Asian Journal of Chemistry Vol. 21, No. 8 (2009), 6335-6342

Syntheses and Characterization of Coordination Compounds of Monobasic Bidentate OS Donor Polystyrene-Anchored Azetidinone

DINESH KUMAR*, AMIT KUMAR†, DURGA DASS‡ and PRAVEEN KUMAR GUPTA†
Department of Chemistry, National Institute of Technology, Kurukshetra-136 119, India
E-mail: dkumar_nitk@yahoo.com

The nucleophillic addition reaction followed by the elimination of one water molecule between polystyrene 3-formylsalicylate ($PSCH_2$-Fsal) and 2-aminoethanethiol in DMF in presence of ethyl acetate and triethylamine results in the formation of polystyrene N-(2-thiohydroxyethyl)-2′-hydroxybenzalideneimine-3′-carboxylate ($PSCH_2$-LH_2). A dioxane suspension of $PSCH_2$-LH_2 reacts with chloroacetyl chloride in presence of triethylamine to form polystyrene N-(2-thiohydroxyethyl)-4-(3'-carboxy-2'-hydroxyphenyl)azetidin-2-one, $PSCH_2$-L'H_2 (**I**). A DMF suspension of **I** reacts with appropriate metal ions and forms [$PSCH_2$-L'HM(OAc)·DMF] [where M = Cu(II), Co(II), Zn(II), Cd(II), UO_2(VI)], [$PSCH_2$-L'HM'(OAc)·3DMF] [here M' = Ni(II), Mn(II)], [$PSCH_2$-L'HMoO_2-(acac)] and [$PSCH_2$-L'HZr$(OH)_3$· 2DMF]. A square planar structure to [$PSCH_2$-L'HM(OAc)·DMF] [here M = Cu(II), Co(II)]; a tetrahedral structure to [$PSCH_2$-L'HM'(OAc)· DMF] [here M' = Zn(II), Cd(II)]; an octahedral structure to [$PSCH_2$-L'HM'(OAc)·3DMF] [here M' = Ni(II), Mn(II)] and [$PSCH_2$-L'HM(OAc)·DMF] [here M = MoO_2(VI), UO_2(VI)] and a pentagonal bipyramidal structure to [$PSCH_2$-L'HZr$(OH)_3$·2DMF] have been suggested. The compounds of Cu(II), Co(II), Ni(II) and Mn(II) are paramagnetic and magnetically dilute, while those of others are diamagnetic. This is the first report on the polystyrene-anchored coordination compounds containing the versatile therapeutic azetidinone moiety.

Key Words: Polystyrene-anchored azetidinone, Magnetically dilute, Paramagnetic.

INTRODUCTION

β-Lactams, the most versatile antibiotics used in medicines are the 2-carbonyl derivatives of azetidine. Their biological activities are associated with the chemical reactivity of the β-lactam ring[1]. The most widely used antibiotics such as penicillins, cephalosporins and the nocardicins all contain β-lactam ring[2]. They are known to be associated with anticancer, analgesic, insecticidal and other powerful therapeutic

---

†Department of Chemistry, Haryana College of Technology & Management, Kaithal-136 027, India.

‡Department of Chemistry, Shri Krishan Institute of Engineering & Technology, Kurukshetra-136 118, India.

activities like antibacterial, antimicrobial, anticonvulsant, antiinflammatory, antitubercular, antifungal, sedatives and antidepressant[3]. They are also employed as intermediates in chemical synthesis and in the treatment of chemotherapeutic diseases[4]. The reaction of polymer-anchored organic ligands with metal ions provides an easy route for the syntheses of immobilized transition metal coordination compounds[5]. A perusal of the literature indicates that several polymer-anchored ligands containing oxygen and sulphur atoms like dithiocarbamates[6] and thiosalicylic acid[7], *etc.* have been reported. However there is no report on the coordination compounds of polymer-anchored ligand containing azetidinone moiety. The present report is related to the syntheses and characterization of some method coordination compounds of polystyrene-anchored azetidinone, $PSCH_2$-L'H_2 (**I**). It is expected that the present compounds will find the therapeutic and biological activities.

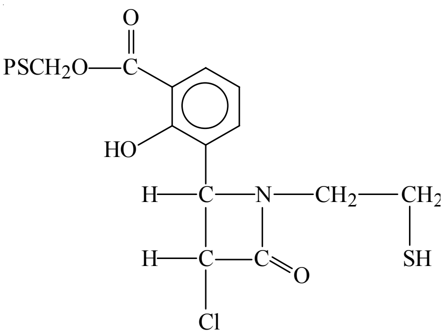

Fig. 1. Structure of polystyrene-anchored azetidinone (**I**)

EXPERIMENTAL

2-Aminoethanethiol hydrochloride [Aldrich], chloroacetyl chloride [Ranbaxy], chloromethylated polystyrene, $PSCH_2$-Cl (containing 1.17 mmol of Cl per g of resin and 1 % crosslinked with divinylbenzene) [Sigma] and other chemicals and solvents used for the syntheses were obtained from the sources mentioned earlier[8].

Analyses and physical measurements: The leaching of metal ions from the corresponding polystyrene-anchored coordination compounds and the estimation of the former was carried out as per reported procedures[9]. The coordinated DMF molecules were determined by heating the corresponding polystyrene-anchored coordination compounds in an air oven at a definite temperature for 3 h.

Synthesis of polystyrene N-(2-thiohydroxyethyl)-2′-hydroxybenzalideneimine-3′-carboxylate ($PSCH_2$-LH_2): CH_3COONa (0.38 g, 4.68 mmol) was added to a DMF-MeOH solution (50 mL) of 2-aminoethanethiol hydrochloride (0.53 g, 4.68 mmol). The mixture was stirred for 5 min and separated NaCl was filtered off. Polystyrene 3-formylsalicylate ($PSCH_2$-Fsal) (1.0 g) was allowed to suspend and swell in DMF (100 mL) for 45 min. To this suspension, the above filtrate and ethyl acetate (100 mL) were added, while stirring magnetically. The mixture was refluxed for 8 h and then was cooled to room temperature. $\text{PSCH}_2\text{-LH}_2$ obtained was suction filtered, washed with DMF and ethyl acetate. The compound was dried under vacuum at room temperature.

Synthesis of polystyrene N-(2-thiohydroxyethyl)-4-[(3'-carboxy-2'-hydroxyphenyl)azetidin-2-one ($\text{PSCH}_2\text{-L'H}_2$) (I): $\text{PSCH}_2\text{-LH}_2$ (1.0 g) was allowed to suspend and swell in dioxane (100 mL) for 1 h. To this suspension, triethylamine (0.35 g, 3.51 mmol) was added and the mixture was cooled to 5 ºC. Chloroacetyl chloride (0.26 g, 2.34 mmol) was added dropwise during a period of 8 h, while constant stirring magnetically. The solid product obtained was washed several times with chilled water. The product was then suction filtered, washed with dioxane and dried under vacuum at room temperature.

Syntheses of coordination compounds of $\text{PSCH}_2\text{-L'H}_2$ (I): $\text{PSCH}_2\text{-L'H}_2$ (**I**) (1.0 g) was allowed to suspend and swell in DMF (100 mL) for 1 h. A DMF solution of appropriate metal salt (2.34 mmol) was added to the above suspension. The mixture was refluxed on water bath for 8-10 h and the products obtained were suction filtered, washed several times with ethyl acetate and DMF. The products were then dried as mentioned above.

RESULTS AND DISCUSSION

Chloroacetyl chloride reacts with polystyrene N-(2-thiohydroxyethyl)-2′-hydroxybenzalideneimine-3′-carboxylate ($\text{PSCH}_2\text{-LH}_2$) in presence of triethylamine in dioxane and forms polystyrene N-(2-thiohydroxyethyl)-4-(3'-carboxy-2'-hydroxyphenyl)azetidin-2-one, $\text{PSCH}_2\text{-L'H}_2$ (**I**). A DMF suspension of **I** reacts with Cu(II), Co(II), Zn(II), Cd(II), Ni(II), Mn(II), Zr(IV), MoO_2(VI) and UO_2(VI) ions in 1:2 molar ratio to form the corresponding coordination compounds. The per cent reaction conversion (PRC) of polystyrene-anchored coordination compound is 50.3-89.3 (Table-1). The metal binding capacity (MBC) of **I** is between 0.35-0.64 mmol per gram of resin. The formation of the polystyrene-anchored azetidinone (**I**) and its coordination compounds takes place as per the **Schemes I** and **II**.

$$\text{PSCH}_2\text{-Fsal} + \text{H}_2\text{N-CH}_2\text{-CH}_2\text{-SH} \xrightarrow[\text{reflux}]{\text{DMF, ethyl acetate}} \text{PSCH}_2\text{-LH}_2 + \text{H}_2\text{O}$$

$$\text{PSCH}_2\text{-LH}_2 \xrightarrow[\text{Triethylamine/Dioxane}]{\text{Chloroacetyl chloride}} \text{PSCH}_2\text{-L'H}_2\ (\mathbf{I})$$

Scheme-I: Method of preparation of polystyrene-anchored Schiff base and its azetidinone

Infrared spectral studies: Infrared spectra of **I** and its coordination compounds were recorded in KBr and the important peaks are shown in Table-2. $\text{PSCH}_2\text{-LH}_2$ exhibits ν(C=N)(azomethine) stretch[8] at 1610 cm^{-1}. This band disappears in **I** and a new band at 1410 cm^{-1} appears due to ν(C–N)(β-lactam) stretch[10] indicating the

TABLE-1
ANALYTICAL, MBC AND PRC VALUES OF POLYSTYRENE-ANCHORED COORDINATION COMPOUNDS[a]

Compounds	Found (Calcd.) %		MBC[b] mmol/g of resin	PRC[c] %
	M	DMF		
$[PSCH_2–L'HCu(OAc)·DMF]$	3.7 (4.83)	4.2 (5.55)	0.58	76.6
$[PSCH_2–L'HCo(OAc)·DMF]$	2.5 (4.50)	3.1 (5.57)	0.42	55.6
$[PSCH_2–L'HZn(OAc)·DMF]$	4.2 (4.97)	4.5 (5.55)	0.64	84.5
$[PSCH_2–L'HCd(OAc)·DMF]$	5.6 (8.25)	3.6 (5.36)	0.50	67.9
$[PSCH_2–L'HUO_2(OAc)·DMF]$	10.9 (15.65)	3.4 (4.80)	0.46	69.6
$[PSCH_2–L'HNi(OAc)·3DMF]$	3.6 (4.03)	13.4 (15.05)	0.61	89.3
$[PSCH_2–L'HMn(OAc)·3DMF]$	1.9 (3.78)	7.5 (15.09)	0.35	50.3
$[PSCH_2–L'HMoO_2(acac)]$	4.3 (7.13)	–	0.45	60.3
$[PSCH_2–L'HZr(OH)_3·2DMF]$	4.1 (6.48)	6.6 (10.38)	0.45	63.3

[a] Abbreviations: $PSCH_2–L'H_2$ = **I**.

[b] MBC = [M % (observed) × 10]/(atomic weight of metal).

[c] PRC = [M % (observed) × 100]/M % (calculated) on the basis of 100 % reaction conversion of polystyrene-anchored ligand to polystyrene-anchored coordination compounds.

$$I + M(OAc)_2 \xrightarrow[Reflux]{DMF} [PSCH_2\text{-}L'HM(OAc)\cdot DMF] + CH_3COOH$$

$$[M = Cu(II), Co(II), Zn(II), Cd(II), UO_2(VI)]$$

$$I + M'(OAc)_2 \xrightarrow[Reflux]{DMF} [PSCH_2\text{-}L'HM'(OAc)\cdot 3DMF] + CH_3COOH$$

$$[M' = Ni(II), Mn(II)]$$

$$I + MoO_2(acac)_2 \xrightarrow[Reflux]{DMF} [PSCH_2\text{-}L'HMoO_2(acac)] + acacH$$

$$I + [Zr_4(OH)_8(H_2O)_{16}](OAc)_8 \xrightarrow[Reflux]{DMF} 4[PSCH_2\text{-}L'HZr(OH)_3\cdot 2DMF] + 8CH_3COOH + 16H_2O$$

Scheme-II: Method of preparation of polystyrene-anchored coordination compounds of **I**

TABLE-2
IR, REFLECTANCE SPECTRAL DATA (cm^{-1}) AND MAGNETIC MOMENTS OF COORDINATION COMPOUNDS

Compound	ν(C=O) (β-lactam)	ν(C=O) (DMF)	$\nu_{as}(CO_2)$ (acetate)	$\nu_s(CO_2)$ (acetate)	ν_{as}(C–S) (thioalcoholic)	ν_{max}	μ_{eff} (BM)
$PSCH_2$–L'H_2 (**I**)	1736	–	–	–	750	–	Diamagnetic
[$PSCH_2$–L'HCu(OAc)·DMF]	1710	1665	1570	1350	700	17150	1.92
[$PSCH_2$–L'HCo(OAc)·DMF]	1715	1650	1565	1360	685	8380, 22900	2.36
[$PSCH_2$–L'HNi(OAc)·3DMF]	1710	1665	1570	1355	690	9460, 16400, 25000	3.12
[$PSCH_2$–L'HMn(OAc)·3DMF]	1724	1650	1575	1370	705	18390, 22850, 25360	5.83
[$PSCH_2$–L'HZn(OAc)·DMF]	1718	1655	1580	1360	695	–	Diamagnetic
[$PSCH_2$–L'HCd(OAc)·DMF]	1708	1660	1585	1365	700	–	Diamagnetic
[$PSCH_2$–L'HZr$(OH)_3$·2DMF]	1700	1650	1570	1370	702	–	Diamagnetic
[$PSCH_2$–L'HMoO_2(acac)]	1720	–	–	–	692	–	Diamagnetic
[$PSCH_2$–L'HUO_2(OAc)·DMF]	1718	1670	1590	1355	705	–	Diamagnetic

formation of corresponding azetidinone. The ν(C-O) ϕ stretch[8] of **I** occurs at 1550 cm^{-1}. This band remains unchanged in coordination compounds indicating the non-involvement of phenolic O atom towards coordination. **I** exhibits ν(C=O) (β-lactam) stretch[11] at 1736 cm^{-1}. This band shifts to lower energy by 12-36 cm^{-1} in coordination compounds indicating the coordination of O atom of β-lactam moiety with metal ions. The ν(C-Cl) stretch[11] of **I** occurring at 735 cm^{-1} remains unchanged in the coordination compounds indicating the non-involvement of Cl atom towards coordination. A medium intense band at 2520 cm^{-1} in **I** is assigned to ν(S-H) stretch[12]. The disappearance of this band in the coordination compounds indicates the deprotonation of thiol group and subsequent coordination of S atom to metal ion[13]. The ν(C-S) (thioalcoholic) stretch[12] of **I** occurs at 750 cm^{-1}. This band undergoes negative shift by 45-65 cm^{-1} in the coordination compounds indicating the involvement of S atom towards coordination. Thus, IR data are indicative of monobasic bidentate OS donor behaviour of **I**. DMF shows a band at 1680 cm^{-1} due to ν(C=O) stretch. This band shifts to lower energy by 10-30 cm^{-1} in the coordination compounds indicating the involvement of O atom towards coordination[14]. The $\nu_{sym}(CO_2)$ and $\nu_{asym}(CO_2)$ stretches of free CH_3COO^- occur at 1416 and 1560 cm^{-1}, respectively. The $\nu_{sy}(CO_2)$ and $\nu_{asy}(CO_2)$ stretches in coordination compounds occur in the range: 1370-1350 and 1590-1565 cm^{-1}, respectively. The magnitude of energy separation ($\Delta\nu$ = 200-235 cm^{-1}) between $\nu_{sy}(CO_2)$ and $\nu_{asy}(CO_2)$ is > 144 cm^{-1} and it indicates the monodentate nature of CH_3COO^- ions, since in the event of bidentate coordination, the energy separation[15] between ν_{sy}(COO) and ν_{asy}(COO) is < 144 cm^{-1}. [$PSCH_2$-L'HUO_2(OAc)·DMF] exhibits ν_{asy}(O=U=O) stretch at 915 cm^{-1} and this band occurs in the usual range (870-950 cm^{-1}) observed for the majority of *trans*-UO_2 compounds[8,15]. [$PSCH_2$-L'$HMoO_2$(acac)] exhibits the ν_{sy}(O=Mo=O) and ν_{asy}(O=Mo=O) stretches at 945 and 915 cm^{-1} and these bands occur in the usual range (892-964 cm^{-1}; 842-928 cm^{-1}) reported for the majority of MoO_2(VI) compounds[8,15]. The presence of ν_{sy}(O=Mo=O) and ν_{asy}(O=Mo=O) bands indicates a *cis*-MoO_2 structure as the compounds with *trans*-MoO_2 structure exhibit only the ν_{asy}(O=Mo=O) since the ν_{sy}(O=Mo=O) is IR inactive[16]. The absence of a band between 850-950 cm^{-1}, characteristic of ν(Zr=O) stretch in Zr(IV) compound suggests its structure as [$PSCH_2$-L'HZr$(OH)_3$·2DMF] and not as [$PSCH_2$-L'HZrOH·2DMF]. The appearance of a band at 1130 cm^{-1} due to δ(ZrOH)[8,15] also supports the suggested structure of the compound.

Magnetic measurements: The room temperature magnetic susceptibilities and magnetic moments of the polystyrene-anchored coordination compounds of **I** are presented in Table-2. The polystyrene-anchored compounds of Cu(II), Ni(II), Co(II) and Mn(II) exhibit magnetic moments of 1.92, 3.12, 2.36 and 5.83 BM, respectively. These values are indicative of the magnetically dilute nature of the compounds[8]. The polystyrene-anchored coordination compounds of Zn(II), Cd(II), Zr(IV) and MoO_2(VI) are diamagnetic as expected. Thus, the data suggest a square planar structure to [$PSCH_2$-L'HCu(OAc)·DMF], [$PSCH_2$-L'HCo(OAc)·DMF]; a tetrahedral structure to [$PSCH_2$-L'HZn(OAc)·DMF], [$PSCH_2$-L'HCd(OAc)·DMF]; an octahedral structure to [$PSCH_2$-L'HNi(OAc)·3DMF], [$PSCH_2$-L'HMn(OAc)·3DMF], [$PSCH_2$-L'$HMoO_2$(acac)], [$PSCH_2$-L'HUO_2(OAc)·DMF] and a pentagonal bipyramidal structure to [$PSCH_2$-L'HZr$(OH)_3$·2DMF].

Reflectance spectral studies: Nujol mull electronic spectra of the compounds could not be recorded as they do not form a good mull and hence their reflectance spectra were recorded (Table-2). The compounds being insoluble in common solvents, their solution electronic spectra also could not be recorded. [$PSCH_2$-L'HCu(OAc)·DMF] exhibits a band at 17150 cm^{-1} which is assigned to $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{2g}$ and ^2E_g transitions for square planar arrangement of ligand around Cu(II) ions[8,15]. The absence of a band between 8000-10000 cm^{-1} precludes the presence of a tetrahedral structure[17]. [$PSCH_2$-L'HCo(OAc)·DMF] exhibits two bands one at 8380 cm^{-1} and another at 22900 cm^{-1} which is in the usual range (8400-8550 and 21000-24500 cm^{-1}) due to $^1A_{1g} \rightarrow {}^1B_{2g}$ and $^1A_{1g} \rightarrow {}^1B_{1g}$ transitions, respectively in a square planar symmetry[18]. [$PSCH_2$-L'HNi(OAc)·3DMF] exhibits three bands at 9460, 16400 and 25000 cm^{-1} due to the $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1), $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$($\nu_2$) and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (ν_3) transitions, respectively in an octahedral symmetry[8,15]. The ν_2/ν_1 value is 1.73 and lies in the usual range (1.60-1.82) reported for majority of octahedral Ni(II) compounds[19]. The spectral parameters[18] are: Dq = 946 cm^{-1}, B' = 790 cm^{-1}, β = 0.75 and β^0 = 25 %. The reduction of Racah parameter from the free ion value (1056 cm^{-1}) to 790 cm^{-1} and β^0 value (25 %) are indicative of the strong covalent nature of the compound[18].

[PSCH$_2$-L'HMn(OAc)·3DMF] exhibits three bands at 18390, 22850 and 25360 cm^{-1} due to $^6A_{1g} \rightarrow {}^4T_{1g}(G)$, $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ and $^6A_{1g} \rightarrow {}^4A_{1g}(G)$ transitions, respectively in an octahedral environment[18,19].

ESR Studies: The presence of diamagnetic large polymer backbone keeps the metal centers in the polystyrene-anchored compounds considerably separated, which avoid dipolar broadening. As a result, reasonably good ESR spectrum was observed in polycrystalline solids in the absence of a host diamagnetic coordination compound diluent. [PSCH$_2$-L'HCu(OAc)·DMF] exhibits two g values ($g_\parallel = 2.24$, $g_\perp = 2.08$) and this indicates the presence of a tetragonal type symmetry about the Cu(II) ion[20]. The spectral parameters are: $A_\parallel = 1.64 \times 10^{-2}$ cm^{-1}, $A_\perp = 3.27 \times 10^{-3}$ cm^{-1}, G = 3.05, $g_\parallel/A_\parallel = 136$, $\alpha^2_{Cu} = 0.77$, $(\alpha')^2 = 0.30$, k = 0.50, $g_{av} = 2.13$ and $P_d = 1.68 \times 10^{-2}$ cm^{-1}. The data indicate that $g_\parallel > g_\perp$ and $A_\parallel > A_\perp$ which are indicative of the presence of the unpaired electron in the $d_{x^2-y^2}$ orbital[21]. For ionic environments, $g_\parallel$ is normally ≥ 2.3 and is < 2.3 for covalent environments. The $g_\parallel$ value (2.24) indicates that the metal-ligand bonding in the compound is covalent. For tetragonal Cu(II) compounds, if G is less than 4.0, the ligand forming the Cu(II) compound is regarded as a strong field ligand. G value (3.05) indicates the strong field nature of the polystyrene-anchored ligand. α^2_{Cu} value (0.77) and $(\alpha')^2 = 0.30$ indicate its covalent nature. The smaller the value of α^2_{Cu}, the more covalent is the bonding; $\alpha^2_{Cu} = 1$ indicates completely ionic bonding, while $\alpha^2_{Cu} = 0.5$ indicates completely covalent bonding[21]. The larger the value of the $(\alpha')^2$, the more covalent is the bonding; $(\alpha')^2 = 0$ suggests a complete ionic bonding[21]. The positive value of κ suggests that $A_\parallel$ should be greater than $A_\perp$ and it has also been observed in present studies. The lower value of P_d in comparison to that of the free ion value (3.5×10^{-2} cm^{-1}) indicates the presence of covalent character between the metal-ligand bonding. The absence of any band *ca.* 1500 G due to the ΔMs = 2 transitions precludes the presence of M-M interaction. The metal atoms are placed on phenyl rings (of polystyrene) which are 6 to 7 styrene units apart when the per cent conversion is < 100 %. This results in a magnetically dilute environment around the metal atom as the pathway for the dimmer formation with M-M interaction is blocked. However, since the polymer is cross-linked with polymer chains overlapped and twisted, some of the reactive groups may come close to one another resulting in some M-M interaction which was not detectable by ESR studies.

Conclusion

The present study reveals that [PSCH$_2$-L'HCu(OAc)·DMF] and [PSCH$_2$-L'HCo (OAc)·DMF] compounds are paramagnetic and exhibit square-planar structure; [PSCH$_2$-L'HNi(OAc)·3DMF] and [PSCH$_2$-L'HMn(OAc)·3DMF] compounds are paramagnetic and have octahedral structure; [PSCH$_2$-L'HCd(OAc)·DMF] and [PSCH$_2$-L'HZn(OAc)·DMF] compounds are diamagnetic and have tetrahedral structure; [PSCH$_2$-L'HMoO$_2$(acac)] and [PSCH$_2$-L'HUO$_2$(OAc)·DMF] compounds are diamagnetic and have octahedral structure; [PSCH$_2$-L'HZr(OH)$_3$·2DMF] compound is diamagnetic with pentagonal bipyramidal structure. The ligand acts as monobasic bidentate OS donor chelating agent in all the compounds. The ESR spectrum studies indicate the magnetically dilute tetragonal type of symmetry around copper(II) ions.

ACKNOWLEDGEMENTS

The authors (Amit Kumar, Praveen Kumar Gupta and Durga Dass) are thankful to the Principals of their Institutes for providing financial support for this work.

REFERENCES

1. R.H. Udupi, N. Kaisnath and A.R. Bhat, *Indian J. Heterocycl. Chem.*, **7**, 121 (1998).
2. E.G. Mata, M. Fraga and C.M.L. Delpiccolo, *J. Comb. Chem.*, **5**, 208 (2003).
3. R.H. Udupi and M. Jeeson, *Indian J. Heterocycl. Chem.*, **5**, 99 (1996); A.S. Gajare, S.B. Bhawsar, D.B. Shinde and M.S. Shingare, *Indian J. Chem.*, **36B**, 449 (1997); B. De and G.V.S. Ramasarma, *Indian Drugs*, **36**, 583 (1999); S.N. Pandeya, D. Shriram and V. Algarsamy, *Acta Pharm. Turc.*, **41**, 153 (1999); K.A. Parikh, P.S. Oza and A.R. Parikh, *Indian J. Chem.*, **39B**, 716 (2000); L. Sun, N.I. Vasilevich, J.A. Fuselier, S.J. Hocart and D.H. Coy, *Bioorg. Med. Chem. Lett.*, **14**, 2041 (2004); M.K. Pataskar and J.T. Rao, *Asian J. Chem.*, **17**, 133 (2005); M.K. Pataskar and J.T. Rao, *Asian J. Chem.*, **17**, 319 (2005).
4. B.S. Vashi, D.S. Mehta and V.H. Shah, *Indian J. Chem.*, **34B**, 802 (1995).
5. M.R. Maurya, M. Kumar and U. Kumar, *J. Mol. Catal. A: Chem.*, **273**, 133 (2007).
6. K. Takashashi, Y. Nakashiro, T. Toyoshima and T. Wakamastsu, *Suiyokaishi*, **20**, 243 (1985).
7. J.Y. Han, *Chingang Uikak*, **47**, 217 (1984); D.W. Lee, C.H. Eum, T.S. Kim, D.S. Shin and K.S. Chung, *Taehan Hwahakhoe Chi*, **31**, 308 (1987).
8. A. Syamal, D. Kumar, A.K. Singh, P.K. Gupta, Jaipal and L.K. Sharma, *Indian J. Chem.*, **41A**, 1385 (2002).
9. R.U. Roy and K.R. Desai, *Int. J. Chem. Sci.*, **3**, 529 (2005).
10. Chandramouli, R.H. Udupi and V.H. Bindu, *Orient. J. Chem.*, **23**, 1077 (2007).
11. A.A. Chavan and N.R. Pai, *Molecules*, **12**, 2467 (2007).
12. A. Syamal and D. Kumar, *Synth. React. Inorg. Met.-Org. Chem.*, **14**, 325 (1984).
13. A. Syamal and D. Kumar, *Indian J. Chem.*, **32**, 625 (1993).
14. D. Kumar, A. Syamal and A.K. Singh, *Indian J. Chem.*, **42A**, 280 (2003).
15. D. Kumar, A. Syamal and L.K. Sharma, *J. Coord. Chem.*, **61**, 1788 (2008).
16. A. Syamal and M.R. Maurya, *Coord. Chem. Rev.*, **95**, 183 (1989).
17. D.W. Warad, C.D. Satish, V.H. Kulkarni and C.S. Bajgur, *Indian J. Chem.*, **39A**, 415 (2000).
18. A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, edn. 2 (1984) and references therein.
19. A. Syamal, *Chem. Educ.*, **4**, 33 (1987).
20. R.S. Drago, Physical Methods in Chemistry, W.B. Saunders Co., Philadelphia, edn. 2 (1976).
21. R.L. Dutta and A. Syamal, Elements of Magnetochemistry, Affiliated East-West Press Pvt. Ltd, New Delhi, edn. 2, pp. 224-228 (1993).

(*Received*: 15 December 2008; *Accepted*: 28 May 2009) AJC-7616