ISSN 1070-3632, Russian Journal of General Chemistry, 2011, Vol. 81, No. 11, pp. 2304–2309. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © G.B. Pethe, A.R. Yaul, A.S. Aswar, 2011, published in Zhurnal Obshchei Khimii, 2011, Vol. 81, No. 11, pp. 1853–1858.

Synthetic, Characterization and Catalytic Studies of Some Coordination Compounds Derived from Unsymmetrical Quadridentate Schiff Base Ligand

G. B. Pethe, A. R. Yaul, and A. S. Aswar

Department of Chemistry, St. Gadge Baba Amravati University, Amravati-444 602, M.S. India
e-mail: aswar2341@rediffmail.com

Received May 25, 2010

Abstract—The stable complexes of VO(IV), Cr(III), Mn(III), Fe(III), MoO_2(VI), and WO_2(VI), with an unsymmetrical tetradentate Schiff base ligand derived from 2-hydroxy-5-methylacetophenone, 2-hydroxy-5-chloroacetophenone and carbohydrazide were synthesized and characterized by the elemental analysis, UV-Vis and IR spectroscopy, magnetic measurements and thermal analysis. The VO(IV) and Mn(III) complexes were tested for the catalytic oxidation of styrene. The conversion of styrene increases with use of VO(IV) catalyst and decreases with use of Mn(III) catalyst.

DOI: 10.1134/S1070363211110144

Schiff bases are an important class of ligands in coordination chemistry due to their synthetic flexibility, selectivity and sensitivity towards a variety of metal atoms [1]. They are found useful in catalysis, in medicine as antibiotics and anti-inflammatory agents [2, 3]. The metal complexes of Schiff bases derived from heterocyclic compounds have been the centres of attraction for many researches in recent years. Tetradentate Schiff bases are well known for their coordination with various metal ions to give the stable compounds. Several symmetrical Schiff bases and their complexes have been studied while comparatively unsymmetrical tetradentate Schiff base complexes were less studied then symmetrical ones. These metal complexes find wide spread applications as heterogeneous and homogeneous catalysts for the epoxidation of styrene [4].

The aim of the present work is to synthesize and characterize unsymmetrical Schiff base ligand derived from the 2-hydroxy 4-methylacetophenone, 2-hydroxy-4-chloroacetophenone, and carbohydrazide and its complexes.

The reaction of 2-hydroxy-5-metylacetophenone, 2-hydroxy-5-chloroacetophenone with carbohydrazide in hot DMF–ethanol yields the Schiff base (H_2L). The reaction of H_2L in DMF and appropriate metal salts in ethanol yields the complexes.

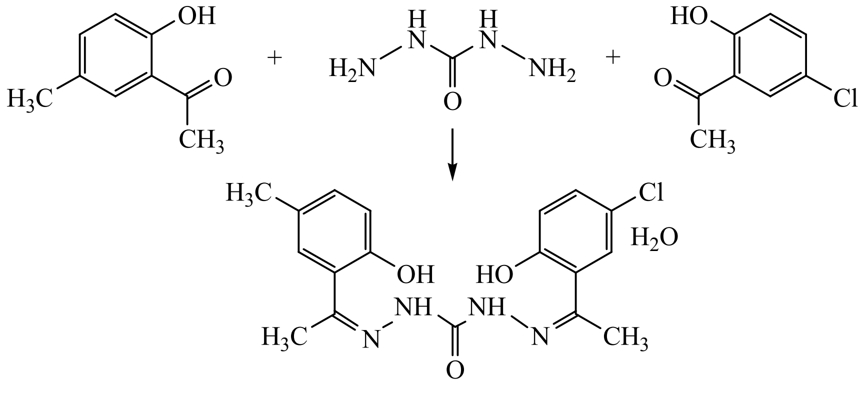

Table 1. Analytical and physical data of the ligand and its complexes

Compound	*M*, g mol^{-1}	Found, %				Calculated, %				σ, Ω^{-1} cm^{-1} at 373 K	E_a, eV
		C	H	N	M	C	H	N	M		
H_2L	374.82	57.32	5.02	14.12	–	57.68	5.11	14.95	–	1.68×10^{-11}	0.9961
[VOL]	439.74	48.88	3.79	12.10	11.14	49.16	3.90	12.74	11.58	3.44×10^{-6}	0.8917
$[CrL(H_2O)Cl]\cdot H_2O$	496.28	43.18	4.19	10.87	9.92	43.56	4.27	11.29	10.48	6.85×10^{-8}	0.8325
[MnLOAc]	486.78	48.83	4.08	11.21	11.03	49.35	4.14	11.51	11.51	2.31×10^{-5}	0.7288
$[FeL(H_2O)Cl]\cdot H_2O$	500.13	43.10	4.19	10.93	11.08	43.23	4.23	11.20	11.17	4.32×10^{-10}	0.6658
$[MoO_2L]$	500.74	42.98	3.11	10.91	18.91	43.17	3.42	11.19	19.16	2.73×10^{-9}	0.6029
$[WO_2LNCS]$	646.72	34.99	2.55	10.69	28.17	35.29	2.65	10.83	28.43	4.87×10^{-7}	0.5417

Table 2. The IR data (ν, cm^{-1}) of the ligand and its complexes

Compound	O–H phenol	N–H	C=N	C=O	C–O	N–N	M–O	M–N	H_2O
H_2L	2982	3270	1633	1702	1246	995	–	–	–
[VOL]	–	3284	1628	1681	1265	1012	549	443	–
$[CrL(H_2O)Cl]\cdot H_2O$	–	3263	1620	1685	1260	1024	511	455	3392, 1614, 892,732
[Mn LOAc]	–	3261	1609	1720	1263	1018	535	435	–
$[FeL(H_2O)Cl]\cdot H_2O$	–	3278	1591	1693	1260	1027	509	439	3361, 1609, 838, 751
$[MoO_2L]$	–	3288	1618	1683	1257	1013	552	424	–
$[WO_2LNCS]$	–	3268	1597	1698	1269	1005	527	412	–

The analytical data for the ligand and complexes are given in Table 1. All the complexes are coloured solids, non-hygroscopic, air stable and insoluble in common organic solvents, but sparingly soluble in DMSO. The elemental analysis shows 1:1 metal to ligand stoichiometry for all the complexes.

IR spectroscopy. The IR spectra of the complexes (Table 2) were interpreted by comparing the spectra with that of the free ligand. The IR spectrum of the free ligand exhibits a band at 2982 cm^{-1} due to the intramolecular hydrogen bonded OH-group. The disappearance of this band upon complexation indicates the breakdown of the H-bonding followed by the deprotonation of phenolic OH-group and the subsequent involvement of phenolic oxygen atoms towards coordination [5]. The phenolic stretching vibrations bands ν(C–O) appear at 1246 cm^{-1} in the ligand and which get shifted to higher region 1257–1269 cm^{-1} in complexes, also suggest the coordination of ligand through phenolic oxygen via deprotonation [6]. The IR spectrum of ligand shows a strong band at 1633 cm^{-1} due to the C=N stretching vibrations. On complexation this shows negative shift by 5–40 cm^{-1}, which indicates the coordination of azomethyne nitrogen atom to the metal ions in the complexes [7–9]. The ν(N–H) and ν(C=O) bands of the ligand at 3270 and 1702 cm^{-1} do not change their position after complexation, indicating that ligand exist in keto-form in free state as well as in all the complexes [10]. Non involvement of amido oxygen in coordination of the acetate group in Mn(III) complexes is confirmed due to the difference between the two bands ($\Delta\nu > 193$ cm^{-1}) appeared at 1619 and 1426 cm^{-1}, belonging to ν_{as}(OCO) and ν_s(OCO). A band at 671 cm^{-1} [δ(O–C–O)] confirms a monodendate ligand formation [11, 12].

Table 3. Thermal decomposition, magnetic properties and electronic spectral data of the ligand and its complexes

Compound	$T_{1/2}$, °C	E_a, kJ mol^{-1}	μ_{ef}, BM	λ, nm
H_2L	292	31.02	–	–
[VOL]	348	48.31	1.58	920 [$d_{xy}(b_2) \rightarrow d_{xy}d_{yz}(e^*)$], 516 [$d_{xy}(b_2) \rightarrow d_{x2-y2}(b_1^*)$], 382 [$d_{xy}(b_2) \rightarrow d_{z2}(a_1^*)$]
$[CrL(H_2O)Cl]\cdot H_2O$	412	37.73	3.81	618 [$^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$], 471 [$^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$], 270 [$^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$]
[Mn LOAc]	427	50.99	4.87	742 ($^5B_1 \rightarrow {}^5B_2$), 609 ($^5B_1 \rightarrow {}^5A_1$), 511 ($^5B_1 \rightarrow {}^5E$), 352 (ligand–metal transition)
$[FeL(H_2O)Cl]\cdot H_2O$	366	49.92	5.69	760 ($^6A_{1g} \rightarrow {}^4T_{1g}$), 639 ($^6A_{1g} \rightarrow {}^4T_{2g}$), 435 ($^6A_{1g} \rightarrow {}^4E_g$)
$[MoO_2L]$	409	31.01	Diamagnetic	–
$[WO_2LNCS]$	420	34.45	″	–

The coordination of water in Cr(III) and Fe(III) complexes is indicated by the appearance of the bands at 3392–3361, 1609–1614, 838–892 and 732–751 cm^{-1} assignable to γ(O–H) , δ(O–H), $\rho_r(H_2O)$, and $\rho_w(H_2O)$ vibrations respectively [13]. The MoO_2(VI) and WO_2 (VI) complexes show new bands at 944 and 930 cm^{-1} belonging to ν_{as}(O=Mo=O) and ν_{as}(O=W=O) vibrations [14]. In the spectrum of WO_2(VI) complex there is the bands at 2075 (CN), 778 (CS), and 487 cm^{-1} (NCS) suggesting that the thiocyanate group act as a ligand, in which bonding through nitrogen takes place [15].

Electronic Spectra. The electronic spectral data for the obtained complexes are given in Table 3. The electronic spectrum of VO(IV) complex contains absorption bands at 920, 516 and 382 nm corresponding to square pyramidal geometry [16]. These bands may be assigned to $d_{xy}(b_2) \rightarrow d_{xy}d_{yz}(e^*)$, $d_{xy}(b_2) \rightarrow d_{x2-y2}(b_1^*)$ and $d_{xy}(b_2) \rightarrow d_{z2}(a_1^*)$ transitions respectively. The Cr(III) complex shows absorption band at 618, 471 and 270 nm owing to $^4A_{2g}(F) \rightarrow {}^4T_{2g}$ (F), $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$, and $^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$ transitions indicating an octahedral geometry of the Cr(III) ion [17]. The spectrum of the Mn(III) complex contains the absorption bands at 742, 609, 511 and 352 nm originating from $^5B_1 \rightarrow {}^5B_2$, $^5B_1 \rightarrow {}^5A_1$, and $^5B_1 \rightarrow {}^5E$ and LMCT transitions, which corresponds to the square pyramidal geometry of the complex [18]. In the spectrum of the Fe(III) complex there are the absorption bands at 760, 639, and 435 nm due to $^6A_{1g} \rightarrow {}^4T_{1g}$, $^6A_{1g} \rightarrow {}^4T_{2g}$, and $^6A_{1g} \rightarrow {}^4E_g$ transitions, respectively, indicating the octahedral geometry for the complex [19].

Magnetic properties. The molar magnetic susceptibility of the VO(IV), Cr(III), Mn(III), and Fe(III) complexes at room temperature is given in Table 3. The μ_{ef} value of VO(IV), Cr(III), Mn(III), and Fe(III) complexes at room temperature is found to be 1.58, 3.81, 4.87 and 5.69 B.M., respectively. These values support to those reported earlier. The MoO_2(VI) and WO_2(VI) complexes are diamagnetic as considered with their electronic configuration.

Electrical conductivity. The solid state electrical conductivity of the ligand and its complexes is given in Table 1. The solid state electrical conductivity was measured in compressed pellet from room temperature to 403 K. The solid state electrical conductivity increases with increasing the temperature [20]. The electrical conductivity (σ) varies experimentally with the absolute temperature according to the relation $\sigma = \sigma_0 \exp(E_a/kT)$, where σ_0 is constant, E_a is the activation energy of electrical conduction, T is the absolute temperature and k is the Boltzmann constant. The dependence $\log\sigma - 1/T$ was found to be linear over the studied temperature range indicating the semiconducting behaviour for the obtained complexes [21]. The values of electrical conductivity lies in the range of 1.68×10^{-11}–2.31×10^{-5} eV, in which accordance the obtained complexes can be arranged as follows: H_2L < Fe(III) < MoO_2(VI) < Cr(III) < WO_2(VI) < VO(IV) < Mn(III).

Thermogravimetric study. In order to know the presence of water molecules and decomposition pattern of the ligand and its complexes TG analysis was carried out. The thermogram reveals three stage

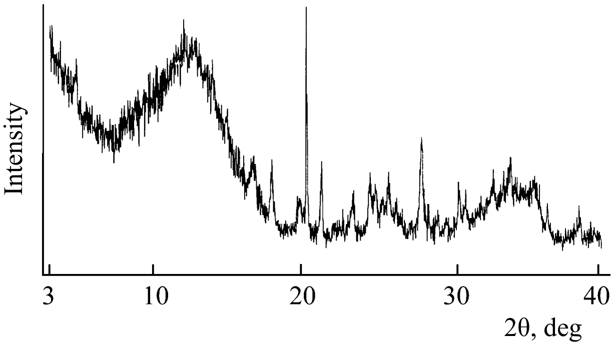

Fig. 1. X-ray Diffraction Spectrum of the VO(IV) complex.

decomposition pattern for Cr(III) and Fe(III) complexes and two stage for VO(IV), MoO_2(VI), and WO_2(VI) complexes. The TG curve of Cr(III) and Fe(III) complexes elimination of an water molecule takes place between 70–120°C, indicating the presence of lattice water molecule, and 145–225°C, indicating the presence of an coordinated water molecule [22]. The Mn(III) complexes is almost stable up to 200°C and then after the thermogram shows gradual weight loss up to ~280°C corresponding to loss of one acetate group. The MoO_2(VI) and WO_2 complexes are almost stable up to 160°C indicating the absence of lattice or coordinated water molecule. The thermogram of the WO_2 complex shows weight loss in the range of 175–225°C, which corresponds to loss of one thiocyanate group [15]. The half decomposition temperature and activation energy values were calculated by the Broido's method and are given in Table 3 [23]. The final stage ends with aerial oxidation of the complexes that includes the decomposition of organic part with increasing temperature and formation of the stable metal oxides.

Powder XRD study of the VO(IV) complex. The X-ray diffraction spectrum of the VO(IV) complex is shown in Fig. 1. The X-ray diffraction spectrum of the VO(IV) complex exhibits sharp peaks indicating the crystalline nature of the complex. The XRD spectrum was recorded with CuK_α-irradiation in the range 2θ 4°–35° with λ 1.5406 Å. All the main peaks were indexed by using the appropriate methodology and PowdMult, Version 2.3 program package. The unit cell lattice parameter of the VO(IV) complex are: a 7.5711, b 19.6694, c 6.4079 Å; α 106.665°, β 101.406°, γ 98.264°, V 875.48 $Å^3$; triclinic system.

Catalytic activity of the complexes obtained in styrene oxidation. In generally, the catalytic oxidation of styrene gives the products like styrene oxide, benzaldehyde, benzoic acid, phenyl acetic acid and 1-phenylethan-1,2-diol and other side products [24]. In the present work the oxidation of styrene catalysed by the VO(IV) and Mn(III) complexes was carried out. The catalytic activity of these complexes was checked as a function of the amount of catalyst and H_2O_2 used as oxidant. The amount of catalyst is used like 0.020, 0.030 and 0.040 g, respectively; amount of styrene and H_2O_2 (1:2) was fixed in the presence of acetonitrile at 80°C. The conversion of styrene using the VO(IV) and Mn(III) complexes was 25–36 and 42–45%, respectively, as shown in Figs 2, 3. The styrene conversion increases with increase in amount of catalyst in presence of fixed amount of H_2O_2 and styrene in case of the VO(IV) complex catalyst, but it decreases as the amount of Mn(III) complex catalyst increases.

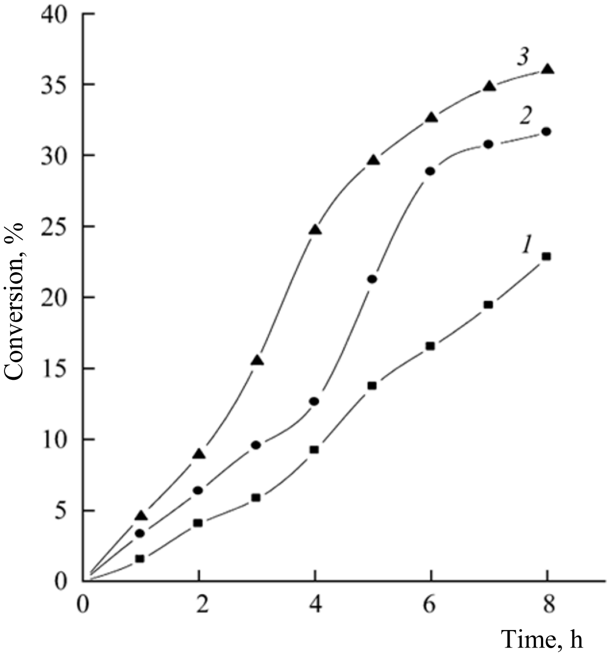

Fig. 2. Effect of [VOL] catalyst on styrene conversion: (*1*) 0.020, (*2*) 0.030, and (*3*) 0.040 g.

EXPERIMENTAL

All the chemicals and solvents were of analytical grade and purchased from commercial sources. Vanadyl sulphate petahydrate, chromium chloride hexahydrate, anhydrous ferric chloride, dioxotungsten tetrathiocyanate and carbohydrazide were of Rankem and SD fine chemicals and use as supplied. $Mn(OAc)_3\cdot 2H_2O$ was prepared by the oxidation of $Mn(OAc)_2\cdot 4H_2O$ using Christensen's method [25]. Bis(acetyl-

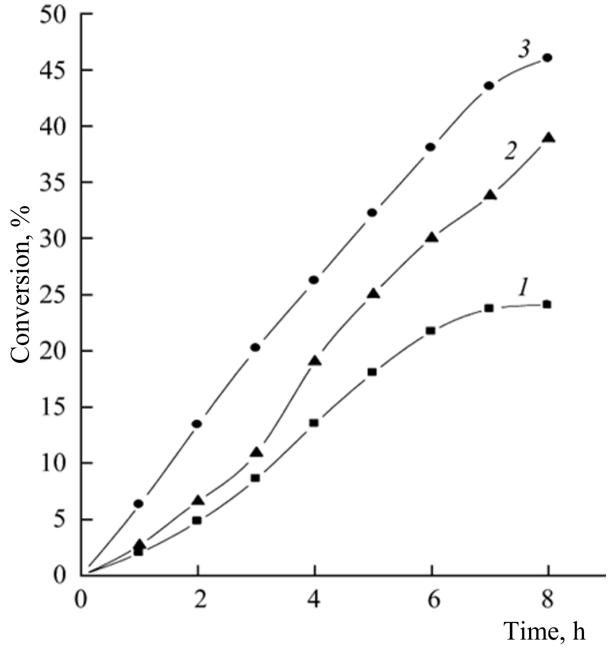

Fig. 3. Effect of [MnLOAc] catalyst on styrene conversion: (*1*) 0.020, (*2*) 0.030, and (*3*) 0.040 g.

acetonato)dioxomolybdenum(VI) was synthesized according to the literature method [26].

The elemental analysis was performed on a Carlo Erba 1108 analyser in micro analytical laboratory (CDRI, Lucknow). The IR spectra were recorded on a Perkin-Elmer 597 spectrophotometer from KBr pellets (SAIF Punjab University, Chandigarh). The ^{1}H NMR spectrum of ligand was obtained on a Bruker Auance-II 400 NMR spectrophotometer in DMSO-d_6 (SAIF Punjab University, Chandigarh). The electronic spectra of the complexes were recorded on Varian SE UV–NIR spectrophotometer using MgO as reference. The magnetic susceptibility was measured at room temperature by Gouy's method using Hg[CO(NCS)$_4$] as a calibrant and the diamagnetic corrections were made using Pascal's constants. The solid state d.c. electrical conductivity of compounds was measured by Zentech Electrometer in their compressed pellet form over 313–403 K temperature range. The TG analysis of the complexes was carried out on a Perkin Elmer TG-2 thermobalance in ambient air with a heating rate of 10°C per minute. Metal contents of the complexes were analysed gravimetrically after decomposing the complexes with a mixture of $HClO_4$, H_2SO_4 and HNO_3 and then igniting to metal oxide. The XRD measurement of the complexes was recorded with a Bruker AXS, D8-Avance instrument equipped with θ/θ gonimeter and a Lynv Eye detector. The gas chromatography was recorded on a Shimandzu 14B gas chromatograph with SE-30 column and FID detector (School of Chemical Science, Devi Ahilya University, Indore).

Synthesis of *N*''-[1-(5-chloro-2-hydroxyphenyl) ethylidene]-*N*'''-[(1-(2-hydroxy-5-methylphenyl)-ethylidene]carbonohydrazide (H_2L). To a mixture of ethanolic solutions of 2-hydroxy-5-methylacetophenone (2.4 g, 0.016 M) and 2-hydroxy-5-chloroacetophenone (2.72 g, 0.016 M.) was added dropwise a hot ethanol–DMF solution (60:40 v/v, 25 ml) of carbohydrazide (1.44 g., 0.016 M.) with stirring. The mixture was refluxed on sand bath for about 7 h. The solvent was then partially evaporated under air and yellow coloured compound formed was filtered off, washed with ethanol, petroleum ether and then dried in vacuum. Yield 72%, mp 292ºC.

^{1}H NMR spectrum, δ, ppm: 12.78 s (1H, OH, phenolic), 12.48 s (1H, OH, phenolic), 11.16–11.41 s (2H, NH-imino), 2.21 s (6H, CH_3), 2.15 s (3H, Ph–CH_3), 6.77–7.94 m (6H, H_{Ph}).

Synthesis of VO(IV), Cr(III), Mn(III), Fe(III), and MoO_2 complexes. To a hot DMF solution (25 ml) of the organic ligand (1.0 mmol) was added a hot ethanolic solution of the appropriate metal salt (1.0 mmol) solution under continuous stirring. The resulting mixture was refluxed for 4–5 h. On cooling to room temperature the precipitate solid metal complexes was filtered off, washed thoroughly with ethanol, DMF and petroleum ether to remove the unreacted ligand and metal salts. Finally all the complexes were dried under vacuum at room temperature. Yield 65–70%.

Synthesis of the WO_2 complex. To a mixture of aqueous solutions of sodium tungstate dihydrate (1.2 g, 0.00363 mol) and ammonium thiocyanate (2.9 g, 0.038 mol) at room temperature was added 7.5 ml of 11 M HCl. The resulting yellow solution was cooled in an ice bath and DMF solution (10 ml) of ligand (0.00363 M.) was added to it. The precipitate formed was filtered off, washed 3–4 times with water containing few drops of HCl and dried in vacuum.

Catalytic oxidation of styrene. The catalytic reactions were carried out in 250 ml reaction flask fitted with water condenser. To a mixture of styrene (1.04 g, 10 mmol) and 30% H_2O_2 (2.27 g, 20 mmol) in 10 ml of MeCN was added and the catalyst tested (0.020 g) and the reaction mixture was heated in an oil bath with continuous stirring at 80°C for 8 h. The reaction progress was monitored at various time periods by the gas chromatography.

ACKNOWLEDGMENTS

The authors are grateful to SAIF Chandigarh and CDRI Lucknow for recording elemental analyses, IR, NMR, electronic spectra and XRD facilities; Dr. R. Prasad, School of Chemical Science, Devi Ahilya University, Indore to gas chromatography analysis of the compounds and University Grants Commission for providing financial assistance.

REFERENCES

1. Schiff, H.S., *Ann. Chim. (Paris)*, 1864, vol. 118, p 131.
2. Maurya, M.R., Bharti, N., Nafui, F., and Azam, A., *Bio-Inorg. Med. Chem. Lett.*, 2002, vol. 10, p. 2243.
3. Chang, Y., Lv, Y., Lu, F., Zha, F. and Lei, Z., *J. Mol. Catal. A*, 2010, vol. 320, nos. 1–2, p. 56.
4. Li, J., Xu, B., Jiang, W., Zhou, B., Zeng, W., and Qin, S., *Trans. Met. Chem.*, 2008, vol. 33, p. 975.
5. Yaul, A.R., Dhande, V.V., Suryawanshi, N.J., and Aswar, A.S., *Polish J. Chem.*, 2009, vol. 83, p. 565.
6. Maurya, M.R., Khurana, S., Schulzke, C., and Rehder, D., *Eur. J. Inorg. Chem.*, 2001, vol. 3, p. 779.
7. Vafazadeh, R. and Kashfi, M., *Bull. Korean Chem. Soc.*, 2007, vol. 28, no.7, p. 1227.
8. Aranha, E.P., Dos. Santos, M.P., Romera, S., and Dockal, E.R., *Polyhedron*, 2007, vol. 26, p. 1373.
9. Bellamy, L.J., *Advances in InfraRed Group Frequencies*, London: Methuen, 1968.
10. Warad, D.U., Satish, C.D., Kulkarni, V.H., and Bajgur, C.S., *Indian J. Chem. A*, 2000, vol. 26, p. 415.
11. Nakamota, K., *Infrared Spectra of Inorganic and Coordination Compounds*, New York: Willey, 1970.
12. Alaudeen, M., and Prabhakaran, C.P., *Indian J. Chem. A*, 1996, vol. 35, p. 517.
13. Adam, D.M., *Metal Ligand and Related Vibrations*, London: Arnold, 1967.
14. Nag, J.K., Pal, S., and Sinha C., *Trans. Met. Chem.*, 2005, vol. 30, p. 523.
15. Pathania, M.S., Hussain, A., Sheikh, H.N., and Kalsotra, B.L., *J. Indian Chem. Soc. A*, 2005, vol. 82, p. 594.
16. Maurya, R.C., Mishra, D.D., and Pillai, V., *Synth. React. Inorg. Met. Org. Chem.*, 1995, vol. 25, p. 1123.
17. Dubey, R.K., Dubey, V.K., and Mishra C.M., *Indian J. Chem. A*, 2008, vol. 47, p. 1210.
18. Thakar, B.T., Patel, I.A., and Thakar, P.B., *Indian J. Chem. A*, 1998, vol. 37, p. 429.
19. Badwaik, V.B., and Aswar, A.S., *Russ. J. Inorg. Chem.*, vol. 54, no. 10, p. 1611.
20. Katon, J.E., *Organic Semiconducting Polymers*, New York: Marcel Dekker, 1968.
21. Koca, M., Dagdelen, F., and Aydogdy, Y., *Matter. Lett.*, 2004, vol. 58, p. 2901.
22. Zigmond, A., Horvath, A., and Notheisz, F., *J. Mol. Catal. A.*, 2001, vol. 171, p. 95.
23. Parekh, H.M., Panchal, P.K., and Patel, M.N., *J. Therm. Anal. Cal.*, 2006, vol. 86, no. 3, p. 803.
24. Broido, A., *J. Phys. Chem. A*, 1969, vol. 27, p. 761.
25. Christensen, O.T., *Z. Anorg. Chem. A*, 1998, vol. 37, p. 325.
26. Syamal, A. and Singh, M.M., *Indian J. Chem. A*, 1998, vol. 37, p. 350.