Journal of Thermal Analysis, Vol. 39 (1993) 65-74

THERMAL AND TEMPERATURE DEPENDENCE OF ELECTRICAL CONDUCTIVITY STUDIES ON Zn, Cd AND Hg HYDRAZONE COMPLEXES

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(Received August 5, 1991; in revised form August 4, 1992)

The complexes of Zn, Cd and Hg of isatin isonicotinoyl hydrazone were prepared at two different *pHs*. Their thermal studies (TG, DTG and DTA) have been made and the DC electrical conductivity of compressed powder samples as a function of temperature was investigated. The activation energies (ΔE) were calculated for the ligand and the complexes which showed that the ligand has a lower value of ΔE than the complexes. The magnitude of ΔE was found to be affected by the nature of the metal and the *pH* of preparation.

Keywords: electrical conductivity, hydrazone complexes, kinetics

Introduction

Hydrazones derived from isonicotinic acid hydrazide (INH) are well known for their antibacterial and antitubercular activities [1, 2], also complexes derived from hydrazones of INH have antibacterial activity [1, 3]. The complex of diacetyl diisonicotinoyl hydrazone (DINH) with Y(III) is fluorescent at *pH* 6.4–7.6 [4], the fluorescence of Sn(IV)-DINH complex has also been studied. Salicylaldehyde isonicotinoyl hydrazone (Sal) has been prepared [5] and used in the determination of Ga(III) and In(III) spectrophotometrically [6]. On the other hand, several hydrazones of isatin exhibit anticonvulsant [7] and anti-bacterial [8] activities. The results of DC electrical conductivity and thermal analyses have been correlated for the Co, Ni, Cu and Zn complexes of isonicotinoyl hydrazone

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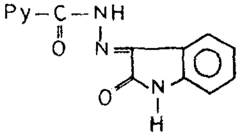
of benzoylacetone, salicylaldehyde and 2-hydroxy-naphthaldehyde and their activation energies for conduction have also been correlated [9].

In this paper we report some thermal studies on isatin isonicotinoyl hydrazone and its Zn, Cd and Hg(II) complexes, the DC electrical conductivity and thermal analyses have been described and their Δ*E* for conduction have been discussed.

Experimental

The ligand, isatin isonicotinoyl hydrazone was prepared according to Sacconi [10]. The complexes of Zn, Cd and Hg were prepared from metal chloride as previously described [11] in neutral solution and at *pH* 10 (using NH_4OH/NH_4Cl buffer). The structure of the ligand is as (I):



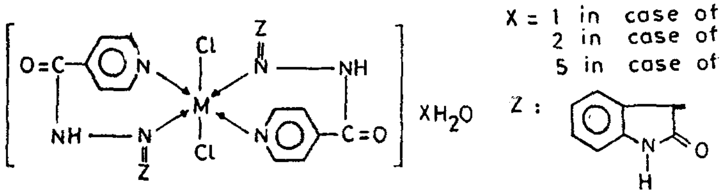
(Orange)

I

TG, DTG and DTA were carried out on a Shimadzu XD-30 thermal analyzer from the room temperature to 750°C at the rate of 10 deg·min^{-1}, full scale represents 100% weight loss. IR-spectra were recorded on a Perkin-Elmer 598 (4000–200 cm^{-1}) infrared spectrophotometer and the DC electrical conductivity was measured as given previously [9], in the temperature range (20°–280°C) for compounds dissociating at 300° and (20°–350°C) for those dissociating at 400°C. The conductivity was measured in S·cm^{-1}.

Results and discussion

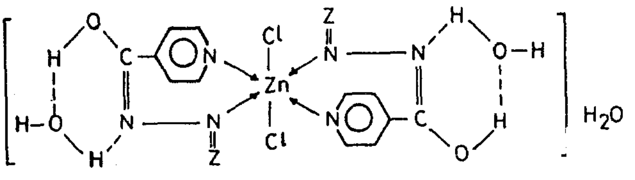
Analytical studies [12] showed that although all the complexes prepared in neutral medium have the same mode of coordination (II), complexes prepared at *pH* 10 have different structures (IIIa, b and c).



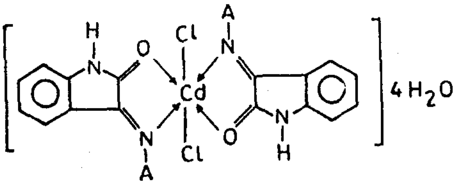
II

X = 1 in case of Zn
2 in case of Hg
5 in case of Cd

M : Zn, Cd and Hg

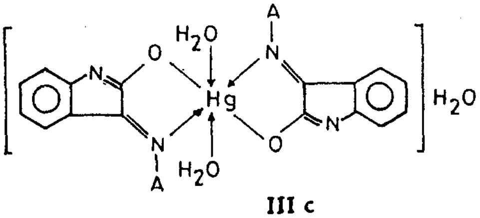


III a



A = Py – CONH –

III b



III c

DTA, TG and DTG thermal analyses

The ligand

Isatin isonicotinoyl hydrazone is thermally stable up to 290°C, its decomposition proceeds without melting in one step (10% weight loss) with strong exothermic peak at 300°–330°C with a liberation of N_2 and the colour changes from orange to brown. The broad endothermic peak that occurs before the decomposition without weight loss may be due to rearrangement (Figs 1, 2).

Comparing the IR spectra of the ligand (I) and that of the compound obtained by heating at 330°C for an hour (IV) Fig. 3, it was found that the ligand exhibits amide group frequencies at 1720, 1550 and 1290 cm^{-1}, beside two bands at 1695 and 1670 cm^{-1} assigned to $\nu_{C=O}$ of the isatin part and the central $\nu_{C=N}$ respectively. The absence of amide I, II and III bands in the spectrum of the compound (IV) indicated the destruction of the amide group of the ligand through enolisation. The spectrum of compound (IV) showed only two strong bands in the range 1800–1600 cm^{-1}, one at 1708 cm^{-1} assigned to $\nu_{C=O}$ and the other at 1610 cm^{-1} assigned to $\nu_{C=C}$ in conjugation, so the following mechanism may be suggested.

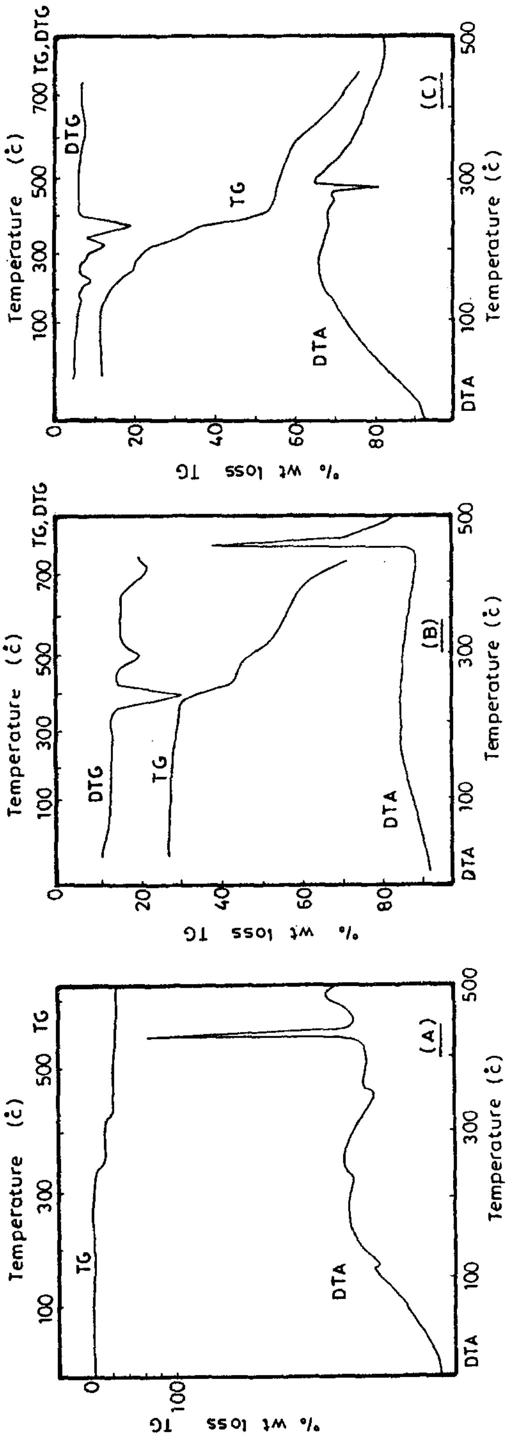


Fig. 1 DTG, DTA and TG curves for complexes prepared in neutral solution

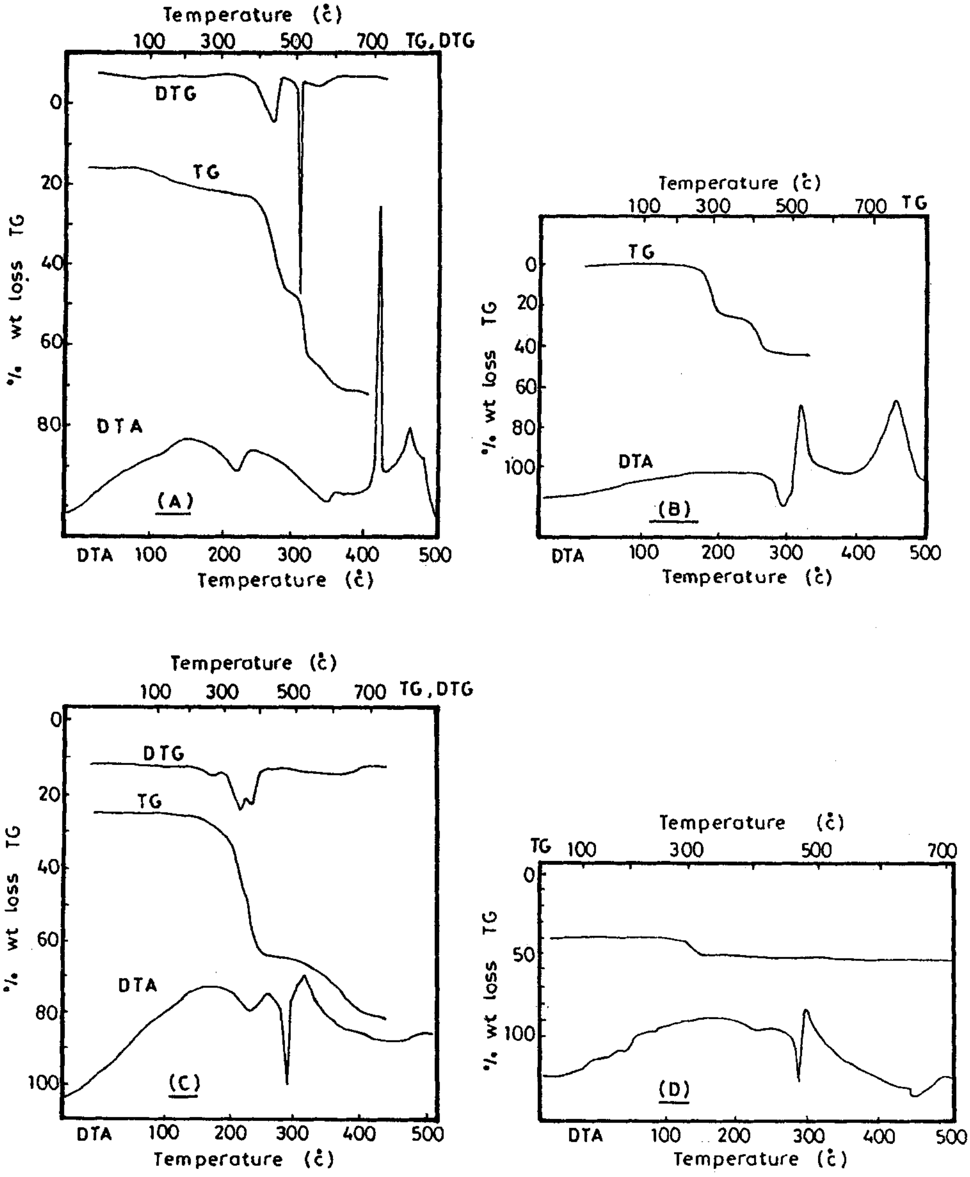
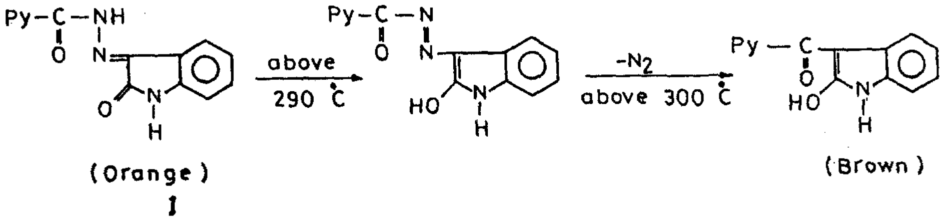


Fig. 2 DTG, DTA and TG curves for the ligand and complexes prepared at $pH = 10$

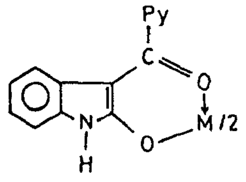


The complexes

These complexes (except the complex of cadmium prepared at *pH* 10) as seen from Table 1 are thermally stable. The decomposition proceeds by losing H_2O and HCl followed by N_2. The high temperature at which the water molecules were evolved may be explained by its presence in the H-bonded form.

The loss of water molecules appeared in the DTA curve as a broad endothermic peak while the loss of HCl appeared as an exothermic peak. The two peaks may overlap when the decomposition temperatures are close to each other.

The liberation of N_2 for zinc and cadmium complexes occurred above 400°C (mercuric complex at ≈300°C) with a strong exothermic effect. The broad weak endothermic peak found before the evolution of N_2 with no weight loss may be due to a rearrangement within the molecule. The decomposition of the complexes was confirmed by subjecting the complex to heat at the decomposition temperature in an oven for an hour and then examined. The product was found to contain no chlorine, and the IR spectrum showed the disappearance of the amide group frequencies (in the region 1800–1600 cm^{-1}) and instead two strong peaks appeared at 1708 and 1610 cm^{-1} which may be assigned to $\nu_{C=O}$ in conjugation and $\nu_{C=C}$ in conjugation also. The complexes obtained may have the following structure.



From the Table, it is clear that the decomposition temperature (D_T) at which the complexes are completely decomposed are as follows:

	Complexes prepared at *pH* 7			Complexes prepared at *pH* 10		
	Zn	Cd	Hg	Zn	Cd	Hg
D_T	457	435	315	455	425	300

Table 1 Thermal analyses data of the ligand and its Zn, Cd and Hg complexes

pH	Formula	M.Wt.	Temp. / °C	% Wt. loss Calc.	% Wt. loss F*	DTA	Temp. / °C	Assignment
	Ligand (HL)	266.262	290	—	0.0	endo (m)	290	may be due to rearrangement and/or melting.
			290–330	10.5	10.0	exo(s)	300	loss of N_2 molecules
7	$[Zn(HL)_2Cl_2]\cdot H_2O$	686.618	220–340	13.2	13.0	endo (m)	300	loss of (H-bonded) $H_2O+2HCl$ molecules
						exo(m)	320	
			340–440	8.2	8.0	endo (br)	400	may be due to rearrangement
						exo(s)	457	loss of $2N_2$ molecules
	$[Cd(HL)_2Cl_2]\cdot 5H_2O$	805.910	290–355	20.3	20.0	mso (br)	340	loss of (H-bonded) $5H_2O+2HCl$
			355–410	—	—	endo (br)	400	may be due to rearrangement
			410–438	7.0	8.0	exo(s)	435	loss of $2N_2$ molecules
	$[Hg(HL)_2Cl_2]\cdot 2H_2O$	840.052	140–360	20.1	20.0	endo (br)	230	
						exo(br)	250	loss of (H-bonded) $2H_2O+2HCl$
						endo (s)	295	loss of $2N_2$ molecules
						exo(m)	315	
10	$[Zn(HL)_2Cl_2]\cdot 3H_2O$	722.848	120	2.5	2.0	—	—	loss of one H_2O molecule (lattice)
			up to 430	13.8	13.0	—	—	loss of (H-bonded) $2H_2O+2HCl$ molecules
			430–450	—	—	endo (br)	440	may be due to rearrangement
			450–545	7.7	8.0	exo(s)	455	loss of $2N_2$
	$[Cd(HL)_2Cl_2]\cdot 4H_2O$	787.894	50–160	4.6	4.5	endo (br)	230	loss of one H_2O (lattice)
			160–400	4.6	4.5	endo (br)	355	loss of (H-bonded) H_2O
						endo (br)	390	rearrangement and loss of $2N_2$
			400–455	16.1	15.0	exo(s)	425	
	$[HgL_2(H_2O)\cdot H_2O$	785.146	140–160	2.5	2.5	—	—	loss of one H_2O (lattice)
			175–255	5.0	5.0	endo (br)	230	loss of (H-bonded) $2H_2O$
			255–260	—	—	endo (s)	260	may be due to rearrangement
			260–350	7.1	6.5	exo(s)	300	loss of $2N_2$

* F: found, (br): broad, (s): strong, (m): medium

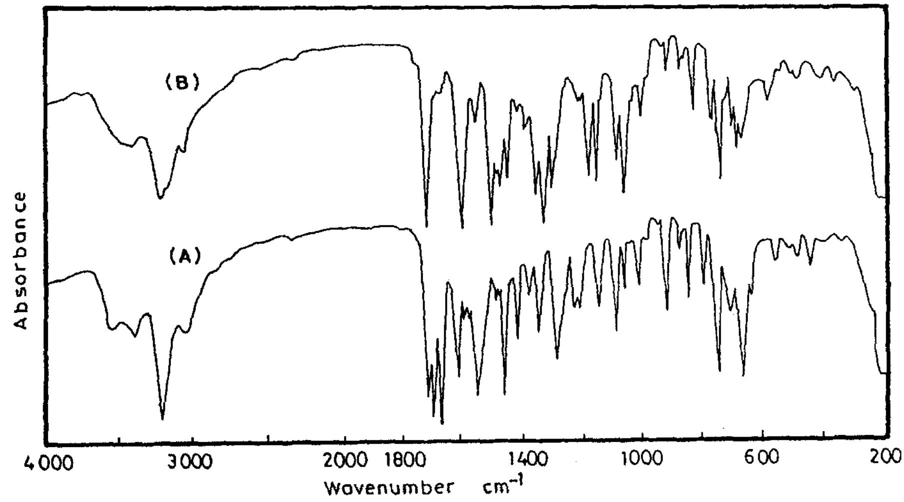


Fig. 3 IR spectra of $[Cd(HL)_2Cl_2]\cdot 5H_2O$, A: The original B: The residual after heating to 330°C

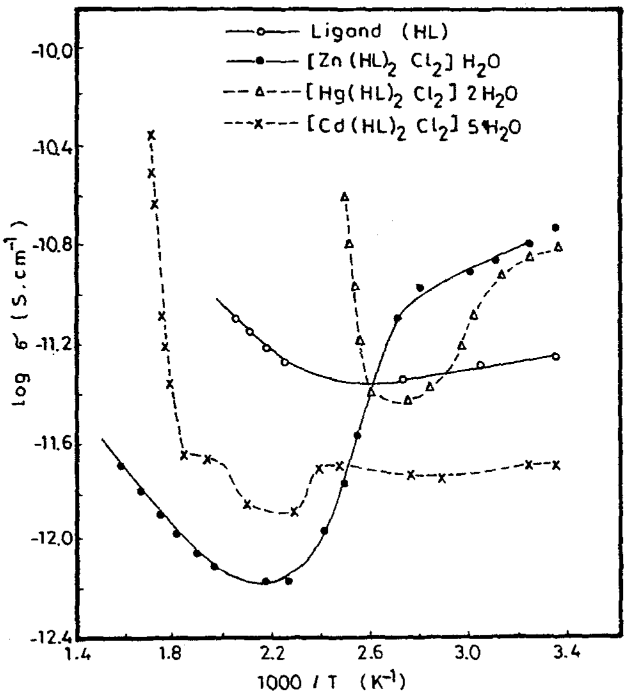


Fig. 4 Variation of log conductivity (S·cm^{-1}) vs. 1000/T (K^{-1}) for the ligand and complexes prepared in neutral solution

which shows that the thermal stability of these complexes is in the sequence Zn > Cd > Hg.

DC electrical conductivity

The variation of log σ (electrical conductivity) *vs.* reciprocal, absolute temperature for the ligand and its Zn, Cd and Hg complexes that prepared in neutral solution and at *pH* 10 are shown in Figs 4 and 5 respectively. The curves are characterized by two regions. The low temperature range is the extrinsic range where dehydration is probable and is separated from the high temperature range by a knee. The knee is not sharp as that generally observed with inorganic semiconductors, probably due to a less degree of crystallinity. The results obtained fit the relation $\sigma = \sigma_o e^{-\Delta E/2kT}$ where σ_o is a preexponential factor, from this relation, the activation energy for conduction ΔE, is calculated from the higher temperature range. The values of ΔE of the tested compounds at both neutral and basic media are compiled in Table 2. From this Table the activation energy for conduction is affected by the medium of preparation, where in neutral medium ΔE in-

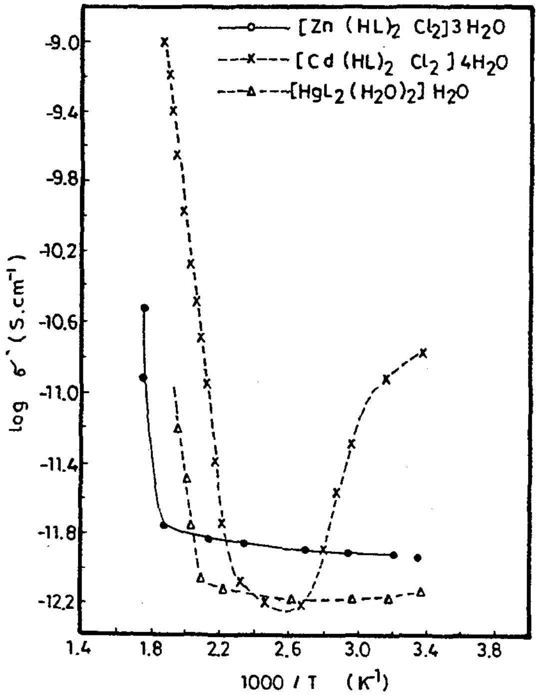


Fig. 5 Variation of log conductivity (S·cm^{-1}) *vs.* 1000/*T* (K^{-1}) for the complexes prepared at *pH*=10

creased as the atomic number increased in the triad Zn, Cd and Hg complexes. This trend is reversed for the preparations performed at the higher *pH*.

Table 2 The activation energies for conduction of the investigated samples (eV)*

Compound 'Neutral'	ΔE	Compound '*pH* 10'	ΔE
$[Zn(HL)_2Cl_2]H_2O$	0.466	$[Zn(HL)_2Cl_2]3H_2O$	3.200
$[Cd(HL)_2Cl_2]5H_2O$	2.470	$[Cd(HL)_2Cl_2]4H_2O$	2.800
$[Hg(HL)_2Cl_2]2H_2O$	3.300	$[HgL_2(H_2O)_2]H_2O$	2.170

* Ligand (ΔE)=0.28 eV

In the present work, the metal complexes showed higher ΔE values than that of the ligand (0.28 eV). This supports our previous work [9], where it was believed that complexation stabilizes the molecular orbitals through the formation of molecular orbitals involving the ligand and the central atom.

The conduction mechanism in metal complexes was proposed to be excitation of electrons from the uppermost filled orbitals to the lowest vacant molecular orbitals [13].

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Zusammenfassung Bei zwei verschiedenen *pH*-Werten wurden die Zn-, Cd- und Hg-Komplexe von Isatinisonicotinoylhydrazon hergestellt. Diese wurden thermisch untersucht (TG, DTG, DTA) und die Gleichstromleitfähigkeit von gepreßten Pulverproben als eine Funktion der Temperatur untersucht. Sowohl für die Liganden als auch für die Komplexe wurden die Aktivierungsenergien (ΔE) berechnet, wobei sich für die Liganden niedrigere Werte ergaben. Man fand, daß die Größe von ΔE durch die Art des Metalles und den *pH*-Wert bei der Herstellung beeinflußt wird.