APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2007; **21**: 788–793

Synthetic and catalytic investigations of ruthenium(III) complexes with triphenylphosphine/triphenylarsine and tridentate Schiff base

S. Priyarega[1], R. Prabhakaran[1], K. R. Aranganayagam[1], R. Karvembu[2] and K. Natarajan[1]*

[1]Department of Chemistry, Bharathiar University, Coimbatore 641 046, India
[2]Department of Chemistry, National Institute of Technology, Tiruchirappalli 620 015, India

Received 19 February 2007; Accepted 5 April 2007

The synthesis and characterization of several hexa-coordinated ruthenium(III) complexes of the type [RuCl(PPh_3)$_2$(L)] (L = dibasic tridentate ligand derived by the condensation of salicylaldehyde/*o*-vanillin with *o*-aminophenol/*o*-aminothiophenol) are reported. IR, electronic, EPR spectral data and redox bahaviour of the complexes are discussed. An octahedral geometry has been tentatively proposed for all the complexes. The new complexes were found to be effective catalysts for the oxidation of benzyl alcohol and cyclohexanol to benzaldehyde and cyclohexanone respectively using *N*-methylmorpholine-*N*-oxide as a co-oxidant. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: ruthenium(III) complexes; Schiff base; triphenylphosphine; triphenylarsine; spectral studies; catalytic oxidation

INTRODUCTION

In the last decade, Schiff base ligands have received much attention because of their application in the fields of synthesis and catalysis. This attention is still growing, so that a considerable research effort is today devoted to the synthesis of new Schiff base complexes with transition metal ions, to further develop applications in the area of catalysis,[1,2] material and pharmaceutical chemistry.[3–5] A recent report reveals that phosphine ligands play a central role in many reactions catalyzed by transition metals.[6–8] In particular, triphenylphosphine complexes of ruthenium have been employed as catalysts for various organic transformations such as oxidation,[9] hydrogenation,[10] C–C couplings,[11] hydroformylation,[12] isomerization,[13] polymerization,[14] racemization,[15] etc. Among these, catalytic oxidation of alcohol to carbonyl compounds is a pivotal reaction due to their utility in fine chemicals and pharmaceutical industries. Ruthenium complexes are known to mediate alcohol oxidation using variety of oxidants such as PhIO,[16] NMO,[17] BrO_3^-,[18] $S_2O_8^-$,[19] *t*-BuOOH,[20] TEMPO[9] and O_2 or air.[21] Our research group has also reported some Ru–PPh_3 complexes as catalysts for oxidation of alcohols in the presence of NMO[22,23] and air.[24,25] In continuation of this, we herein describe synthesis, characterization and catalytic properties of Ru(III) complexes containing PPh_3 or $AsPh_3$ as well as tridentate Schiff bases. The tridentate Schiff bases used in this work are derived from salicylaldehyde/*o*-vanillin and *o*-amino phenol/*o*-aminothiophenol (Scheme 1).

Although monovalent Ru(I),[26] bivalent Co(II), Ni(II), Cu(II), Zn(II) and Ru(II)[27–30] and tetravalent VO(IV)[31,32] metal complexes of H_2L^1 and H_2L^3 have been widely investigated, few studies have been done with trivalent metal complexes.[33,34]

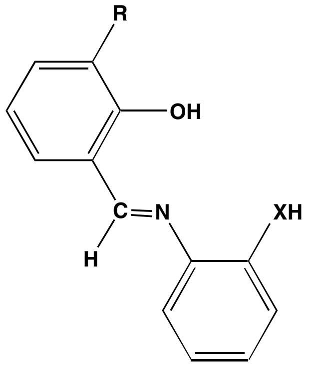
RESULTS AND DISCUSSION

The H_2L3 and H_2L4 ligands exist in two forms as shown in Scheme 2. The yellow compound was isolated and used to prepare the new complexes. Stable ruthenium(III) complexes of the general formula [RuB(EPh_3)$_2$(L)] (B = Cl or Br; E = P or As; L = tridentate Schiff base dianion) have been prepared by reacting [RuB_3(EPh_3)$_3$] (B = Cl or Br; E = P or As) with the respective Schiff bases in a 1 : 1 molar ratio in benzene (Scheme 3).

All the complexes are soluble in most of the common organic solvents. Their purity was checked by thin-layer

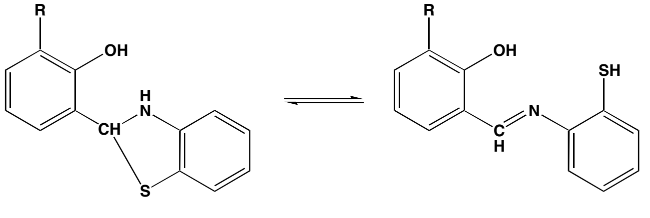
---

*Correspondence to: K. Natarajan, Department of Chemistry, Bharathiar University, Coimbatore 641 046, India.
E-mail: k_natraj6@yahoo.com



R	X	Abbreviation
H	O	H_2L1
OCH_3	O	H_2L2
H	S	H_2L3
OCH_3	S	H_2L4

Scheme 1. Structure of Schiff base ligands (R = H or OCH_3).



White form

Yellow form

Scheme 2. Equilibrium reactions of the H_2L3 and H_2L4 ligands (R = H or OCH_3).

chromatography on silica gel. The analytical data obtained for the new complexes agree well with the proposed molecular formulae. In all of the above reactions, the Schiff bases behave as binegative tridentate ligands.

UV–vis spectra

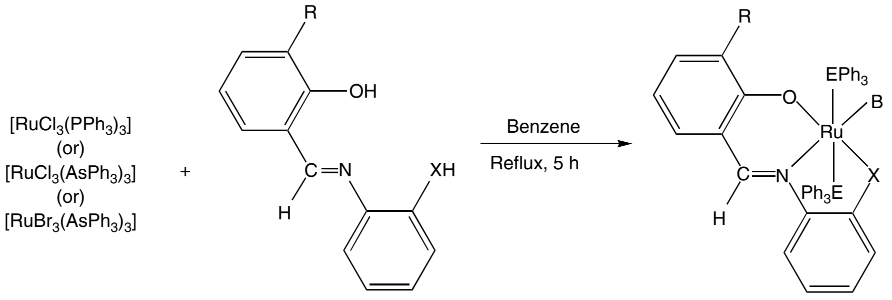
The ground state of ruthenium(III) is $^2T_{2g}$ and the first excited doublet levels in the order of increasing energy are $^2A_{2g}$ and $^2A_{1g}$ which arises from the $t_{2g}{}^4e_g{}^1$ configuration.[35] In most of the ruthenium(III) complexes, the UV–vis spectra show only charge transfer bands.[36] In a d^5 system, and especially in ruthenium(III), which has relatively high oxidizing properties, the charge transfer bands of the type $L_{\pi y} \rightarrow t_{2g}$ are prominent in the low energy region, which obscures the weaker bands due to d–d transition. It therefore becomes difficult to assign conclusively the bands of ruthenium(III) complexes which appear in the visible region.

The electronic spectra of all the complexes in dichloromethane showed two to three bands in the region 440–243 nm (Table 1). These bands have been assigned to charge transfer transitions. Similar observations have been made for other ruthenium(III) octahedral complexes.[5]

IR spectra

The IR spectra of all the ligands exhibited a strong band in the 1600–1635 cm^{-1} region, characteristic of the azomethine (C=N) group. All the Schiff bases displayed a band around 3000 cm^{-1}, which could be due to ν(O–H). The spectra of H_2L3 and H_2L4 showed a weak absorption in the 2500–2600 cm^{-1} region due to ν(S–H).

The IR spectra of the ligands were compared with those of the ruthenium complexes in order to confirm the binding mode of the Schiff base ligands to the ruthenium ion in the complexes (Table 1). In all the complexes, the ν(C=N) band is shifted to lower frequency, 1588–1599 cm^{-1}, indicating coordination of the Schiff bases through the azomethine nitrogen atom.[5] A strong band observed around 1280–1290 cm^{-1} in the free Schiff bases has been assigned to phenolic C–O stretching. On complexation, this band has been shifted to higher frequency (1318–1304 cm^{-1}), showing that the other coordination site is through the phenolic oxygen atom.[23] This is further supported by the disappearance of broad band at 3000 cm^{-1} due to O–H in the complexes. The band corresponding to S–H also disappears in the complexes containing H_2L3 and H_2L4 ligands. Moreover the absorption due to ν(C–S) of H_2L3 and H_2L4 at 1240 cm^{-1} is shifted to 1255–1260 cm^{-1} in the these complexes, indicating



Scheme 3. Formation of new Ru(III) Schiff base complexes (R = H or OCH_3; X = O or S; B = Cl or Br).

Table 1. IR and UV–vis spectral data of ligands and ruthenium(III) complexes[a]

Compounds	ν (C=N)	ν (C–O)	ν (C–S)	Bands due to PPh_3–$AsPh_3$	λ_{max}
H_2L1	1632	1280	—	—	—
H_2L2	1632	1285	—	—	—
H_2L3	1614	1279	1240	—	—
H_2L4	1600	1285	1240	—	—
$[RuCl(PPh_3)_2(L1)]$	1590	1310	—	1433, 1094, 695	420, 300, 270
$[RuCl(PPh_3)_2(L2)]$	1588	1304	—	1433, 1092, 694	440, 306, 243
$[RuCl(PPh_3)_2(L3)]$	1599	1318	1260	1434, 1093, 695	385, 307, 244
$[RuCl(PPh_3)_2(L4)]$	1589	1305	1255	1434, 1091, 696	383, 307, 243
$[RuCl(AsPh_3)_2(L1)]$	1591	1290	—	1431, 1070, 692	428, 309, 247
$[RuCl(AsPh_3)_2(L2)]$	1586	1285	—	1434, 1070, 693	430, 310, 244
$[RuCl(AsPh_3)_2(L3)]$	1593	1314	1235	1436, 1080, 692	450, 307, 245
$[RuCl(AsPh_3)_2(L4)]$	1560	1300	1250	1435, 1079, 692	425, 306, 245
$[RuBr(AsPh_3)_2(L1)]$	1586	1304	—	1433, 1078, 691	410, 300, 245
$[RuBr(AsPh_3)_2(L2)]$	1576	1294	—	1434, 1077, 692	435, 310, 246
$[RuBr(AsPh_3)_2(L3)]$	1589	1295	1270	1436, 1080, 689	435, 307, 245
$[RuBr(AsPh_3)_2(L4)]$	1560	1300	1260	1435, 1075, 692	420, 300, 240

[a] ν in cm^{-1}; λ in nm.

that the third coordination site is a phenolic sulfur atom.[5] The characteristic bands due to triphenylphosphine were observed in the expected regions.

EPR spectra

The solid-state EPR spectra of powdered samples of some of the complexes were recorded at room temperature and the g values are listed in Table 2. The spectra of complexes $[RuCl(PPh_3)_2(L4)]$ and $[RuCl(AsPh_3)_2(L4)]$ showed a single isotropic resonance with g values of 1.84 and 1.75 respectively (Fig. 1). Such isotropic lines are usually observed either due to intermolecular spin exchange, which can broaden the lines, or occupancy of the unpaired electron in a degenerate orbital. However the spectra of complexes $[RuCl(AsPh_3)_2(L2)]$ and $[RuBr(AsPh_3)_2(L3)]$ exhibit three lines with three different g values indicating magnetic anisotropy in these system (Fig. 2). The average g value is in the range 1.73–1.77. The presence of three g values is an indication of rhombic distortion in these complexes. These assignments have been made for similar other octahedral ruthenium complexes of the types $[RuX_2(EPh_3)(L)]$ (where X = Cl or Br; E = P or As; L = tridentate Schiff base anion)[37] and $[RuX(EPh_3)(L)]$ (where X = Cl or Br; E = P or As; L = tetradentate Schiff base dianion).[5]

Table 2. EPR spectral data of ruthenium(III) complexes

Complex	g_x	g_y	g_z	$< g >$[a]
$[RuCl(PPh_3)_2(L4)]$	—	1.84	—	—
$[RuCl(AsPh_3)_2(L2)]$	1.61	1.75	1.82	1.73
$[RuCl(AsPh_3)_2(L4)]$	—	1.75	—	—
$[RuBr(AsPh_3)_2(L3)]$	1.69	1.78	1.83	1.77

[a] $< g > = [1/3\, g_x^2 + 1/3\, g_y^2 + 1/3\, g_z^2]^{1/2}$.

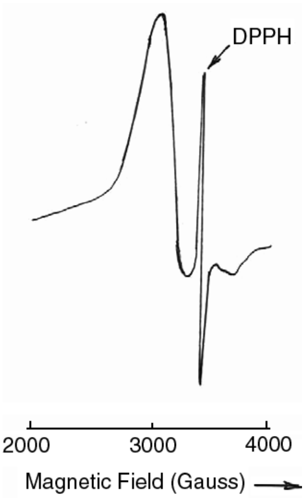


Figure 1. EPR spectrum of $[RuCl(PPh_3)_2(L4)]$.

Electrochemistry

Complexes were electrochemically examined at a glassy carbon working electrode in dichlromethane solution using cyclic voltammetry. A representative voltammogram has been depicted in Fig. 3 and the potential data are listed in Table 3. The complexes display the Ru(III)–Ru(II) and Ru(III)–Ru(IV) couples in the potential ranges −0.43 to −0.67 and 0.83 to 1.17 V respectively vs SCE. In this, the Ru(III)–Ru(II) redox couple is quasi-reversible in nature, with a peak-to-peak separation (ΔE_p) of 120–370 mV, and the Ru(III)–Ru(IV) couple is irreversible. The reason for

Table 3. Cyclic voltammetric data[a] for ruthenium(III) Schiff base complexes

	Ru^{III}–Ru^{IV}				Ru^{III}–Ru^{II}			
Complex	E_{pa} (V)	E_{pc} (V)	ΔE_p (mV)[b]	$E_{1/2}$ (V)[c]	E_{pa} (V)	E_{pc} (V)	ΔE_p (mV)[b]	$E_{1/2}$ (V)[c]
$[RuCl(PPh_3)_2(L1)]$	0.96	—	—	—	−0.64	−0.43	210	−0.535
$[RuCl(PPh_3)_2(L3)]$	1.17	—	—	—	−0.67	−0.55	120	−0.610
$[RuCl(AsPh_3)_2(L4)]$	1.07	—	—	—	−0.64	−0.27	370	−0.625
$[RuCl(AsPh_3)_2(L3)]$	0.83	—	—	—	−0.60	−0.44	160	−0.520

[a] Supporting electrolyte: $[NBu_4]ClO_4$ (0.1 M); scan rate, 100 mV s^{-1}; reference electrode, Ag–AgCl.

[b] $\Delta E_p = E_{pa} - E_{pc}$

[c] $E_{1/2} = 0.5\ (E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are the anodic and cathodic peak potentials in Volts, respectively.

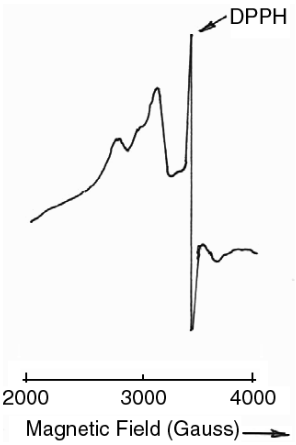


Figure 2. EPR spectrum of $[RuCl(AsPh_3)_2(L2)]$.

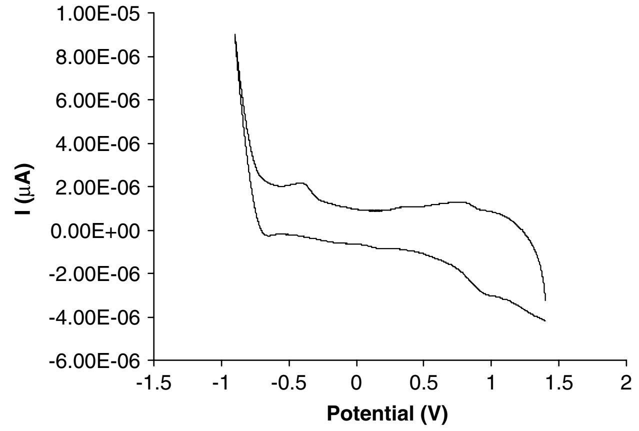
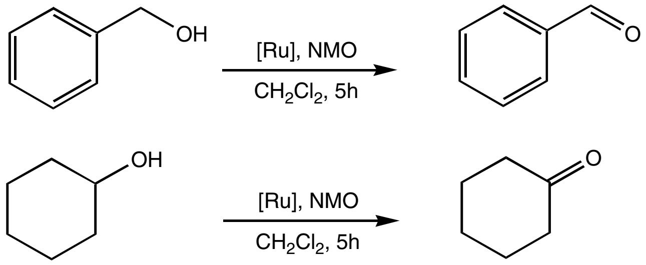


Figure 3. Cyclic voltammogram of $[Ru(L1)(PPh_3)_2Cl]$.

the irreversibility of these complexes may be oxidative degradation or the short-lived oxidized state of the metal ion.[38] The $E_{1/2}$ value of a complex containing a thiophenolato donor is more cathodic than that of a complex containing phenolato donor. Coordination of the sulfur atom makes the metal center more electron-rich and shifts the oxidation potential towards more negative values.[39]



Scheme 4. Catalytic oxidation of alcohols by Ru(III) complexes.

On the basis of the analytical and spectral results discussed so far, a hexa coordinated octahedral geometry is suggested for new ruthenium(III) complexes (Scheme 3).

Catalytic studies

The oxidation of benzyl alcohol and cyclohexanol was carried out with new ruthenium complexes in the presence of *N*-methylmorpholine-*N*-oxide (NMO) as cooxidant and dichloromethane as solvent (Scheme 4). Benzaldehyde was formed from benzyl alcohol and cyclohexanol was converted into cyclohexanone after refluxing for about 5 h, which was then quantified as its 2,4-dinitrophenylhydrazone derivatives. There was no detectable oxidation of alcohol in the presence of NMO alone. All the synthesized complexes were found to catalyze the oxidation of alcohols to aldehydes, but the yield and the turnover vary with the different catalysts used (Table 4). The relatively higher product yield obtained for oxidation of benzyl alcohol compared with cyclohexanol is due to the fact that α-CH unit of benzylalcohol is more acidic than cyclohexanol.[33] The yields obtained from the reactions catalyzed by Ru-PPh_3 complexes (entries 1–8) are greater compared with that of Ru–$AsPh_3$ complexes (entries 9–12). A high valency Ru(V)–oxo complex is expected to be the active species in the catalytic processes as reported previously.[23]

EXPERIMENTAL

All the solvents used were dried and purified by standard methods. IR spectra were recorded as KBr pellets with

DOI: 10.1002/aoc

Table 4. Catalytic activity data[a] of ruthenium(III) complexes

Entry	Complexes	Substrate	Product	Yield (%)[b]	Turnover number[c]
1	$[RuCl(PPh_3)_2(L1)]$	Benzyl alcohol	A	62	65
2		Cyclohexanol	K	45	47
3	$[RuCl(PPh_3)_2(L2)]$	Benzyl alcohol	A	67	68
4		Cyclohexanol	K	44	45
5	$[RuCl(PPh_3)_2(L3)]$	Benzyl alcohol	A	65	67
6		Cyclohexanol	K	39	40
7	$[RuCl(PPh_3)_2(L4)]$	Benzyl alcohol	A	67	69
8		Cyclohexanol	K	34	36
9	$[RuCl(AsPh_3)_2(L1)]$	Benzyl alcohol	A	51	53
10		Cyclohexanol	K	32	33
11	$[RuBr(AsPh_3)_2(L1)]$	Benzyl alcohol	A	48	50
12		Cyclohexanol	K	38	40

[a] A, benzaldehyde; K, cyclohexanone; reaction time, 5 h.
[b] Yields based on substrate.
[c] Turnover number = moles of product per mole of catalyst.

a Nicolet FT-IR spectrophotometer in the 4000–400 cm^{-1} range. Electronic spectra of the complexes were recorded in dichloromethane solutions using a Shimadzu spectrophotometer in the 800–200 range. Magnetic susceptibility measurements were made with an EG & G-Parc vibrating sample magnetometer. Microanalyses were carried out with a VarioEL AMX-400 elemental analyzer. EPR spectra of powdered samples were recorded with a Jeol TEL-100 instrument at X-band frequencies at room temperature. Cyclic voltammetric studies were carried out with a BAS CV-27 model electrochemical analyzer in acetonitrile using a glassy-carbon working electrode and the potentials were referenced to an Ag–AgCl electrode. Melting points were recorded with a Boetius micro heating table and were uncorrected. The starting complexes $[RuCl_3(PPh_3)_3]$,[40] $[RuCl_3(AsPh_3)_3]$,[41] $[RuBr_3(AsPh_3)_3]$[42] and the ligands[43,44] were prepared by reported literature methods.

Preparation of ruthenium(III) complexes

To a solution of $[RuB_3(EPh_3)_3]$ (B = Cl or Br; E = P or As) (0.9–0.1g; 0.1 mmol) in benzene (25 ml), an appropriate Schiff base ligand (0.1 mmol) was added (molar ratio of ruthenium complex to Schiff base was 1 : 1). The solution was heated under reflux for 6 h. Then it was concentrated to a small volume (3 ml) and the new complex was separated from it by the addition of a small quantity (6 ml) of petroleum ether (60–80 °C). The product was filtered, washed with petroleum ether and crystallized from CH_2Cl_2–petroleum ether (60–80 °C) mixture and dried *in vacuo*. Yield: 65–72%.

Procedure for catalytic oxidation

To a solution of alcohol (1 mmol) in dichloromethane (20 ml), *N*-methylmorpholine-*N*-oxide (3 mmol) and the ruthenium complex (0.01 mmol) were added. The solution was refluxed for 5 h. The mixture was evaporated to dryness and extracted with petroleum ether (60–80 °C). The combined petroleum ether extracts were filtered and evaporated to give the corresponding carbonyl compound which were then quantified as their 2,4-dinitrophenylhydrazones.

REFERENCES

1. Leung WH, Chan EYY, Chow EKF, Williams ID, Peng SM. *J. Chem. Soc. Dalton Trans.* 1996; 1229.
2. Wong WK, Chen XP, Guo JP, Chi YG, Pan WX, Wong WY. *J. Chem. Soc. Dalton Trans.* 2002; 1139.
3. Katsuki T. *Curr. Org. Chem.* 2001; **5**: 663.
4. Ramesh R, Maheshwaran S. *J. Inorg. Biochem.* 2003; **96**: 457.
5. Prabhakaran R, Geetha A, Thilagavathi M, Karvembu R, Krishnan V, Bertagnolli H, Natarajan K. *J. Inorg. Biochem.* 2004; **98**: 2131.
6. Pignolet LH (ed.). *Homogeneous Catalysis with Metal Phosphine Complexes*. Plenum Press: New York, 1983.
7. Simpson MC, Cole-Hamilton DJ. *Coord. Chem. Rev.* 1996; **155**: 163.
8. Cornils B, Herrmann WH (eds). *Applied Homogeneous Catalysis with Organometallic Compounds*. VCH: Weinheim, 1996.
9. Sheldon RA, Arends IWCE, Brink G-JT, Dijksman A. *Acc. Chem. Res.* 2002; **35**: 774.
10. Doucet H, Ohkuma T, Murata K, Yokozawa T, Kozawa M, Katayama E, England AF, Ikariya T, Noyori R. *Angew. Chem. Int. Edn* 1998; **37**: 1703.
11. Baratta W, Herrmann , Kratzer RM, Rigo P. *Organometallics* 2000; **19**: 3664.
12. Ahn HS, Han SH, Uhm SJ, Seok WK, Lee HN, Korneeva GA. *J. Mol. Cat. A: Chem.* 1999; **144**: 295.
13. Serron SA, Haar CM, Nolan SP. *Organometallics* 1997; **16**: 5120.
14. Ando T, Kamigaito M, Sawamoto . *Macromolecules* 2000; **33**: 5825.
15. Persson BA, Larsson ALE, Ray ML, Backvall JE. *J. Am. Chem. Soc.* 1999; **121**: 1645.
16. Muller P, Godoy J. *Tetrahedron Lett.* 1981; **22**: 2361.
17. Bhowon MG, Li Kam WH, Narain R. *Polyhedron* 1998; **17**: 341.
18. Griffith WP. *Coord. Chem. Rev.* 1992; **21**: 179.
19. Bailey AJ, Cother LD, Griffith WP, Hankin DM. *Transition Met. Chem.* 1995; **20**: 590.
20. El-Hendawy AM, Al-Kubaisi AH, Al-Madfa HA. *Polyhedron* 1997; **16**: 3039.

DOI: 10.1002/aoc

21. Wolfson A, Wuyts S, De Vos DE, Vankelecom IFJ, Jacobs PA. *Tetrahedron Lett.* 2002; **43**: 8107.
22. Karvembu R, Natarajan K. *Polyhedron* 2002; **21**: 1721.
23. Karvembu R, Hemalatha S, Prabhakaran R, Natarajan K. *Inorg. Chem. Commun.* 2003; **6**: 486.
24. Karvembu R, Natarajan K. *Polyhedron* 2002; **21**: 219.
25. Kaveri MV, Prabhakaran R, Karvembu R, Natarajan K. *Spectrochim. Acta A* 2005; **61**: 2915.
26. Khalil MMH, Aboaly MM. Ramadan RM. *Spectrochim. Acta A* 2005; **61**: 157.
27. Aboaly MM, Khalil MMH. *Spectrosc. Lett.* 2001; **34**: 495.
28. Soliman AA, Linert W. *Thermochim. Acta* 1999; **338**: 67.
29. Jayabalakrishnan C, Natarajan K. *Transition Met. Chem.* 2002; **27**: 75.
30. Sinha PK, Falvello LR, Bhattacharya S. *Indian J. Chem.* 2004; **43A**: 1846.
31. Ando R, Ono H, Yagyu T, Maeda M. *Inorg. Chim. Acta* 2004; **357**: 817.
32. Maurya MR. *Coord. Chem. Rev.* 2003; **237**: 163.
33. Chatterjee D, Mitra A, Mukherjee S. *J. Mol. Cat. A: Chem.* 2001; **165**: 295.
34. Chatterjee D, Mitra A, Roy BC. *React. Kinet. Catal. Lett.* 2000; **70**: 147.
35. Ballhausen CJ. *Ligand Field Theory*. McGraw Hill: New York, 1962.
36. Lever ABP. *Inorganic Electronic Spectroscopy.* Elsevier: New York, 1989.
37. Saridha K, Karvembu R, Viswanathamurthi P, Yasodhai S. *Synth. React. Inorg. Met.- Org. Nano-Met. Chem.* 2005; **35**: 707.
38. Bond AM, Colton R, Mann DR. *Inorg. Chem.* 1990; **29**: 4665.
39. Chatterjee D, Mitra A. *J. Coord. Chem.* 2004; **57**: 175.
40. Chatt J, Leigh G, Mingos DMP, Paske RJ. *J. Chem. Soc. (A)* 1968; 2636.
41. Poddar RK, Khullar IP, Agarwala U. *Inorg. Nucl. Chem. Lett.* 1974; **10**: 221.
42. Natarajan K, Poddar RK, Agarwala U. *J. Inorg. Nucl. Chem.* 1977; **39**: 431.
43. Mazzi U, Refosco F, Tisato F, Bandoli G, Nicolini M. *J. Chem. Soc. Dalton Trans.* 1986; 1623.
44. Tisato F, Refosco F, Mazzi U, Bandolin U, Nicolini M. *J. Chem. Soc. Dalton Trans.* 1987; 1693.

DOI: 10.1002/aoc