Int. J. Chem. Sci.: 8(2), 2010, 951-960

MIXED - LIGAND ORGANOMETALLIC COMPLEXES OF Pt-GROUP METALS WITH TRIPHENYL PHOSPHINE AND HETEROCYCLIC THIOAMIDES

R. N. PANDEY*, GUNJAN KUMARI, AMARESH KUMAR and RAJNISH Kr. SINGH

P.G. Centre of Chemistry (M.U.), College of Commerce, PATNA – 800 020 (M.S.) INDIA

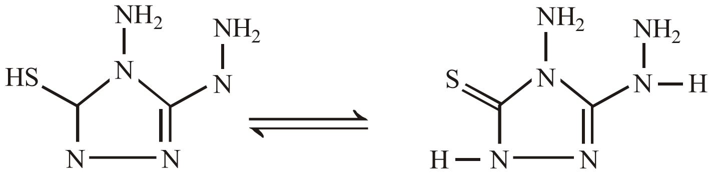
ABSTRACT

Mixed-ligand organometallic complexes of Pt-group metals with triphenyl phosphine and 4-amino-3-hydrazino-5-mercapto-1, 2, 4, triazole have been prepared and characterised using various physico-chemical techniques. The rhodium (I), palladium (II) and platinum (II) complexes are square planar but ruthenium (II), rhodium (III) and iridium (III) complexes have octahedral configuration. The value of crystal field parameters and Far – IR specta confirm their assigned structure.

Key Words: Organo-platinum group metals, Thioamide ligands, Structure, Bonding, Complexes.

INTRODUCTION

The versatile catalytic property[1-3] and the anti – cancer activity[4-6] of organometallic complexes of Pt-group metals tempted us to prepare and to investigate some new organometallic derivatives of Pt-group metals in continuation of our previous reports.[7-9] Some monomeric organometallic complexes have been prepared and characterised in the present work using triphenyl phosphine as primary and 4-amino-3-hydrazino-5-mercapto-1, 2, 4-triazole (Fig. I) as secondary ligand.



(Thiol-form) (Thione-form)

Fig. 1

---

*Author for correspondence; E-mail: rameshwarnath.pandey@yahoo.com; rajnish_sinha09@ymail.com

EXPERIMENTAL

All chemicals used were of CP-grade or AR-grade. The ligand (AHtTH) was prepared by the slightly modified method reported in literature[10] (MP = 268°C). The precursor complexes $[Rh(P\phi_3)X]$[11] ($X = Cl^-, Br^-, I^-, NCS^-$ and $SnCl_3^-$), $[Pd(P\phi_3)_3(AHtTH)]$[12] $[Pt(P\phi_3)_3(AHtTH)]$[12], $[RuH(CO)\ (P\phi_3)_3Cl]$[13] and $[Ir(CO)\ (P\phi_3)_2Cl]$[14] were prepared by the methods reported in literature. The palladium (II) and platinum (II) complexes were prepared by oxidative addition between precursor complexes and ethanolic solution of inorganic acids as our previous report.[15] The preparation of rhodium (I) and ruthenium (II) complexes was similar to our earlier method[29].

Infrared spectra of ligand and complexes were recorded on a Perkin – Elmer 577 spectrophotometer in the range of 4000-200 cm^{-1} and electronic spectra on a Beckmann DU-6 spectrophototometer. The molar conductance (10^{-3}M) of complexes were measured in DMF using wiss-wekstatter weitheim obb type LBR conductivity meter. The magnetic measurements were made on a Gouy balance.

RESULTS AND DISCUSSION

All organometallic complexes are stable solid and did not melt up to 250°C. However, ruthenium (II) complexes melted at 187°C (S. No. 1) and at 218°C (S. No. 2). Analytical results were satisfactory and possible composition is presented in Table 1. The oxidative addition to zerovalent platinum complexes with 15% ethanolic solution of inorganic acids produced hydrido-complexes of platinum (II).

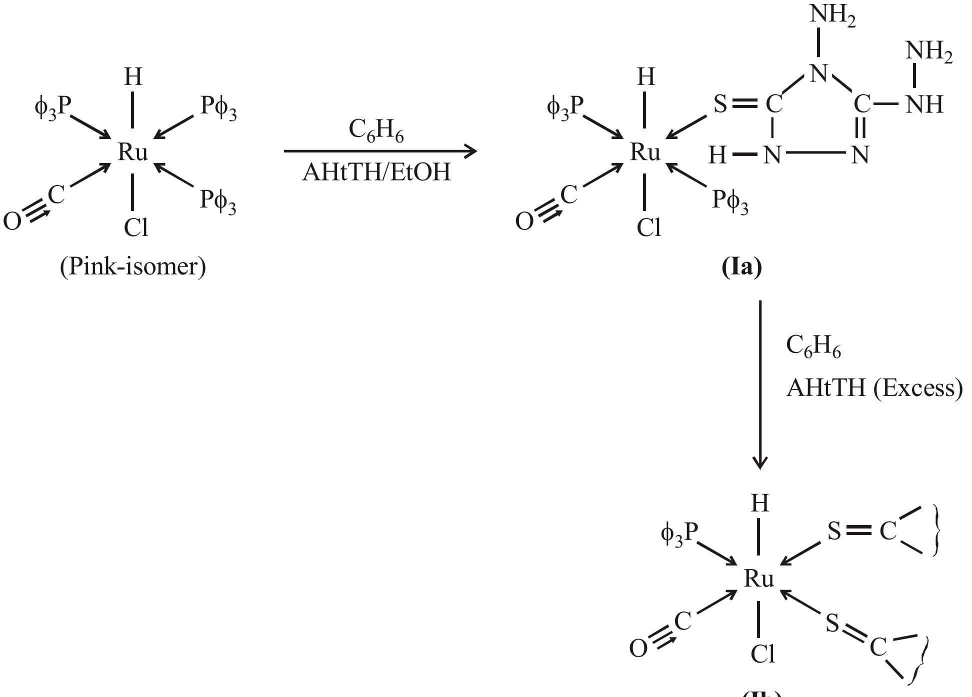
$$[Pt^{\circ}(P\phi_3)_3\ (AHtTH)] + HX \xrightarrow{EtOH} [Pt\ H\ (P\phi_3)_2(AHtTH)]\ X + P\phi_3$$
$$(X = Cl^-,\ NO_3^-,\ HSO_4^- \text{ and } ClO_4^-)$$

Under identical conditions zerovalent, palladium complexes did not form hydrides.

$$[Pd(P\phi_3)_3(AHtTH)] + 2\ HCl \xrightarrow{EtOH} H_2\ (g) + [Pt\ (P\phi_3)_3\ (AHtTH)]\ Cl_2$$

The presence of ionic chlorides were confirmed by the quantitative analysis of Na_2CO_3 extract solution of complexes, where white precipitate of AgCl was obtained for total chlorine with $AgNO_3$.

The replacement reactions of pink-isomer of $[RuH(CO)(P\phi_3)_3Cl]$ with ligand (AHtTH) in benzene medium produced products in which two $P\phi_3$ molecules are replaced by two AHtTH molecules. However, the bonded hydride ion as well as chlorine and $C\overset{\leftarrow}{\equiv}O$ group are not replaced even if the replacement reaction was carried out with large excess of ligand or increasing time of stirring.

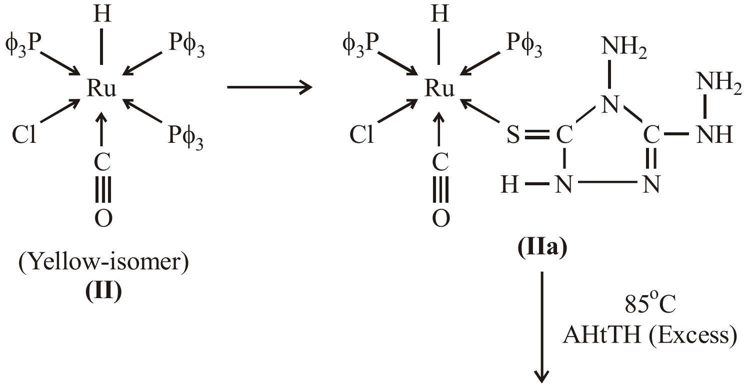


(Pink-isomer)

(Ia)

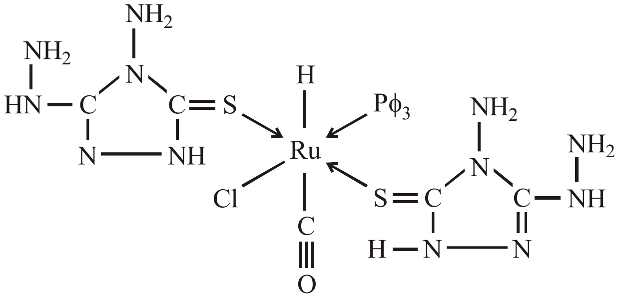
(Ib)

Since CO is having much greater trans-effect than $P\phi_3$ and $P\phi_3$ has greater trans-effect than chlorine, the formation of **(Ib)** can be explained. The yellow–isomer **(II)** yielded [RuH(CO) $(P\phi_3)_2$ (AHtTH)Cl] most easily as expected **(IIa)**. The further replacement occur under more vigorous conditions by increasing time of stirring on magnetic stirrer.



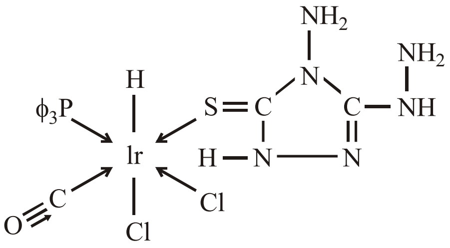
(Yellow-isomer)
(II)

(IIa)



(IIb)

Iridium (III) is a 'b' – class acceptor, which readily forms complexes with soft sulphur donor AHtTH ligand and incoming ligand takes up cis-position **(III)** on oxidative addition to Vaska compound, [Ir^1 (CO) (Pϕ)$_2$Cl].



(Str. III)

The Wilkinson catalyst [Rh(Pϕ_3)$_3$Cl] and analogues [Rh(Pϕ_3)$_3$X] (X = Br$^-$, I$^-$, NCS$^-$, $SnCl_3^-$] undergo replacement reactions with AHtTH and forms stable solid (Table 1).

Table 1: Analytical and physical data of complexes

S. No.	Complex/ Colour	Analysis (%) Found/ (Calcd)			Molar Cond. ($\Omega^{-1}cm^2mol^{-1}$)
		Cl	N	Metal	
1.	[RuH(CO)(Pϕ_3)$_2$ (AHtTH)Cl] (Light grey)	4.55 (4.24)	10.20 (10.04)	12.22 (12.16)	NC
2.	[Ru H(CS) (Pϕ_3)$_2$ (AHtTH)Cl] (Yellow)	4.20 (4.16)	10.01 (9.85)	12.00 (11.93)	NC
3.	[Pd (Pϕ_3)$_2$ (AHtTH)$_2$]Cl$_2$ Light yellow	7.01 (7.14)	17.01 (16.91)	11.01 (10.71)	51.62

Cont…

S. No.	Complex/ Colour	Analysis (%) Found/ (Calcd)			Molar Cond. ($\Omega^{-1}cm^2mol^{-1}$)
		Cl	N	Metal	
4.	$[Pt\ H(P\phi_3)_2\ (AHtTH)]Cl$ (White)	4.11 (3.71)	8.88 (8.76)	20.50 (20.37)	22.30
5.	$[PtH(P\phi_3)_2(AHtTH)]NO_3$ (White)	- -	10.11 (9.94)	19.90 (19.79)	24.32
6.	$[PtH(P\phi_3)_2(AHtTH)]HSO_4$ (White)	- -	8.25 (8.23)	19.22 (19.11)	21.42
7.	$[Pt\ H\ (P\phi_3)_2\ (AHtTH)]$ ClO_4 (White)	4.72 (4.70)	8.31 (8.21)	19.06 (19.07)	20.11
8.	$[Rh\ (P\phi_3)_2\ (AHtTH)Cl]$ (Golden yellow)	4.44 (4.39)	10.40 (10.38)	12.85 (12.73)	NC
9.	$[Rh\ (P\phi_3)_2(AHtTH)Br]$ (Golden brown)	- -	9.82 (9.84)	12.21 (12.07)	NC
10.	$[Rh\ (P\phi_3)_2(AHtTH)I]$ (Brownish – red)	- -	9.41 (9.33)	11.45 (11.44)	NC
11.	$[Rh\ (P\phi_3)_2\ (AHtTH)$ $(NCS)]$ (Yellow)	- -	11.80 (11.79)	12.40 (12.39)	NC
12.	$[Rh\ (P\phi_3)_2\ (AHtTH)$ $(SnCl_3)]$ (Orange)	10.60 (10.66)	8.51 (8.41)	10.41 (10.31)	NC
13.	$[RhH\ (P\phi_3)_2(AHtTH)\ Cl_2]$ (Yellow)	8.34 (8.40)	10.01 (9.94)	12.10 (12.18)	NC
14.	$[Ir\ H(CO)\ (P\phi_3)(AHtTH)$ $Cl_2]$ (Brownish yellow)	10.11 (10.13)	12.01 (11.96)	27.32 (27.46)	NC

NC = Non-conducting

Electronic spectra

All Pd (II) complexes are diamagnetic indicating their low-spin square planar configuration. The spectral bands at 18370 cm^{-1} ($^1A_{1g} \rightarrow {}^1A_{2g}$), 21310 cm^{-1} ($^1A_{1g} \rightarrow {}^1B_{1g}$)

and at 22860 cm^{-1} ($^{1}A_{1g} \rightarrow {}^{1}E_{1g}$) confirm their square planar stereochemistry[16]. The high intensity bands at 38315 cm^{-1} is due to CT band. However, hydridophosphine complexes of platinum (II) display a single ligand field transition at 23230 cm^{-1} assignable to $^{1}A_{1g} \rightarrow {}^{1}B_{1g}$ transition similar to planar complexes (Gray et al.[17]).

The ligand field bands in the rhodium (III) and iridium (III) complexes are analogous[18] to those observed in isoelectronic ruthenium (II) complexes of octahderally disposed strong ligand fields. The spectra exhibited two spin – forbidden $^{1}A_{1g} \rightarrow {}^{3}T_{1g}$ (16640 cm^{-1}) and $^{1}A_{1g} \rightarrow {}^{3}T_{2g}$ (19140 cm^{-1}) and two spin – allowed transitions $^{1}A_{1g} \rightarrow {}^{1}T_{1g}$ (23396 cm^{-1}) and $^{1}A_{1g} \rightarrow {}^{1}T_{2g}$ (30230 cm^{-1}) for octahedral structure[19]. In addition to d-d transition bands; one L → M CT band[20] of high intensity near 38315 cm^{-1} is also observed in each spectrum. The absorption bands of rhodium (III) complexes (S. No. 13) at 21780 and 30760 cm^{-1} are assigned to spin-allowed transitions $^{1}A_{1g} \rightarrow {}^{1}T_{1g}$ (ν_1) and $^{1}A_{1g} \rightarrow {}^{1}T_{2g}$ (ν_2) transition and at 13760 cm^{-1} is probably due to spin-forbidden $^{1}A_{1g} \rightarrow {}^{3}T_{1g}$ transition[20]. The value of ligand field parameters, $\nu_2/\nu_1 = 1.41$, $B = 560.2$, $\beta = 0.77$, $10Dq = 22840$ cm^{-1}, LFSE = 27.38 K.cal mol^{-1} confirms distorted octahedral configuration around rhodium (III) ion with diamagnetism nature of complexes. The reduced value of B obtained in comparison to free-ion value (720 cm^{-1}) indicates increased covalent character in metal-ligand σ bond as well as reduced effective cationic charge (Z*).

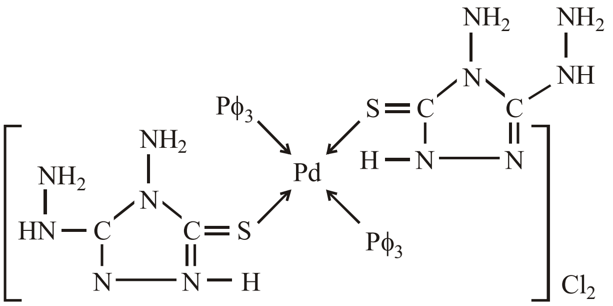
All rhodium (I) complexes display high intensity band in the region 25000-28000 cm^{-1} due to charge transfer from filled 4dz^2 orbital to empty ligand n-orbital characteristic to square planar configuration around Rh (I) ion[21]. The other d-d transition bands are obscured by high intensity charge transfer band[9] due to very strong reducing Rh^{+} species. However, the reflectance spectra of [Rh(Pϕ_3)$_2$(AHtTH)Cl] exhibits three absorption bands at 13810, 18210 and 23610 cm^{-1}. The first band (13810 cm^{-1}) is broad and weak and assigned to spin-forbidden $^{1}A_{1g} \rightarrow {}^{3}A_{2g}$ transition. The band at 18210 cm^{-1} may be due to either spin-forbidden $^{1}A_{1g} \rightarrow {}^{3}B_{1g}$ transition or spin allowed $^{1}A_{1g} \rightarrow {}^{1}B_{1g}$ transition. The high value of the extinction coefficient suggest it to be the singlet-singlet transition. Thus, square planar configuration to all rhodium (I) complexes may be assigned, based on previous literature[21-23].

All complexes of ruthenium (II) display two spin-allowed transition $^{1}A_{1g} \rightarrow {}^{1}T_{1g}$ (20410 cm^{-1}) and $^{1}A_{1g} \rightarrow {}^{1}T_{2g}$ (18720 cm^{-1}) and a weak spin –forbidden transition $^{1}Ag \rightarrow {}^{3}T_{1g}$ (15120 cm^{-1}) are assignable to octahedral configuration[24]. A strong intensity band at 36230 cm^{-1} is probably due to CT band. Iridium (III) complex (S. No. 14) exhibits spin-allowed transition at 25000 ($^{1}A_{1g} \rightarrow {}^{1}T_{1g}$), 29400 cm^{-1} ($^{1}A_{1g} \rightarrow {}^{1}T_{2g}$) and one spin-forbidden transition at 24200 cm^{-1} ($^1A_{1g} \rightarrow {}^3T_{1g}$). The value of crystal field parameters, ν_1/ν_2 = 1.17, 10Dq = 26270 cm^{-1} and B = 660 cm^{-1} are consistent with octahedral structure[20].

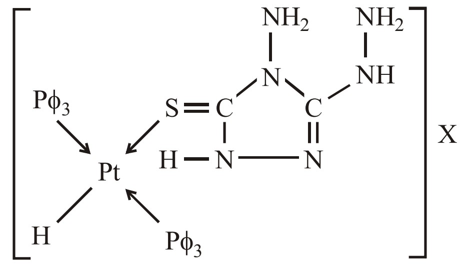
IR Spectra

There are four medium bands at 3230, 3190, 3070 and 3010 cm^{-1} in the IR spectrum of ligand (AHtTH) due to interaction between NH_2 group and –NH – NH_2 group of stretching modes of vibrations.[25] Almost same pattern of multiplet bands are observed in all complexes at the same position indicating absence of bonding through N–atoms. Thioamide band I is a mixed bands[26,27] having major contribution from δNH is either identical or blue shifted (10-20 cm^{-1}) on compexation indicating the intactness of imino nitrogen atom of the ligand. Thioamide band II (1330 cm^{-1}), band III (1090 cm^{-1}) and band IV (715 cm^{-1}) of ligand undergoes red shift on complexation indicating bonding through thione sulphur of ligand (AHtTH).[28-30].

All hydridophosphine complexes of platinum (II) display an infrared absorption band of medium intensity between 2210-2160 cm^{-1} assigned to ν_{Pt-H} and another less intense one between 810 – 800 cm^{-1} due to $\delta_{Pt\text{-}H}$ are in good agreement with the criteria suggested by Chatt et al.[31] A weak band observed at 580 cm^{-1} in Pt (II) complexes and at 575 cm^{-1} in Pd (II) complexes are characteristics of square planar configuration. This new band is neither present in the spectrum of ligand nor in Ru (II), Rh (III) and Ir (III) complexes. Palladium (II) complex exhibits a doublet band[32] below 300 cm^{-1} separated by 10 cm^{-1} due to metal – S stretching mode supports two AHtTH ligands are at trans – position in square planar structure **(IV)**. The presence of a single band at 350 cm^{-1} in all hydrido complexes of platinum (II) also indicates two $P\phi_3$ molecules in trans-position in square planar structure **(VI)**.



(IV)



(VI)

(X = Cl^-, NO_3^-, HSO_4^- and ClO_4^-)

The metal- H stretching mode and bending mode of ruthenium complexes (2120 & 720 cm^{-1}) and at 2225 cm^{-1} and 810 cm^{-1} for rhodium (III) complexes and at 2240 and 790 cm^{-1} for iridium (III) complexes are in agreement with previous reports[33-35]. The presence of single ν_{Ru-P} (445 cm^{-1}), ν_{Rh-P} (435 cm^{-1}) and ν_{Ir-P} (415 cm^{-1}) band in Far – IR indicates two $P\phi_3$ molecules are at trans-position in octahedral structure.

The absorption associated with anions in platinum (II) compexes are indentified at 1360 and 810 cm^{-1} for ionic nitrate[36], at 1090 and 615 cm^{-1} for ionic perchlorate[37] and at 3440, 1260 – 1230, 1060 and 1020 cm^{-1} for bisulphate[38]. The non – ligand bands at 2080 – 2120 cm^{-1} (ν_{CN}), 780-860 cm^{-1} (ν_{CS}) and 460 – 480 cm^{-1} (δ_{NCS}) in thiocyanato complexes of rhodium (I) indicates bonding through nitrogen atom[39] and at 340 and 325 cm^{-1} for coordinated trichlorostannate (II) ion[40]. The ν_{Sn-Cl} of free $SnCl_3^-$ ion are generally observed at 289 and 252 cm^{-1} and shifted to higher frequencies upon coordination to metal ion[41].

Thus, on the basis of aforesaid observations, square planar structure to Rh (I), Pd (II) and Pt (II) and octahedral structure to Ru (II), Rh (III) and Ir (III) complexes may be tentatively assigned.

REFERENCES

1. L. Malatesta, Prog. Inorg. Chem., **1**, 283 (1962).
2. W. Wegman and D. C. Busby, J. Mol. Catal., **n32**, 125 (1985).
3. A. Fouda and G. L. Rempel, Inrog. Chem., **18**, 1 (1979).
4. R. G. Hughes, J. L. Bear and A. P. Kimball, Proc. Am. Assoc. Cancer Res., **13**, 120 (1972).
5. Pattrringg and J. A. Grim, Cancer Res., **27**, 1278 (1967).
6. J. L Bear, H. B. Gray, Jr. L. Rainen, I. M. Chang, R. Howard, G. Cerio and A. P. Kimball, Cancer Chemother. Rep. Part I, **59**, 611 (1975).
7. R. N. Pandey, Arun Kumar, R. S. P. Singh, A. N. Sahay and Shashi Kant Kumar, J. Indian Chem. Soc., **69**, 804 (1992).
8. R. N. Pandey, Sunil Kumar, Shahshikant Kumar, (Miss) Rita Roy Choudhary and A. N. Sahay, Indian J. Chem., **32 A**, 987 (1993).
9. R. N. Pandey and J. N. Das, J. Indian Chem. Soc., **71**, 187 (1997).
10. C. H. L. Kennard and N. W. Issacc, J. Chem. Soc., **36**, 1270 (1971).

11. J. A. Osborn, F. H. Jardine, J. F. young and G. Wilkinson, J. Chem. Soc., A, 1711 (1966).
12. R. N. Pandey, R. N. Sharma, A. N. Sahay, Rita Roy Choudhary and J. N. Das, Asian J. Chem., **Vol. 5**, 639 (1993).
13. U. Agarwala and R. K. Poddar, Indian J. Chem., **9**, 477 (1971).
14. L. Vaska and J. W. Dl. Luzio, J. Am. Chem. Soc., **83**, 2784 (1961).
15. R. N. Pandey, Ashok Kumar and R. N. Sharma, J. Ultra. Chem., **3**, 163 (2007).
16. H. B. Grey and C. J. Ballhausen, J. Am. Chem. Soc., **85**, 260 (1963).
17. W. R. Mason and H. B. Gray, J. Am. Chem. Soc., **90**, 5721 (1968).
18. D. K. Rastogi, A. K. Srivastava, P. C. Jain and B. R. Agarwal, J. Less – Common. Met., **24**, 383 (1971).
19. P. L. Goggin, R. J. Goodfellow and F. J. S. Reed, J. Chem. Soc. Dalton Trans., 1298 (1972).
20. R. K. Upadhyay, J. Indian. Chem. Soc., **72**, 589 (1995).
21. D. K. Datta and M. M. Singh, Transition Met. Chem., **5**, 244 (1980).
22. R. Bandy, B. R. Flynn, G. L. Geoffery, H. B. Gray, J. Peonl, JR. and L. Vaska, Inorg. Chem., **15**, 1485 (1976).
23. N. K. Roy, J. Indian Chem. Soc., **66**, 131 (1989).
24. T. Singh and J. P Singh, J. Indian. Chem. Soc., **69**, 158 (1992).
25. R. V. Gadag and M. R. Gajendragad, J Indian. Chem. Soc., **55**, 789 (1978).
26. C. N. R. Rao and R. Venkataraghavan, Can. J. Chem., **42**, 43 (1964).
27. I. Suzuki, Bull Chem. Soc. Japan, **35**, 1286, 1449 (1962).
28. R. N. Pandey, Manju Sharma and R. N. Sharma, Asian J. Chem., **16**, 1479 (2004).
29. R. N. Pandey, Sanjay Kumar Singh, A. N. Sahay and R. N. Sharma, Oriental J. Chem., **10**, 227 (1994).
30. R. N. Pandey, L. M. Roy Choudhary, (Mrs.) Pramila Sharma, A. N. Shahay and R. N. Sharma, Indian J. Chem., **32A**, 450 (1993).
31. J. Chatt, L. A. Duncanson and B. L. Shaw, Chem. Ind. (Lodon), 859 (1958).
32. D. M. Adams and J. B. Cornell, J. Chem. Soc., A, 884 (1967).

33. D. S. Moore and S. D. Robinson, Chem. Soc. Rev., 415 (1983).

34. G. G. Hlatky and R. H. Crabtree, Coord. Chem. Rev., 65 (1985).

35. R. G. Pearson, Chem. Rev., **85**, 41 (1985).

36. C. C. Addition, R. Davis and N. Logan, J. Chem. Soc., A, 3333 (1970).

37. J. G. Bullitt, F. A. Cotton and J. J. Marks, Inorg. Chem., **11**, 671 (1972).

38. F. Cariati, R. Ugo and F. Bonati, Inorg, Chem., **5**, 1128 (1966).

39. M. A. Jennings and Andrew Wojciki, Inorg. Chem., **6**, 1854 (1967).

40. R. N. Pandey and Shashi Kant Kumar, J. Indian Chem. Soc., **70**, 563 (1993).

41. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 4th Edn, John Wiley and Sons, Inc. New York, (1986) p. 325.

Accepted : 03.12.2009