

Synthetic and Spectroscopic Studies of Chelate Polymers Involving Azelaoyl Bis-*N*-phenyl Hydroxamic Acid with Transition Metal Ions

Vaishali V. Ukey, Harjeet D. Juneja

Department of Chemistry, PGTD Campus, Rashtrasant Tukadoji Maharaj (RTM), Nagpur University, Nagpur 440033, India

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ABSTRACT: Chelate polymers of azelaoyl bis-*N*-phenyl hydroxamic acid with Mn(II), Co(II), Ni(II), and Zn(II) were synthesized for the first time in a dimethylformamide (DMF) medium. These newly synthesized chelate polymers were characterized on the basis of several analytical techniques, namely, elemental analyses, infrared and reflectance spectral studies, magnetic moment, and thermal analyses. On the basis of data obtained with these techniques, the composition of the polymeric units, the structure, and the geometry were ascertained. It was found that the Mn(II) and Zn(II) chelate polymers had a tetrahedral geometry, whereas the Co(II) and Ni(II) chelate polymers were octahedral. Thermal

analytical data clearly indicated that the Ni(II) chelate polymer was highly thermally stable relative to the Mn(II), Co(II), and Zn(II) chelate polymers. Since these chelate polymers are highly insoluble in almost all the organic solvents, including alcohol, acetone, chloroform, carbon tetrachloride, DMF, and DMSO, and have high thermal stability, they may be used as surface-coating materials and as thermally stable materials. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 273–278, 2006

Key words: inorganic polymer; thermogravimetric analyses (TGA); thermal properties; transition metal chemistry

INTRODUCTION

Polymers are important materials used in commodities such as textiles, tires, and packaging (e.g., film and containers). Polymers, particularly thermosets, also are widely used as composite materials in applications in the transportation industry, including automotive, marine, and aerospace. Most of these markets are now mature, and future growth is expected to be small; however, there are many more applications for polymers that may be less obvious but have great potential and offer challenges for new technology and growth into the 21st century. Some of these uses include polymeric membranes for air and water purification and for important separations in the chemical and biotech industries. IR spectra have shown potential bidentate behavior of ligands having complexing sites at hydroxyl and carbonyl groups, which could give rise to complexes of varied coordination numbers depending on the amount of acid used. Recently, a large number of applications for chelate polymers have been reported.^{1–4} Chelate polymers of hydroxamic acid with high thermal stability were reported by Gandhi et al.⁵

In continuation of our earlier work,⁶ we report here the preparation and characterization of azelaoyl bis-*N*-phenyl hydroxamic acid and its Mn(II), Co(II), Ni(II), and Zn(II) chelate polymers.

EXPERIMENTAL

Chemicals

All the chemicals used were AR grade. The solvents used were doubled-distilled before use.

Instruments

C, H, and N content was analyzed on an EA 1108 Carlo Erba elemental analyzer from CDRI Lucknow (India). FTIR spectra of the chelate polymers and ligand were recorded at the Regional Sophisticated Instrumentation Center, IIT Chennai, India, on a Bruker IFS 66V spectrometer (Germany), using the KBr technique in the range of 400–4000 cm⁻¹. Reflectance spectra of the chelate polymers in solid state were recorded on a single-beam Karl-Zeiss Jena, Specord M-400 spectrophotometer in the range 250–600 nm. Finely powdered magnesium oxide was used as a reference material. Magnetic susceptibility of the chelate polymers was determined by Gouy's method at room temperature using mercury tetrathiocyanatocobaltate(II) as the standard. Metal content was esti-

Correspondence to: Vaishali V. Ukey (Vaishali296@rediffmail.com).

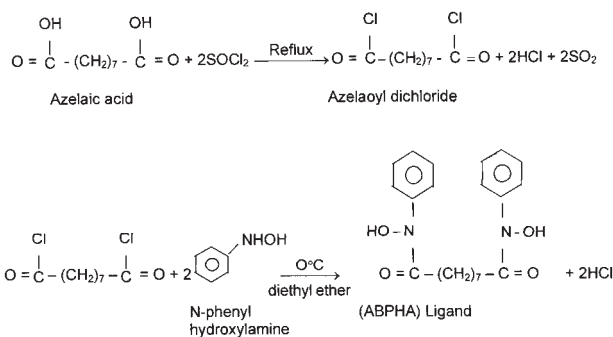


Figure 1 Synthesis of azelaoyl-bis-*N*-phenyl hydroxamic acid (ABPHA).

mated by the standard oxide method using platinum crucible.⁷⁻⁸ Thermogravimetric analysis was carried out at RSIC, RTM Nagpur University, Nagpur, India on an TGA/SDTA-851, Mettler Toledo. The thermocouple used was Pt-Pt-Rh with a temperature range of 20°C–1000°C at a heating rate of 15°C/min. A 12-mg sample was used in the thermal analyses, which were carried out in an air atmosphere. Mass loss was recorded continuously on the recorder.

Synthesis of ligand

In the present investigation, a modified version of the method of Priyadarshini and Tandon,⁹ based on the Schotten–Baumann reaction, was used for the preparation of hydroxamic acid. In this method, freshly prepared *N*-phenyl hydroxylamine and vacuum-distilled acid dichloride in a stoichiometric ratio were reacted at low temperature (0°C or lower) in a diethyl ether medium containing an aqueous suspension of sodium bicarbonate.

Preparation of acid dichloride

First 18.82 g (0.1M) of azelaic acid and 23.78 g (0.2M) of thionyl chloride were placed in a dry 250-mL round-bottomed flask fitted with a perfectly dry Leibig water condenser with a guard tube containing calcium chloride. The mixture was heated in a water bath until a clear yellow liquid was obtained. An air condenser was then used, and the mixture was heated to 70°C–80°C for a half hour for complete evolution of HCl gas. Then the acid dichloride was distilled off under reduced pressure. The azelaoyl dichloride was a yellowish liquid.

Preparation of *N*-phenyl hydroxylamine

N-phenyl hydroxylamine was prepared by controlled reduction of nitrobenzene.¹⁰

Synthesis of azelaoyl bis-*N*-phenyl hydroxamic acid (ABPHA)

To a 500-mL beaker were added 27.25 g (0.25M) of freshly prepared, crystallized *N*-phenyl hydroxylamine, diethylether (100 mL), 25.23 g (0.3M) of sodium bicarbonate, and 30 mL of distilled water, and the mixture was cooled to 0°C or lower. To this mixture, a solution of 22.55 g (0.1M) of azelaoyl dichloride in 150 mL of diethylether was added dropwise with constant stirring for about 1 h. The separated product was filtered and washed thoroughly with a saturated solution of sodium bicarbonate to remove any acidic impurities. The product obtained was crystallized from a 2 : 1 ethanol–dimethylformamide mixture. The ABPHA was cream in color with an mp of 142°C. This is the first report of azelaoyl-bis-*N*-phenyl hydroxamic acid, and hence it has been characterized by elemental analyses, infrared spectra, and so forth. The reactions of ligand formation are shown in Figure 1.

Synthesis of chelate polymers

Chelate polymers of ABPHA with Mn(II), Co(II), Ni(II), and Zn(II) were prepared by the reaction between equimolar quantities (0.01) of metal acetates

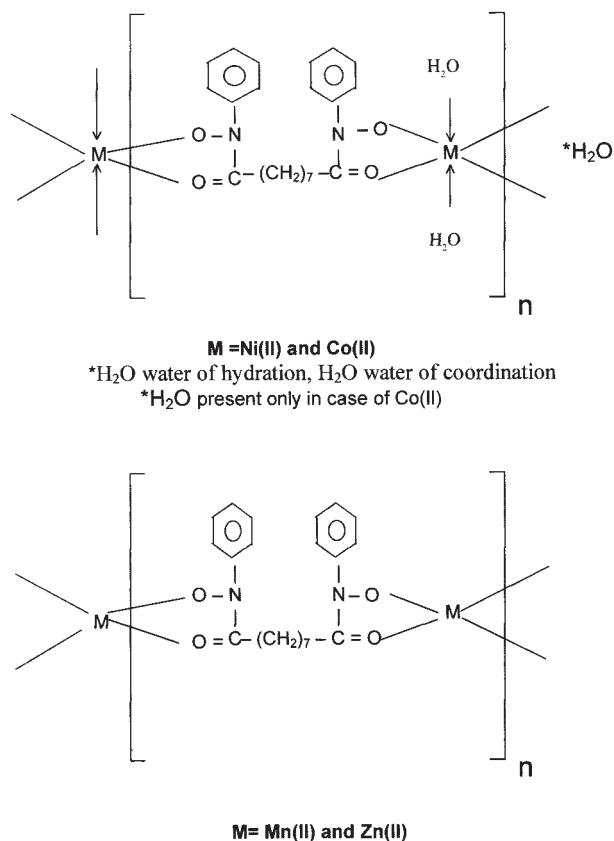


Figure 2 Proposed structure of chelate polymers of azelaoyl-bis-*N*-phenyl hydroxamic acid.

TABLE I
Analytical Data of ABPHA Ligand and Its Chelate Polymers

Proposed composition of chelate polymers	Empirical formula	Formula weight	Yield (%)	Elemental analysis calc. (found)			
				C	H	N	M
ABPHA ligand	C ₂₁ H ₂₆ O ₄ N ₂	370.00	80	68.10 (68.08)	7.02 (7.05)	7.56 (7.40)	—
Mn(II)(ABPHA)	C ₂₁ H ₂₄ O ₄ N ₂ M _n	422.93	60	59.58 (59.00)	5.67 (5.55)	6.62 (6.55)	12.98 (12.80)
Co(II)(ABPHA)	C ₂₁ H ₃₀ O ₇ N ₂ Co	480.93	70	52.39 (52.02)	6.23 (6.62)	5.82 (5.55)	12.25 (12.50)
Ni(II)(ABPHA)	C ₂₁ H ₂₈ O ₆ N ₂ Ni	462.71	70	54.46 (54.05)	6.05 (6.62)	6.05 (6.56)	12.68 (12.12)
Zn(II) (ABPHA)	C ₂₁ H ₂₄ O ₄ N ₂ Zn	433.37	80	58.14 (58.12)	5.53 (5.40)	6.64 (6.44)	15.08 (15.02)

and bis ligand azelaoyl bis-*N*-phenyl hydroxamic acid (ABPHA) in a dimethylformamide medium. The reaction mixtures were then heated in an oil bath with constant stirring until the polymers separated as an insoluble solid. They were then digested in an oil bath for about 24 h from 120°C to 150°C. Chelate polymers generally appeared after 24 h of heating in the oil bath. They were filtered, washed thoroughly, first with hot DMF and then with absolute alcohol, and dried. These newly synthesized chelate polymers were found to be insoluble in almost all organic solvents including alcohol, acetone, chloroform, carbon tetrachloride, dimethylformamide, dioxane, and dimethyl sulfoxide. Their purity was ascertained by repeated washing, as recrystallization was not possible. The final products appeared as amorphous powder. The chelate polymers were all stable at room temperature.

RESULTS AND DISCUSSION

On the basis of elemental analyses, infrared spectra, reflectance spectra, and thermal studies, the proposed structures of these chelate polymers were determined, which are shown in Figure 2. The analytical data on the chelate polymers of azelaoyl-bis-*N*-phenyl hydroxamic acid are given in Table I. The presence of water of crystallization as well as water of coordination was ascertained on the basis of the thermal studies.

Infrared spectral studies

The infrared spectra of the chelate polymers were nearly identical. The frequencies of some significant

bands of the free ligand and of the chelate polymers are reported in Table II. A free O—H stretching frequency appeared at 3179 cm⁻¹ in the ABPHA ligand.¹¹ A sharp band at 1684 cm⁻¹ in ABPHA was assigned to the C=O stretching vibration. Two consecutive bands at 1661–1715 cm⁻¹ in ABPHA resulted from various resonating structures of the ligand. An N—O stretching vibration was observed at 901 cm⁻¹. As anticipated, the O—H band disappeared in the polymers. The carbonyl band was found to have been displaced toward a lower frequency with an increase in intensity.¹² The same was observed for ABPHA polymers.

With the Co(II) chelate polymer, only a medium band appeared at 3513 cm⁻¹, which was a result of the H—OH of lattice water, as only the Co(II) polymer was found to contain lattice water in addition to coordinated water. With the Co(II) and Ni(II) chelate polymers, bands appearing in the region of 755–761 cm⁻¹ could be assigned to π H—OH mode of coordinated water. The presence of an M—O band in the chelate polymers was indicated by bands around 646–687 cm⁻¹.

Electronic spectral studies and magnetic susceptibility data of chelate polymers

In the [Mn(II)(ABPHA)]_n chelate polymer, a band appeared at 27.80 kK that could be assigned because of the 6A₁→4E (D) transition in a tetrahedral field. The magnetic moment value also supported the tetrahedral geometry of the [Mn(II)(ABPHA)]_n chelate polymer.¹³

TABLE II
IR Spectral Assignment of ABPHA Ligand and Its Chelate Polymers (cm⁻¹)

Ligand/chelate polymers	Lattice (H—O—H)	(Coord.) H—O—H	O—H	>C—O at	N—O	M—O
				>C—O M		
ABPHA ligand	—	—	3179.7 (b)	1684	901 (s)	—
Mn(II)(ABPHA)	—	—	—	1593 (s)	945 (w)	687 (w)
Co(II)(ABPHA)	3513 (m)	755 (w)	—	1562 (b)	934 (b)	655 (w)
Ni(II) (ABPHA)	—	761 (b)	—	1525 (s)	984 (s)	661 (b)
Zn(II) (ABPHA)	—	—	—	1529 (s)	953 (w)	646 (s)

TABLE III
Electronic Spectral and Magnetic Susceptibility Data on ABPHA Chelate Polymers

Chelate polymers	Color	μ_{eff} (B.M.)	Electronic spectra		Stereochemistry
			Absorbance (kk)	Assignments	
Mn(II)(ABPHA)	Light brown	5.82	27.80	$6A_1 \rightarrow 4E$ (D)	Tetrahedral (high spin)
Co(II)(ABPHA)	Light pink	4.82	22.20	$4 T_{1g} \rightarrow 4T_{1g}$	Octahedral (high spin)
Ni(II) (ABPHA)	Light green	4.28	18.50 22.12	$3 A_{2g} \rightarrow 3T_{1g}$ (P)	Octahedral (high spin)
Zn(II) (ABPHA)	Pale white	Diamagnetic	16.66 —	$3 A_{2g} \rightarrow 3T_{1g}$ (F) —	Tetrahedral

In the $\{[\text{Co(II)(ABPHA)(H}_2\text{O)}_2] (\text{H}_2\text{O})\}_n$ chelate polymer, the bands that appeared at 18.50 and 22.20 kK may be attributed to the $4T_{1g} \rightarrow 4T_{1g}$ (P) transition in the octahedral field. The octahedral geometry was further supported by the magnetic moment value.

In the $[\text{Ni(II)(ABPHA)(H}_2\text{O)}_2]_n$ chelate polymer, the bands that appeared at 22.12 and 16.66 kK could be assigned to the $3A_{2g} \rightarrow 3T_{1g}$ (P) and $3A_{2g} \rightarrow 3T_{1g}$ (F) transitions, respectively, in octahedral field, which was further supported by the magnetic moment value.

Because $[\text{Zn(II)(ABPHA)}]_n$ is a d^{10} system, it is diamagnetic. However, the results of elemental analyses, an infrared spectrum, and thermal decomposition analysis suggested that its most probable geometry was tetrahedral. The electronic spectral and magnetic susceptibility data of the chelate polymers are given in the Table III.

Thermogravimetric studies of ABPHA chelate polymers

The results of thermogravimetric analysis of the ABPHA chelate polymers are presented in Table IV. All chelate polymers decomposed in two or three stages.¹⁴ Thermal analyses confirmed the presence of lattice and coordinated water molecules in the Co(II) chelate polymer and only coordinated water molecules in the Ni(II) chelate polymer. According to Nikolaev et al.,¹⁵

water eliminated below 150°C can be considered crystal water, and water eliminated above 150°C–200°C may be considered water of coordination.

Mn(II) (ABPHA) chelate polymer

The Mn(II) chelate polymer (Fig. 3) showed degradation after 200°C because of the absence of water of hydration as well as water of coordination. After 200°C, a gradual mass loss was observed up to 400°C, after which no mass loss was observed, indicating the formation of a metal oxide, MnO. TG analysis suggested a four-coordinate geometry for the Mn(II) chelate polymer. The decomposition temperature was found to be 353°C (total mass loss: calc. 61.02%; obs. 60%).

Co(II) (ABPHA) chelate polymer

The thermogram of the Co(II) chelate polymer (Fig. 4) showed loss of weight (calc. 3.75%, obs. 3.28%) between 120°C–140°C, which may have been a result of the presence of one lattice water molecule. After 160°C, more weight loss was observed up to 200°C (calc. 7.50%, obs. 7.45) because of the presence of two coordinated water molecules. TG analysis favored a six coordinated geometry for the Co(II) chelate poly-

TABLE IV
Thermoanalytical Data on ABPHA Chelate Polymers

Chelate polymers	Loss due to lattice water (%) Calc. (Obs.)	Loss due to coordinated water (%) Calc. (Obs.)	Loss due to Decomp. (%)	Decomp. range (°C)	Probable composition of residue	Decomposition temperature (°C)
$[\text{Mn(II)(ABPHA)}]_n$	—	—	60	200–400	MnO	353
$\{[\text{Co(II)(ABPHA)(H}_2\text{O)}_2] (\text{H}_2\text{O})\}_n$	3.75 (3.28)	7.5 (7.63)	70	220–430	CoO	370
$[\text{Ni(II)(ABPHA)(H}_2\text{O)}_2]_n$	—	7.78 (7.45)	70	220–800	NiO	530
$[\text{Zn(II)(ABPHA)}]_n$	—	—	80	200–550	ZnO	453

120–150°C, Water of crystallization. 150–200°C, Water of coordination.

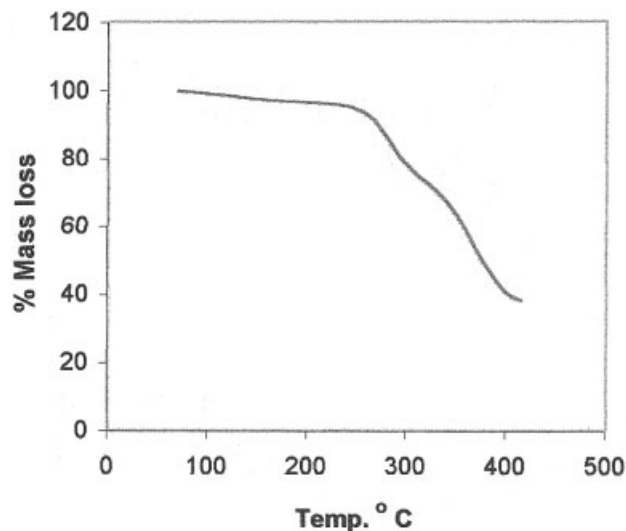


Figure 3 Thermogram of Mn(II) ABPHA chelate polymer.

mer. After 220°C, there a gradual mass loss was observed up to 430°C, after which no mass loss was observed because of the formation of a metal oxide, CoO. The decomposition temperature for the Co(II) chelate polymer was found to be 370°C (total mass loss: calc. 70.08%; obs. 70%).

Ni(II) (ABPHA) chelate polymer

No mass loss was observed up to 150°C, indicating the absence of lattice water (Fig. 5). However, weight loss was observed after 150°C up to 200°C, corresponding to two molecules of coordinated water. Thus, octahedral geometry for the Ni(II) chelate polymer was supported. After 220°C, a gradual mass loss was observed up to 800°C, which may be attributed to the decom-

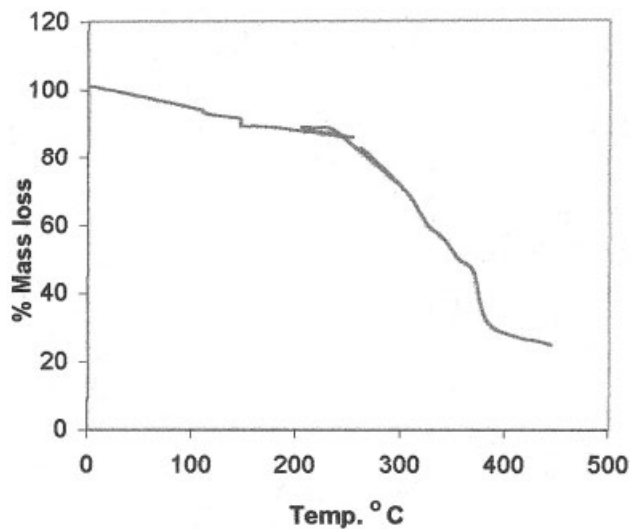


Figure 4 Thermogram of Co(II) ABPHA chelate polymer.

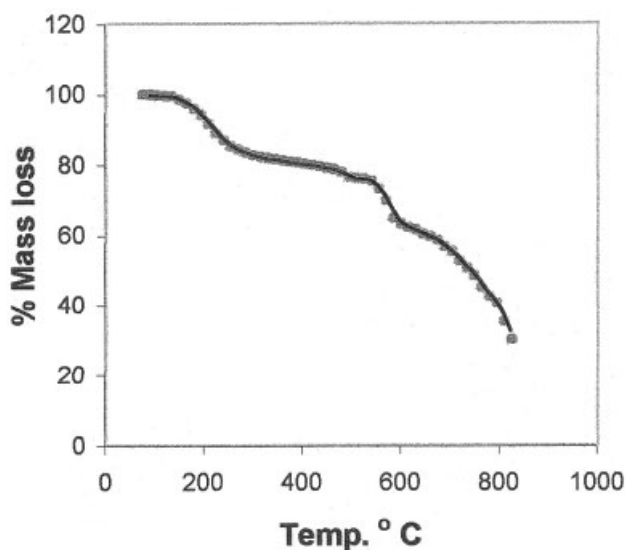


Figure 5 Thermogram of Ni(II) ABPHA chelate polymer.

position of the chelate polymer, and then it formed a stable metal oxide, NiO. The decomposition temperature is found to be 530°C. (Total mass loss: calc. 70.12%; obs. 70%)

Zn(II) (ABPHA) chelate polymer

The TG curve of Zn(II) ABPHA (Fig. 6) showed an absence of both water of hydration and water of coordination because no mass loss was observed up to 220°C, thus favoring four coordinated geometry for the Zn(II) chelate polymer. After 220°C up to 550°C, rapid loss of mass was observed because of the decomposition of the chelate polymer. The decomposition temperature of the Zn(II) chelate polymer was

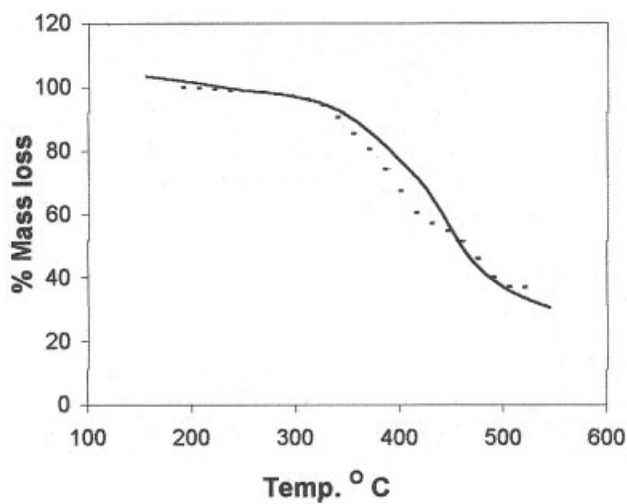


Figure 6 Thermogram of Zn(II) ABPHA chelate polymer.

found to be 453°C (total mass loss: calc. 80.50%; obs. 80%).

The trend in thermal stability of the chelate polymers was found to be: Ni(II) > Zn(II) > Co(II) > Mn(II). The thermoanalytical data of the chelate polymers of ABPHA are given in Tables IV and V. The thermograms of all chelate polymers are shown in Figures 3–6.

CONCLUSIONS

According to the analytical techniques used, both the Mn(II) and Zn(II) chelate polymers have a tetrahedral geometry, whereas the Ni(II) and Co(II) chelate polymers have an octahedral geometry. Thermal stability of the chelate polymers was in the order Ni > Zn > Co > Mn, and the order of reaction was close to 1.

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References

1. Michalak, A.; Ziegler, T. *Macromolecules* 2003, 36, 928.
2. Davies, J. A.; Griffiths, P. C. *Macromolecules* 2003, 36, 950.
3. Prabhumirashi, L. S.; Khoje, J. K. *Indian J Chem* 2004, 43, 299.
4. Dholakiya, P. P.; Patel, M. N. *Synth Reactivity Inorg Metal Org Chem* 2004, 34, 383.
5. Gandhi, N. R.; Munshi, K. N. *J Indian Chem Soc* 1982, 59, 1290.
6. Saxena, N.; Juneja, H. D.; Munshi, K. N. *J Indian Chem Soc* 1993, 70, 943.
7. Roy, S. M.; Juneja, H. D.; Munshi, K. N. *Synth Reactivity Inorg Metal Org Chem* 2001, 31, 1612.
8. Roy, S. M.; Juneja, H. D.; Munshi, K. N. *J Therm Anal Calorimetry* 2001, 65, 197.
9. Priyadarshini, U.; Tandon, S. G. *J Chem Eng Data* 1967, 12, 143.
10. Marvel, C. S.; Kamma, O. *J Am Chem Soc* 1919, 40, 276.
11. Shukla, P.; Agrawal, Y. K.; Kuchya, K. P. *J Indian Chem Soc* 1954, 51, 143.
12. Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1970; p 270.
13. Lever, A. B. P. *Inorganic Electronic Spectroscopy*; Elsevier: New York, 1968; p 297.
14. DeGeiso, R. C.; Donaruna, L. G.; Tomic, E. A. *J Org Chem* 1962, 27, 1424.
15. Nikolaev, A. V.; Logvienko, V. A.; Myachina, L.T. *Thermal Analysis*; Academic Press: New York, 1969; Vol. 2, p 779.