The thermal stability and temperature dependence of the electrical conductivity of Mn(II), Fe(III), Co(II), Ni(II), and Cu(II) indazole Schiff base complexes

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Abstract

The thermal stabilities of the indazole Schiff base complexes of Mn(II), Fe(III), Co(II), Ni(II), and Cu(II) were studied. The stabilities are discussed in terms of structure and type of metal ions. The activation energies E_α of the different processes were evaluated and discussed in accordance with the structure of the complexes. The electrical properties of the metal complexes were also investigated with reference to the types of metal ion and organic ligand.

Keywords: Conductivity; DTA; Indazole; Ligand; Schiff base; Semiconductor; Stability

1. Introduction

In recent years, considerable attention has been paid to the use of thermal analysis as a technique for studying the bonding and structure of coordination compounds [1–11]. The synthesis and characterization of the studied complexes have been reported previously [12]. Their general formulae are M(SB)Cl · nH$_2$O for M is Mn(II), Co(II), Ni(II) and Cu(II) and M(SB)Cl$_2$ · nH$_2$O for M is Fe(III), where SB indicates Schiff bases derived from 5-aminoindazole and 2-hydroxy-1-naphthaldehyde (**I**), 2,4-dihydroxybenzaldehyde (**II**) or salicylaldehyde (**III**).

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In this study, the thermal and semiconducting behaviour of this group of related complexes is reported. This is based on a differential thermal analysis study and the temperature dependence of the electrical properties of the solid complexes.

2. Experimental

The ligands (**I–III**) as well as their complexes were prepared and characterized as reported earlier [12]. The ligand structure is
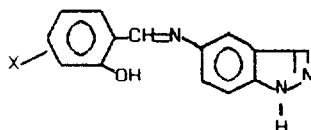
where X is C_4H_4 (**I**), p-OH (**II**) and H (**III**).

Differential thermal analysis (DTA) measurements were carried out using a Du Pont TA 900 thermal analyser; 15–20 mg of the sample was heated up to 1173 K at a heating rate of 293 K min^{-1} in flowing air. The electrical conductivity measurements were carried out using a Super Megohmmeter electrometer (Model 170), as described previously [8]. Measurements were undertaken at room temperature and at temperatures up to ≈ 460 K.

3. Results and discussion

3.1. Differential thermal analysis (DTA)

The DTA thermograms of the complexes under investigation (Fig. 1) display weak endothermic peaks within the range 337–382 K, which is consistent with loss of water from the surface of the crystals [13]. Weak to medium endothermic peaks occur within the range 385–493 K and are assigned to the removal of the coordinated water molecules. The thermograms of complexes 1, 4 and 5 exhibit medium to strong exothermic peaks at 596, 536 and 608 K, respectively, which are assigned to the crystallization of the anhydrous complexes. The appearance of medium to strong exothermic peaks at 641–740 K may correlate with lattice rearrangement of the crystalline complexes. The strong broad exothermic peaks lying within the range 825–1121 K include the thermal decomposition of the complexes [14] and the loss of their organic portion, with the formation of the corresponding metal oxides as final products. The appearance of medium exothermic peaks at 979, 1063 and 936 K for complexes 7, 9 and 11, respectively, indicates the formation of Co_2O_3,

Fig. 1. (a), (b) Arrhenius plots constructed from differential thermal analysis (DTA) thermograms of indazole Schiff base complexes.
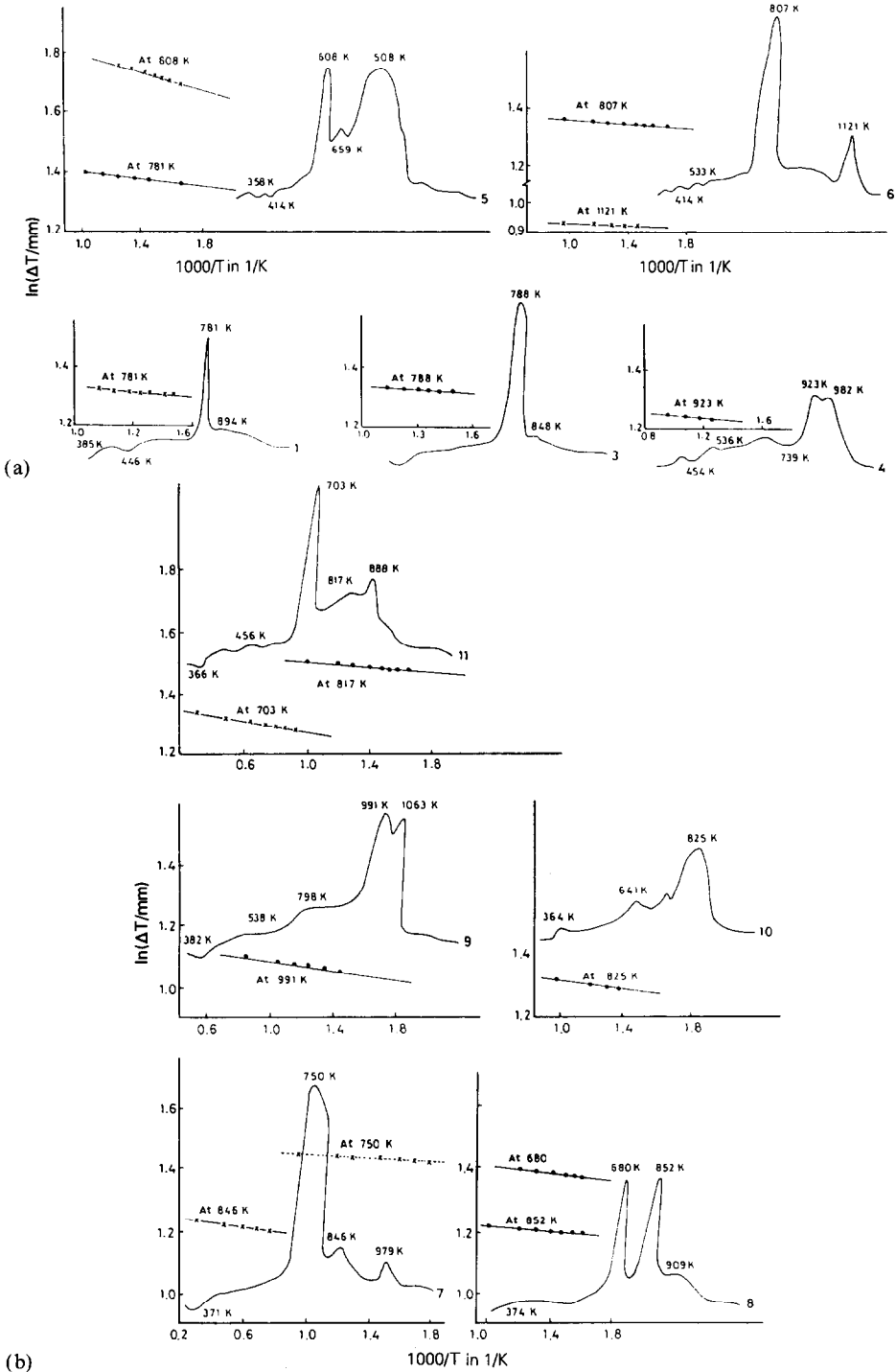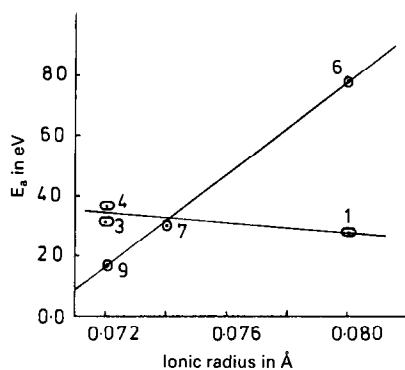
Fig. 2. The relation between ionic radii of the metal ions and the activation energy values calculated from DTA thermograms of complexes 1, 3, 4, 6, 7 and 9.

CuO and MnO_2 as final products. For complex 3, the strong exothermic peak at 788 K includes the various changes, namely, the melting of the complex and its decomposition with loss of its organic portion and the formation of NiO as a final product.

The values of the activation energies for some selected thermal processes were evaluated using the method of Piloyan et al. [15]. Arrhenius plots were constructed (Fig. 2) and E_α values were obtained from the slope, as listed in Table 1. Using Reich's empirical relation [16], the order of rection n of the thermal processes is given by $n = 1.26 \sqrt{a/b}$, where (a/b) is the shape factor of the peak. In general the data ($n = 0.82-1.1$) indicate that the processes follow first-order kinetics.

Figure 2 shows the relationship between ionic radii and activation energy values. For complexes derived from ligand **I**, the activation energy decreases with increasing ionic radii of the metal ions, confirming that the stability of the complexes decreases with increasing ionic radii. Thus the deactivation energy for the thermal decomposition of these complexes increases in the same direction due to the decrease in the affinity for complexation of the metal ions. For complexes of ligand **II**, the activation energy increases with increasing ionic strength. This opposite trend can be explained by the presence of the free OH group on the benzole ring of these complexes which occupies the para-position on the azomethine group, and may cause an induced strong electronic delocalization over the whole complex molecule. This high induced electronic delocalization is a major contribution and affects the stability of the complex. As the ionic radii of the metal ion increases, the delocalization along the azomethine group increases and the complex stability increases in the same direction.

3.2. Electrical conductivity

The electrical conductivity σ in organic molecular solids differs in several important ways from that in metals and typical semiconductors such as silicon. The

Table 1
The obtained values of the activation energies calculated from the Arrhenius plot derived from DTA and electrical conductivity temperature data

No.	Lig. (L)	Complex	Activation energy from DTA		Activation energy from conductivity	
			Temp./K	$E_a/(kJ\ mol^{-1})$	$\Delta E_1/(J\ mol^{-1})$	$\Delta E_2/(J\ mol^{-1})$
1	I	$[MnLCl(H_2O)_3]H_2O$	781	119.3	15.44	54.99
2	I	$[CoLCl(H_2O)_3]H_2O$	–	–	21.23	128.3
3	I	$[NiLCl(H_2O)]$	788	129.7	–	–
4	I	$[CuLCl(H_2O)]H_2O$	923	148.5	18.33	156.3
5	II	$[FeLCl_2(H_2O)_3]4H_2O$	608	57.3		
					112.9	114.8
			781	110.0		
6	II	$[MnLCl(H_2O)_3]2H_2O$	807	192.10		
					18.33	119.6
			1121	329.3		
7	II	$[CoLCl(H_2O)_3]2H_2O$	750	139.8		
					46.3	46.3
			846	121.3		
8	II	$[NiLCl(H_2O)]4H_2O$	740	142.7		
					46.3	193.0
			852	203.3		
9	II	$[CuLCl(H_2O)]4H_2O$	991	69.9	46.3	91.7
10	III	$[FeLCl_2(H_2O)_2]2H_2O$	825	89.1	46.3	168.8
11	III	$[MnLCl(H_2O)_3]2H_2O$	703	118.4		
					–	–
			817	82.0		

experimental behaviour of the electrical conductivity of the compounds investigated was found to fit the well-known Arrhenius equation of the form

$$\sigma = \sigma_0\, e^{-\Delta E/KT}$$

where σ is the electrical conductivity at temperature T, σ_0 the pre-exponential constant, ΔE the activation energy of the conduction, and K the Boltzmann constant.

Figure 3 shows that the conductivity of ligand I and its complexes increases with temperature rise, i.e. there is a positive temperature coefficient of the electrical conductivity ($d\sigma/dT$). Thus the material possesses semiconducting character. As a general trend, it can easily be seen that on going from the organic ligand to its corresponding metal complexes, the electrical conductivity increases and the activation energy for conduction decreases. This could be explained by the metal ion in the complex acting as a bridge, facilitating the flow of the current [17] throughout the organic ligands. The conductivity curve for complexes of ligand I shows an abrupt change within the range 376–445 K, corresponding to a phase change as detected in the DTA data, thought to be brought about by loss of humidity and
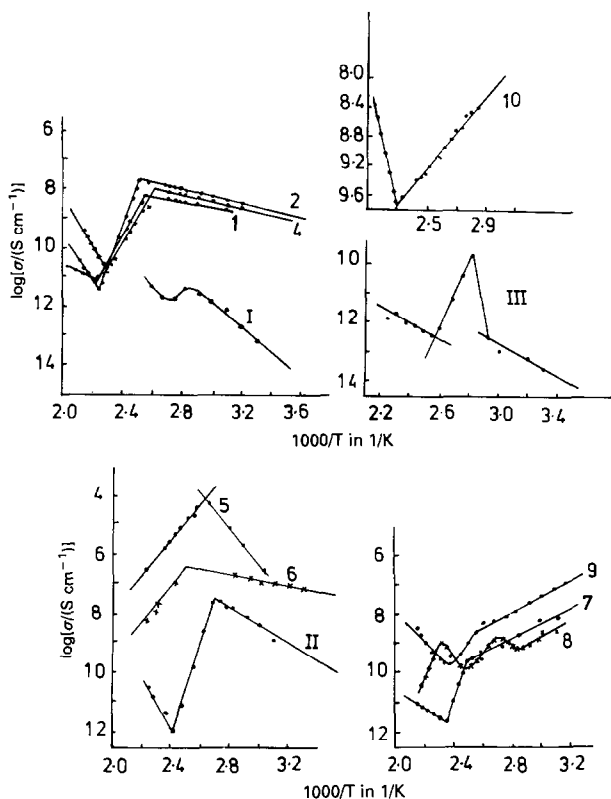
Fig. 3. Log σ vs. 1000/T relationship of ligands I–III and their metal complexes.

coordinated water molecules. This phase change may also induce lattice rearrangement and, hence, may change the geometrical structure of the complexes for which the conductivity gets lower and its attendant activation energy for conduction ΔE gets higher (Fig. 3), because values of the activation energy of the complexes are high compared to those of the corresponding free ligands, in addition to its rapid decrease in the high temperature zones. Hence the conduction mechanism undergoes inversion from electronic to ionic. Values of the activation energies (ΔE_1 and ΔE_2) of the complexes derived from ligand I follow the order Co > Cu > Mn and Cu > Co > Mn, as shown in Fig. 4. Thus it can be suggested that the conductivity strongly depends on the ionic radii of the metal ions in the complex [18,19].

The conductivity curve for the free ligand II displays two activation energies, ΔE_1 and ΔE_2. The inflection observed can be attributed to a change in the conduction mechanism on passing through the phase change. As already noted, this phase change includes lattice rearrangement caused by loss of humidity and water of crystallization molecules. The first step in the conduction process is due to electronic conduction via π-electron delocalization, while at higher temperatures the conduction is due to electronic excitation from the highermost filled π-molecular
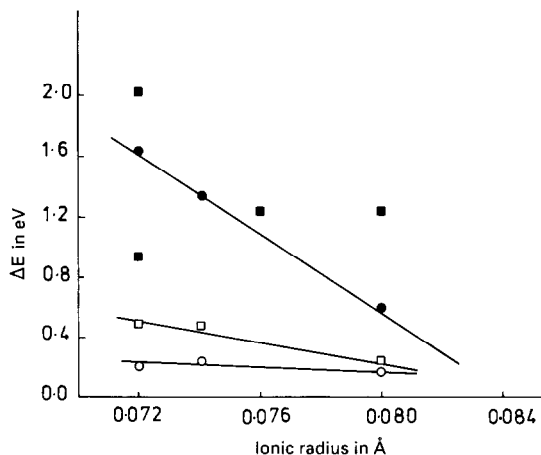
Fig. 4. The relationship between the ionic radii of the metal ions and the ΔE values evaluated from the electrical conductance temperature relationship: $\bigcirc$, ΔE_1 for complexes 1, 2, and 4; $\bullet$, ΔE_2 for complexes 1, 2, and 4; $\square$, ΔE_1 for complexes 5–9; and $\blacksquare$, ΔE_2 for complexes 5–9.

orbitals to the lowermost unfilled π-molecular orbitals. Thus, the electron is assumed to tunnel to an equivalent empty level of a neighbouring molecule in the anodic direction. Alternatively, a hopping conduction mechanism might prevail. The data indicate that the conductivity of the Ni(II) complex (8) decreases with temperature rise, i.e. it shows metallic behaviour. The behaviour of the Co(II) and Cu(II) complexes (7 and 9) is similar, i.e. the conductivity decreases in the lower temperature range then increases again in the higher temperature range. The electrical conductivity of complexes 6–9 increases and the activation energy decreases on going from the free ligand to its complex. The dependence of ΔE_1 on the ionic radii for divalent ions was found to be in the order Mn < Co $\approx$ Ni $\approx$ Cu, i.e. the higher the ionic radii, the lower the activation energy (ΔE_1) values. The second activation energy values (ΔE_2) at higher temperatures show irregular behaviour, see Fig. 4. The metallic conductivity behaviour as traced for the Mn(II), Fe(III), and Ni(II) complexes can be explained by the cationic disproportionation of these complexes into lower (metallic) and higher valency states.

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