ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2010, Vol. 36, No. 4, pp. 254–258. © Pleiades Publishing, Ltd., 2010.

Synthesis, Spectral, Catalytic, and Thermal Studies of Vanadium Complexes with Quadridentate Schiff Bases[1]

A. R. Yaul, G. B. Pethe, and A. S. Aswar*
Department of Chemistry, Sant Gadge Baba Amravati University, Amravati 444602, India
**E-mail: anandaswar@yahoo.com*

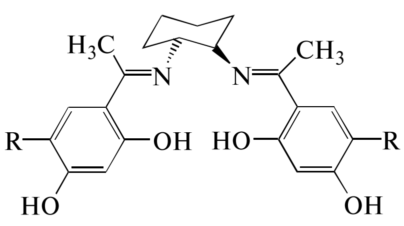
Received September 6, 2009

Abstract—The paper reports the synthesis and characterization of vanadium complexes of N,N'-(±)-*trans*-*bis*(2,4-dihydroxyacetophenone)-1,2-cyclohexanediamine (H_2L^1) and N,N'-(±)-*trans*-bis(2,4-dihyroxy-5-nitroacetophenone)-1,2-chyclohexanediamine (H_2L^2). All the complexes were characterized by elemental analysis, magnetic susceptibility measurements, infrared and electronic spectra, and thermogravimetric analysis. The X-ray patterns of the $[VO(L^1)] \cdot H_2O$ (**I**) and $[VO(L^2)] \cdot H_2O$ (**II**) complexes show the monoclinic system with the unit cell parameters $a = 26.1352$, $b = 11.7149$, $c = 6.0401$ Å, $\beta = 115.38°$ and $a = 29.3787$, $b = 12.9398$, $c = 5.9175$ Å, $\beta = 96.84°$, respectively. The complexes **I** and **II** catalyze the oxidation of styrene in the presence of hydrogen peroxide.

DOI: 10.1134/S1070328410040032

INTRODUCTION

Vanadium chelates containing tetradentate Schiff base ligands derived from 1,2-diamines were subjects of several recent reports [1–3]. The salen complexes of vanadium metal were used in solution as biomimetic catalysts for oxygen atom transfer and as catalysts for aziridination, sulfoxidation, and other oxidative processes [4–6]. In addition, selective epoxidation of olefins catalyzed by the vanadium Schiff base complexes became the most important industrial processes. More recently the vanadium coordination compounds were shown to catalyze the selective oxidation of alkenes by molecular oxygen [7]. The Schiff base vanadium complexes are also very interesting as model compounds for the clarification of several biochemical processes [8–10]. The present work describes the synthesis and characterization of the vanadium(IV) and (V) complexes with the tetradentate Schiff base ligands: N,N'-(±)-*trans*-bis(2,4-dihydroxyacetophenone)-1,2-cyclohexanediamine (**H_2L^1**) and N,N'-(±)-*trans*-bis(2,4-dihyroxy-5-nitroacetophenone)-1,2-chyclohexanediamine (**H_2L^2**).



,

where R = H (for H_2L^1), NO_2 (for H_2L^2).

We also report oxidation of styrene by hydrogen peroxide using the $[VO(L^1)] \cdot H_2O$ (**I**) and $[VO(L^2)] \cdot H_2O$ (**II**) complexes.

EXPERIMENTAL

Materials and Solvents

The solvents were used after purification employing standard methods [11]. The reagents used in the synthesis of the Schiff base ligands and their complexes were used as received. Vanadyl sulfate ($VOSO_4 \cdot 5H_2O$), ammonium metavanadate, and vanadium pentoxide were received from Qualigens Chemicals. *trans*-1,2-Diaminocyclohexane was purchased from Across Organics.

Physical Measurements

Carbon, hydrogen, and nitrogen contents were recorded on a Carlo Erba 1108 elemental analyzer. ^1H NMR spectra of the ligands were recorded with a Bruker DRX-300NMR spectrophotometer in DMSO-d_6 using tetramethylsilane as internal reference. FT-IR spectra were obtained as KBr pellets using a Shimadzu 8201 spectrophotometer in the range 400–4000 cm^{-1}. The solid state reflectance spectra of the complexes were recorded in the range 200–1000 nm (as MgO) on a Beckman DK-2A spectrophotometer. Magnetic measurements were carried out at room temperature by the Gouy method using $Hg[Co(SCN)_4]$ as calibrant. Thermogravimetric analysis was performed on a TGA-2 PerkinElmer thermal analyzer in the temperature range 40–800°C with a

---

[1] The article is published in the original.

Table 1. Elemental analysis data for the ligands and their complexes

Compound	Formula weight	Contents (found/calcd.), %			
		C	H	N	V
H_2L^1	382.45	69.27/69.09	6.81/6.85	7.57/7.32	
$[VO(L^1)] \cdot H_2O$	465.39	56.92/56.78	5.69/5.63	5.89/6.02	10.87/10.95
$[VO(Cl)(L^1)]$	482.83	54.80/54.73	5.12/5.01	5.87/5.80	10.53/10.50
$K[VO_2(L^1)] \cdot 2H_2O$	538.50	49.12/49.07	5.09/5.24	5.23/5.20	9.54/9.46
H_2L^2	472.44	55.87/55.93	5.27/5.12	11.81/11.86	
$[VO(L^2)] \cdot H_2O$	555.38	47.65/47.58	4.32/4.36	10.24/10.09	9.14/9.17
$[VO(Cl)(L^2)]$	572.82	46.29/46.13	3.56/3.87	9.83/9.78	8.95/8.89
$K[VO_2(L^2)] \cdot 2H_2O$	628.50	42.16/42.04	4.21/4.17	9.02/8.91	8.23/8.11

heating rate of 10°C min^{-1}. Gas chromatography experiments were performed with a Shimadzu 14B gas chromatograph equipped with a SE-30 column and a flame-ionization detector. X-ray diffraction patterns were obtained with a BRUKER AXS, D8 ADVANCE instrument (GmbH, Karlsruhe, West Germany) equipped with a θ/θ goniometer and a Lynx Eye detector.

Synthesis of Schiff base ligands. Both the Schiff bases H_2L^1 and H_2L^2 were prepared by a similar method. A solution of *trans*-1,2-diaminocyclohexane (10 mmol) in 10 ml of methanol was added dropwise to a hot methanolic solution of respective ketones (20 mmol in 40 ml), and the reaction mixture was heated under reflux on a water bath for 2 h. After cooling to room temperature, the yellow precipitates separated were filtered off, wash with methanol, and finally dried over calcium chloride. The purity of the synthesized compounds was monitored by TLC. The yield was 75–78%, m.p. H_2L^1: 214°C and H_2L^2: 229°C. ^1H NMR (δ, ppm) H_2L^1: 16.87 (s., 2H, OH C_2), 9.74 (s., 2H, OH C_4), 7.32–6.00 (m., 6H, Ar–H), 3.84 (m., 2H, CH), 2.22 (s., 6H, CH_3), 1.03–1.87 (br., 8H, CH_2CH_2); H_2L^2: 17.28 (s., 2H, OH C_2), 10.02 (s., 2H, OH C_4), 8.33–6.08 (m, 4H, Ar–H), 4.24 (m., 2H, CH), 2.43 (s., 6H, CH_3), 1.97–1.06 (br., 8H, CH_2CH_2).

Synthesis of complexes I and II. Equimolar quantities (10 mmol) of metal salt ($VOSO_4 \cdot 5H_2O$) and the ligand were dissolved separately in absolute methanol (25 ml). Both solutions were filtered and mixed under hot conditions. The reaction mixture was refluxed for 4–6 h in a water bath, and a colored solution was concentrated and cooled to yield the complexes. The latter were washed with diethyl ether and dried over calcium chloride. The yield was 62–70%.

Synthesis of $[VO(Cl)(L^1)]$ (III) and $[VO(Cl)(L^2)]$ (IV) complexes. An aqueous (15 ml) solution of NH_4VO_3 (1.17 g) was treated with 6 ml of concentrated HC1 and stirred until a yellow solution was obtained. This solution was added to a methanolic solution (30 ml) of the ligand (10 mmol) with stirring. The reaction mixture was refluxed in a water bath for 3–4 h. The colored solid obtained was filtered off, washed with diethyl ether, and dried over calcium chloride. The yield was 55–60%.

Synthesis of $K[VO_2(L^1)] \cdot 2H_2O$ (V) and $K[VO_2(L^2)] \cdot 2H_2O$ (VI) complexes. V_2O_5 (0.46 g, 5 mmol) dissolved in 10 ml of KOH (0.29 g, 5 mmol) was added to a hot solution of the ligands (5 mmol) dissolved in dry methanol (20 ml). The resulting mixture vigorously was stirred, and on stirring a colored precipitate was formed, filtered off, washed with diethyl ether, and dried in vacuum. The yield was 47–50%.

Oxidation of styrene. The catalytic oxidation of styrene was carried out using the complexes **I** and **II** in a 50-ml reaction flask fitted with a water condenser. A general procedure was applied for all reactions. In typical reactions, styrene (1.04 g, 10 mmol) and 30% aqueous hydrogen peroxide (2.27 g, 20 mmol) were mixed in 10 ml of MeCN, and the reaction mixture was heated in an oil bath with continuous stirring at 80°C for 8 h. The catalyst to be tested (0.025 g) was added to the reaction mixture, and the reaction was considered to begin. The progress of the reaction was monitored by withdrawing a small amount of the reaction mixture at different time intervals and analyzing them quantitatively by gas chromatography. The effect of an amount of the catalyst was studied to obtain suitable reaction conditions.

RESULTS AND DISCUSSION

All the complexes are nonhygroscopic and stable in the solid state at room temperature. Analytical and physical data of the ligands and their vanadium complexes are presented in Table 1.

The infrared spectra of the vanadium complexes were compared with those of the free ligands. Both ligands exhibit a broad band at 2912–2947 cm^{-1} due to hydrogen bonding between phenolic hydrogen and nitrogen of the azomethine group. The ligands are relatively planar with an adequate intramolecular distance that favors the formation of hydrogen bonds

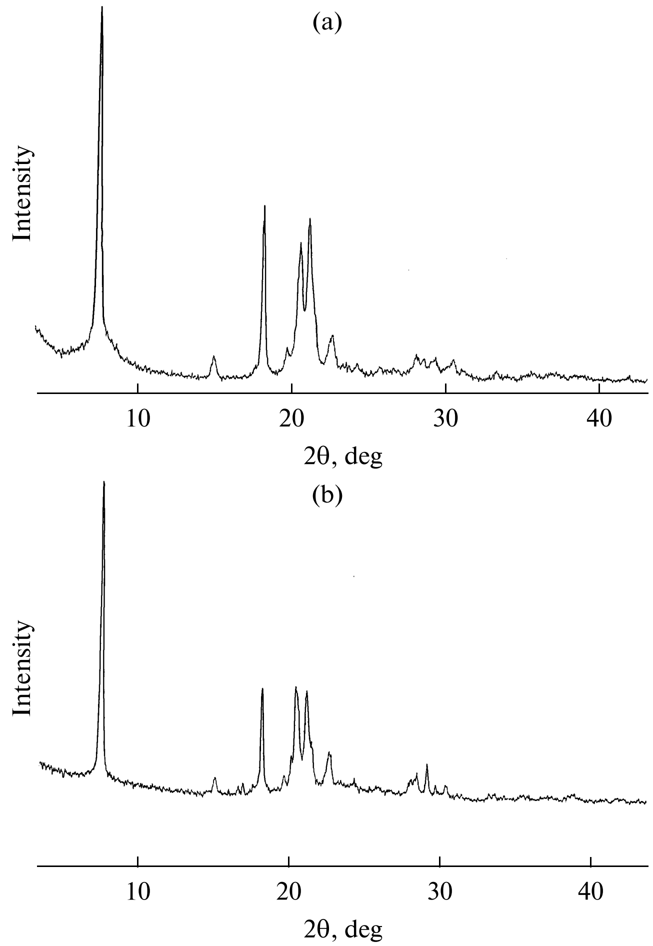


Fig. 1. X-ray diffraction pattern of for **I** (a) and **II** (b).

[12]. The presence of electron-donating groups on nitrogen also favors intramolecular hydrogen bond formation [12]. The absence of these bands in the spectra of the complexes indicates the destruction of the hydrogen bond followed by the coordination of phenolic oxygen after deprotonation. This is also supported by the upfield shift (by 9–24 cm^{-1}) of the phenolic ν(C–O) mode [13, 14]. Both ligands exhibit a strong band around 1620 cm^{-1} attributable to the C=N stretching vibration, undergoing a shift to lower frequency (by 9–25 cm^{-1}) after complexation, indicating the coordination of azomethine nitrogen to the vanadium ion. This can be explained by the donation of electrons from nitrogen to the empty *d* orbital of the vanadium ion [15–17].

The oxovanadium(IV) complexes exhibit an additional strong absorption band near ~980 cm^{-1}, which is assigned to ν(V=O) [18]. The dioxovanadium complexes show a significant pair of the V=O stretching frequency around 980 and 920 cm^{-1} for the asymmetric and symmetric modes, respectively. Complexes **III** and **IV** display one sharp band at 950 and 948 cm^{-1} respectively, and a decrease reduction in the stretching frequency as compared to the oxovanadium(IV) complexes, which may be due to the weakening of the V=O bond by the *trans* effect of the added ligand. Conclusive evidence of the bonding is also shown by the new bands in the spectra of the complexes appeared at 468–480 and 527–549 cm^{-1} assigned to the V–O and V–N stretching vibrations that are not observed in the spectra of the ligands. On the basis of these results, we conclude that the Schiff bases in the vanadium complexes behave as dibasic tetradentate molecules.

Complexes **I** and **II** exhibit the μ_{eff} value 1.73 and 1.82 μ_B, respectively, which are very close to the spin-only value for the d^1 system [19, 20]. These complexes show all the expected three bands in the regions 13570–13630, 16680–16698, and 21837–22102 cm^{-1}, which result from the ${}^2B_2 \to {}^2E$, ${}^2B_2 \to {}^2B_1$ and ${}^2B_2 \to {}^2A_1$ transitions, respectively [21]. The fourth band observed in the region 28010–29472 cm^{-1} may be due to the charge transfer transition. Thus, keeping in view the tetradentate nature of the ligands, 5-coordinated square-pyramidal structures in which the ligand lies in the basal plane and oxygen occupies the apical position may be suggested for both VO(IV) complexes. Vanadium(V) is a d^0 species, and no *d–d* traditions are expected or observed. However, these complexes display low-energy bands, which are assigned to the ligand-to-metal charge transfer (LMCT) transition from the phenolic oxygen to the empty *d* orbitals on the vanadium [22].

The X-ray diffraction (**XRD**) studies of the complexes **I** and **II** (Fig. 1) were carried out using CuK_α radiation with $\lambda = 1.5418$ Å. The XRD patterns of the both complexes were recorded at 2θ values between 3° and 45°. The X-ray crystal system was worked out by the trial and error methods for finding the best fit between the observed and calculated values. The unit cell parameters for complex **I**: $a = 26.1352$, $b = 11.7149$, $c = 6.0401$ Å, $\beta = 115.38°$, $V = 1670.00$ Å^3; for complex **II**: $a = 29.3787$, $b = 12.9398$, $c = 5.9175$ Å, $\beta = 96.84°$, $V = 2233.51$ Å^3. It was found that both complexes belong to the monoclinic system.

The catalytic properties of complexes **I** and **II** were investigated in the oxidation of styrene by using H_2O_2 as an oxidant. Styrene oxide, phenyl acetaldehyde, benzaldehyde, benzoic acid, and 1-phenylethane-1,2-diol were formed along with minor amounts of unidentified products. These are common products and were identified as well [23, 24]. Catalyst concentrations were varied to study their effect on the oxidation activity of the catalytic system. The catalytic study of both the complexes toward oxidation of styrene using H_2O_2 as an oxidant results in the 27–32% styrene conversion. Three different amounts of **I**, viz., 0.015, 0.025 and 0.035 g were considered while keeping fixed amounts of styrene (10 mmol) and H_2O_2 (20 mmol) in 10 ml of MeCN. The reaction was carried out at 80°C. Figure 2 shows that the conversion intensifies on increasing the amount of the catalyst and a maximum of 32% conversion were achieved with 0.025 g of the

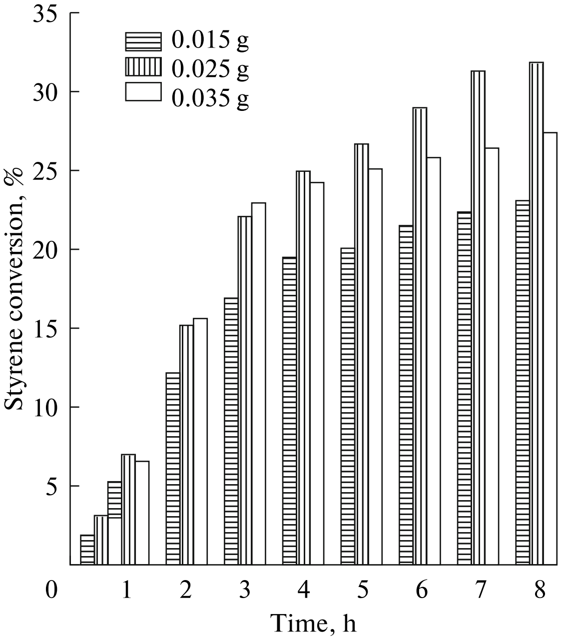


Fig. 2. Effect of amount of catalyst on the oxidation of styrene.

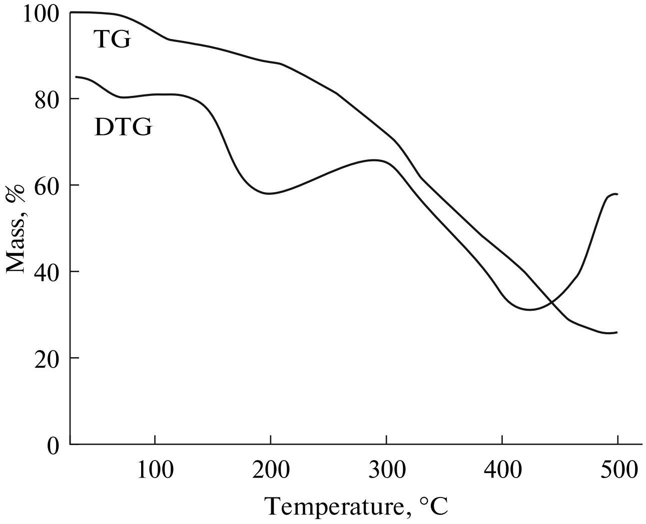


Fig. 3. TG and DTG curves of complex **V**.

catalyst. The conversion decreases with further increasing the catalyst conversion. Hence, 0.025 g of the catalyst can be considered as optimum conditions for the maximum conversion.

The present study aims at evaluating the thermal behavior of the representative vanadium complexes on the basis of the TG/DTG method. The stages of decomposition, temperature ranges, and the observed and calculated weight loss percentages are listed in Table 2. The TG/DTG curves of complex **V** is shown in Fig. 3. The dioxovanadium complex undergoes three-stage decomposition. The first weight loss 6.42% (calcd. 6.68%) was observed in the temperature range 60–115°C and corresponds to the loss of two moles of the lattice water molecules [25], The second stage of decomposition started at about 115°C and completed at 260°C corresponding to a weight loss of 11.59%, which could be attributed to the loss of one part of the ligand moiety. The third stage of decomposition occurred in the range 260–490°C with a weight loss of 55.68%, which can be due to the loss of the remaining part of the ligand and leaving KVO_3 as a final product. The three stages were denoted by the DTG peaks at about 82, 208, and 423°C, respectively.

Complex **I** slowly started to decompose in the temperature range 40–110°C. The first weight loss 3.80% (calcd. 3.86%) is attributed to the removal of one lattice water molecule [25]. In the temperature range 110–340°C, the weight loss of 14.02% is due to the pyrolysis of one part of the ligand. The weight loss

Table 2. Thermal decomposition data for the vanadium complexes

Complex	TG range, °C	DTG peak, °C	Weight loss, % (obs./calcd.)	Assignment
I	40–110	92	3.80/3.86	Loss of one mole of lattice water molecule
	110–340	334	14.02	Removal of one part of the ligand
	340–800	743	63.98	Removal of remaining part of the ligand
			81.80*/82.08	Leaving of metal oxide residue
III	170–255	212	12.96	Removal of one part of the ligand
	255–740	629	69.18	Removal of remaining part of the ligand
			82.14*/82.73	Leaving of metal oxide residue
V	60–115	82	6.42/6.68	Loss of two moles of lattice water molecules
	115–260	208	11.59	Removal of one part of the ligand
	260–490	423	55.68	Removal of remaining part of the ligand
			73.69*/74.27	Leaving of metal oxide residue

* Total weight loss.

63.98% is observed in the range 340–800°C, which corresponds to the loss of the remaining part of the ligand. The three stages were also denoted by the DTG peaks at about 92, 334, and 743°C, respectively. The final residue vanadium oxide has the observed weight 17.92% against the calculated value 17.81%.

The thermal decomposition of complex **III** showed two decomposition stages in the temperatures ranges 170–255 and 255–740°C. They were donated by the DTG peaks at 212 and 629°C. The first stage of decomposition agreed with a weight loss of 12.96%, which may be due to the loss of 50% of the ligand. The second stage indicates a weight loss of 69.18%, which may correspond, to the loss of the remaining part of the ligand and the oxidation of the metal to a residue of VO_2, which is stable above this temperature [26].

ACKNOWLEDGMENTS

The authors are grateful to the Director, C.D.R.I. Lucknow for recording the IR spectra and elemental analyses; S.A.I.F., IIT Chennai for recording the electronic spectra. We also thank Prof. R. Prasad, School of Chemical Sciences, D.A. University, Indore, for recording the gas chromatograms. One of the authors (A.R. Yaul) is grateful to the University Grant Commission (New Delhi, India) for providing financial support.

REFERENCES

1. Dey, K., Bhaumik, B.B.., and Sarkar, S., *Indian J. Chem., Sect. A: Inorg., Bio-inorg., Phys., Theor. Anal. Chem.* 2004, vol. 43, p. 773.
2. Lu, Z. and Anson, F.C., *Inorg. Chem.*, 2001, vol. 40, p. 1329.
3. Ando, R., Ono, H., Yagyu, T., and Maeda, M., *Inorg. Chim. Acta*, 2004, vol. 357, p. 817.
4. Maurya, M.R., Kumar, M., and Arya, A., *Catal. Commun.*, 2008, vol. 10, p. 187.
5. Boghaei, D.M. and Mohebbi, S., *Tetrahedron*, 2002, vol. 58, p. 5357.
6. Masuda, Y. and Shishido, S., *Thermochim. Acta*, 1979, vol. 28, p. 377.
7. Mohebbi, J., Nikpour, S., and Rayati, S., *J. Mol. Catal., A*, 2006, vol. 256, p. 265.
8. Butler, A. and Carrano, C.J., *Coord. Chem. Rev.*, 1991, vol. 109, p. 152.
9. Masuda, Y., *Thermochim. Acta*, 1983, vol. 60, p. 203.
10. Jeyraja, G.L. and House (Jr.), J.E., *Thermochim. Acta*, 1983, vol. 66, p. 289.
11. Furniss, B.S., Hannaford, A.J., Smith, P.W.G., and Tatchell, A.R., *Vogel'S Textbook of Practical Organic Chemistry*, London: Logmans, 1989.
12. Freedman, H.H., *J. Am. Chem. Soc.*, 1961, vol. 83, p. 2900.
13. Natarajan, K., Karvembu, R., Hemalatha, S., and Prabhakaran, R., *Inorg. Chem. Commun.*, 2003, vol. 6, p. 486.
14. Gupta, K.C. and Sutar, A.K., *J. Mol. Catal., A*, 2007, vol. 272, p. 64.
15. Yaul, A.R., Dhande, V.V., Suryawanshi, N.J., and Aswar, A.S., *Pol. J. Chem.*, 2009, vol. 83, p. 565.
16. Aranha, E.P., Dos Santos, M.P., Romera, S., and Dockel, E.R., *Polyhedron*, 2007, vol. 26, p. 1373.
17. Vafazadef, R. and Kashfi, M., *Bull. Korean Chem. Soc.*, 2007, vol. 2817, p. 1228.
18. Garg, R., Fahmi, N., and Singh, R.V., *J. Indian Chem. Soc.*, 2009, vol. 86, p. 670.
19. Raman, N., Pitchaikaniraja, Y., and Kulandaisamy, A., *Proc. Indian Acad. Sci.*, 2001, vol. 113, p. 183.
20. Dutta, S.K. and Edward, R.T., *Polyhedron*, 1997, vol. 16, p. 1863.
21. Lever, A.B.P., *Inorganic Electronic Spectroscopy*, Amsterdam: Elsevier, 1997.
22. Ghosh, T., Bhattacharya, S., Das, A., et al., *Inorg. Chem. Acta*, 2005, vol. 358, p. 989.
23. Joseph, T., Srinivas, D., Gopinath, C.S., and Halligudi, S.B., *Catal. Lett.*, 2002, vol. 83, p. 209.
24. Zsigmond, A., Horvath, A., and Notheisz, F., *J. Mol. Catal., A*, 2001, vol. 171, p. 95.
25. Wasi, N. and Singh, H.B., *Synth. Ract. Inorg. Met.-Org. Chem.*, 1988, vol. 18, p. 473.
26. Modi, C.K. and Thaker, B.T., *J. Therm. Anal. Cal.*, 2008, vol. 94, p. 567.