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SOME NEW COBALT(II) COMPLEXES
Synthesis, characterization and thermal studies

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Abstract

Cobalt(II) complexes of tetradentate Schiff bases of the type CoL [$H_2L=C_{20}H_{16}N_2O_2$ (H_2dsp), $C_{21}H_{18}N_2O_2$ (H_2dst), $C_{20}H_{15}N_3O_4$ (H_2ndsp) and $C_{16}H_{16}N_2O_2$ (H_2salen)] have been synthesized and characterized by UV-visible, IR, and magnetic studies. Various thermodynamic parameters have been calculated for the decomposition step using TG/DTA. $C_{20}H_{14}N_2O_2Co$ complex has the minimum and $C_{16}H_{14}N_2O_2Co$ complex has the maximum activation energy.

Keywords: cobalt(II), Schiff base, thermal studies

Introduction

Tetradentate Schiff base cobalt(II) complexes have been extensively studied. Their ability to form stable organometallic derivatives [1, 2], to bind reversibly molecular oxygen [3–5] and carbondioxide [6] to the metal centre and to act as complex ligand [7] for alkalimetal ions and other metallic elements [8] have been widely investigated and discussed in terms of electronic and structural properties. However no significant work has been done on thermal studies of tetradentate Schiff base complexes of cobalt(II). Hence, this paper describes the synthesis, spectral and thermal studies of new Co(II) complexes derived from N,N'-disalicylidene-1,2-phenylenediamine (H_2dsp), N,N'-disalicylidene-3,4-diaminotoluene(H_2dst), 4-nitro-N,N'-disalicylidene-1,2-phenylene-diamine(H_2ndsp) and N,N'-disalicylidene ethylenediamine (H_2salen). Kinetic and thermodynamic parameters have been calculated using Coats and Redfern [21] and Zsakó [22] method.

Experimental

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

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Ligand syntheses

All the tetradentate Schiff base ligands except H_2dst 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.

H_2dst was prepared by dissolving 25 mmol (3.050 g) of 3,4-diaminotoluene in 100 mL of ethanol and stirred for 3 h. After that 50 mmol (6.106 mL) of salicylaldehyde was mixed in 150 mL of ethanol. 3,4-diaminotoluene solution was added to the salicylaldehyde solution using an overhead stir for complete mixing. It resulted in some yellow precipitate. The crude product was recrystallised from dichloromethane/hexane (1:2) mixed solvent. Melting point: 120°C, yield ~ 80%, proton ^{1}H NMR in $CDCl_3$, 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)].

Synthesis of complexes

H_2dsp, H_2ndsp and H_2salen were synthesized according to a reported procedure with slight modification [9] and preparation of H_2dst is given in the ligand syntheses.

The requisite ligand 1 mmol suspended in 30 mL of ethanol was added to the solution of $CoAC_2\cdot 4H_2O$, 1 mmol in ethanol, the mixture was stirred for 4 h at room temperature and then refluxed on waterbath for 4 h. The coloured precipitate so formed was filtered, washed with ethanol and diethyl ether and dried over P_4O_{10}.

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. TG and DTA were recorded on Rigaku 8150 thermoanalyser at the heating rate of 10 deg min^{-1}. 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 [21]. Apparent activation entropy was calculated by Zsakó [22] method.

Results and discussion

All the complexes were found to be crystalline, brown coloured substances, non-hygroscopic and insoluble in non-polar solvents but partially soluble in DMF and DMSO. All the complexes were decomposed in the range of 470–560 K on heating and by dilute mineral acids. Microanalyses data are presented in Table 1.

Table 1 Analytical and magnetic data for Co(II) complexes of Schiff base

No.	Complex	Composition	Analysis found, calc./%				
			C	H	N	M	μ_{eff} (BM)
1.	Co (dsp)	$C_{20}H_{14}N_2O_2Co$	64.30 (64.36)	3.70 (3.75)	7.50 (7.51)	15.80 (15.80)	2.11
2.	Co (dst)	$C_{21}H_{16}N_2O_2Co$	65.90 (65.13)	4.38 (4.13)	7.20 (7.24)	15.22 (15.23)	2.53
3.	Co (ndsp)	$C_{20}H_{13}N_3O_4Co$	57.40 (57.43)	3.10 (3.11)	10.01 (10.05)	14.09 (14.10)	2.62
4.	Co (salen)	$C_{16}H_{14}N_2O_2Co$	59.08 (59.09)	4.29 (4.31)	8.60 (8.62)	18.13 (18.14)	2.75

UV-visible spectra

The electronic spectra (Table 2) of all the complexes showed intense absorption bands around 400 nm which are assigned to charge transfer transition from the Pπ orbitals of the donor atoms to the *d* orbitals of the metal [10], $d\rightarrow\pi^*$ [11] and intraligand $n\rightarrow\pi^*$ transition [12]. In the complexes the $n\rightarrow\pi^*$ transitions due to the azomethine group are shifted to the lower energy. From these results, the imine group nitrogen atom appears to be coordinated to the metal ion [13]. Bands due to the $n\rightarrow\pi^*$ transition of the C=N chromophores which occur between 380–410 nm in ligand shifts to lower or higher energy upon complexation (330–495 nm). Bands between 320–350 nm is assigned as an n–π^* transition involving molecular orbitals of the C=N chromophore and the benzene ring. The remainders of the observed bands at about 290–320 nm are assigned as π–π^* type transitions involving molecular orbitals located on the phenolic chromophore. In the ligands this band was observed at about 280–320 nm. This blue shift in the complexes may be due to the donation of a lone pair of electrons by the oxygen of the phenoxy group to the central metal atom [14].

The study of the electronic spectra to identify the *d–d* transitions in the presence of a ligand field has encountered difficulties because several bands fall in the near-infrared region with a low intensity while a large part of the visible region is obscured by intense charge transfer and intraligand (π–π^*) transitions.

IR spectra

IR spectra (Table 2) of the ligand exhibit broad medium intensity bands in the 2500–2750 and 3338–3353 cm^{-1} range which are assigned to the intramolecular H bonding vibration (O–H---N). In the spectra of the complexes these bands disappear [15].

The vibrations of the azomethine group of the free ligands are observed at 1614–1635 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 [16]. Coordination of azomethine nitrogen is affirmed with the presence of a new bands at 450–480 cm^{-1} region assignable to νCo–N for these complexes [17]. The νC–O stretching 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 400–460 cm^{-1} range in the spectra of the complexes is assignable to νCo–O [19].

Magnetic susceptibility measurements

Magnetic moments in the present study of Co(II) complexes lie in the range 2.1–2.80 BM at room temperature (Table 1). The reason for departure from the spin-only value lies partly in the existence of the second order Zeeman effect between the ground and the higher ligand field terms [20]. However, it lies mainly in

Table 2 IR and electronic spectral data of the ligands and their Co(II) complexes/cm^{-1}

No.	Compound	νC=N	νC–O	νO–H	νCo–O	νCo–N	λ_{max}/nm
	H_2dsp	1614.59 (s)	1325 (w)	2500-2680 (bw)			384, 337, 284
1.	Co(dsp)	1598 (w), 1623.67 (s)	1310 (m)		425.27 (s)	473.74 (s)	432.9, 402.8, 341.24, 301.6
	H_2dst	1617.46 (s)	1350 (w)	2550-2750 (bw)			393, 348, 303
2.	Co(dst)	1600 (s), 1624.85 (s)	1379.45 (w)		422.08 (s)	468.32	462.81, 423.47, 394, 357, 310.54
	H_2ndsp	1615 (s)	1277 (m)	3338-3353 (b)			405, 344, 316
3.	Co(ndsp)	1595 (w) 1615.46 (s)	1317.10 (w)		424.24 (s)	471.10 (s)	494.74, 435.81, 394, 349.82, 317.9
	H_2salen	1635 (s)	1313 (w)	2650-2750 (bw)			408, 345, 316
4.	Co(salen)	1623.86 (s)	1332.44 (m)		430.70 (s)	468.32 (s)	431.58, 410.53, 380, 302.46, 296.8, 289.8

Table 3 Thermal data for Co(II) complexes

Complex	Step	Order of rk^n/n	E/J mol^{-1}	ln$A$/min^{-1}	$\Delta H^{\#}$/J mol^{-1}	$\Delta S^{\#}$/J K^{-1} mol^{-1}	$\Delta G^{\#}$/kJ mol^{-1}
Co(dsp)	1	1	59.11	3.83	+25.26	–3.87	+1.952
Co(dst)	1	1	61.07	3.85	+35.49	–3.89	+1.99
Co(ndsp)	1	1	61.55	7.93	+198.79	–3.90	+2.199
Co(salen)	1	1	65.82	3.82	+8.15	–3.92	+2.058

the fact, that in the presence of spin-orbit coupling, the quenching effect of the ligand field cannot be complete.

Thermal studies

From TG curves (Fig. 1), the order of reaction (*n*), activation energy (*E*) and frequency factor (ln*A*) of the reactions have been enumerated and are given in Table 3. The Coats and Redfern method [21] has been used to derive kinetic parameters. All the complexes start decomposing above 498 K. All complexes showed the same reaction order (n=1) and similar trend of decomposition over the temperature range of study and decompose in one step. The final product of decomposition at about 780 K in all the complexes corresponds to CoO and Co_3O_4 which was confirmed by compar-

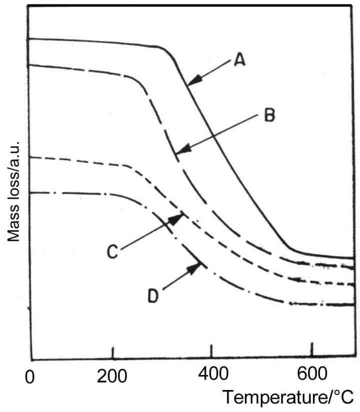

Fig. 1 TG curves for (A) Co (dsp), (B) Co (dst), (C) Co (ndsp), (D) Co (salen) complexes

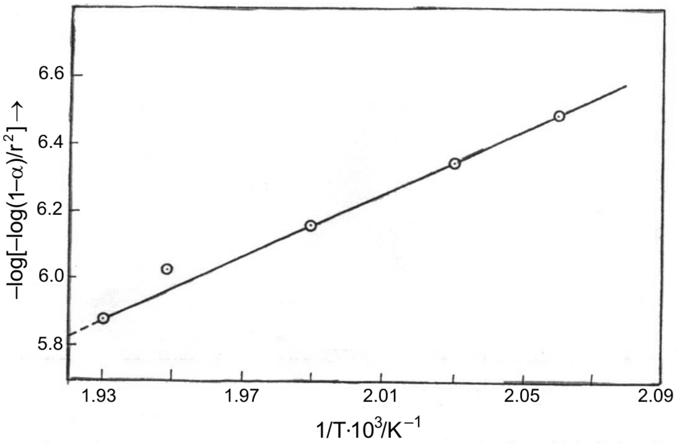

Fig. 2 Kinetic parameters of Co (dsp) complex

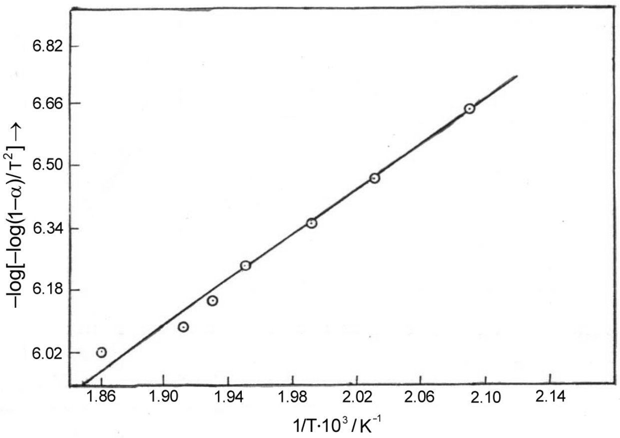

Fig. 3 Kinetic parameters of Co (dst) complex

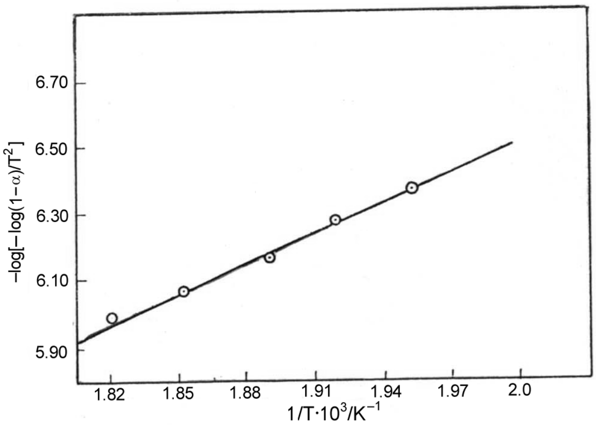

Fig. 4 Kinetic parameters of Co (ndsp) complex

ing observed and calculated masses of pyrolysis product. The relevant data needed for plotting linearization curve are recorded in Table 4 and linearization plots are shown in Figs 2–5. The calculation of heat of reaction ($\Delta H^{\#}$) (Table 3) from the DTA curves (Fig. 6) was done by using

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

where M is the molar mass of the complex.

Apparent activation entropy ($\Delta S^{\#}$) is calculated by Zsakó [22] method (Table 3).

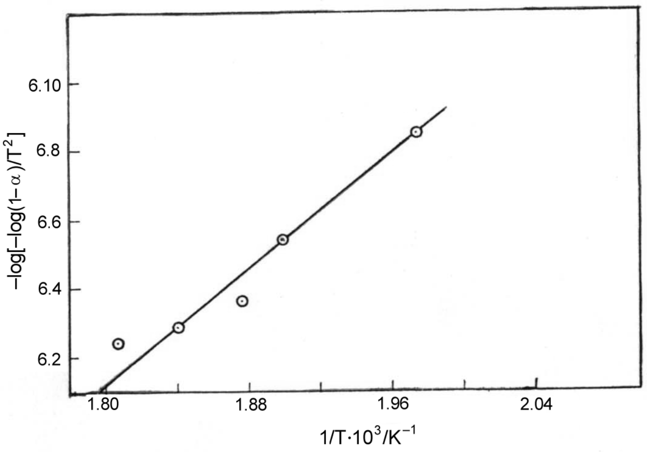

Fig. 5 Kinetic parameters of Co (salen) complex

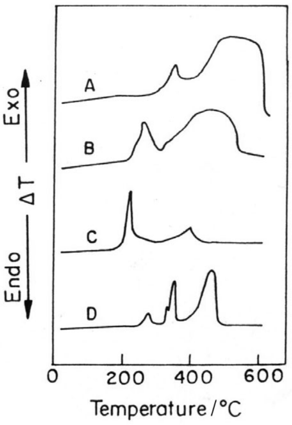

Fig. 6 DTA curves for (A) Co (dsp), (B) Co (dst), (C) Co (ndsp), (D) Co (salen) complexes

$$\Delta S^{\#}=2.303\log\frac{\beta A}{kT_{1/2}}$$

Free energy of activation (Table 3) is calculated by Gibbs' equation

$$\Delta G^{\#}=\Delta H^{\#}-T\Delta S^{\#}$$

The $\Delta S^{\#}$ values were found to be negative, which indicate a more ordered activated state that may be possible through the chemisorption of oxygen and other decomposition products [23]. The negative values of the entropies of activation are compensated by the values of the enthalpies of activation, leading to almost the same values (1.9–2.2 kJ mol^{-1}) for the free energies of activation.

Table 4 Kinetic parameters from TG for Co(II) complexes

T/K	Co(dsp)			Co(dst)			Co(ndsp)			Co(salen)		
	X	Y	Z	X	Y	Z	X	Y	Z	X	Y	Z
478				0.12	2.090	6.63						
483	0.16	2.070	6.49									
493	0.22	2.030	6.35	0.18	2.030	6.46						
503	0.33	1.990	6.16	0.23	1.990	6.35						
506										0.08	1.976	6.85
508							0.21	1.968	6.37			
513	0.44	1.949	6.02	0.29	1.950	6.24						
518	0.55	1.930	5.88	0.35	1.930	6.15	0.28	1.930	6.27			
523				0.41	1.910	6.07				0.17	1.902	6.54
528							0.35	1.893	6.17			
533										0.25	1.876	6.36
538				0.47	1.860	6.02	0.43	1.858	6.07			
543										0.29	1.840	6.29
548							0.50	1.820	5.99			
553										0.33	1.808	6.24

where $X=\alpha$, $Y=1/T\cdot 10^3$, $Z=-\log\left[-\frac{\log(1-\alpha)}{T^2}\right]$

Hence, one can postulate that the structure of the complexes as square planar, –ONNO– donor atoms occupying the four sites of the plane. The tentative structure for the complexes is shown in Fig. 7.

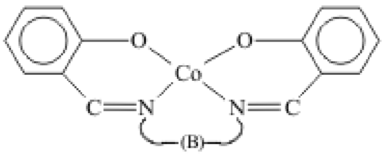

Fig. 7 Proposed structure of Co(II) complexes

where *B*=Ph, H_3C–Ph, O_2N–Ph and $–CH_2–CH_2–$

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