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Thermochemical and electrical properties of Zincon complexes with Mg(II), Ca(II), Sr(II), Ba(II) and Bi(III)

M. Gaber [a,1], H.E. Mabrouk [a] and M. Mounir [b]

[a] *Chemistry Department, Faculty of Science, Sana'a University, Sana'a (Yemen)*
[b] *Physics Department, Faculty of Science, Cairo University (Egypt)*

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Abstract

The thermal behaviour of Zincon complexes with the divalent metal ions Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} and Bi^{3+} has been studied. The structure of the complexes were characterised by elemental analysis and infrared spectra. The thermal stability of the investigated complexes is discussed in terms of the type of metal ions. The kinetics of the thermal decompositions are discussed. The energies of activation were determined. The electrical resistivities were measured and the activation energies of the complexes were also calculated.

INTRODUCTION

The Zincon ligand used in this investigation has been widely used as an analytical reagent for the microdetermination of zinc ions [1–3]. Only a few studies have considered its ability to form chelate compounds with divalent transition metal ions [4]. In continuation of the work on the chelates of Zincon, the present article reports on studies of the complexes formed by the interaction of Zincon with Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} and Bi^{3+} ions using IR and DTA, as well as the conductivity measurements.

EXPERIMENTAL

All the chemicals used in the present study were pure laboratory grade BDH chemicals. The solid complexes were prepared by mixing 0.01 mmol of Zincon in ethanol with 0.01 mmol of the metal salt in the same solvent. The mixture was then refluxed for 2 hours. The isolated solid complexes were then filtered off, washed with ethanol and dried over anhydrous $CaCl_2$.

Thermal analysis of the complexes was carried out using a Du Pont TA 900 thermal analyser. Infrared spectra were measured in KBr discs using a Perkin–Elmer 598 (200–4000 cm^{-1}) spectrophotometer. The electrical con-

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[1] Author to whom correspondence should be addressed.

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ductivity of the solid compounds was measured in a continuous regime at a rate of about 0.5 °C min^{-1}. The conduction current was measured using an electrometer, type 610 °C (Keithly instrument). Compressed pellets 1 cm^2 in area and 0.1–0.15 cm thick were moulded at 25 °C at a pressure of 10 tons cm^{-2}.

RESULTS AND DISCUSSION

All the prepared complexes were subjected to elemental microanalysis; the data are listed in Table 1. The isolated metal complexes were $ML(EtOH)_n$ where n = zero for M = Ca(II) and Sr(II); $n = 2$ for M = Mg(II); and $n = 3$ for M = Ba(II). The composition of the Bi(III) complex is $[BiLCl](H_2O)_4$.

Infrared spectra

Comparing the solid state IR spectra of the complexes with that of the ligand (Table 1) shows the following: (i) The bands at 3120, 1670 and 1540 cm^{-1} corresponding to NH, ν(C=O) and ν(N=N) respectively, are shifted to lower wavenumbers in the spectra of the complexes; this indicates that the NH, COO and N=N groups are coordination sites for the Zincon. (ii) The absence in the complex spectra of the δ(OH) of the phenolic (1320 cm^{-1}) and carboxylic (1350 cm^{-1}) groups of the free ligands indicates that these groups participate in complex formation through H^+-ion displacement. (iii) The ν(C=N) band of the free ligand at 1630 cm^{-1} is not affected by

TABLE 1

Analytical, IR, DTA and electrical conductance data of the Zincon complexes

No.	Complex	Microanalysis [a]			IR spectra				ΔE_a^b	T decom. (°C)	ΔE [c] (eV)
		% C	% H	% M	NH	C=O	C=N	N=N			
1	$MgL(EtOH)_2$	50.9	4.0	3.91	3120	1670	1630	1540	50.6	403.5	M
		(49.97)	(4.34)	(4.22)	3100	1640	1620	1520		500 sh [d]	
2	CaL	48.1	2.5	7.4					48.1	407	0.38
		(48.0)	(2.6)	(8.0)	3090	1650	1605	1525			
3	$BiLCl(H_2O)_4$	30.2	2.5	26.2						480	0.38
		(30.9)	(2.7)	(26.9)	3110	1655	1620	1515	55.7		
4	$BaL(EtOH)_3$	42.7	4.0	17.9						434	0.38
		(42.4)	(4.2)	(18.7)	3095	1645	1615	1518	159.4	490	
5	$SrL(H_2O)$	41.9	2.4	15.3						418	1.01
		(42.4)	(2.65)	(15.5)	3100	1655	1615	1520	145	464 sh	

[a] Found (calc). [b] From DTA. [c] From the Arrhenius plot: M = metallic. [d] sh = shoulder.

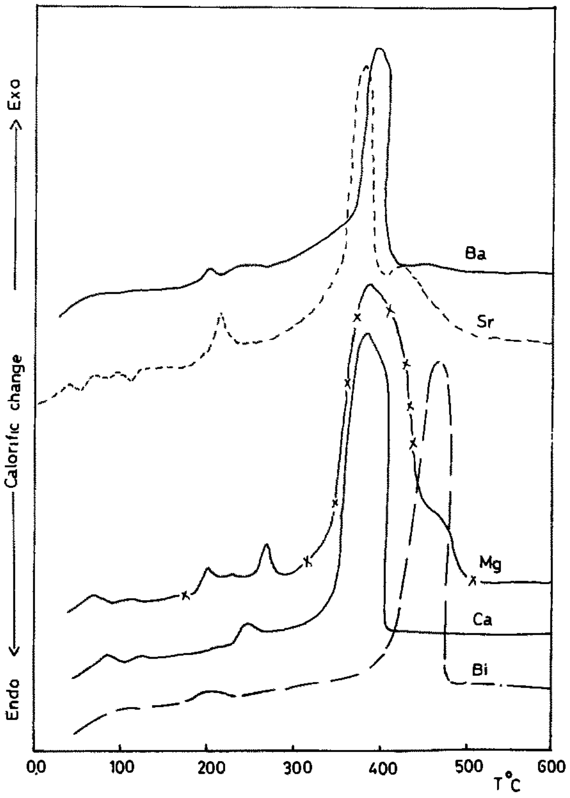
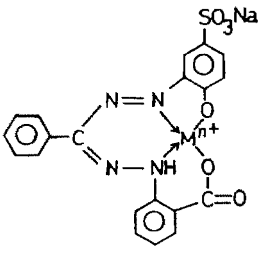


Fig. 1. DTA of the solid Zincon complexes.

coordination, i.e. it is not involved in complex formation. Based on the IR spectra, the bonding between metal and ligand can be represented as follows



where ($n+$) = 0 for Mg, Ca, Ba, Sr; ($n+$) = +1 for Bi.

Differential thermal analysis of the solid complexes

DTA can be used to solve problems concerning the structure of the coordination compounds as well as to calculate the kinetics and thermodynamics data for the solid state reactions [5–12]. Therefore, the structures of the complexes under investigation can be determined by DTA.

The DTA curve of the Mg complex (Fig. 1) consists of a medium-sized exothermic peak at 203° C consistent with the loss of ethanol molecules

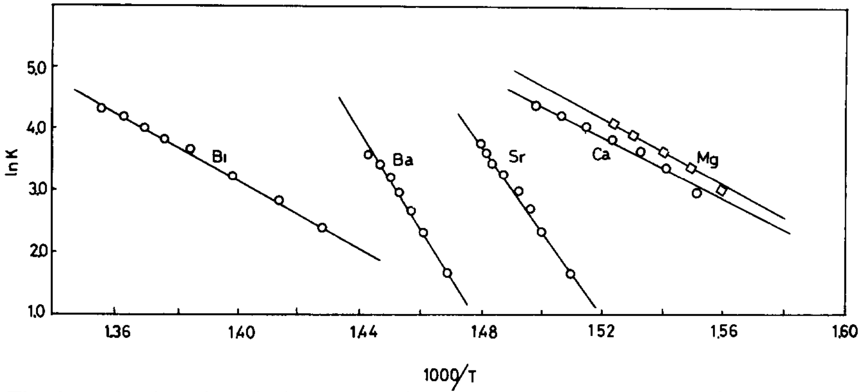


Fig. 2. Arrhenius plot of Zincon complexes constructed from DTA thermograms.

from the surface of the crystal. The appearance of a similarly sized exothermic peak at 276 ° C may be correlated with the overlapping of two adjacent processes, melting and phase transformation. The broad exothermic peak at 404 ° C includes the decomposition [13] and the loss of the organic portion, with subsequent formation of the metal oxide. The disappearance of any thermal change above 403 ° C is consistent with the formation of only one metal oxide MgO, because it shows good stability on further heating up to 700 ° C. The energy of activation (E_a) of the thermal decomposition of the complex was evaluated from the DTA curve as in previous studies [7,14]. In general, the reaction follows first-order kinetics. An arrhenius plot was constructed (Fig. 2) and the energy of activation (50.6 kcal mol^{-1}) was obtained from the slope.

For the Ca complex, the weak endothermic peak at 109 ° C is correlated with the loss of water from the surface of the crystals (moisture content) [15]. The broad, medium exothermic peak at 256 ° C corresponds to the melting of the anhydrous complex. The strong, broad exothermic peak at 407 ° C corresponds to the decomposition of the complex and loss of the organic ligand, leaving CaO as the final product. No thermographic changes are observed up to 700 ° C. Figure 2 shows the Arrhenius plot from which the energy of activation of thermal decomposition was calculated (48 kcal mol^{-1}).

The DTA thermogram of the Sr complex shows an endothermic peak at 118 ° C corresponding to the loss of a water molecule. The exothermic peak at 234 ° C corresponds to the melting of the complex and the strong exothermic peak at 418 ° C, with a broad shoulder at 464 ° C, includes various changes, including the decomposition of the complex to the final product. The thermal decomposition follows a first-order kinetic law from which the rate constant (K) is obtained from the DTA curves at a certain temperature, T. An Arrhenius plot was then constructed as shown in Fig. 2

and the energy of activation, E_a, was obtained from the slope (144.9 kcal mol^{-1}).

For the Ba complex, all peaks are exothermic with loss of ethanol molecules at 222° C, a weak, broad peak at 266° C corresponding to the melting of the complex, and the decomposition of the complex and loss of the ligand at 434° C, leading to the formation of BaO as the final product.

The energy of activation (E_a) of the thermal decomposition was calculated from the Arrhenius plot (159.4 kcal mol^{-1}, see Fig. 2).

The DTA thermogram of the Bi complex shows a weak endothermic peak at 120° C corresponding to the loss of water molecules from the surface of the complex. The exothermic peak at 192° C may be assigned to the loss of chlorine. The appearance of a strong, broad exothermic peak at 480° C may be correlated with the decomposition along the chelate bond by loss of the organic ligand. The complex is stable up to 750° C. The energy of activation of the latter process is 55.65 kcal mol^{-1}, see Fig. 2.

Electrical conductivity

The electrical conductivity in organic molecular solids differs in several important ways from that in metals and typical semiconductors such as silicon. The electrical conductivity (σ) of solids normally varies according to the Arrhenius equation

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

where σ_0 and ΔE are the conductivity constant and the activation energy, and K is the Boltzmann constant.

Figure 3 shows the electrical conductivity of the Zincon and its metal complexes. It can be shown that the conductivity of all the complexes, except the Mg complex, increases with temperature, i.e. there is a positive coefficient of the electrical conductivity ($d\sigma/dT$).

The conductivity curve for the free ligand shows a break at 70° C. Therefore the ligand has two activation energies, see Table 1. The inflection observed can be attributed to a change in the conduction mechanism. The first step in the conduction process is due to the electronic conduction through π-electron delocalisation, while at higher temperatures the conduction is due to the excitation of an electron from the uppermost filled π-molecular orbital to the lowest unfilled π-molecular orbital. Thus, the electron is assumed to tunnel to an equivalent empty level of a neighbouring molecule in the anodic direction.

The conductivity of the Sr complex is very low at room temperature (i.e. very high resistivity), but it increases with temperature. Thus the Sr complex behaves in a manner similar to semiconductor materials. The conductivity of the magnesium complex decreases with temperature, i.e. it shows metallic

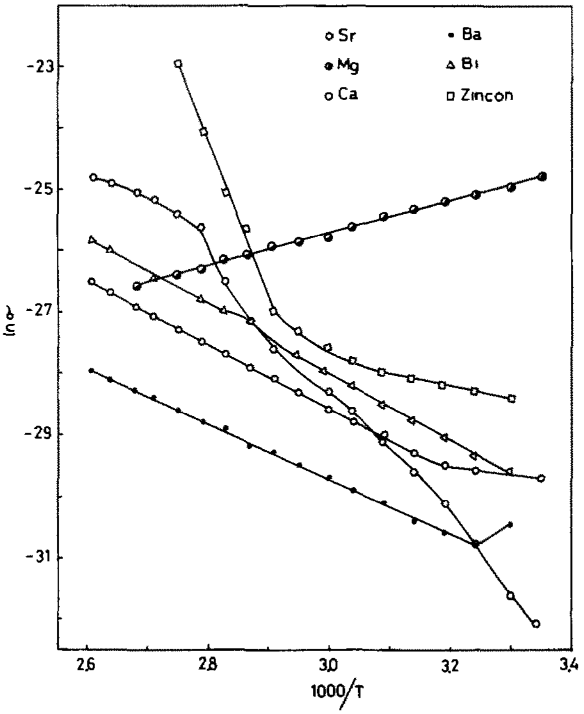


Fig. 3. Electrical resistivities of some Zincon complexes.

behaviour. This decrease may be due to high recombination between the free carriers.

The behaviour of the Ca, Ba and Bi complexes is similar, i.e. they have the same activation energy values.

The conductivities of the metal complexes are lower than that of the ligand at high temperature ($\Delta E = 1.12$ eV). This can be ascribed to an increase in the mobility as a consequence of the replacement of the hydrogens of the OH and COOH groups with a metal ion, to form new molecular orbitals which are delocalised over the whole complex.

It has been suggested that the conductivity depends on the ionic radius of the cation, as well as on the stability of the complexes [16,17]. The observed activation energies of the Zincon complexes studied show an irregular trend that is independent of the ionic radius of the cation.

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