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PREPARATION, CHARACTERIZATION AND THERMAL STUDY OF NEW CERIUM(IV) COMPLEXES WITH THE SALICYLIDENE-2-AMINOTHIOPHENOL SCHIFF BASE

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ABSTRACT

New complexes of the titled Schiff base with cerium(IV) ion have been synthesized and characterized by elemental analyses, conductimetric, IR and ^{1}H NMR studies and thermogravimetric analysis. The results suggest that the Schiff base acts as a bivalent anion with tridentate ONS donors derived from the phenolic oxygen, azomethine nitrogen and thiophenolic sulfur. The complexes formed are non-electrolytes with the general formulae $[ML(NO_3)_2H_2O]$ and $[M(HL)_2(NO_3)_2]$. The thermal decomposition of the complexes follows

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first order kinetics and the thermodynamic parameters of the decomposition are reported.

INTRODUCTION

A large number of Schiff bases and their complexes have been studied for their interesting and important properties, *e.g.* their ability to reversibly bind oxygen[1], catalytic activity in the hydrogenation of olefins[2], transfer of an amino group[3], photochromic properties[4], complexing ability towards some toxic metals[5] and so on. Metal complexes of Schiff bases derived from substituted salicylaldehydes and various amines have been widely investigated[6-12]. However, little attention has been given to Schiff bases which include an ONS donor system. The aim of the present work is to synthesize and study the chelate formed between the salicylidene-2-aminothiophenol Schiff base (Fig. 1) and the Ce(IV) ion.

EXPERIMENTAL

All the chemicals used in this work were of analytical grade or equivalent quality. Cerium(IV) was used as the $(NH_4)_2Ce(NO_3)_6$ salt. The organic solvents used were obtained as pure grade materials from BDH or purified by recommended methods[13].

Preparation of the Schiff Base

The Schiff base was prepared by a condensation reaction between 0.5 mole of salicylaldehyde (6.10 g, 5.24 mL (d = 1.164-1.167)) and 0.5 mole of 2-aminothiophenol (6.23 g, 5.31 mL (d =

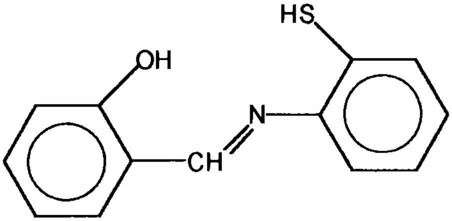


Fig. 1. Structure of the Schiff Base H_2L

1.179)) in 100 ml ethanol. The Schiff base obtained was filtered and recrystallized from dilute acetic acid to a sharp melting point of 127.8°C (literature m.p.: 128° C). The structure was confirmed by elemental analysis, IR, ^{1}H NMR and thermal analysis[14].

Measurements

The pH-potentiometric titrations were carried out in alcohol-water mixture (70% v/v), to insure the complete solubility of the Schiff base, at 25° C and μ = 0.1 ionic strength, (by the addition of appropriate amounts of 1 M sodium chloride solution), using a Jenway 3010 pH meter. The ionization constants of the investigated Schiff base and its metal chelates were determined using the technique of Sarin and Munshi[15] and Irving and Rossotti[16].

The IR spectra were recorded as KBr pellets using a 1430 Perkin-Elmer spectrometer. The ^{1}H NMR spectra were recorded on a Varian Gemini 200 (200 MHz) spectrometer. DMSO-d_6 was used as solvent and the spectra were measured in the 0-14 ppm range with TMS as the internal standard. The conductimetric measurements were carried out in DMF using a TOA conductivity bridge model CM-1K. The thermal analyses of the complexes were carried out using a Shimadzu thermogravimetric analyzer with a TGA-50H detector in nitrogen atmosphere, (flow rate = 30.0 mL/min). The % weight loss was measured from the ambient temperature up to 800° C at a heating rate of 10° C/min.

Preparation of Solid Complexes

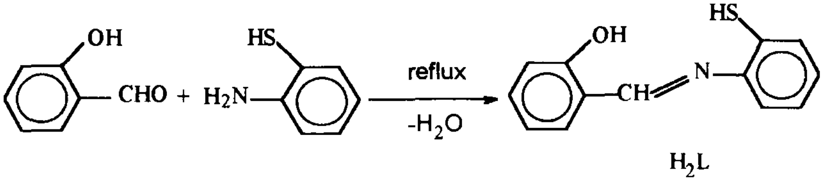
The 1:1 complex was prepared by addition of 20 mmol of the hot ethanolic solutions of the Schiff base under investigation, (0.23 g in 50 mL ethanol), to 20 mmol of $(NH_4)_2Ce(NO_3)_6$, (0.55 g in 50 mL ethanol), the solution was made 85% v/v ethanol/water by addition of ethanol and water in the dilution of the volume to 250 mL. The pH was adjusted to 5.0-6.0 using alcoholic ammonium hydroxide, (a few drops of conc. NH_4OH in ethanol), and the solution was then refluxed for 2 h, concentrated under vacuum to 100 mL and cooled overnight to separate the solid complex which was filtered and washed several times with ethanol until the filtrate became colourless. The isolated complex was recrystallized by dissolving it in the least possible amount of DMF, filtered while hot and diluted with ethanol to 100 mL and left overnight. The solid complex separated was filtered and washed first with ethanol, then with diethyl ether, dried in a vacuum desiccator and then subjected to elemental microanalysis.

The 1:2 complex was prepared by addition of 10 mmol of $(NH_4)_2Ce(NO_3)_6$, (0.2741 g in 50 mL ethanol), to 20 mmol of the hot solution of the Schiff base (0.229 g in 50 mL ethanol) and proceeding the same way as above. The analyses in each case, (C, H, N and S), were repeated twice. The metal contents of the complexes were determined by the method of MacDonald[17].

RESULTS AND DISCUSSION

Synthesis of Complexes

The Schiff base complexes with Ce(IV) of the general formulae [$CeL(NO_3)_2H_2O$] and [$Ce(HL)_2(NO_3)_2$] were prepared by refluxing $(NH_4)_2Ce(NO_3)_6$ and the Schiff base prepared by the condensation of salicylidine and 2-aminothiophenol according to the following scheme:



$$H_2L + (NH_4)_2Ce(NO_3)_6 \xrightarrow[2h]{\text{reflux}} \underset{1:1}{CeL(NO_3)_2.H_2O} + 2\,NH_4NO_3 + 2HNO_3$$

$$2H_2L + (NH_4)_2Ce(NO_3)_6 \xrightarrow[2h]{\text{reflux}} \underset{1:2}{Ce(HL)_2(NO_3)_2} + 2\,NH_4NO_3 + 2HNO_3$$

The results of the elemental analyses of the Schiff base H_2L and its 1:1 and 1:2 (M:H_2L) complexes are listed in Table I and are in good agreement with those required by the proposed formulae. The metal percentages found are average values of three metal content determinations[17] and those obtained from thermal analysis, (metal oxides residue). Electrical conductivities of the complexes in DMF, (0.001 M) are 2.10 and 2.61 S cm^{-2} mol^{-1} for Ce:H_2L (1:1) and Ce:H_2L (1:2), respectively, indicating that the complexes are non-electrolytes.

TABLE I. Elemental Analysis Data.

Compound (Empirical Formula) (Formular weight)	Yield (%)	Colour	Decom-position Temp. (°C)	% C	% H	% N	% S	%M
H_2L ($C_{13}H_{11}NOS$) (229)	98	faint yellow	128 (m.p.)	67.3 (68.0)	4.8 (4.8)	6.3 (6.3)	13.9 (14.0)	—
[$CeL(NO_3)_2H_2O$] ($C_{13}H_{11}CeN_3O_8S$) (509.12)	90	Blue	328	31.0 (30.6)	2.2 (2.2)	8.2 (8.3)	6.2 (6.3)	27.4 (27.5)
[$Ce(HL)_2(NO_3)_2$] ($C_{26}H_{20}CeN_4O_8S_2$) (720.12)	85	dark blue	310	43.3 (43.3)	2.8 (2.8)	7.7 (7.8)	8.8 (8.9)	19.5 (19.5)

Formation Constants

The ionization constants of the Schiff bases are found to be $pK_1 = 9.3$ and $pK_2 = 10.35$ for the OH and SH groups, respectively[18].

$$H_2L \Leftrightarrow HL^- + H^+ \qquad K_1 = [HL^-][H^+]/[H_2L]$$

$$HL^- \Leftrightarrow L^{2-} + H^+ \qquad K_2 = [L^{2-}][H^+]/[HL^-]$$

The formation constants of the Ce(IV) complexes are $\log\beta_1 = 12.74$ and $\log\beta_2 = 23.56$, (where $\log\beta_1 = \log K_1$ and $\log\beta_2 = \log K_1K_2$). The equations of the formation reactions are given below, (M represents Ce(IV) for simplicity).

$$M + H_2L \Leftrightarrow ML^{2-} + 2H^+ \qquad K_1 = [ML^{2-}][H^+]^2/[M][H_2L]$$

$$2ML^- + 2H^+ \Leftrightarrow 2M(HL)_2 \qquad K_2 = [M(HL_2]^2/[ML^-]^2[H^+]^2$$

The formation constant values reflect the high affinity of the Schiff bases for chelation with Ce(IV) ions. The high values of the free energy change, ($-\Delta G_1 = 72.81$ and $-\Delta G_2 = 134.65$ kJmol^{-1} for $\log\beta_1$ and $\log\beta_2$, respectively), indicate that the complex formation reaction is a spontaneous one.

IR Spectra

The IR spectra of the cerium complexes were compared with those of the Schiff base H_2L in order to determine the coordination sites involved in chelation. The significant IR bands are listed in Table II.

The OH stretching vibration, ν(OH), which is found as a medium band at 3254 cm^{-1} in the spectrum of the Schiff base has disappeared in the spectra of the 1:2 complex ($Ce(HL)_2(NO_3)_2$) indicating the

TABLE II. Significant IR Bands of the Schiff Base and its Ce(IV) Complexes (cm^{-1}).

complex	ν(OH)	ν(C=N)	δ(OH) in-plane	ν(C-O) str.	ν(C-S) str.	γ(OH) (Water)	ν(M-O)	ν(M-N)
H_2L	3254 m	1619 s	1406 m	1236 s	759 s	—	—	—
$[CeL(NO_3)_2$ H2O]	3421 vb	—	1384 m	1201 m	727 m	972 w	675 w	457 w 430 w
$[Ce(HL)_2(NO_3)_2]$	—	1608 m	1380 m	1203 m	735m	—	636 w	457 w 434 w

participation of the OH group in chelate formation via proton displacement. On the other hand, the presence of water of coordination in the spectra of the 1:1 complex ($CeL(NO_3)_2.H_2O$) as a broad band at 3421 cm^{-1} renders it difficult to obtain conclusions from the ν(OH) frequency of the OH group of the Schiff base. However, this OH vibration disappeared on drying the 1:1 complex at 290° C indicating the participation of the OH group in chelation. The participation of the OH group is further evidenced by the shift in the position of the δ(OH) in-plane vibration (1406 cm^{-1} in the free ligand) to 1384 cm^{-1} in the spectrum of the complex and the shift of the strong ν(C-O) stretching vibration in the Schiff base (1236 cm^{-1}) to a medium vibration at 1201 cm^{-1} in the spectrum of the complex. The presence of water in the 1:1 complex is confirmed by the presence of a weak band at 972 cm^{-1} which may be attributed to the bending vibration of water molecules, γ(OH). The other bending vibration of water molecules, δ(OH), is usually found around 1600 cm^{-1} which always interferes with the C=C skeleton vibration of the benzene ring.

The SH stretching vibrations, ν(SH), are not helpful since they displayed very weak bands in both the free ligand and the spectra of the complexes. However, the participation of the SH group in chelation is ascertained from the shift of the ν(C-S) band to lower frequencies, from 759 cm^{-1} in the free ligand to 727 and 735 cm^{-1} in the spectra of the 1:1 and 1:2 complexes, respectively.

The ν(C=N) stretching vibration, found in the free ligand at 1619 cm^{-1}, disappeared in the spectra of the 1:1 complex and has shifted to lower wave numbers in the spectra of the 1:2 complexes (1608 cm^{-1}), indicating the participation of the azomethine nitrogen in coordination (M←N). New bands observed at 675 and 636 cm^{-1} may be attributed to M-O vibrations. Two other new bands observed at 457 and 430 cm^{-1} in the spectra of the 1:1 complex and at 457 and 434 cm^{-1} in the spectra of the 1:2 complex may be attributed to M-N vibrations from CH=N and nitrate groups.

^{1}H NMR Spectra

The ^{1}H NMR spectrum of the Schiff base has three peaks[14], at 10.9, (s, 1H, OH), 6.4-7.6, (m, 9H, ArH and azomethine), 3.4, (s, 1H, SH). When comparing the spectra of the diamagnetic 1:1 and 1:2 complexes with those of the free ligand, the OH singlet appearing at 10.9 ppm in the case of the free ligand has disappeared in the spectra of the two complexes, indicating the participation of the OH group in chelation through proton displacement. The SH signal present in the spectrum of the free ligands at 3.4 ppm is absent in the spectra of the 1:1 complex, indicating that the SH proton is removed by chelation. However, this signal is found deshielded in the spectra of the 1:2 complex at 3.7 ppm which indicates that the SH group may participate in coordination without proton displacement. A new signal is observed at 3.5 ppm in the spectrum of the 1:1 complex, with an integration corresponding to two protons, corresponding to one water molecule.

Thermogravimetric Analysis

Studies on the thermal decomposition and kinetics of metal chelates with Schiff bases have been done by several workers[19,20]. The complexes under investigation have two decomposition steps. The first decomposition step started at 328 and 310° C in case of the 1:1 and 1:2 complexes, respectively, and ended at 493° C in both cases. The second decomposition is in the range 515-659° C for the 1:1 complex and 493-720° C for the 1:2 complex with the formation of stable oxide CeO_2 as end product, (Table III). The initial mass loss observed in the thermogram of the 1:1 complex in the range of 156-290° C corresponding to one water molecule, was attributed to water of coordination[20, 21].

On the basis of the above observations, the following general scheme for the thermal decomposition may be proposed:

For the 1:1 complex:

$$[ML(NO_3)_2H_2O] \xrightarrow[\text{156-290}^\circ\text{C}]{H_2O\text{ (decoordination)}} [ML(NO_3)_2]$$

$$[ML(NO_3)_2] \xrightarrow[\text{328-493}^\circ\text{C}]{\text{partial decomposition}} \underset{\text{(unstable)}}{\text{Intermediate}}$$

$$\text{Intermediate} \xrightarrow[\text{515-659}^\circ\text{C}]{\text{final decomposition}} \text{metal oxide } (CeO_2)$$

For the 1:2 complex:

$$[M(HL)_2(NO_3)_2] \xrightarrow[\text{310-493}^\circ\text{C}]{\text{partial decomposition}} \underset{\text{(unstable)}}{\text{Intermediate}}$$

$$\text{Intermediate} \xrightarrow[\text{493-720}^\circ\text{C}]{\text{final decomposition}} \text{metal oxide } (CeO_2)$$

TABLE III. Thermal Data of Schiff base-Ce(IV) Complexes.

Complex	Water elimination				Decomp. stages °C	Oxide formation (% metallic residue)		
	Temp. range; °C	% H_2O Loss calc.	% H_2O Loss found	No. of H_2O molecules		Temp. °C found		calc.
[CeL$(NO_3)_2$ H_2O]	156-290	3.5	3.60	1	328-493	659	27.5	27.4
					515-659			
[Ce$(HL)_2(NO_3)_2$]	---	---	---	---	310-493	720	19.5	19.5
					493-720			

Based on the elemental analyses, IR, NMR and TG studies, the Schiff base acts as a dibasic tridentate NSO ligand in the 1:1 complex and monobasic tridentate NSO ligand in the 1:2 complex. The complexes were found to have the general formulae $[CeL(NO_3)_2H_2O]$ and $[Ce(HL)_2(NO_3)_2]$ in which cerium(IV) is suggested to have the coordination numbers six and eight, respectively (Fig. 2).

Determination of Reaction Order of Decomposition

The Horowitz and Metzger[22] equation, $C_s = (n)^{1/1-n}$, where C_s is the weight fraction of the substance present at the DTG peak temperature, T_s, is given as

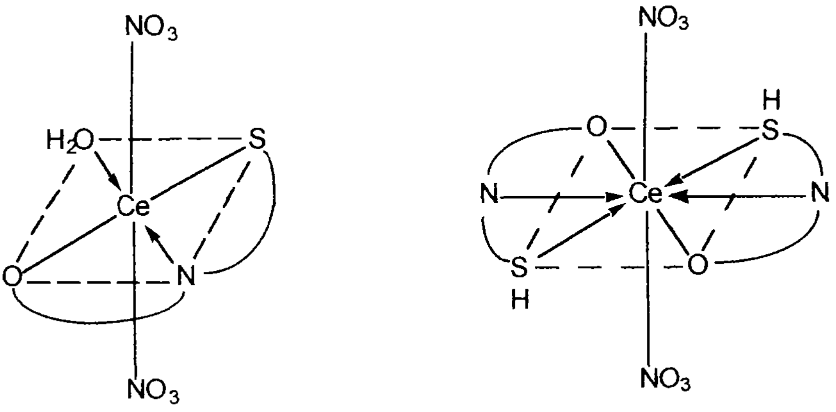
$$C_s = (W_s-W_f)/(W_i-W_f) \qquad (1)$$

and was used for the determination of the values of the reaction order (n). Here W_s stands for the weight remaining at a given temperature T_s, i.e. the DTG peak temperature, W_i and W_f are the initial and final weights of the substance, respectively. The values of C_s for the thermal decomposition of complexes are in the range 0.30-0.39 which indicates that the decomposition follows first order kinetics[22].

Integral Method using the Coats-Redfern Equation[23]

For a first order process the Coats-Redfern equation may be written in the form:

$$\log\left[\ln\frac{W_f}{(W_f - W)/T^2}\right] = \log\left[\frac{AR}{\theta E *}\left(1 - \frac{2RT}{E *}\right)\right] - \frac{E *}{2.303RT} \qquad (2)$$



1:1 complex

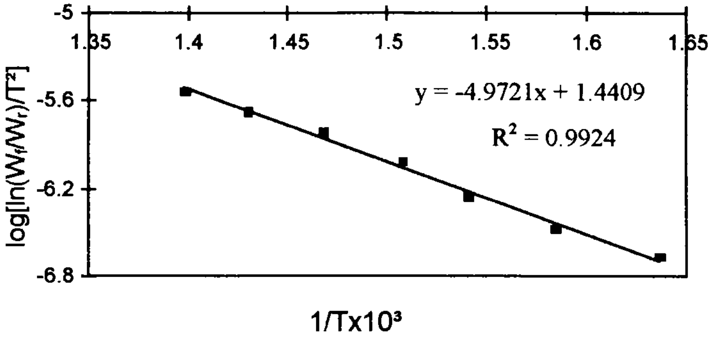
1:2 complex

Fig. 2. Suggested Structures of the Complexes

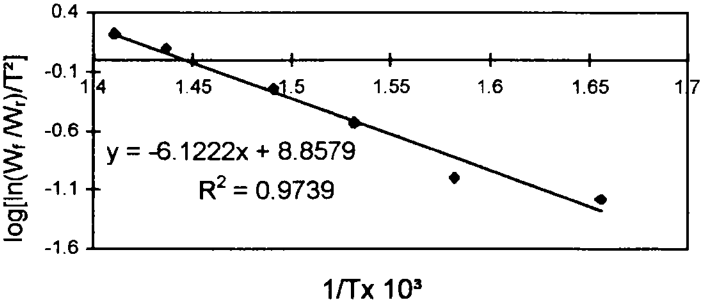
where W_f is the mass loss at the completion of the reaction, W is the mass loss up to the temperature T; (W_r = W_f-W), R is the gas constant, E* is the activation energy in Jmol^{-1}, θ is the heating rate. Since 1-2RT/E* ≅ 1, a plot of the left hand side of equation (2) against 1/T was drawn (Figs. 3 and 4) and E* was calculated from the slope and A (Arrhenius constant) was found from the intercept.

The activation entropy S*, the activation enthalpy H* and the free energy of activation G* were calculated using the following equations:

$$S^* = 2.303\ (\log\frac{Ah}{KT})\ R \qquad (3)$$

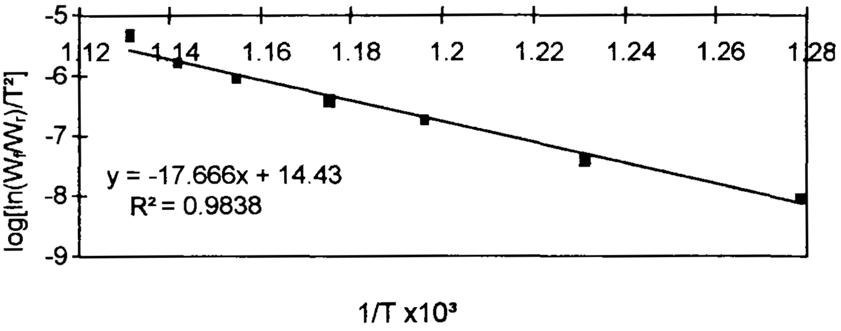


1:1 complex

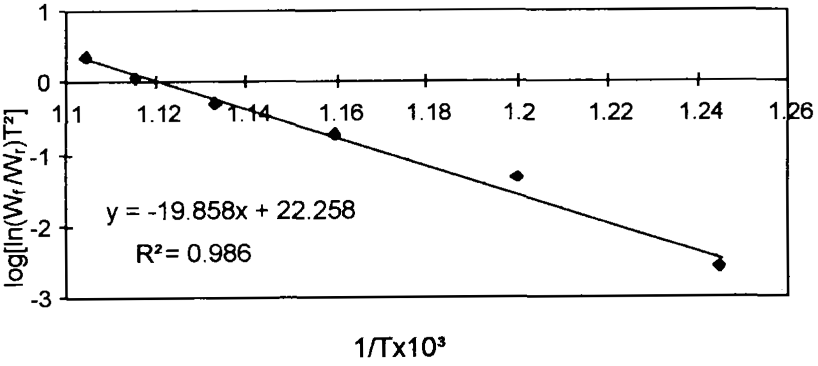


1:2 complex

Fig. 3. Coats-Redfern Plots for the First Decomposition Steps of the Schiff Base Complexes.



(1:1) complex



(1:2) complex

Fig. 4. Coats-Redfern Plots of the Second Decomposition Step of the Schiff Base Complexes

TABLE IV. Kinetic Data of the Thermal Decomposition of the Schiff Base Complexes

Complex	Decomp. steps °C	E* kJmol^{-1}	A s^{-1}	S* JK^{-1}mol^{-1}	H* kJmol^{-1}	G* kJmol^{-1}	C$_s$
[CeL(NO$_3$)$_2$H$_2$O]	328-493	95.3	3.2×10^{6}	-15.3	89.6	100.0	0.4
	515-659	338.5	1.2×10^{20}	15.7	331.2	317.5	0.3
[Ce(HL)$_2$(NO$_3$)$_2$]	310-493	117.3	$1. \times 10^{14}$	2.0	111.7	110.4	0.4
	493-720	380.5	8.3×10^{27}	47.3	373.1	330.6	0.3

$$H^* = E^* - RT \tag{4}$$

$$G^* = H^* - T_s S^* \tag{5}$$

where k and h are the Boltzman and Planck constants respectively. The calculated values of E*, A, S*, H* and G* for the two decomposition steps are given in Table IV.

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REFERENCES

1. R. D. Jones, D. A. Summerville and F. Basolo, Chem. Rev., 79, 139 (1979).
2. G. Henrici-Olive and S. Olive, "The Chemistry of the Catalyzed Hydrogenation of Carbon Monoxide", Springer, Berlin, pp. 152 (1984).
3. H. Dugas and C. Penney, "Bioorganic Chemistry", Springer, New York, pp. 435 (1981).
4. J. D. Margerum and L. J. Miller, " Photochromism", Interscience, Wiley, pp. 569 (1971).
5. W. J. Sawodny and M. Riederer, Angew. Chem., Int. Edn. Engl., 16, 859 (1977).

6. S. Yamada, H. Kuma and K. Yamanouchi, Inorg. Chim. Acta, 10, 151 (1974).
7. G. C. Percy and H. S. Stenton, Spectrochim. Acta, 32A, 1615 (1976).
8. B. A. Kushekar and D. D. Khanolkar, Indian J. Chem., 22A, 881 (1983).
9. V. V. Dixit and B. H. Mehta, Natl. Acad. Sci. Lett., 9, 179 (1986).
10. A. A. Abd El-Gaber, A. M. A. Hassaan, M. El-Shabasy and A. M. El-Roudi, Synth. React. Inorg. Met.-Org. Chem., 21, 1265 (1991).
11. A. Taha, S. El-Shetary and W. Linert, Monatsh. Chem., 124, 135 (1993).
12. G. Wang and J. C. Chang, Synth. React. Inorg. Met-Org. Chem., 24, 623 (1994).
13. A. I. Vogel, "Vogel's Textbook of Practical Organic Chemistry", 5th Edn., Longman, London (1989).
14. Y. M. Issa, M. M. Omar, H. M. Abdel-Fattah and A. A. Soliman, J. Indian Chem. Soc., 73, 55 (1996).
15. R. Sarin and K. N. Munshi, J. Inorg. Nucl. Chem., 34, 581 (1972).
16. H. M. Irving and H. S. Rossotti, J. Chem. Soc., 3397 (1953).
17. A. M. G. MacDonald and P. Sirichanya, Microchem. J., 14, 199 (1969).
18. Y. M. Issa, H. M. Abdel Fattah, M. M. Omar and A. A. Soliman, Monatsh. Chem., 126, 163 (1995).
19. V. Indira and G. Parameswaran, J. Therm. Anal., 32, 1151 (1987).
20. Y. M. Issa, H. M. Abdel Fattah and A. A. Soliman, J. Therm. Anal., 42, 1175 (1994).
21. N. T. Abdel-Ghani and O. E. Sherif, Thermochim. Acta, 156, 69 (1989).
22. H. H. Horowitz and G. Metzger, Anal. Chem., 35, 1464 (1963).
23. A. W. Coats and J. P. Redfern, Nature, 201, 68 (1964).

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