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Notes

Spectral characterization of tetradentate Schiff base complexes of N_2O_2 donor groups

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Copper(II) complexes of tetradentate Schiff bases N, N’–disalicylidene–1, 2–phenylenediamine(H_2dsp), N, N’–disalicylidene–3, 4–diaminotoluene(H_2dst), 4–nitro-N, N’–disalicylidene–1, 2–phenylenediamine(H_2ndsp), N, N’–disalicylideneethylenediamine(H_2salen) have been synthesized and characterized by elemental analysis, electronic spectra, IR spectra, magnetic susceptibility measurement, EPR, CV and thermal studies. TG studies show that Cu(dsp) and Cu(ndsp) complexes thermally degrade in two steps and Cu(dst) and Cu(salen) in one step. Kinetic and thermodynamic parameters have been computed from thermal decomposition data. The activation energies of both the thermal degradation step is found to lie in between 52–74 kJ mol^{-1}.

Keywords*:* Spectral data, Schiff base, Copper(II), Thermal studies

Schiff bases are an important class of compounds in inorganic chemistry. Research on these compounds has expanded very rapidly over the time. Recognization of different Schiff bases has increased the interest in the development of this field of bioinorganic chemistry[1].

Schiff bases have C=N linkage which is essential for biological activity. Several azomethines were reported to have remarkable antibacterial, antifungal, anticancer and diuretic activities. Schiff bases have wide applications in food industry, dye industry, analytical chemistry, catalysis, fungicidal, agrochemical and biological activities[2,3]. Schiff base complexes are considered to be among the most important stereo chemical models in main group and transition metal coordination chemistry due to their preparative accessibility and structural variety[4]. They have played a seminal role in the development of modern coordination chemistry, inorganic biochemistry, catalysis and optical materials[5,6]. Metal complexes of Schiff bases derived from aromatic carbonyl compounds have been widely studied in connection with asymmetric catalysis, metalloprotein models, electrochemical reduction processes[7,8] and catalytically active materials to develop surface modified electrodes for sensing applications. The high thermal and moisture stabilities of many Schiff base complexes were useful for their application as catalysts in reactions at high temperatures[9].

Schiff base ligands with oxygen or nitrogen donor atoms are good class of organic compounds capable of binding to different metal ions with interesting medicinal and non medicinal properties[10]. Several model systems including those with bidentate, tridentate, tetradentate, multidentate Schiff base ligands and their coordination chemistry of copper attracts much attention because of their biological relevance and their own interesting coordination chemistry such as geometry, flexible redox property and oxidation state[11]. It is believed that the biological activity is related to the hydrogen bonding through the imino group of Schiff bases with the active centres of the cell constituents[12]. Steric and electronic effects around the metal core can be finely tuned by an appropriate selection of bulky and/or electron withdrawing or donating substituent incorporated into the Schiff bases, the two donor atoms, N and O of the chelated Schiff base exert two opposite electronic effects: the phenolic oxygen is a hard donor and stabilizes the higher oxidation state whereas the imine nitrogen is a border line donor and stabilizes the lower oxidation state of the metal ion[13].

In view of recent interest in the energetic of metal ligand binding in metal chelates involving N, O donor ligands, we started to study Schiff base complexes derived from N, N'-bridged tetradentate ligand involving an N_2O_2 donor atoms. However, literature survey reveals that little work has done on thermal studies of copper (II) complexes containing N_2O_2 donor groups. The present paper describes the synthesis, spectroscopic and thermal studies of the copper(II) complexes with N_2O_2 donor atoms of the synthesized ligands.

Materials and methods

All the chemicals and metal salts used in the synthesis were of reagent grade and were used without further purification. The solvents were dried before use by conventional methods.

Synthesis of ligands

Ligands H_2dsp, H_2dst, H_2ndsp and H_2salen were prepared according to a reported procedure with slight modifications[14] and were characterized by elemental analysis, mass spectra, UV-visible, IR, ^{1}H NMR and ^{13}C NMR spectroscopy. The structures of the ligands are shown in Fig. 1.

Synthesis of complexes

The ligand (1 mmol suspended into 20 mL of ethanol) was added to the solution of $CuCl_2.2H_2O$ (1 mmol in ethanol) and the mixture was stirred for 3 h at room temperature. The yellow/blue coloured product was filtered off, washed with ethanol and diethyl ether and dried over $P_4O_{10.}$

Physical measurements

The metal content of each complex was determined by atomic absorption spectroscopy technique on a AA-640-13, Shimadzu (Japan) machine. Magnetic measurements carried out in the polycrystalline state by vibrating sample magnetometer (model: 155, Princeton applied research) at 5500 Gauss Field strength. UV-visible absorption spectra were recorded in DMF on Beckman DU-64 spectrophotometers. IR spectra were recorded on Perkin–Elmer FTIR spectrophotometers (model: Spectrum 2000) using KBr and polyethylene pellets. X-band EPR spectra were recorded on a Varian model E-112 EPR spectrometers using DPPH (g = 2.0023) as the standard with a variable temperature nitrogen cryostat. Cyclic voltammetry (CV) measurements were carried out using a BAS-50W electrochemical analysing system. A mixed solvent DMSO: CH_3CN (1:9) was employed using 0.1 M $NaClO_4$ as supporting electrolyte. A three electrode configuration was used, comprising of a platinum disk working electrode, platinum wire counter electrode and $Ag/AgNO_3$ reference electrode. Electrode performance was monitored by observing ferrocenium/ferrocene (Fc^+/Fc) couple in DMSO:CH_3CN solvent system under dry nitrogen atmosphere. TG and DTA were simultaneously recorded on Rigaku 8150 thermo analyser in static air at the heating rate of 10 °C min^{-1}. A platinum crucible was used with alumina as the reference material. The number of decomposition steps was identified using TG. The activation energy (E) and frequency factor (logA) of the degradation process were obtained by Coats and Redfern method[42] and apparent activation entropy was calculated by Zsako[43] method.

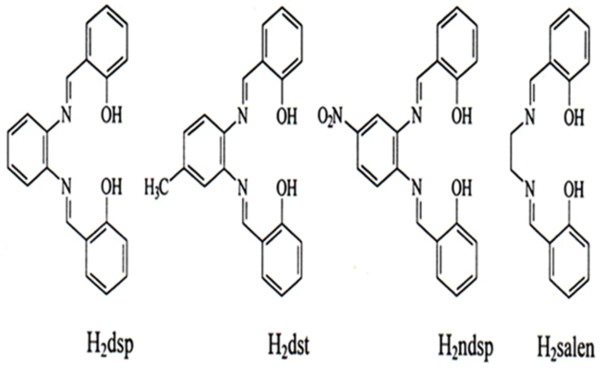

Fig. 1 — Structures of the ligands.

Results and Discussion

The entire complex was crystalline, yellow/blue coloured, non-hygroscopic and insoluble in non-polar solvents but freely or partially soluble in DMF and DMSO. All the complexes were decomposed in the range of 513–567 K and by dilute mineral acids. Analytical data of all complexes were obtained and possible compositions were calculated (Table 1).

UV–visible absorption spectra

UV-visible absorption spectra of the investigated complex (as shown in Fig. 2) were recorded in DMF

Table 1 — Analytical and physical data for Cu(II) complexes of Schiff bases

S. No.	Complex	Composition	Colour	Found/ (Calc)%				$\mu_{eff}{}^a$ (BM)
				C	H	N	M	
1	Cu(dsp)	$C_{20}H_{14}N_2O_2Cu$	yellow	63.5 (63.6)	3.6 (3.7)	7.5 (7.4)	16.7 (16.8)	1.80
2	Cu(dst)	$C_{21}H_{16}N_2O_2Cu$	yellow	64.40 (64.37)	4.4 (4.08)	7.2 (7.1)	16.2 (16.2)	2.11
3	Cu(ndsp)	$C_{20}H_{13}N_3O_4Cu$	yellow	56.7 (56.8)	3.1 (3.08)	10.0 (9.9)	14.98 (15.0)	1.82
4	Cu(salen)	$C_{16}H_{14}N_2O_2Cu$	blue	28.3 (58.3)	4.2 (4.25)	8.6 (8.5)	19.3 (19.2)	1.92

[a] Per metal ion and measured at room temperature

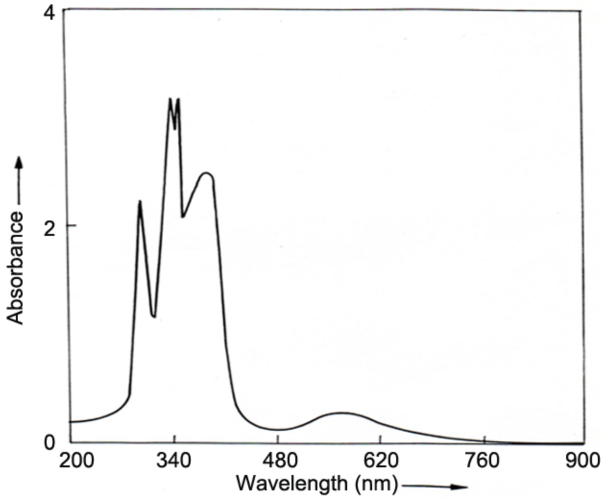

Fig. 2 — Electronic spectrum of Cu(salen) complex.

solvent. The electronic spectra are used to assign the stereochemistry of the metal ion in the complex based on the position and number of d–d transition bands[15]. The copper(II) complex under present investigation exhibit only one broad band ranging from 540–600 nm due to d–d transition which suggests a square planar (D_{4h}) symmetry around copper (II)[16,17]. The d–d absorption bands are due to symmetric forbidden electronic transition between the d orbital of the copper(II) ion. They appear as vibronic transitions, i.e., coupled with the vibrational modes. Charge transfer (CT) bands are observed if the energies of empty and filled ligand and metal centred orbital are similar and it is symmetry allowed bands[15]. The direction of the electron transfer is determined by the relative energy levels of ligand and metal orbital. Complexes show an intense band around 380–395 nm having a mainly metal to ligand [Cu($3d_{xy}$), O($2p_z$), ph(π)$\rightarrow$C=N(π^*), ph(π^*) charge transfer (MLCT) character[18,19], there is a transition from the HOMO (Partially filled MO), which is principally composed of Cu ($3d_z$), O($2p_z$), ph(π) orbital to the LUMO [C=N(π^*)] orbital. The spectra of the complexes 1–3 show a medium intensity band around 400–460 nm which can be attributed to MLCT transition, copper (II)→phenolate(π^*) transition, i.e., CT band from the filled d ($3d_{xz}$, $3d_{yz}$) orbital of copper(II) to the antibonding orbital of the phenolic residue[20]. The position of MLCT bands is mostly defined by the ligand properties. The band corresponding to the azomethine(C=N) showed a slight shift to longer wavelength on complexation indicating coordination of ligands to metal through the azomethine moiety[21]. The intense bands around 270–370 nm in the complexes is due to $\pi\rightarrow\pi^*$ and intraligand $n\rightarrow\pi^*$ transition[22,23].

IR Spectra

The IR spectra of the complexes, when compared with that of the free ligands, show remarkable differences and revealed that the ligand is bonded to the metal ions in a quadridentate mode[24].

The IR spectra of the ligands exhibit broad medium intensity bands in the 2500-2750 cm^{-1} and 3330–3360 cm^{-1} range which are assigned to the intramolecular H bonding vibration (O-H---N). In the spectra of complexes these bands are found to disappear[23].

The vibrations of the azomethine ($\nu_{C=N}$) groups of the free ligands are observed around 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[25]. Coordination of the Schiff base to the metal ions through the nitrogen atom is expected to reduce electron density in the azomethine link and lower the $\nu_{C=N}$ absorption frequency[26].

Low frequency IR spectra (Far Infrared region) of the metal complexes provide very useful information regarding the type of metal–ligand bond arising from the coordination of ligands to the metal centre. However, the IR spectra of the ligands having aromatic rings which show bands due to out of plane ring deformation[1] and out of plane deformation of C-H bonding in the low frequency region, complicate the spectral features[27]. From a stereochemical point of view $\nu_{(Cu\text{-}O)}$ and $\nu_{(Cu\text{-}N)}$ bands are expected in the complexes under investigation.

Coordination of azomethine nitrogen is further confirmed with the presence of a new bands at 438–470 cm^{-1} region assignable to $\nu_{(Cu\text{-}N)}$ for these complexes[25]. The $\nu_{(C\text{-}O)}$ stretching frequency shifts in the complexes towards lower or higher values as a result of coordination of the oxygen to the metal ion[28]. A new band in the 390–436 cm^{-1} range in the spectra of the complexes is assignable to $\nu_{(Cu\text{-}O)}$[22]. Accordingly it confirmed that the ligand binds the metal ion in tetradentate fashion with N, O coordination to copper(II) ion. The bonding sites are the azomethine nitrogen and hydroxyl oxygen atoms[29].

Magnetic susceptibility measurement

The Cu(II) complexes with all the ligands are paramagnetic. μ_{eff} values (Table 1), corresponding to the presence of one unpaired electron (1.80–2.11 BM).

It has generally been found that under conditions of adequate magnetic dilution the cupric ion exhibits magnetic moment a little above the spin-only value for the one unpaired electron of d^9 configuration, i.e., 1.73 BM.

In square planar complex the unpaired electron of d^9 configuration is in the b_{1g} orbital giving a $^2B_{l\ g}$ ground term and μ_{eff} may be expected to be some 15% above spin only value[30].

Electron Paramagnetic Resonance (EPR) spectra

The EPR spectra of complexes are shown in Fig. 3. In EPR, the observed signal arises from the interaction between the magnetic moments of unpaired electron and an external magnetic field, according to the Zeeman interaction. For a single unpaired electron in a magnetic field, the energy splitting (ΔE_{Zeeman}) is given by:

$$\Delta E_{Zeeman} = g_e\mu_B\beta_o \text{ and } \Delta E_{Zeeman} = h\nu \qquad \ldots(1)$$

Where β_o is the applied magnetic field strength, g_e is the electron g value, μ_B is the Bohr magneton and transitions can be observed when the resonance condition is met by radiation of the appropriate frequency (ν)[30]. In practice, EPR transitions typically do not occur at a magnetic field corresponding to the free electron g value but rather are influenced by the effective field generated by contributions from the local chemical environment. This is expressed in terms of g value given by $g = h\nu/\mu_B\beta_o$, g values depending on the orientation of the metal complex in the applied magnetic field[31].

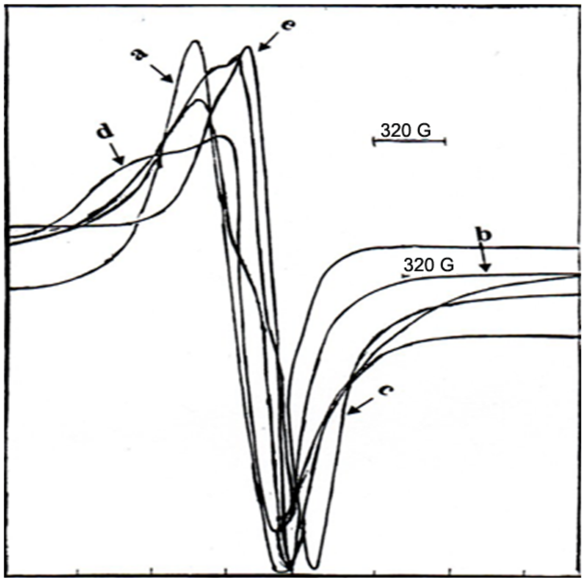

Fig. 3 — X-band EPR spectra of (a) Cu(dsp), (b) Cu(dst), (c) Cu(ndsp) (d) Cu(salen) complex in polycrystalline state at liquid nitrogen temperature (LNT) and (e) Cu(salen) complex in DMSO solution at LNT.

All the complexes showed an isotropic sharp signal which is attributable to less dipolar interaction and spin-lattice relaxation[20,32] of the coordinating ligand and spin exchange interaction between Cu(II) ions[33]. Hyperfine coupling due to the metal ion (A^{Cu}) could not be resolved even at liquid nitrogen temperature (LNT) due to exchange narrowing of EPR lines[34]. The nitrogen having planar conformation, sp^2 type conformation, show large superhyperfine (shf) coupling constant as compared to the nitrogen having tetrahedral, sp^3 (less s-character) conformation. An effect of distortion from the planar array to a tetrahedral array in the first coordination sphere may also lead to some reduction in nitrogen shf coupling[35], since it results in a reduction of overlap of the copper unpaired electron orbital with the ligand and hence causes the decrease in the spin density on nitrogen and consequently nitrogen coupling constants. In the present study, complexes 1, 2 & 3 showed sharp isotropic signal with g values equal to 2.097, 2.94 and 2.096, respectively. As a consequence of the relatively high rigidity of the structure of complexes 2 and 3 the planarity of copper surrounding and the spectral parameters are not affected by the methylation/nitration of the phenyl bridge. For Cu(salen) complex $g_{||} = 2.41$, $g_\perp = 2.13$ and $< g > = 2.22$ and G = 3.15 in polycrystalline state at LNT and in DMSO solution at LNT, this complex shows $g_{||} = 2.14$, $g_\perp = 2.06$ and $< g > = 2.08$ and G = 2.33. The axial symmetry parameter, G is less than four indicates considerable exchange interaction in the complex[36]. The trend $g_{||} > g_\perp > 2.0023$ observed for all the complexes indicate that the unpaired electron most likely resides in the $d_{X^2-Y^2}$ orbital. Kivelson and Neiman[37] have shown that $g_{||}$ is a moderately sensitive function for indicating covalency. Relatively speaking $g_{||} > 2.3$ is characteristics of an ionic environment and $g_{||} < 2.3$ of a covalent environment in M-L bonding. In solid state for complex 4, $g_{||} > 2.3$ indicates ionic character in Cu–L bonding but in solution $g_{||} < 2.3$ was observed which indicated a fair degree of covalent character in the Cu–L bonding.

Cyclic voltammetry

Cyclic Voltammetry (shown in Fig. 4) is a powerful tool to probe reactions involving electron transfers. The Nerst equation relates the potential of an electrochemical cell (E) to the standard potential of a species(E^o) and the relative activities[38] of the oxidized (Ox) and reduced (Red) analyte in the system at equilibrium. In the equation:

$$E = E^o + RT/nF \ln[Ox]/[Red] \qquad \ldots(2)$$

Where F is faraday's constant, R is the universal gas constant, n is the number of electrons and T is the temperature.

The Nerst equation provides a powerful way to predict how a system will respond to a change of concentration of species in solution or a change in the electrode potential. Electron transfer processes are at the centre of the reactivity of inorganic complexes. Analytes that react in homogeneous chemical processes upon reduction (such as ligand loss or degradation) are not chemically reversible. Electrochemical reversibility refers to the electron transfer kinetics between the electrode and the analyte. When there is a low barrier to electron transfer, the Nerstian equilibrium is established immediately upon any change in applied potential and vice versa[39].

Complexes 1 and 2 do not give any redox peak in the CV scan in the range of 0.0–1.30 V and 0.80–0.70 V respectively (vs Ag/$AgNO_3$) under dry nitrogen atmosphere. But complex 4 shows very weak peak near 0.65 V. This may be due to the fact that copper(II) to copper(I) redox processes are influenced by the coordination number, stereochemistry and hard/soft character of the ligand donor atom[21]. However, due to inherent difficulties in relating coordination number and stereochemistry of the species present in solution, redox processes are generally described in terms of the nature of the ligands present[40]. Patterson and Holm[41] have shown that softer ligands tend to produce more positive E^o values, while hard acids give rise to negative E^o values. In present study, it appears that copper(II) oxidation state is stabilized by N_2O_2 donor ligands in square planar arrangement and voltammetry at a platinum electrode gave result which were complicated by electrode kinetics at the scan rates 35–1000 mV s^{-1}.

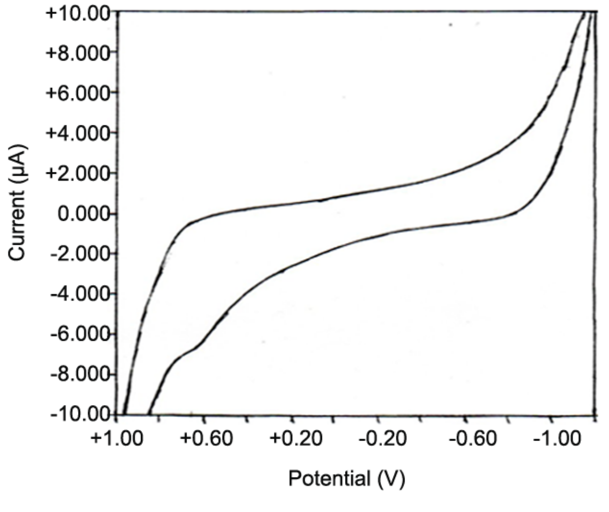

Fig. 4 — Cyclic voltammograms of Cu(salen) complex in DMSO: CH_3CN (1:9) solution at a scan rate of 300 mV/s.

Thermal studies

TG and DTA studies were carried out on the complexes in the temperature range of 20–600 °C. TG studies of all the complexes showed no weight loss upto 150 °C indicating the absence of water molecule in the complex. The first step in the decomposition sequence at 220–405 °C for Cu(dsp) and 150–335 °C for Cu(ndsp) corresponds to the loss of benzene and nitro group respectively. The inflection of the TG curve at a temperature range above 440 °C for Cu(dsp) and 338 °C for Cu(ndsp) indicates the decomposition of the organic part of the chelate leaving metallic oxide at the final temperature. From TG, the order of reaction (n), activation energy (E) and frequency factor (logA) of the reactions have been enumerated and are given in Table 2 and shown in Figs 5–8. The weight change is plotted on the ordinate with decreasing weight downwards and temperature (T) on the abscissa increasing from left to right. The method of Coats and Redfern[42] has been used for deriving kinetic parameters. Apparent activation entropy (ΔS) is calculated by Zsako[43]

Table 2 — Thermal data and kinetic parameters for Cu(II) complexes of Schiff bases

Complex	Step	Orderf rk^n (n)	E (KJ mol^{-1})	logA (min^{-1})	ΔH ($Jmol^{-1} \times 10^{-3}$)	ΔS	ΔG
Cu(dsp)	I	1	65.80	8.42	+15.418	-3.93	+2.08
	II	1	85.88	3.38	+28.36	-4.28	+3.19
Cu(dst)	I	I	80.64	3.33	+8.15	-4.13	+2.67
Cu(ndsp)	I	1	52.21	8.30	+1177.18	-3.83	+2.99
	II	1	75.43	3.51	+17.43	-4.09	+2.54
Cu(salen)	I	I	73.88	3.41	+198.71	-4.10	+2.76

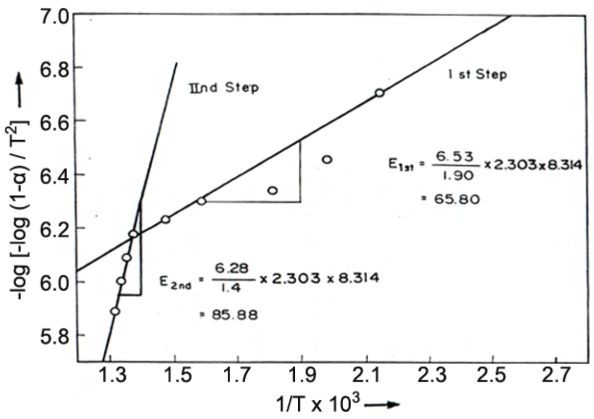

Fig. 5 — Kinetic parameters of Cu(dsp) complex.

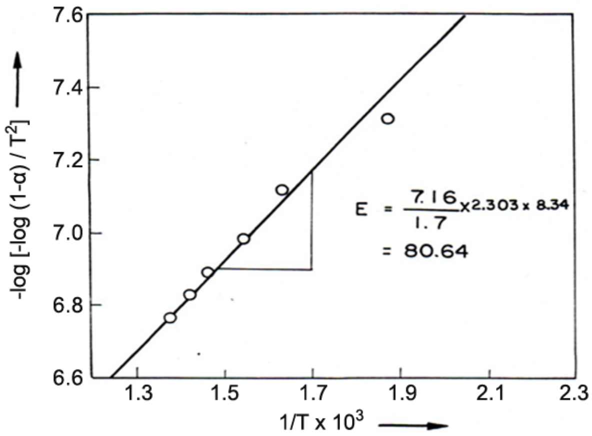

Fig. 6 — Kinetic parameters of Cu(dst) complex.

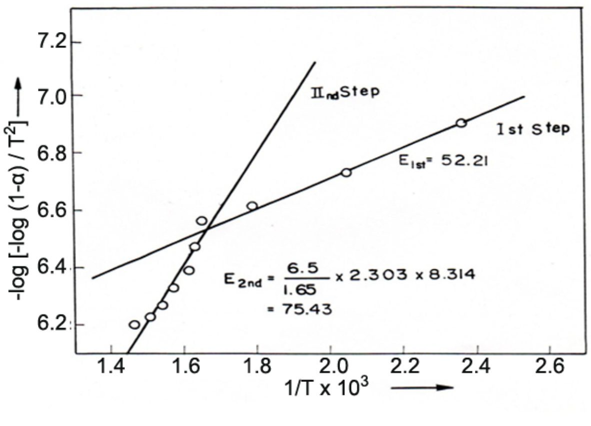

Fig. 7 — Kinetic parameters of Cu(ndsp) complex.

method. Free energy of activation is calculated by Gibb’s equation.

The ΔS values were negative which indicates a more ordered activated state that may be possible through the chemisorptions of oxygen and other decomposition products. The negative values of the entropies of activation are compensated by the values of the enthalpies of activation leading to almost the same values (2.0–3.20 kJ mol^{-1}) for the free energies of activation. The order of activation energy for first step of decomposition is Cu(dst) > Cu(salen) > Cu(dsp) > Cu(ndsp) and activation energy for second step of decomposition is Cu(dsp) > Cu(ndsp). The literature contains various explanations of the relative order of thermal stability of complexes[44]. The energy of activation of for first step decomposition is highest in Cu(dst) and hence it is found to be the most stable among all the synthesized complexes.

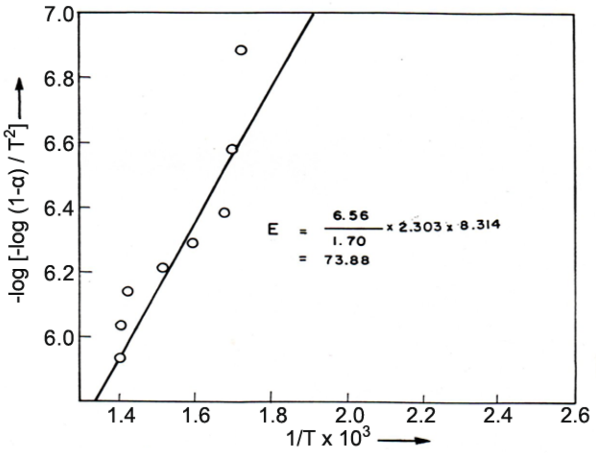

Fig. 8 — Kinetic parameters of Cu(salen) complex.

Conclusions

All complexes give only one d–d transition. Magnetic moment corresponds to one unpaired electron present in all complexes. On the basis of result of analysis of UV-visible, IR, EPR, CV best possible structure of all complexes is square planar.

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