow{\text{Reflux, benzene}} [SnO_2TiAl(O\text{-}i\text{-}Pr)_{5-n}(RSal)_n] + nHO\text{-}i\text{-}Pr$$

(n=1; Rsal=deprotonated methyl salicylate)

The liberated *iso*propanol was continuously fractionated at 72-78 °C as binary azeotrope of *iso*propanol-benzene. The azeotrope formed during the course of reaction was collected and checked for completion of the reaction.[37,39] 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 $[SnO_2TiAl(O\text{-}i\text{-}Pr)_3(MeSal)_2]$.

The preparation of other salicylate derivatives of $[SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ 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 °C.

**Result and discussion**

The reaction of heterotrimetallic [Al(III);Sn(II);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 $[SnO_2TiAl(O\text{-}i\text{-}Pr)_4(RSal)]$ and $[SnO_2TiAl(O\text{-}i\text{-}Pr)_3(RSal)_2]$ respectively according to the following general reaction :

$$[SnO_2TiAl(O\text{-}i\text{-}Pr)_5] + HRSal \xrightarrow{\text{Reflux, benzene}} [SnO_2TiAl(O\text{-}i\text{-}Pr)_{5-n}(RSal)_n] + nHO\text{-}i\text{-}Pr$$

(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 heterotrimetallic [Al(III);Sn(II);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.

**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 | $[SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ 0.623 (1.200) | HMeSal 0.182 (1.200) | 1:1 | 3 | $[SnO_2TiAl(O\text{-}i\text{-}Pr)_4(MeSal)]$ 0.585 (82.0) | 0.059 (0.055) | 19.31 (16.05) | 7.69 (6.17) | 4.41 (3.50) |
| 2 | $[SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ 0.588 (1.132) | HMeSal 0.344 (2.264) | 1:2 | $5^{1/2}$ | $[SnO_2TiAl(O\text{-}i\text{-}Pr)_3(MeSal)_2]$ 0.635 (83.7) | 0.111 (0.101) | 16.78 (14.20) | 6.68 (5.65) | 3.84 (2.95) |
| 3 | $[SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ 0.612 (1.179) | HEtSal 0.195 (1.179) | 1:1 | $3^{1/2}$ | $[SnO_2TiAl(O\text{-}i\text{-}Pr)_4(EtSal)]$ 0.591 (82.8) | 0.058 (0.052) | 18.88 (15.86) | 7.52 (6.06) | 4.32 (3.40) |
| 4 | $[SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ 0.427 (0.822) | HEtSal 0.272 (1.644) | 1:2 | 6 | $[SnO_2TiAl(O\text{-}i\text{-}Pr)_3(EtSal)_2]$ 0.479 (84.1) | 0.080 (0.076) | 16.14 (13.81) | 6.42 (5.07) | 3.69 (3.05) |
| 5 | $[SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ 0.590 (1.136) | HPhSal 0.243(1.36) | 1:1 | $3^{1/2}$ | $[SnO_2TiAl(O\text{-}i\text{-}Pr)_4(PhSal)]$ 0.621 (84.8) | 0.056 (0.050) | 17.53 (14.87) | 6.98 (5.86) | 4.01 (3.10) |
| 6 | $[SnO_2TiAl(O\text{-}i\text{-}Pr)_5]$ 0.379 (0.730) | HPhSal 0.312 (1.46) | 1:2 | $5^{1/2}$ | $[SnO_2TiAl(O\text{-}i\text{-}Pr)_3(PhSal)_2]$ 0.480 (85.4) | 0.072 (0.067) | 14.26 (12.31) | 5.68 (4.76) | 3.26 (2.60) |

**Infrared Spectral Studies**

1:1 salicylate derivatives show absorption bands in the region 1360-1330 $cm^{-1}$, 1160-1150 $cm^{-1}$ and 1120-1090 $cm^{-1}$ are characteristics of *gem*-dimethyl portion and combination band *ν*(C-O + O-*i*-Pr) of the terminal and bridging *iso*propoxy groups respectively.[40,41] 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 ~3100$cm^{-1}$ due to *ν*(O-H) in salicylates is found absent in derivatives of [$SnO_2TiAl(O\text{-}i\text{-}Pr)_5$] 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 1240 $cm^{-1}$ 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 760 $cm^{-1}$ and lower are due to M-O stretching vibrations.[42]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.

**NMR Spectral Studies**

**$^1$H NMR spectra**

The $^1$H NMR spectrum of 1:1 derivative show number of peaks in the regions δ 0.7-1.3 ppm are due to methyl protons of the *iso*propoxy groups.[43] A multiplet centered at δ 4.1 ppm in [$SnO_2TiAl(O\text{-}i\text{-}Pr)_5$] due to methine proton of the *iso*propoxy groups[37] 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 [$SnO_2TiAl(O\text{-}i\text{-}Pr)_5$] 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 6.7 –δ 7.7 ppm) in all the derivatives.

**$^{13}$C NMR spectra**

The $^{13}$C NMR spectra of 1:1 salicylate derivatives of heterotrimetallic [Al(III);Sn(II);Ti(IV)]-μ-oxo-*iso*propoxide shows two prominent peaks at δ ~ 26.5 ppm and δ ~ 28.6 ppm assignable to the methyl carbon of terminal and bridged *iso*propoxy groups. Two different type of methine carbons of *iso*propoxy groups[44] is confirmed by the two signals observed at δ ~ 64.0 ppm and δ ~ 64.4 ppm. 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).[45]

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 [$SnO_2TiAl(O\text{-}i\text{-}Pr)_5$]:

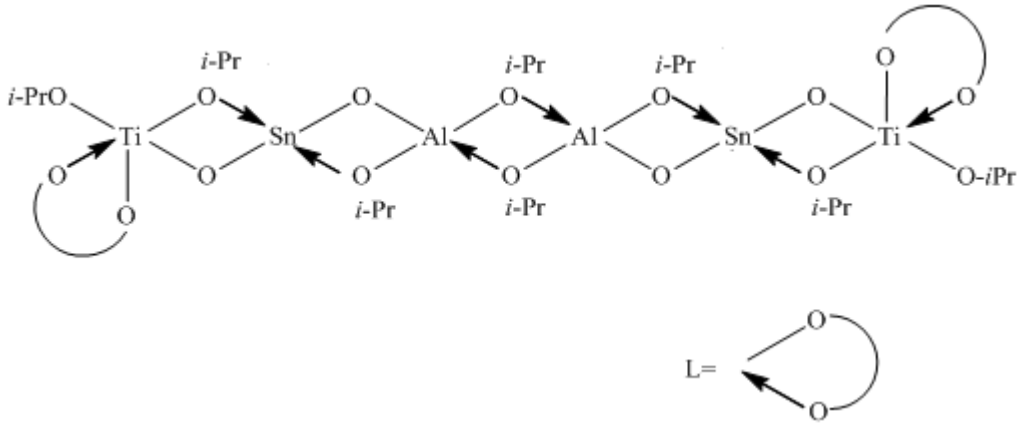


**Fig. 1** [$SnO_2TiAl(O\text{-}i\text{-}Pr)_4(MeSal)$]

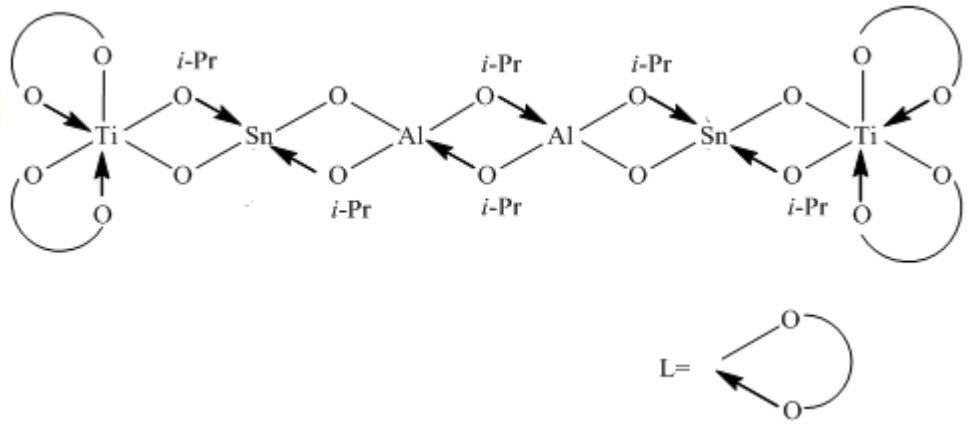


**Fig. 2**: [$SnO_2TiAl(O\text{-}i\text{-}Pr)_3(MeSal)_2$]

**Acknowledgements:** My sincere thanks are due to DAV College (Lahore) Ambala City for providing the necessary facilities and SAIF, P.U. Chandigarh for spectral and elemental analysis.

**References**

1. Brune, V.; Grosch, M.; Weißing, R.; Hartl, F.; Frank, M.; Mishra, S.; Mathur, S. Influence of the Choice of Precursors in the Synthesis of Two Dimensional Transition Metal Dichalcogenides. *Dalton Trans*. 2021, *50*, 12365-12385.

2. Mishra, S.; Daniele, S. Molecular engineering of metal alkoxides for solution phase synthesis of high-tech metal oxide nanomaterials. *Chem. Eur. J.* 2020, *26*, 9292–9303.

3. Mishra, S.; Daniele, S. Metal-Organic Derivatives with Fluorinated Ligands as Precursors for Inorganic Nanomaterials. *Chem. Rev*. 2015, *115*, 8379-8448.

4. Seisenbaeva, G. A.; Kessler, V. G. Precursor directed synthesis – "molecular" mechanisms in the Soft Chemistry approaches and their use for template-free synthesis of metal, metal oxide and metal chalcogenide nanoparticles and nanostructures. *Nanoscale* 2014, *6*, 6229-6244.

5. Bloor, L. G.; Carmalt, C. J.; Pugh, D. Single-source precursors to gallium and indium oxide thin films. *Coord. Chem. Rev*. 2011, *255*, 1293-1318.

6. Mishra, S.; Daniele, S.; Hubert-Pfalzgraf, L. G. Metal 2-ethylhexanoates and related compounds as useful precursors in materials science. *Chem. Soc. Rev.* 2007, *36*, 1770-1787.

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

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

9. 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.

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

11. 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 the synthesis of ternary coinage metal chalcogenides. *Inorg. Chem*. 2020, *59*, 7727-7738.

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

13. Chen, Y.; Mishra, S.; Ledoux, G.; Jeanneau, E.; Daniel, M.; Zhang, J.; Daniele, S. Direct synthesis 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.

14. 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.

15. Mishra, S.; Mendez, V.; Jeanneau, E.; Caps, V.; Daniele, S. A single source precursor route to 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.

16. 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.

17. 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.

18. 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**.**

19. Goulas, K. A.; Mironenko, A. V.; Jenness, G. R.; Mazal, T.; Vlachos, D. G., Fundamentals of C–O bond activation on metal oxide catalysts. *Nat. Catal.* **2019,** *2* (3), 269-276.

20. Puigdollers, A. R.; Pacchioni, G., CO Oxidation on Au Nanoparticles Supported on $ZrO_2$: Role of Metal/Oxide Interface and Oxide Reducibility. *ChemCatChem* **2017,** *9* (6), 1119-1127.

21. Dlugosz, O.; Szostak, K.; Staron, A.; Pulit-Prociak, J.; Banach, M., Methods for Reducing the Toxicity of Metal and Metal Oxide NPs as Biomedicine. *Materials* **2020,** *13* (2).

22. Nikolova, M. P.; Chavali, M. S., Metal Oxide Nanoparticles as Biomedical Materials. *Biomimetics* **2020,** *5* (2).

23. Maier, S. A.; Brongersma, M. L.; Kik, P. G.; Meltzer, S.; Requicha, A. A.; Atwater, H. A., Plasmonics—a route to nanoscale optical devices. *Adv. Mater.* **2001,** *13* (19), 1501-1505.

24. Ney, A.; Pampuch, C.; Koch, R.; Ploog, K. H., Programmable computing with a single magnetoresistive element. *Nature* **2003,** *425* (6957), 485-7.

25. Atwater, H. A.; Polman, A., Plasmonics for improved photovoltaic devices. *Nat. Mater.* **2010,** *9* (3), 205-13.

26. Noginov, M. A.; Zhu, G.; Belgrave, A. M.; Bakker, R.; Shalaev, V. M.; Narimanov, E. E.; Stout, S.; Herz, E.; Suteewong, T.; Wiesner, U., Demonstration of a spaser-based nanolaser. *Nature* **2009,** *460* (7259), 1110-2.

27.Jing, L.; Zhou, W.; Tian, G.; Fu, H., Surface tuning for oxide-based nanomaterials as efficient photocatalysts. *Chem. Soc. Rev.* **2013,** *42* (24), 9509-49.

28. Huang, M. H.; Rej, S.; Chiu, C. Y., Facet-Dependent Optical Properties Revealed through Investigation of Polyhedral Au-Cu(2)O and Bimetallic Core-Shell Nanocrystals. *small* **2015,** *11* (23), 2716-26.

29. Rothschild, A.; Komem, Y., The effect of grain size on the sensitivity of nanocrystalline metal-oxide gas sensors. *J. Appl. Phys.* **2004,** *95* (11), 6374-6380.

30. Lane, M. K. M.; Zimmerman, J. B., Controlling metal oxide nanoparticle size and shape with supercritical fluid synthesis. *Green Chem.* **2019,** *21* (14), 3769-3781.

31. Wu, Z.; Li, M.; Overbury, S. H., On the structure dependence of CO oxidation over $CeO_2$ nanocrystals with well-defined surface planes. *J. Catal.* **2012,** *285* (1), 61-73.

32. Li, Z.; Ji, S.; Liu, Y.; Cao, X.; Tian, S.; Chen, Y.; Niu, Z.; Li, Y., Well-Defined Materials for Heterogeneous Catalysis: From Nanoparticles to Isolated Single-Atom Sites. *Chem. Rev.* **2020,** *120* (2), 623-682.

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

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

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

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

37. Jashmer Singh, *international Journal of Novel Research and development ;*. **10(10),** 573 (2025).

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

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

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

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

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

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

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

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