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Spectral studies of complexes of nickel(II) with tetradentate schiff bases having N₂O₂ donor groups

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Abstract

Complexes of nickel(II) of N,N'-disalicylidene-1,2-phenylenediamine (H₂dsp), N,N'-disalicylidene-3,4-diaminotoluene (H₂dst), 4-nitro-N,N'-disalicylidene-1,2-phenylenediamine (H₂ndsp) and N,N'-disalicylidene ethylenediamine (H₂salen) have been prepared and characterised by elemental analysis, electronic, IR, magnetic susceptibility measurement, ¹H NMR and thermal studies. TG studies show that the Ni(dsp) and Ni(salen) complex decomposed in one step and Ni(dst) and Ni(ndsp) complex in two steps. Kinetic and thermodynamic parameters were computed from the thermal decomposition data. The activation energy of either one step decomposition or two step decomposition of complexes lies 72–95 kJ mol⁻¹ range.

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1. Introduction

Tetradentate schiff base complexes of nickel afford two main differences relative to macrocyclic ligands: easier access to mixed donor environments and an open equatorial ring, the hole size of which can in principle accommodate more easily the expected changes in metal size upon oxidation/ reduction [1]. A considerable number of schiff base complexes have potential biological interest, being used as more or less successful models of biological compounds [2]. On the other hand, the use of these compounds in catalytic reactions has been considered [3]. These studies dealing mainly with synthesis, spectroscopic, structural, electrochemical and magnetic properties, photo and thermochroism have been extensively reviewed [4–7].

In view of recent interest in the energetics of metal ligand binding in metal chelates involving N, O donor ligands [8–10] we started to study schiff base complexes derived from N,N'-bridged tetradentate ligands involving an N₂O₂ donor atoms. However, very little work has been done on thermal studies of tetradentate schiff base complexes of Ni(II). Hence, this paper describes the synthesis, spectral, and thermal studies of new Ni(II) complexes derived from N,N'-disalicylidene-1,2-phenylenediamine (H₂dsp), N,N'-disali-

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cylidene-3,4-diaminotoluene (H_2 dst), 4-nitro-N,N'-disalicylidene-1,2-phenylenediamine (H_2 ndsp) and N,N'-disalicylidene ethylenediamine (H_2 salen). Kinetic and thermodynamic parameters have been calculated using Coats and Redfern [20] and Zsako [21] method.

2. Experimental

All the chemicals used were of A.R. grade and were used as such. Solvents were dried before use by conventional methods.

2.1. Ligand syntheses

All the tetradentate schiff base ligands except H_2 dst were prepared by condensations between diamines and hydroxyaldehydes in ethanol or methanol and were purified by recrystallization from a dichloromethane/ hexane mixed solvent through the partial evaporation of the more volatile dichloromethane.

H₂dst was prepared by dissolving 25 mmol (3.050 g) of 3,4-diaminotoluene in 100 ml of ethanol and stirred for 3h. After that 50 mmol (6.106 ml) of salicylaldehyde was mixed in 150 ml of ethanol. The 3,4-diaminotoluene solution was added to the salicylaldehyde solution using an overhead stirr for complete mixing. Some yellow precipitate resulted. The crude product was recrystallised from dichloromethane/hexane (1:2) mixed solvent. Melting point: 120° C, yield ~ 80%, ¹H NMR in CDCl₃, phenolic O–H [13.14 (s, 1), 13.08 (s, 1)], aldimine proton [8.58 (s, 1) 8.57 (s, 1)], aromatic protons [7.26–7.36 (m, 4), 6.94– 7.11 (m, 5), 6.7–6.9 (m, 2)], methyl proton [2.30 (s, 3)] (Fig. 2(a)).

2.2. Synthesis of complexes

One mmol of NiAc₂·4H₂O was dissolved in ethanol and stirred for 2 h and 1 mmol of requisite ligand was suspended in hot ethanol and stirred for 3 h. Ethanolic solutions of the schiff base were added to ethanolic nickel(II) (Ni(II)) acetate tetrahydrate solutions and the resulting mixtures refluxed, after cooling, brown or red brown microcrystalline solids were filtered off, washed with ethanol and diethyl ether and dried under vacuum over P_4O_{10} .

2.3. Analysis and physical measurements

The metal content of each complex was determined by Atomic absorption spectroscopy technique on AA-640-13, Shimadzu (Japan) machine. Magnetic moments were measured at room temperature by vibrating sample magnetometer (VSM) model 155 (Princeton applied research) at 5500 Gauss field strength. UV-visible spectra were recorded in DMSO on Beckman DU-64 spectrophotometers. IR spectra was recorded on Perkin-Elmer FT-IR spectrophotometers spectrum 2000 in KBr and polyethylene pellets. ¹H NMR was recorded on a Bruker Advance 300 machine. TG and DTA were simultaneously recorded on Rigaku 8150 thermoanalyser, in static air at the heating rate of 10deg min⁻¹. A platinum crucible was used with alumina as the reference material. The number of decomposition steps were identified using TG. The activation energy (E) and frequency factor $(\ln A)$ of the degradation process were obtained by Coats and Redfern method [20]. Apparent activation entropy was calculated by Zsako [21] method.

3. Results and discussion

All the complexes were brown or red and microcrystalline, non-hygroscopic and insoluble in water, methanol, ethanol, dichloromethane and acetone but soluble in hot DMF and DMSO. These were decomposed in the range of $217-297^{\circ}$ C. Possible compositions of the complexes were calculated and compared with the experimental values as presented in Table 1.

3.1. UV-visible spectra

The electronic spectral data are given in Table 1. The very intense bands at low wavelengths have been assigned to charge transfer transition [11,12], for complexes with aromatic bridges these bands occur at longer wavelengths, as expected from the

Table 1 Analytical and electronic spectral data for Ni(II) complexes

S. no.	Complex	Composition	Found (calcd)%				d-d transition	Charge transfer
			С	Н	Ν	М	- (IIII)	transition (iiii)
1	Ni(dsp)	$C_{20}H_{14}N_2O_2Ni$	64.41	3.75	7.52	15.73		479, 450, 380
			(64.40)	(3.76)	(7.51)	(15.74)		
2	Ni(dst)	$C_{21}H_{16}N_2O_2N_1$	65.15	4.39	7.23	15.16		481, 450, 380, 354
			(65.17)	(4.14)	(7.24)	(15.17)		
3	Ni(ndsp)	$C_{20}H_{13}N_3O_4N_1$	57.45	3.10	10.10	14.05		486, 422, 386, 300
			(57.46)	(3.11)	(10.05)	(14.05)		
4	Ni(salen)	$C_{16}H_{14}N_2O_2Ni$	59.13	4.30	8.61	18.06	537	450, 404, 326
			(59.13)	(4.31)	(8.62)	(18.07)		

higher aromaticity of the ligands which eases delocalisation of electron density.

The weaker band in the region 530-600 nm in the spectra of complexes with aliphatic imines is assigned to unresolved transitions from the four low-lying d-orbitals to the empty d_{xy} orbital [11,12]. This band could not be observed for complexes with aromatic imine bridges since it is masked by the high-intensity charge transfer transitions.

The energy of the band assigned to d-d transitions can provide a rough estimate of the ligand field strength, since one of the electronic transitions comprised in the band envelope is $d_{xy} \leftarrow d_{x^{2-}}$ y^2 and the energy associated with this transition is 10 D_q-C [12]. No comparison is possible between energies for d-d transitions for complexes with aliphatic and aromatic imine bridges, as they are not observed in the latter complexes (Fig. 1).

3.2. IR spectra

The spectra of the ligand exhibit broad medium intensity bands in the $2500-2750 \text{ cm}^{-1}$ and $3338-3353 \text{ cm}^{-1}$ range which are assigned to the intramolecular H bonding vibration (O-H...N). In the spectra of complexes these bands disappear [13,14].

The vibrations of the azomethine groups of the free ligands are observed at $1614-1635 \text{ cm}^{-1}$. In the complexes these bands are shifted to the lower frequencies, indicating that the nitrogen atom of the azomethine group is coordinated to the metal

ion [15]. Coordination of azomethine nitrogen is confirmed with the presence of a new bands at $430-480 \text{ cm}^{-1}$ region assignable to v(Ni-N) for these complexes [16,17]. The v(C-O) frequency shifts in the complexes towards lower or higher values as a result of coordination of the oxygen to the metal ion [18]. A new band in the 400-450 cm⁻¹ region in the spectra of the complexes is assignable to v(Ni-O).

3.3. Magnetic susceptibility measurement and ¹H NMR spectroscopy

All complexes are diamagnetic at RT revealing the square planar geometry around Ni(II) ion. ¹H NMR spectra of all the complexes were recorded in DMSO-d₆ solution at 300 MHz (Fig. 2(b)). The solvent impurity DMSO resonates near 2.0 ppm.

The ¹H NMR spectra of all the schiff bases indicate the presence of either one or two azomethine groups. Due to different chemical environments two signals are recorded for the azomethine protons in the H₂dst and H₂ndsp. H₂dsp and H₂salen gives one signal. Intramolecular hydrogen bonding also accounts for the high frequency of the signals for the orthophenolic hydrogens in all the schiff bases.

The ¹H NMR spectra of all the schiff base Ni(II) complexes, show a down-field shift in the frequency of azomethine protons of aromatic bridge and upfield shift in the aliphatic bridge confirming coordination of the metal ion to both groups. In all the complexes, no signals is recorded for a



Fig. 1. (a) UV spectra of Ni(dsp) complex. (b) UV spectra of Ni(dst) complex. (c) UV spectra of Ni(ndsp) complex and (d) UV spectra of Ni(salen) complex. (e) Visible spectra of Ni(salen) complex.



Fig. 2. (a) ¹H NMR (300 MHz) spectra of H_2dst and (b) Ni(dst) in DMSO-d₆.

phenolic hydrogen in the 12–13.5 ppm region, as in the case of the schiff base indicating deprotonation of the orthohydroxyl group.

The coordination of all ligand is also affirmed by the almost 1 ppm upfield change in chemical shift for certain aromatic protons in its aldehydic ring. But there is no upfield change in complex Ni(salen). The imine proton signal is a doublet. This is explained by the restricted freedom of motion present in the complex, which do not average the chemically inequivalent imine protons and largely retain upon coordination and in Ni(ndsp) complex not obscured by the nitrodeshielded aromatic proton signals. For Ni(salen)

Table 2 Thermal data and kinetic parameters for Ni(II) complexes

Complex ^a	Step	Order of rk^n (<i>n</i>)	E (kJ mol ⁻¹)	$\ln A (\min^{-1})$	$\Delta H^{\#}$ (J mol ⁻¹ × 10 ⁻³)	$\frac{\Delta S^{\#}}{(\mathrm{JK}^{-1} \mathrm{mol}^{-1})}$	$\Delta G^{\#}$ (kJ mol ⁻¹)
1	Ι	1	95.03	3.36	-326.13	-4.27	+2.84
2	Ι	1	72.33	8.55	-27.90	-3.30	+1.83
	II	1	83.60	3.78	+457.35	-3.52	+2.91
3	Ι	1	93.46	3.86	-8.09	-3.51	+2.43
	II	1	89.91	3.75	+1597.33	-3.56	+4.18
4	Ι	1	82.14	3.60	+1527.55	-4.09	+4.08

complex the integrated intensities showed the single resonance at 3.46 ppm (low field shifts) which was derived from protons in the ethylene linkage which are equivalent under the prevailing conditions.

3.4. Thermal analyses

TG and DTA studies were carried out on the ligand and its complexes in the temperature range of $20-700^{\circ}$ C. The thermal analyses show that there are two endothermic peak in the DTA curve of the ligand. The first is the melting point of the ligand, because no loss of weight was observed in the TG curve and second corresponds to decomposition of the ligand. TG studies of all the complexes showed no weight loss upto 150° C, indicating the absence of water molecule in the



Fig. 3. Kinetic parameter of Ni(dsp) complex.

complex. The first step in the decomposition sequence at $150-250^{\circ}$ C corresponds to the loss of methyl and nitrogroup in complex 2 and 3 respectively. The inflexion of the TG curve at a temperatures range above 390° C indicates the decomposition of the organic part of the chelate, leaving metallic oxide at the final temperature [19].

The thermal degradation of the complex can be depicted as follows:

$$C_{20}H_{14}N_{2}O_{2}Ni \xrightarrow[650 \circ C]{} NiO$$

$$H_{3}C-C_{20}H_{13}N_{2}O_{2}Ni \xrightarrow[150-200 \circ C]{} C_{20}H_{13}N_{2}O_{2}Ni \xrightarrow[650 \circ C]{} NiO$$

$$O_{2}N-C_{20}H_{13}N_{2}O_{2}Ni \xrightarrow[150-250 \circ C]{} C_{20}H_{13}N_{2}O_{2}Ni \xrightarrow[650 \circ C]{} NiO$$

$$C_{16}H_{14}N_2O_2Ni \xrightarrow{upto}_{650^\circ C} NiO$$

From the TG curves the order of reaction (n), activation energy (E) and frequency factor $(\ln A)$ of the reactions have been enumerated and are given in Table 2. The weight change is plotted on the ordinate with decreasing weights downwards and temperature (T) on the abscissa increasing from left to right. The methods of Coats and Redfern [20] has been used for deriving kinetic parameters (Fig. 3). The calculation of the heat of the reaction $(\Delta H^{\#})$ from the DTA curves was done by using:

$$\Delta H^{\#} = \frac{\Delta H(\text{muv}) \times 60 \times 10^{-6} \times M}{1000} \quad \text{kJ mol}^{-1}$$

where M = molecular weight of the complex.

Apparent activation entropy $(\Delta S^{\#})$ is calculated by Zsako [21] method and free energy of activation is calculated by Gibb's equation.

The $\Delta S^{\#}$ values were negative, which indicate a more ordered activated state that may be possible through the chemisorption of oxygen and other decomposition products [22]. The enthalpies of activation are negative for complex 1 and first step decomposition of complexes 2 and 3 and is positive for second step decomposition of complexes 2 and 3 and for complex 4 also. However, the negative values of the entropies of activation are compensated by the values of the enthalpies of activation leading to almost the same values (1.80–4.20 kJ mol⁻¹) for the free energies of activation. The order of activation energy (*E*) is Ni(dsp) > Ni(ndsp) > Ni(salen) > Ni(dst).

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