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SYNTHESIS, THERMAL AND ELECTRICAL STUDIES ON ZIRCONYL COMPLEXES WITH SCHIFF BASES DERIVED FROM 2-HYDROXY-1-NAPHTHALDEHYDE AND SOME AROMATIC DIAMINES

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ABSTRACT

The complexes of zirconyl chloride with some Schiff bases derived from 2-hydroxy-1-naphthaldehyde and various aromatic diamines were prepared and characterized by elemental analysis, electronic absorption spectra and TG and DTA studies. The electrical properties and ($I-V$) characteristics for the metal complexes were also investigated.

INTRODUCTION

In recent years considerable attention has been paid to the investigation of oxo–metal complexes because of their interesting coordination chemistry as well as their role in synthetic organic chemistry [1]. Zirconium(IV) is of interest since it is used to synthesise novel organic complexes which may be used as agents for oxygen transfer to various substrates [2]. Also, Zr is used to synthesis tractable Schiff base chelate polymers [3]. A series of new zirconium(IV) complexes with Schiff bases derived from different salicylaldehydes and 2-hydroxy-1-naphthaldehydes with *o*-aminophenol [4] and also with tetradentate Schiff bases, bis-salicylaldehyde-*o*-phenylenediimine and bis-salicylaldehyde-*p*-phenylenediimine in 1 : 1 and 1 : 2 molar ratios [5] have been reported.

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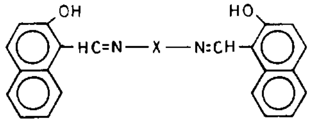
In the present article the synthesis of zirconyl chloride ($ZrOCl_2 \cdot 8H_2O$) complexes with Schiff bases derived from 2-hydroxy-1-naphthaldehyde and some aromatic diamines was studied. The thermal properties, electrical conductivity and current–voltage (I–V) characteristics of these complexes were also investigated.

EXPERIMENTAL

Preparation

The chemicals used were pure products obtained from BDH. The ligands derived from 2-hydroxy-1-naphthaldehyde with *o*- and *m*-phenylenediamines and with 2,3-, 1,5- and 1,8-diaminonaphthalenes were synthesized using the usual procedures. The structures of these ligands are shown below



where X = *o*-phenylenediamine (H_2L_I), *m*-phenylenediamine (H_2L_{II}), 2,3-diaminonaphthalene (H_2L_{III}), 1,5-diaminonaphthalene (H_2L_{IV}) or 1,8-diaminonaphthalene (H_2L_V).

The Zr complexes were prepared as described elsewhere [6,7]. Their chemical formulae and designations are listed in Table 1.

Apparatus

Electronic absorption spectra were measured using a Pye–Unicam SP 8000, while the infrared spectra were recorded on a Perkin–Elmer 598 infrared spectrophotometer using KBr discs.

TABLE 1

Analytical data and electronic absorption spectra of zirconyl complexes

Complex	Empirical formula	Zr (%)	N (%)	UV and visible absorption (nm)
I	$[ZrOL_I] \cdot 4H_2O$	14.8 (15.34)	3.9 (4.7)	480, 405, 325
II	$[(ZrOCl)_2L_{II}] \cdot 5H_2O$	24.0 (23.8)	3.3 (3.5)	475, 450, 360
III	$[ZrOL_{III}] \cdot 2.5H_2O$	14.0 (14.85)	4.3 (4.56)	515, 415, 330
IV	$[ZrOClHL_{IV}] \cdot H_2O$	13.8 (14.85)	4.4 (4.5)	510, 470, 360
V	$[ZrOL_V] \cdot 2H_2O$	14.3 (15.0)	5.8 (4.6)	510, 480, 330

The thermal analyses (DTA and TG) were carried out on a Du Pont 900 Thermal Analyzer: 10–14 mg of the sample was heated up to 750 ° C, using a heating rate of 10 ° C min^{-1} in air.

The electrical conductivity and the current–voltage ($I-V$) measurements were carried out using a Super Megohmmeter electrometer (Model 170) as described by Ayad et al. [8].

RESULTS AND DISCUSSION

Electronic absorption spectral study

The electronic absorption spectra of all the samples were measured on Nujol mulls. In almost all complexes, three prominent bands appear in the spectra; see Table 1. The bands in the wavelength range 480–515 nm can be assigned to charge transfer transitions [6]. However, the other bands located in the ranges 480–405 and 325–360 nm could be attributed to K-band [9] and $\pi-\pi^*$ transitions between the benzal ring and the imine group, respectively.

Infrared spectral analysis

The IR spectra (Table 2) show a strong absorption band in the range 3365–3350 cm^{-1}. This band could be assigned to the stretching vibration ν_{OH}, indicating the presence of water of crystallization. The band at 1620 cm^{-1}, assigned to the C=N stretching of the free Schiff bases [10], is observed in the region 1610–1620 cm^{-1} in the spectra of the complexes. This shift of about 5–10 cm^{-1} towards lower and higher frequencies suggests the possible coordination of the Schiff base in the anionic form through the azomethine nitrogen and oxygen of the phenolic OH groups. These observations agree with those of previous studies [11,12]. The suggested coordination of the ligands in the anionic form finds support in the

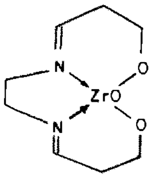
TABLE 2

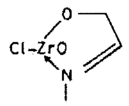
Infrared wavenumbers (cm^{-1}) of zirconyl complexes and their assignments [a]

Complex	ν_{OH}	ν_{C-H} Aromatic	$\nu_{C=N}$	$\nu_{C=C}$ Aromatic	ν_{C-O} Stretching	δ_{OH}	$\nu_{Zr=O}$
I	3350 (3440)	2940 (3030)	1620 (1621)	1570 (1595)	1310 (1288)	1244	990 (–)
II	3358 (3430)	2910 (2918)	1620 (1625)	1570 (1590)	1307 (1290)	1248	985 (–)
III	3365 (3440)	2940 (2920)	1610 (1620)	1570 (1570)	1310 (1305)	1245	990 (–)
IV	3350 (3430)	2940 (2920)	1620 (1620)	1550 (1590)	1320 (1310)	1260	980 (–)
V	3350 (3440)	2960 (2930)	1625 (1620)	1580 (1590)	1265 (1315)	1250	980 (–)

[a] Figures in parentheses indicate wavenumber for ligand.

disappearance of the δ_{OH} and ν_{C-OH} bands in the spectra of the complexes with ligands I, II, III and IV, denoting the displacement of the two phenolic OH groups. For ZrO^{2+} complexes with ligand IV, the δ_{OH} and ν_{C-OH} bands at 1260 and 1320 cm^{-1}, respectively, display an obvious decrease in intensity due to the removal of only one proton, leaving the other unaffected. The difference in behaviour for the two groups of ligands (I, III or V, and II or IV) stems from the formation of stable six- and five-membered rings in the former case involving the two nitrogens and two oxygens, which is not possible for the other compounds [7]. This can be depicted as follows





A band due to the Zr=O stretching vibration for each complex is also observed in the range 980–990 cm^{-1}. This is in agreement with the assignment of the band at 980 cm^{-1} to Zr=O, as reported by Patel et al. [13,14].

Thermal studies

The TG and DTA curves in the temperature range 20–800 °C for all the metal complexes show that they are thermally stable up to 70 °C, when dehydration begins; this is characterized by endothermic peaks within the temperature range 70–100 °C corresponding to the loss of hydration water [15]. The dehydration processes could be interpreted further by using the information given by the TG curves, which indicates that this process takes place in one step.

The DTA curve of complex II, shown in Fig. 1, exhibits exothermic peaks at 274 and 378 °C associated with the thermal dissociation of halogen [16] and rearrangement of the molecular lattice. This is followed by an exothermic peak at 518 °C corresponding to partial decomposition of the complex [17]. In the final stage of degradation, in the temperature range 600–650 °C, the complete decomposition of the complex leads to the formation of ZrO_2, from which the metal content was determined; see Table 2. Thus the thermal decomposition for complex II can be represented by the following scheme

$$[(ZrOCl)_2L_{II}] \cdot 5H_2O \rightarrow [(ZrOCl)_2L_{II}] + 5H_2O$$

$$[(ZrOCl)_2L_{II}] \rightarrow [(ZrO)_2L_{II}]^{2+} + 2Cl^-$$

$$[(ZrO)_2L_{II}]^{2+} \rightarrow ZrO_2$$

The DTA curves were measured for complexes I, III, IV and V, but TG

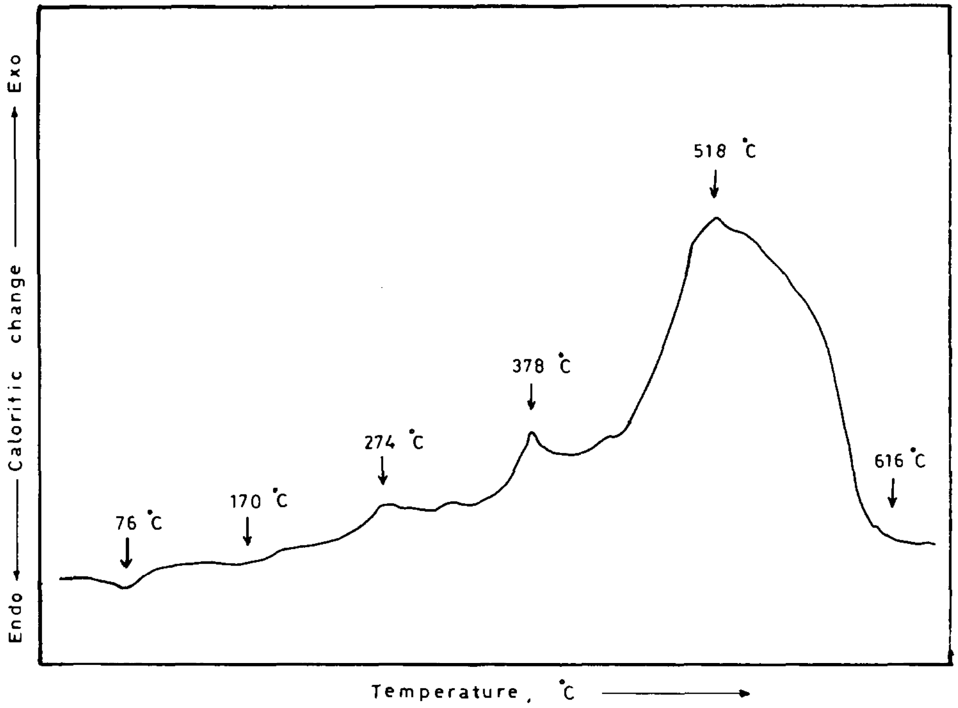


Fig. 1. DTA curve of complex II.

TABLE 3

DTA peaks and their assignments for some zirconyl complexes

Complex	DTA peak (°C)		Assignment
	Endo	Exo	
II	76		Dehydration process
		274	Slow dissociation of halogen
		378	Thermal dissociation of halogen
		518	Decomposition and formation of metal oxide
III	80		Dehydration process
		308	Melting of complex
		392	Partial decomposition of complex
		502	Final degradation of complex
IV	74		Dehydration process
		211	Crystalline transition and chemisorption
		300	Melting of complex
		398	Thermal dissociation of halogen
		476	Decomposition of complex
V	98		Dehydration process
		356 400	Successive melting of complex
		492	Decomposition of complex

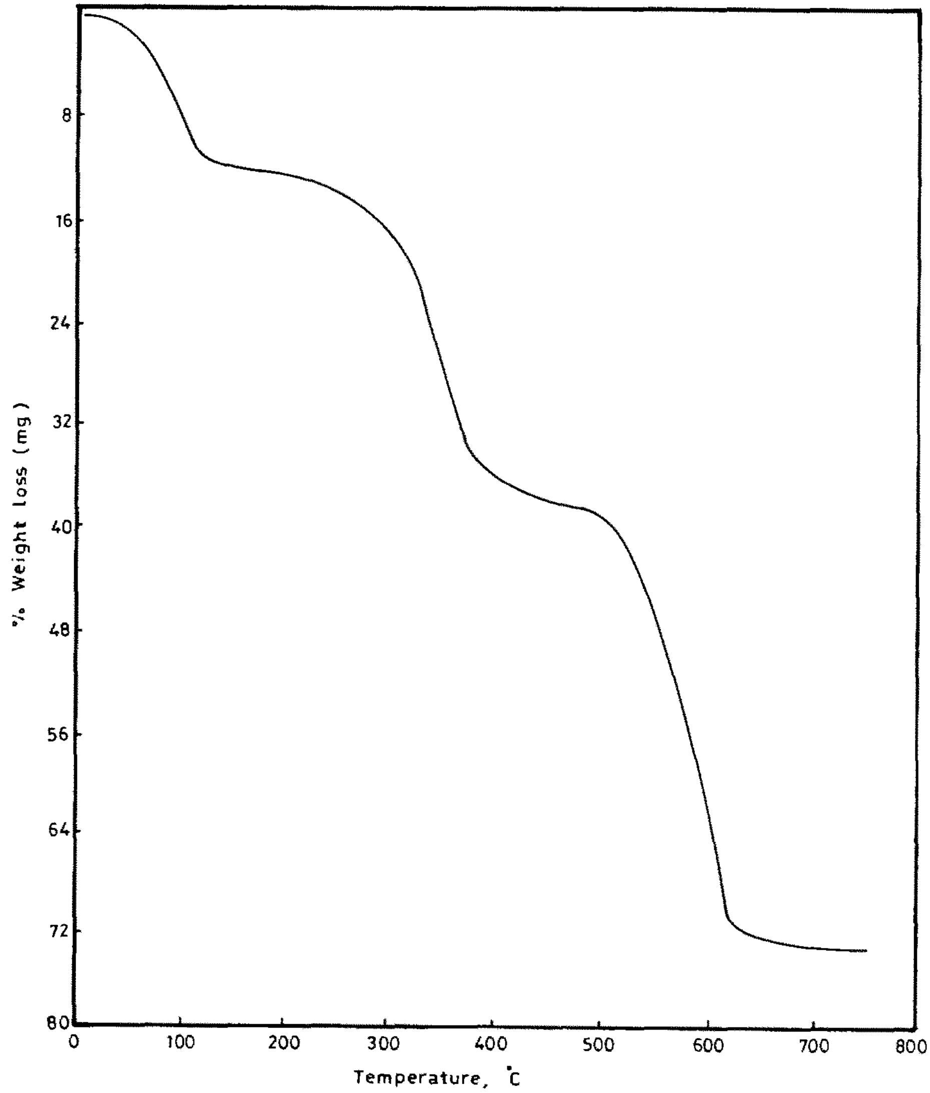


Fig. 2. TG curve of complex II.

TABLE 4

Thermogravimetric analysis for some zirconyl complexes

Complex	H_2O (%)			ZrO_2 (%)		
	Temperature (°C)	Calc.	Found	Temperature (°C)	Calc.	Found
I	70	12.14	11.16	700	20.77	19.0
II	75	11.40	11.10	650	31.20	28.0
III	70	7.32	7.0	650	20.06	20.0
IV	75	2.89	3.10	650	19.75	18.2

measurements were carried out only for complexes I, III and IV. The DTA and TG curves for the different complexes show a number of phenomena similar to those observed for complex II (see Fig. 2). The deduced data are collected in Tables 3 and 4. It can be seen that the decomposition of the anhydrous complexes follows immediately after the dehydration process,

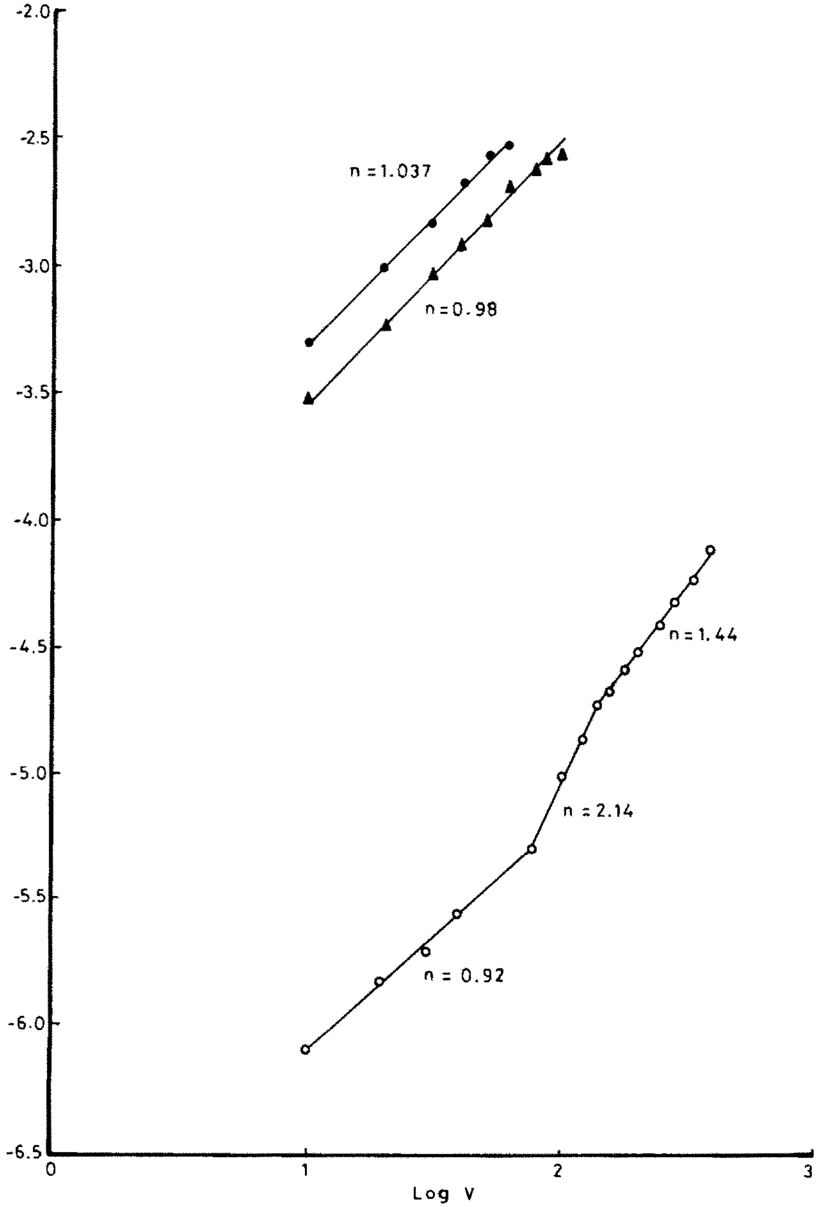


Fig. 3. Log *I* vs. log *V* for complexes: (○) II; (▲) III; (●) V; and values of *n* at different applied voltages.

and the residual weights are in close agreement with the values for the metallic oxide (ZrO_2).

Electrical conductivity

The $I-V$ characteristic on a log–log scale for complex II is shown in Fig. 3. As can be observed, the data fit the proportionality $I \propto V^n$ with $n = 0.92$ at applied voltages $10 < V < 90$. However, in the ranges $90 < V < 160$ and $160 < V < 400$, values of n equal to 2.14 and 1.44, respectively, were obtained. This indicates that the complex proceeds from ohmic conduction to space charge limiting current (SCLC) and finally to nearly ohmic conduction in the three respective ranges of applied voltages [18]. The log I versus log V plots for complexes III and V (Fig. 3) show that these complexes obey Ohm's law in the range of applied voltages $10 < V < 100$ and $10 < V < 60$, respectively.

The electrical resistivity for each complex at 30 °C was measured. The deduced conductivities were 6.50×10^{-6}, 4.17×10^{-9}, 1.95×10^{-6}, 3.89×10^{-6} and 5.51×10^{-6} Ω^{-1} cm^{-1} for complexes I, II, III, IV and V, respectively. It is evident that complexes I, III, IV and V have approximately equal conductivities. The low conductivity of complex II could be attributed to its structural formula. The replacement of two hydrogen atoms by two ZrO^{2+} ions could cause a distortion in the conduction pathways between the metal and the ligand, and hence decrease the electron migration [19].

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REFERENCES

1 R.C. Fay, Coord. Chem. Rev., 80 (1987) 131.
2 M.T.H. Tarafder and M.A.L. Miah, Inorg. Chem., 25 (1986) 2265.
3 R.C. Fay and J.K. Howie, J. Am. Chem. Soc., 101 (1979) 115.
4 A. Syamal and D. Kumar, Indian J. Chem., Sect. A, 24 (1985) 62.
5 J. Uttamchandani and R.N. Kapoor, Trans. Met. Chem., 3 (1978) 79.
6 M.I. Ayad, Ph.D. Thesis, University of Menofia, Egypt, 1989.
7 M. Gaber, R.M. Issa, F.A. Aly and M.I. Ayad, Thermochim. Acta, in press.
8 M.M. Ayad, S. Amer and R.M. Issa, Thermochim. Acta, 140 (1989) 277.
9 M.L. Illingworth and A.L. Rheingold, Inorg. Chem., 26 (1987) 4312.
10 N.S. Biradar and V.H. Kulkarni, J. Inorg. Nucl. Chem., 33 (1971) 2451.
11 N.S. Biradar, V.H. Kulkarni and N.N. Sirmokadam, Monatsh Chem., 101 (1970) 551.
12 V.A. Kogan, O.A. Osipov, V.I. Minkin and V.P. Sokolov, Zh. Neorg. Khim., 10 (1965) 83.
13 V. Krishnan and C.C. Patel, J. Inorg. Nucl. Chem., 26 (1964) 2201.

14 V.V. Savant and C.C. Patel, J. Inorg. Nucl. Chem., 31 (1969) 2319.
15 W.W. Wendlandt, J. Inorg. Nucl. Chem., 25 (1963) 833.
16 Yu.Ya. Kharitonov, M.M. Bekhit and S.F. Belevskii, Russ. J. Inorg. Chem. (Engl. Transl.), 28 (8) (1983) 1109.
17 C.F. Bell and D.R. Rose, Inorg. Chem., 7 (1968) 325.
18 F. Gutmann and L.E. Lyons, Organic Semiconductors, Wiley, New York, 1967.
19 M.G. Abd El-Wahed, M. Abd El-Mottalb and A.K. Abd El-Kader, Thermochim. Acta, 124 (1988) 171.