



Synthesis and Characterization of Phosphine and Arsinic Complexes of Ruthenium (II & III) Ligated With 3-(4-pyridyl)-4-substituted-triazoline-5-thione

R.N. PANDEY* and NISHA KUMARI

P.G. Centre of Chemistry (M.U.), College of Commerce, Patna - 800020 (India)

*Corresponding author E-mail: rameshwarnath.pandey@yahoo.com

<http://dx.doi.org/10.13005/ojc/300480>

(Received: September 23, 2014; Accepted: November 03, 2014)

ABSTRACT

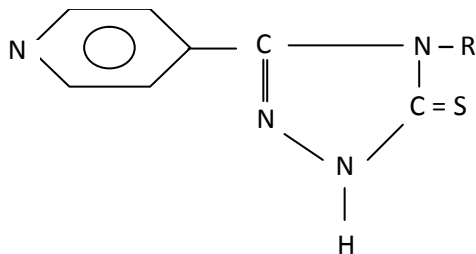
Organometallic complexes of ruthenium (II & III) with the formula $[\text{RuH}(\text{CO})(\text{E}\phi_3)_2\text{L}]$ and $[\text{RuCl}_2(\text{E}\phi_3)_2\text{L}]$ (E = P/As; L = deprotonated mononegative bidentate 3-(4-pyridyl)-triazoline-5-thione and its 4-phenyl substituted derivative) were synthesized and characterized by elemental analysis, physico-chemical and spectroscopic methods. All new compounds were iso-structural with precursor complexes. Two triphenyl phosphine or triphenylarsine molecules are at trans-disposition and thioamide ligands behaves as bidentate (N, S) donor in assigned octahedral structure.

Key words: Organo-ruthenium (II & III), N, S-chelating thioamide, oh-species

INTRODUCTION

nating ability and interesting insights into structure and bonding¹⁻³. Bowman-James's group⁴⁻⁵ and Kanbara and Co-worker⁶⁻⁸ have reported that thioamide based Pincer complexes are photoluminescent and have catalytic activity. The group of Henderson⁹⁻¹¹ has reported the synthesis and structural characterization of various transition metal complexes containing chelating thioamide derivatives. The reactions, structures and anti-tumour activity of transition metal ions with

thioamide ligands are reported by Mohr et al¹². The current interest in organometallic ruthenium complexes with anti-tumour activity¹³⁻¹⁵ prompted us to investigate this class of complexes with 3-(4-Pyridyl)-4-substituted-Triazoline-5-thione which contains secondary thioamide group. Prior to this work low-valent Pd(0), Pt(0) and Rh(I) complexes of this ligand are reported in our previous communication¹⁶. The present study embodies synthesis and characterization of some novel organometallic derivatives of ruthenium (II & III) with 3-(4-Pyridyl)-4-substituted-triazoline-5-thione (I).



(I)

(R = H/C₆H₅)**EXPERIMENTAL**

All chemicals used were either CP grade or AR grade. Solvents were distilled and dried before use. The ligands 3-(4-Pyridyl)-triazoline-5-thione (PytTH) and 3-(4'-Pyridyl)-4-phenyl-triazoline-5-thione (PPytTH) were prepared by the method of Dutta et al¹⁷. The ligands were recrystallized from ethanol before use. The precursor complexes, [RuX₃(Ef₃)₃] (X = Cl/Br; E = P/As), [RuH(CO)(Ef₃)₃Cl] (E = P/As) were prepared following the literature pathway¹⁸⁻²².

Preparation of new ruthenium (II) complexes

All ruthenium (II) complexes were prepared by ligand substitution reactions using precursors [RuH(CO)(Ef₃)₃Cl] (E = P/As)¹⁸⁻¹⁹ and ethanolic solution of ligands, PytTH or PPytTH in equimolar ratio using our previous method²³.

Analysis

- S. No.1 : [RuCl(CO)(Pφ₃)₂(PytT)]
(deep brown) : Calculated (%) for RuC₄₄H₃₅N₄OSCIP₂Ru (865.5) : C = 61.00; H = 5.08; N = 6.47; Ru = 11.66; Found (%) : C = 61.18; H = 5.18; N = 6.50; Ru = 11.72;
- S. No.2 : [RuCl(CO)(Asφ₃)₂(PytT)]
(Brown) : Calculated (%) for RuC₄₄H₃₅N₄OSAs₂Cl (953.34) : C = 55.38; H = 3.67; N = 5.87; Ru = 10.59; Found (%) : C = 55.42; H = 3.77; N = 5.92; Ru = 10.62;
- S. No.3 : [RuCl(CO)(Pφ₃)₂(PPytT)]
(yellowish brown) : Calculated (%) for RuC₅₀H₃₉N₄SP₂Cl (941.50) : C = 63.72; H = 4.14; N = 5.95; Ru = 10.72;

Found (%) : C = 63.82; H = 4.21; N = 6.02; Ru = 10.77;

- S. No.4 : [RuCl(CO)(Asφ₃)₂(PPytT)] (yellowish brown) : Calculated (%) for RuC₅₀H₃₉N₄SAs₂Cl (1025.5) : C = 58.50; H = 3.80; N = 5.46; Ru = 9.84; Found (%) : C = 58.62; H = 3.91; N = 5.38; Ru = 9.92;

Preparation of ruthenium (III) complexes

All the reactions were carried out strictly anhydrous conditions and the complexes were prepared using a general method. Benzene solution of [RuX₃(Eφ₃)₃] (X = Cl/Br; E = P/As) and ligand were mixed in equimolar ratios and stirred on magnetic stirrer for 15 mints and heated on reflux till the brown colour changed to yellowish green. The working mixture was concentrated and cooled. Addition of light petroleum ether produced solid products which was filtered and dried in vacuo over anhydrous CaCl₂. (yield = 76%)

Analysis

- S. No.5 : [RuCl₂(Pφ₃)₂(PytT)] (yellowish green) : Calculated (%) for RuC₄₃H₃₅N₄P₂SCl₂ (873) : C = 59.10; H = 4.00; N = 6.41; Ru = 11.56; Found (%) : C = 59.01; H = 3.98; N = 6.38; Ru = 11.49;
- S. No.6 : [RuCl₂(Asφ₃)₂(PytT)] (greenish yellow) : Calculated (%) for RuC₄₃H₃₅N₄As₂SCl₂ (960.84) : C = 53.70; H = 3.64; N = 5.82; Ru = 10.51; Found (%) : C = 54.01; H = 3.70; N = 5.78; Ru = 10.60;
- S. No.7 : [RuBr₂(Pφ₃)₂(PytT)] (brownish green) : Calculated (%) for RuC₄₃H₃₅N₄P₂SBr₂ (962) : C = 53.63; H = 3.63; N = 5.82; Ru = 10.49; Found (%) : C = 55.63; H = 3.68; N = 5.80; Ru = 10.52;
- S. No.8 : [RuBr₂(Asφ₃)₂(PytT)] (brownish green) : Calculated (%) for RuC₄₃H₃₅N₄As₂SBr₂ (1049.74) : C = 49.15; H = 3.33; N = 5.33; Ru = 9.62; Found (%) : C = 49.32; H = 3.40; N = 5.23; Ru = 9.68;
- S. No.9 : [RuCl₂(Pφ₃)₂(PPytT)] (yellowish green) : Calculated (%) for RuC₄₉H₃₉N₄SP₂Cl₂ (949) : C = 61.95; H = 4.10; N = 5.90; Ru = 10.64; Found (%) : C = 62.11; H = 4.20; N = 6.01; Ru = 10.68;
- S. No.10 : [RuCl₂(Asf₃)₂(PPytT)] (yellowish green)

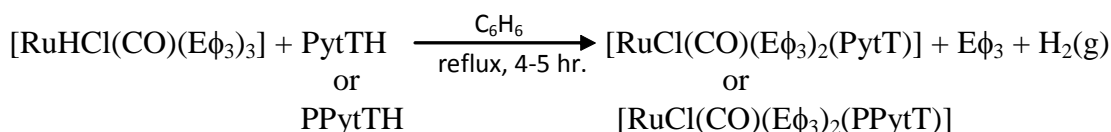
- : Calculated (%) for $\text{RuC}_{49}\text{H}_{39}\text{N}_4\text{SAs}_2\text{Cl}_2$ (1033) : C = 56.92; H = 4.74; N = 6.42; Ru = 9.77; Found (%) : C = 57.01; H = 4.80; N = 5.50; Ru = 9.89;
- S. No.11 : $[\text{RuBr}_2(\text{P}\phi_3)_2(\text{PPyT})]$ (greenish brown) : Calculated (%) for $\text{RuC}_{49}\text{H}_{39}\text{N}_4\text{SP}_2\text{Br}_2$ (1037.8) : C = 56.65; H = 3.75; N = 5.39; Ru = 9.73; Found (%) : C = 56.66; H = 3.88; N = 5.42; Ru = 9.80;
- S. No.12 : $[\text{RuBr}_2(\text{Asf}_3)_2(\text{PPyT})]$ (greenish brown) : Calculated (%) for $\text{RuC}_{49}\text{H}_{39}\text{N}_4\text{SAs}_2\text{Br}_2$ (1125.64) : C = 52.23; H = 3.46; N = 4.97; Ru = 8.97; Found (%) : C = 52.40; H = 3.50; N = 5.01; Ru = 9.00;

The analysis of C, H and N were performed at CDRI, Lucknow, India. IR spectra of ligand and complexes were recorded on a Perkin Elmer 577

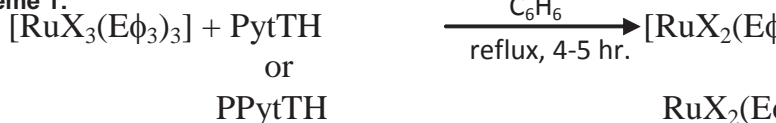
spectrophotometer in the range of 4000-200 cm^{-1} as KBr pellet technique. Electronic spectra of ligand and complexes were recorded on a Beckmann Du-6 spectrophotometer. The molar conductance of complexes (10^{-3} M) were measured in DMF using Wiss-Werkstatter Weihem obb type LBR conductivity meter. The magnetic susceptibility was measured on a gouy balance using $\text{Hg}[\text{CO}(\text{SCN})_4]$ as calibrant.

RESULTS AND DISCUSSION

The reactions of $[\text{RuHCl}(\text{CO})(\text{E}\phi_3)_2]$ (E = P/As) (Scheme I) and $[\text{RuX}_3(\text{E}\phi_3)_3]$ (X = Cl/Br; E = P/As) with thioamide ligands (Scheme II) in 1:1 molar ratio in benzene afforded new hexa-coordinated complexes and ligands acts as mononegative bidentate anion.



Scheme 1:



(X = Cl/Br; E = P/As)

The analytical data are in good agreement with

Scheme 2:

The analytical data are in good agreement with general molecular formula proposed. The mononegative bidentate thioamide ligands replaces are triphenyl phosphine or triphenyl arsine molecule, one chlorido or bromido group from precursors $[\text{RuX}_3(\text{E}\phi_3)_3]$ and hydrido group and one $\text{P}\phi_3$ or Asf_3 from precursors, $[\text{RuHCl}(\text{CO})(\text{E}\phi_3)_3]$. All the isolated products were air-stable and non-hygroscopic nature and fair soluble in acetone, EMK, DMF & DMSO.

Magnetic moment and UV-Vis Spectra

The substitution products $[\text{RuCl}(\text{CO})(\text{E}\phi_3)_2(\text{PytT})]$ and $[\text{RuCl}(\text{CO})(\text{E}\phi_3)_2(\text{PPyT})]$ were

diamagnetic indicating Ru^{++} (d^6) and $^1\text{A}_{1g}$ ground state. The d – d transition bands (table 2) consistent with octahedral structure²⁴.

The magnetic moment value of $[\text{RuX}_2(\text{E}\phi_3)_2(\text{PytT})]$ or $[\text{RuX}_2(\text{E}\phi_3)_2(\text{PPyT})]$ (X = Cl/Br; E = P/As) are in the range of 1.80-1.95 BM corresponding to a single unpaired electron in a low spin $\text{T}_{2g}^{5\text{eg}^0}$ configuration and oxidation state of ruthenium is +3. So, the ground state of Ru (III) is $^2\text{T}_{2g}$ and first excited doublet level in order of increasing energy are $^2\text{A}_{2g}$ and $^2\text{A}_{1g}$ which arises from $\text{t}_{2g}^{4\text{eg}^1}$ configuration²⁵. The electronic spectra of complexes exhibit bands around 18585 ($^2\text{T}_{2g} \rightarrow$

Table 1: Assignment of Major infrared bands of 3-(4-Pyridyl)-4-substituted-triazoline-5-thione and their Ru (II & III) complexes in (cm⁻¹)

Compounds	νN-H + νCH	Thioamide Bands				νRu-S	νRu-N	νRu-X
		Band I	Band II	Band III	Band IV			
PyTTH (ligand)	3120 m 3080 m	1570 (sb)	1205 (s)	960 (s)	850 (ms)	-	-	-
[Ru ^{II} Cl(CO)(Pt ₃) ₂ (PyT)]	3080 m	1535 (s)	1210 (s) 1200 (m)	925 (m)	810 (m)	406 w	441 (m)	370 w 340 w
[Ru ^{II} Cl(CO)(Asf ₃) ₂ (PyT)]	3085 m	1530 (s)	1220 m 1200w	935 (m)	820 (m)	410 w	445 (m)	370 w 350 w
[Ru ^{III} Cl ₂ (Pt ₃) ₂ (PyT)]	3060 m	1545 (s)	1215 m 1200 m	945 (m)	830 (m)	425 (m)	448 (m)	364 m 343 m
[Ru ^{III} Cl ₂ (Asf ₃) ₂ (PyT)]	3070 m	1540 (s)	1215 (m) 1200 (m)	940 (m)	825 (m)	430 m	450 m	356 m 335 m
[Ru ^{III} Br ₂ (Pt ₃) ₂ (PyT)]	3065 m	1535 (s)	1200 w 1185 m	945 (m)	820 (m)	430 w	445 m	355 m 330 m
[Ru ^{III} Br ₂ (Asf ₃) ₂ (PyT)]	3070 m	1545 (s)	1220 m 1190 m	950 (s)	825 (m)	430 w	430 m	360 m 330 m
PPyTTH (ligand)	3060 m	1480 (s)	1290 (s) 1240 (m)	1090 (m)	785 m	³ / ₄	³ / ₄	³ / ₄
[Ru ^{II} Cl(CO)(Pt ₃) ₂ (PPyT)]		1435 (s)	1235 (s)	1035 (m)	765 m	428 w	464	364 m
[Ru ^{II} Cl(CO)(Asf ₃) ₂ (PPyT)]		1460 (s)	1210 (m) 1240 (s)	1040 w	765 m	436 (w)	458 m	356
[Ru ^{III} Cl ₂ (Pt ₃) ₂ (PPyT)]		1445 m	1220 (m) 1250 (s)	1065 (m)	770 (m)	440 w	476	365 m 345
[Ru ^{III} Cl ₂ (Asf ₃) ₂ (PPyT)]		1440 (ms)	1230 (m) 1245 (s)	1070 (m)	772 (m)	436 w	458 m	356 m 335 m
[Ru ^{III} Br ₂ (Pt ₃) ₂ (PPyT)]		1465 (m)	1235 (m) 1250 m	1065 (m)	760 m	440 w	460 m	350 m 330 m
[Ru ^{III} Br ₂ (Asf ₃) ₂ (PPyT)]		1460 (m)	1235 m 1250 m 1220 (m)	1065 (m)	765 m	438 w	470 m	345 m 332 m

${}^2A_{2g}$), 22935 ($T_{2g} \rightarrow \pi^*$, MLCT), 38760 ($n \rightarrow \pi^*$) and 49020 cm^{-1} ($\pi \rightarrow \pi^*$) are consistent with octahedral structure of other ruthenium (III) complexes²⁶.

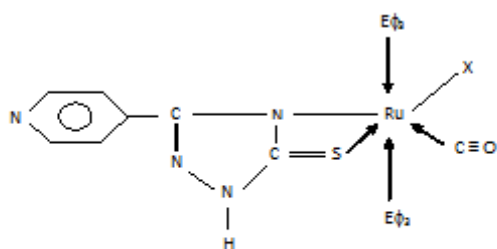
Infrared Spectra

The IR bands of interest of ligands and complexes are given in Table 1. A comparison of the infrared bands of the ligands and complexes indicate the simultaneous formation of Ru – N and Ru – S bonds.

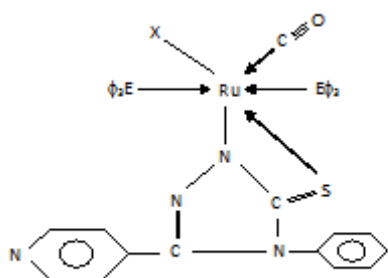
(i) Two bands having contribution from nNH and nCH are present at 3120 cm^{-1} and 3080 cm^{-1} in PytTH and at 3060 cm^{-1} in PPytTH. But there is only one band centred at 3080 cm^{-1} in the spectra of complexes of PytTH and found to be absent in the complexes PPytTH. This suggests that H-atom of N-H group of ligands has been replaced by the Ru(II) and Ru(III) ions leading to the formation of Ru^{II}-N and Ru^{III}-N bonds.

Table 2: Magnetic, Conductometric and Electronic spectral data of ruthenium (II & III) complexes

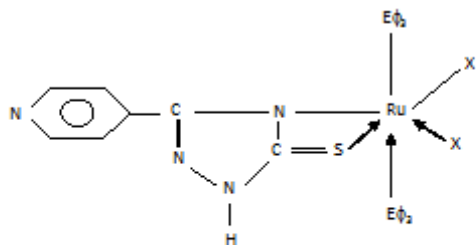
Complexes	$\mu_{\text{eff.}}$ (BM)	Molar cond. $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$	λ_{max} (cm^{-1}) (Assignment)
[Ru ^{II} Cl(CO)(P ϕ_3) ₂ (PytT)]	Dia Mag.	15.60	19240 (${}^1A_{1g} \rightarrow {}^1T_{1g}$) 21740 (${}^1A_{1g} \rightarrow {}^1T_{2g}$) 31250 (CT Band)
[Ru ^{II} Cl(CO)(As ϕ_3) ₂ (PytT)]	Dia Mag.	20.60	19800 (${}^1A_{1g} \rightarrow {}^1T_{1g}$) 20405 (${}^1A_{1g} \rightarrow {}^1T_{2g}$) 28985 (CT Band)
[Ru ^{III} Cl ₂ (P ϕ_3) ₂ (PytT)]	1.86	15.30	18585 (${}^2T_{2g} \rightarrow {}^2A_{2g}$) 22935 ($T_{2g} \rightarrow \pi^*$) 38760 ($n \rightarrow \pi^*$) 49020 ($\pi \rightarrow \pi^*$)
[Ru ^{III} Cl ₂ (As ϕ_3) ₂ (PytT)]	1.95	15.00	18690 (${}^2T_{2g} \rightarrow {}^2A_{2g}$) 22725 ($T_{2g} \rightarrow \pi^*$) 37735 ($n \rightarrow \pi^*$) 48305 ($\pi \rightarrow \pi^*$)
[Ru ^{III} Br ₂ (P ϕ_3) ₂ (PytT)]	1.80	10.32	18690 (${}^2T_{2g} \rightarrow {}^2A_{2g}$) 22470 ($T_{2g} \rightarrow \pi^*$) 37735 ($n \rightarrow \pi^*$) 48780 ($\pi \rightarrow \pi^*$)
[Ru ^{III} Br ₂ (As ϕ_3) ₂ (PytT)]	1.90	12.30	18665 (${}^2T_{2g} \rightarrow {}^2A_{2g}$) 18510 ($T_{2g} \rightarrow \pi^*$) 38165 ($n \rightarrow \pi^*$) 49015 ($\pi \rightarrow \pi^*$)
[Ru ^{II} Cl(CO)(P ϕ_3) ₂ (PPytT)]	Dia, Mag.	15.35	19230 (${}^1A_{1g} \rightarrow {}^1T_{1g}$) 21740 (${}^1A_{1g} \rightarrow {}^1T_{2g}$) 34480 (CT Band) 29760 (CT Band)
[Ru ^{II} Cl(CO)(As ϕ_3) ₂ (PPytT)]	Dia, Mag.	15.30	19605 (${}^1A_{1g} \rightarrow {}^1T_{1g}$) 21740 (${}^1A_{1g} \rightarrow {}^1T_{2g}$) 35715 (CT Band) 30305 (CT Band)
[Ru ^{III} Cl ₂ (P ϕ_3) ₂ (PPytT)]	1.88	10.35	18868 (${}^2T_{2g} \rightarrow {}^2A_{2g}$) 22470 ($T_{2g} \rightarrow p^*$) 38460 ($n \rightarrow p^*$) 48780 ($p \rightarrow p^*$)



Str. I (X = Cl/Br; E = P/As)



Str. II (X = Cl/Br; E = P/As)



Str. III (X = Cl/Br; E = P/As)

- (ii) Thioamide band IV has main contribution from $\nu_{\text{C-S}}$ observed at 850 cm^{-1} (PytTH) and at 785 cm^{-1} (PPyTH) in the spectra of the ligands shift to lower frequency by $30\text{-}50 \text{ cm}^{-1}$ indicating coordination of thioamide ligands through thione sulphur and formation of ruthenium – S bond following our previous observations²⁶.
- (iii) The simultaneous Ru-N and Ru-S bonding results in a decrease in the frequency of thioamide band IV by $30\text{-}50 \text{ cm}^{-1}$, blue shift to higher frequency of $10\text{-}15 \text{ cm}^{-1}$ of band II and red shift to the extent of $35\text{-}55 \text{ cm}^{-1}$ in thioamide band I. These observations are in good agreement with previous literature²⁷. New bands at $435\text{-}465 \text{ cm}^{-1}$ (Ru-N) and $405\text{-}410 \text{ cm}^{-1}$ (Ru-S) due to stretching modes further supports these observations.
- (iv) The presence of bands near $540, 680, 750$ and 1550 cm^{-1} are attributed to coordinated PF_3/Asf_3 in complexes²⁹⁻³⁰. The presence of single Ru-P stretching modes at $510\text{-}500 \text{ cm}^{-1}$ confirms two bulky PF_3 groups are at mutual Trans-disposition in octahedral structure of complexes (Str. I & II). However, more than one Ru-X stretching mode in Ru (III) complexes indicates cis-disposition of two chlorine or two bromine atoms in octahedral structure (Str. III & IV).
- (v) The non-ligand band at $1950\text{-}1960 \text{ cm}^{-1}$ in carbonyl complexes of ruthenium (II) supports terminal $\text{C}=\text{O}$ group slightly higher frequency than in precursor complex.

Thus, the ligands behaves as mononegative bidentate (N, S) donor.

REFERENCES

- Jagodzinski, T.S., *Chem. Rev.* **2003**, 103, 197.
- Pandiarajan, D. and Ramesh, R., *J. Organometallic Chem.* **2013**, 723, 26.
- Murai, T., *Top. Curr. Chem.* **2005**, 251, 247.
- Begum, R.A., Powell, D., Bowman-James, K., *Inorg. Chem.* **2006**, 45, 964.
- Hossain, M.A., Lucarini, S., Powell, D. & Bowman-James, K., *Inorg. Chem.* **2004**, 43, 7275.
- Kanbara, T., Okada, K., Yamamoto, T., Ogawa, H. and Inoue, T., *J. Organomet. Chem.* **2004**, 689, 1860.
- Okamoto, K., Kanbara, T., Yamamoto, T. and Wada, T., *Organometallics*, **2006**, 25, 4026.
- Koizumi, T., Teratani, T., Okamoto, K., Yamamoto, T., Shimoi, Y. and Kanbara, T., *Inorg. Chem. Acta*, **2010**, 363, 2474.
- Henderson, W., Nicholson, B.K. and Tiekink, E.R.T., *Inorg. Chim. Acta*, **2006**, 359, 204.

10. Henderson, W. and Rickard, C.E.F., *Inorg. Chim. Acta*, **2003**, 343, 74.
11. Henderson, W., Nicholson, B.K., Dinger, M.B. and Bennett, R.L., *Inorg. Chim. Acta*, **2002**, 338, 210.
12. Alagoz, C., Brauer, David J. and Mohr Fabian, *J. Organometallic Chem.* **2009**, 694, 1283.
13. Clarke, M.J., *Coord. Chem. Rev.* **2003**, 236, 209.
14. Gielen, M., Tiekink, E.R.T., *Metallotherapeutic Drugs and Metal-based Diagnostic Agents*, John Wiley and Sons, Chichester, **2005**.
15. Yan, Y.K., Melchart, M., Habtemariam, A. and Sadler, P.J., *Chem. Commun.* **2005**, 4764.
16. Pandey, R.N., Kumar Arun, Singh, R.S.P., Sahay, A.N. and Kumar, Shashikant, *J. Indian Chem. Soc.* **1992**, 69, 804.
17. Dutta, S., Acharya, A.K. and Basu, U.P., *J. Indian Chem. Soc.*, **1968**, 45, 338.
18. Ahmad, N., Levison, J.J., Robinson, S.D. and Uttley, M.F., *Inorg. Synth.* **1975**, 15, 45.
19. Balasubramanian, K.P., Manivannanand, S. and Chinusamy, V., *J. Ultra Chem.* **2008**, 4, 15.
20. Poddar, R.K., Khullar, I.P. and Agarwala, U., *J. Inorg. Nucl. Chem. Lett.* **1974**, 10, 221.
21. Natarajan, K., Poddar, R.K. and Agarwala, U., *J. Inorg. Nucl. Chem.* **1977**, 39, 431.
22. Chatt, J., Leigh, C.J., Mingos, D.M.P. and Paske, R.J., *J. Chem. Soc. A*, **1968**, 2636.
23. Pandey, R.N., Bala, Renu and Sinha, A.K., *Oriental J. Chem.* **2011**, 27(1), 293.
24. Pandey, R.N. and Gautam, K.V., *J. Ultra Chem.* **2014**, 10(1), 35.
25. Pandiarajan, D. and Ramesh, R., *Polyhedron*, **2012**, 34, 136.
26. Kannan, S. and Ramesh, R., *Polyhedron*, **2006**, 25, 3095.
27. Singh, B., Singh, R., Choudhary, R.V. and Thakur, K.P., *Indian J. Chem.* 11, 174 (1973).
28. Singh, B. and Singh, R., *J. Inorg. Nucl. Chem.* **1972**, 34, 3449.
29. Pandiarajan, D. and Ramesh, R., *J. Organomet. Chem.* **2003**, 723, 26.
30. Kumar, K.N., Ramesh, R. and Liu, Y., *J. Mol. Catal. A Chem.*, **2007**, 265, 218.