THERMAL–CONDUCTIMETRIC STUDIES ON SOME ISONICOTINOYL HYDRAZONE DERIVATIVES AND THEIR METAL COMPLEXES

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ABSTRACT

The cobalt, nickel, zinc and copper complexes of the isonicotinoyl hydrazones derived from benzoylacetone (Bz), salicyaldehyde (Sal) and 2-hydroxynaphthaldehyde (Naph) derivatives were prepared. The solid materials were subjected to thermal analysis, and their d.c. electrical conductivities were measured at varying temperatures. The results of conductivity and thermal analyses were correlated. The activation energy for conduction was calculated and discussed with respect to likely conduction mechanisms.

INTRODUCTION

The electrical conductivity of solid metal complexes has received attention in the last few years, because such complexes are promising materials for use in electronic devices and because of the increasing importance of electrical conductivity as a characterizing parameter for the structure and mode of association of metal complexes. Electrical conductivity in both metal complexes and charge-transfer complexes may arise from any one of the following factors.

(1) Improved intramolecular overlap of orbitals due to the more diffuse d-orbitals of the transition metal;

(2) Extension of the intramolecular conduction path by conjugation of the d-orbitals and the electron system of the ligand;

(3) Even if conjugation is still restricted, improved conductivity is possible because of hopping of electrons as a result of variable valency of the metal, without the participation of the organic framework.

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The conductivity of compressed discs can be considered to be characteristic of the single crystal [1–3] and is usually determined by the concentration and/or mobility of the charge carrier and by the dependence of these properties on temperature. The variation of conductivity is generally described by the exponential relation [4]

$$\sigma = \sigma_0 \exp(-\Delta E / 2kT)$$

where σ_0 is a pre-exponential factor and ΔE is the activation energy.

EXPERIMENTAL

The ligands, isonicotinoyl hydrazones of benzoylacetone (Bz), salicylaldehyde (Sal) and 2-hydroxynaphthaldehyde (Naph) were prepared as described by Sacconi [5]. Their structures and those of the resulting metal complexes, were characterised by the methods of ref. 6.

Bz   Sal   Naph
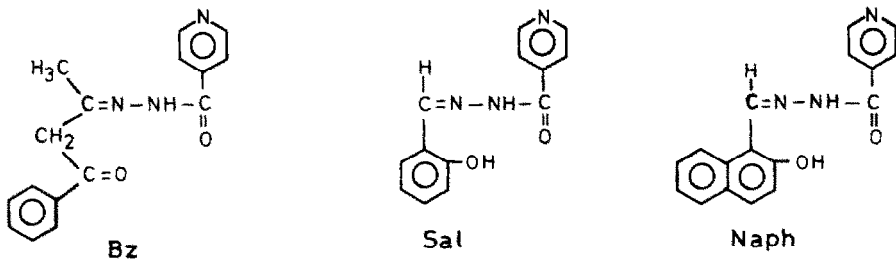
The solid complexes were ground by hand using an agate pestle and mortar, then compacted into discs at 5 ton cm^{-2} for 3 min to ensure a sample having pressure-independent conductivity [7].

For conductivity measurements the samples were held between spring-loaded copper electrodes and heated in a tubular furnace, fitted with a Variac transformer and calibrated chromel-alumel thermocouple, up to 30°C below the m.pt. During measurements the polarity was frequently reversed and ohmic behaviour was validated by applying a potential of 200V to both sample and a standard resistance. The results were reproducible to within experimental error.

Thermal analysis was made by heating a weighed amount of the sample in a drying oven at different temperatures (70–270°C) for at least 3 h, at each temperature tested. TG and DTA were carried out on some selected samples on a Shimadzu XD 30 thermal analyzer from room temperature up to 300°C, at a heating rate of 10°C min^{-1} and a sensitivity of 10 μg inch^{-1}. The full scale represents a 100% weight loss.

RESULTS AND DISCUSSION

The results of thermal analysis are presented in Figs. 1–4. Sal, Naph and the yellow form of Bz are anhydrous but the white form of Bz loses one molecule of water (changing to the yellow form) at 120°C. The results show that cobalt complexes are monohydrated but all the others are anhydrous while TG and DTA curves of the white form of Bz and the cobalt complexes are shown in Fig. 5. The weight loss data indicate loss of one molecule of water from the white form of Bz ligand. Co–Sal and Co–Bz complexes also lose one molecule of water, while the weight loss for the Co–Naph complex corresponds to one molecule each of NH_3 and H_2O.
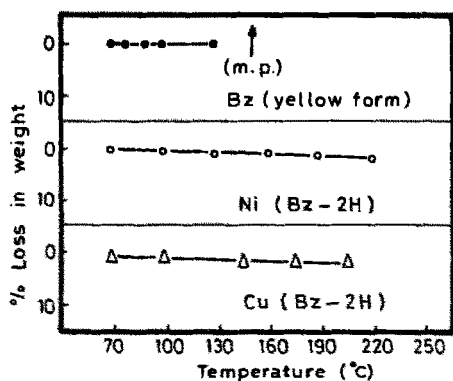
Fig. 1. Thermal analysis curves of benzoylacetone isonicotinoyl hydrazone and some of its complexes, measured in a drying oven.
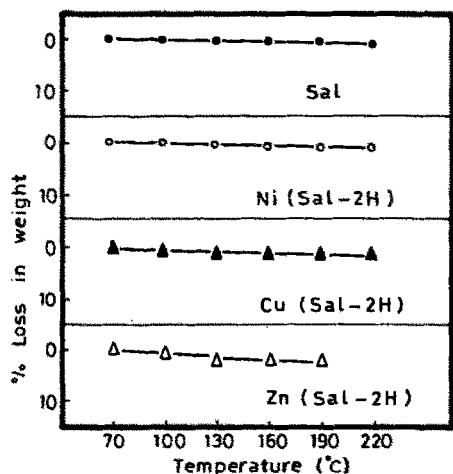

Fig. 2. Thermal analysis curves of salicylaldehyde isonicotinoyl hydrazone and some of its complexes, measured in a drying oven.
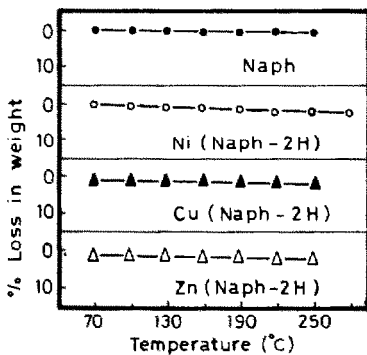
Fig. 3. Thermal analysis curves of 2-hydroxynaphthaldehyde isonicotinoyl hydrazone and its complexes, measured in a drying oven.

Plots of log σ vs. the reciprocal of the absolute temperature are shown in Figs. 6–8. The activation energies were calculated and are shown in Table 1. From these results it is observed that a decrease in activation energy generally correlates with an increase in conductivity. However, $Cd(Bz-H)_2$ deviates from this trend. This complex has metal : ligand molar ratio 1 : 2 [6] and lower metal ratios are known to decrease the conductivity. The relatively high conduction in this complex, in spite of the higher energy-gap width, suggests electron hopping as a probable mechanism for conduction. An increase in conduction, which is associated with a decrease in the energy-gap width, is observed on going from Co to Zn. This observation supports the assumption that the d electrons are involved in the formation
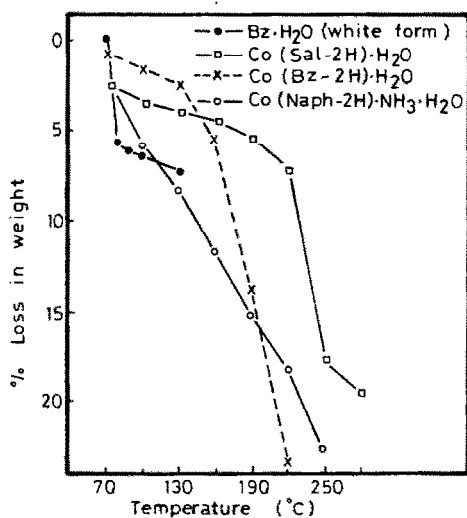

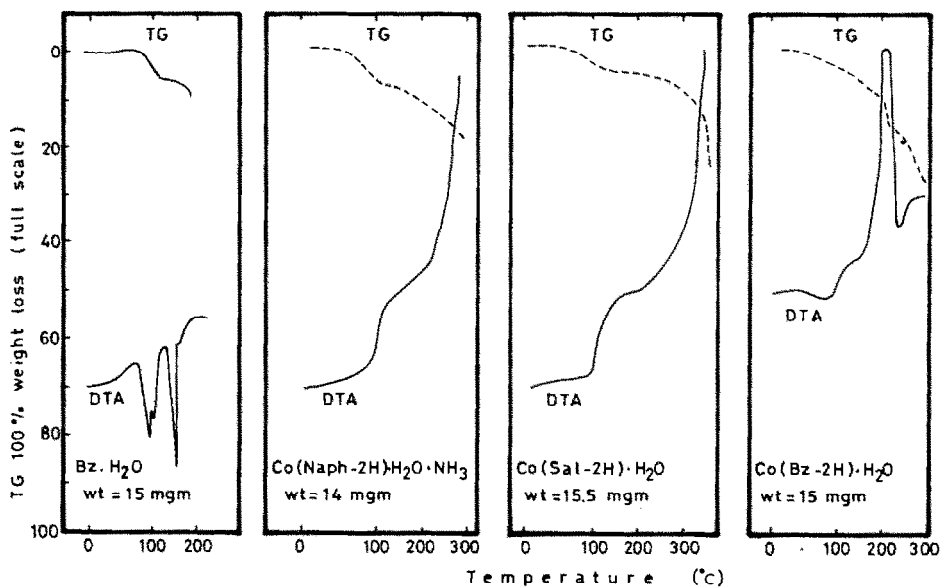Fig. 4. Thermal analysis curves of some Co complexes, measured in a drying oven.

Fig. 5. Thermal analyses (TG and DTA) of the white form of benzoylacetone isonicotinoyl hydrazone ($Bz \cdot H_2O$) and of some complexes.
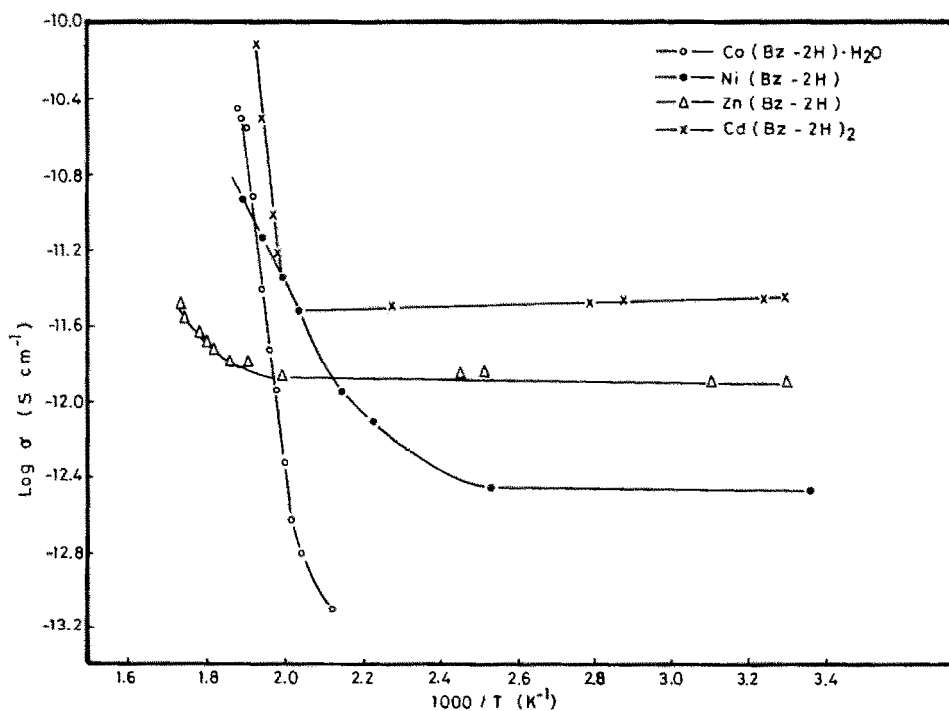

Fig. 6. Variation of log electrical conductivity (S cm^{-1}) of Bz complexes with reciprocal of absolute temperature ($1000/T$ K^{-1}).
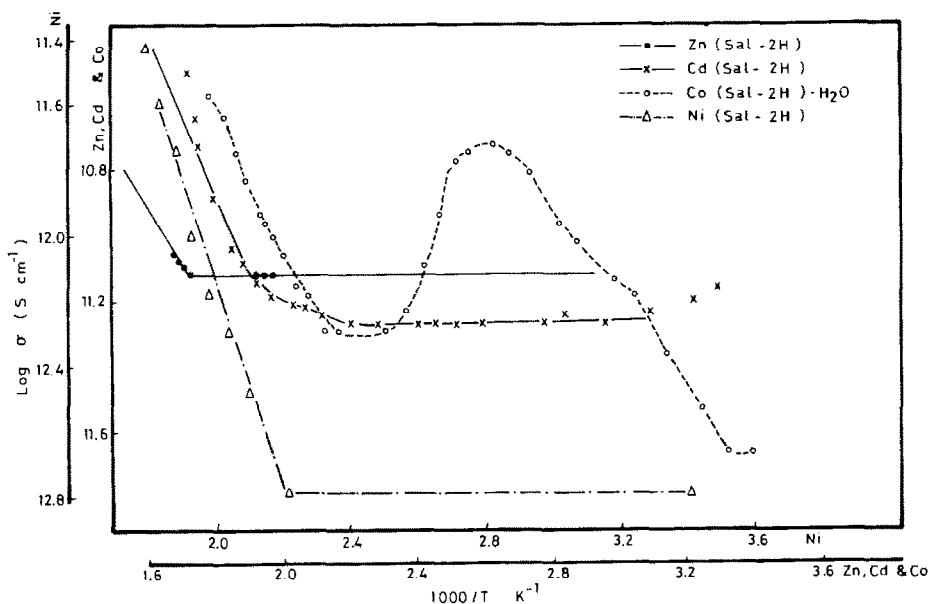
Fig. 7. Variation of log electrical conductivity (S cm^{-1}) of Sal complexes with reciprocal of absolute temperature (1000$/T$ K^{-1}).

of new molecular orbitals covering the entire molecule [8,9]. Most of the complexes which have been studied show similar results.

In the cases of Co(Sal–2H) · H$_2$O and Co(Naph–2H) · H$_2$O · NH$_3$ (Figs. 7 and 8) an inversion in the slope of the log σ vs. 1000$/T$ curves is observed in the ranges 112–167°C and 81.6–93°C, respectively. Such inversions in

TABLE 1

Activation energies and log σ (S cm^{-1}) for the complexes

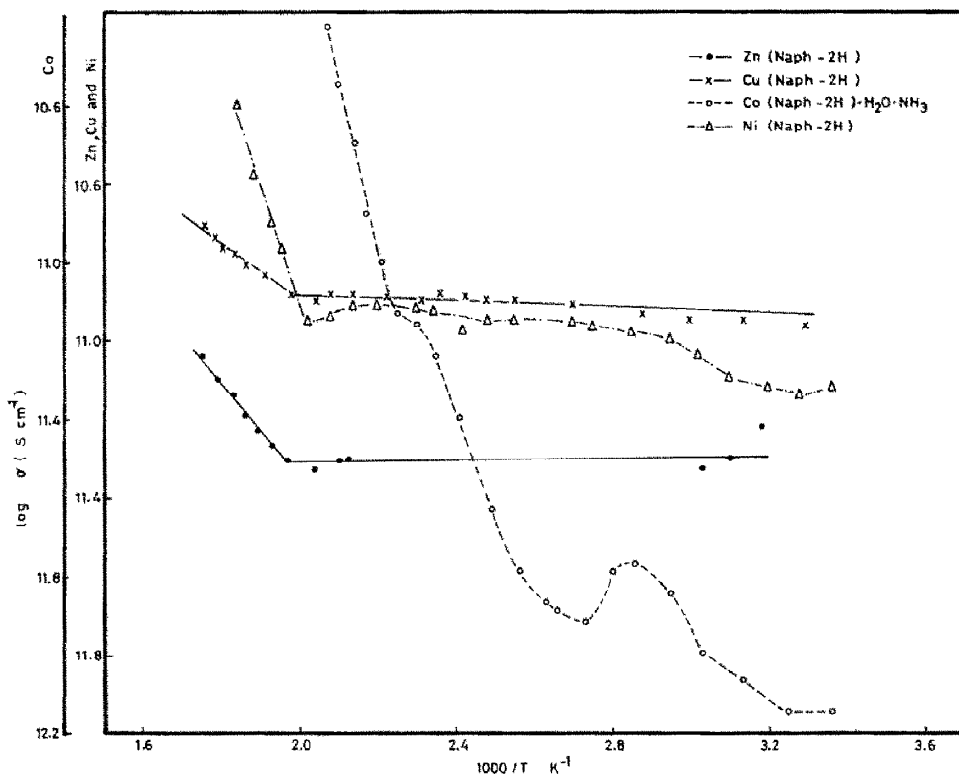| Complex	ΔE_g (eV)	log σ (room temp.)	Remarks
Co(Bz–2H)·H$_2$O	5.71	− 13.10	No detectable conductivity up to 187°C
Ni(Bz–2H)	1.84	− 12.44	
Zn(Bz–2H)	0.97	− 11.85	
Cd(Bz–H)$_2$	5.60	− 11.43	
Co(Sal–2H)·H$_2$O	0.83	− 11.65	Inversion in slope at 112–167°C
Ni(Sal–2H)	1.44	− 12.79	
Zn(Sal–2H)	0.76	− 11.12	
Cd(Sal–2H)	0.94	− 11.22	
Co(Naph–2H)·H$_2$O·NH$_3$	2.20	− 12.15	Inversion in slope at 81.6–93°C; change in slope at 162°C
Ni(Naph–2H)	1.28	− 11.13	
Cu(Naph–2H)	0.31	− 10.30	
Zn(Naph–2H)	0.46	− 11.30	

Fig. 8. Variation of log electrical conductivity (S cm^{-1}) of Naph complexes with reciprocal of absolute temperature (1000/T K^{-1}).

slope were not noticed for Co(Bz–2H) · H$_2$O because no detectable readings could be made up to 187°C. There is a good correlation between these results and the endothermic peaks detected in the thermal analyses (Fig. 5). Heating in the inversion range does not increase the thermal mobility of electrons (which would increase the conduction) but heat is consumed in dehydration (and/or evolution of ammonia in the case of Co(Naph–2H) · H$_2$O · NH$_3$). Changes in the slope of the curve, and hence in activation energy, may be correlated with a change in the conduction mechanism.

Copper complexes are generally characterized by higher conductivity and lower activation energy, as shown in Fig. 8. In such complexes, the unpaired electron which occupies the d$_{x^2-y^2}$ orbital may contribute significantly to conduction.

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