Spectroscopic and Conductometric Studies on Zr^{4+}, In^{3+}, La^{3+}, Ce^{3+} and UO_2^{2+} Complexes with Zincon

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Abstract

The complexes of type [$ML\cdot XH_2O$] and [$ML_2\cdot XH_2O$] in which M = Zr(IV), In(III), La(III), Ce(III) and UO_2(II) ions and L is Zincon, [1-(2-hydroxy-5-sulphophenyl)-3-phenyl-5-(2-carboxyphenyl)-Formazan], were prepared and their structures characterized by elemental analysis, infrared, proton NMR and electronic absorption spectra.

Conductometric measurements of the solid complexes were performed in the temperature range 400–700 K. A phase transition was illustrated for all the complexes, and their activation energies calculated. The latter showed dependence on the charge and ionic readius of each metal ion. The complexes have less activation energies than do the free ligands.

Introduction

The interest of zincon in view of its specific ability as complexing agent for the microanalytical determination of zinc ion at pH 9–10 [1–4]. However, only a few studies have considered the spectral behaviour of this indicator; its ability to form chelate compounds with rare earth and transition metal ions has not been adequately reported.

The electrical properties of different organic compounds have been measured by a number of investigators [5–9]. It is apparent that no investigations have been made on the electrical properties of zincon complexes.

In continuation of our studies on metal complexes with zincon [10], the present work deals with complexes formed by the interaction of zincon with Zr^{4+}, In^{3+}, La^{3+}, Ce^{3+} and UO_2^{2+} ions using spectroscopic techniques (IR, ^1H NMR and visible spectra). Also conductometric measurements of the solid complexes were performed in order to ascertain the effect of transition metal ions on the electrical resistivity and related properties of the reagent.

Experimental

All compounds used in the present work were laboratory grade BDH or Merck chemicals.

1. Preparation of the Solid Complexes

The solid complexes were prepared by mixing equimolecular amounts of the ligand and metal dissolved in acetone. The mixture was then stirred for about half an hour, and then reduced in volume. The solid complexes were isolated by addition of ether and then filtered immediately. Recrystallization of the solid complexes from acetone/ether, to ensure the isolation of pure compounds, was carried out and the solid complexes were then filtered off, washed and dried over P_2O_5.

2. Spectrophotometric Measurements

A Perkin-Elmer Model 598 spectrophotometer was used to obtain the IR spectra of the complexes by a KBr disk technique. Electronic spectra were recorded on a Unicam SP 8000 spectrophotometer. NMR spectra were recorded on a Varian Associates Model A 60 spectrometer equipped with a 60 Mc/s Radiofrequency source.

3. Electrical Measurements

The samples were in the form of discs 8 mm in diameter and 2 mm thick, prepared under a pressure of 3 ton/cm^2. The electrical contact was made with silver paste. The cell used in the measurements was as described previously [9]. The temperature was measured by a copper-constant thermocouple placed close to the sample and the direct current was measured with a Multiflex galvanometer with a sensitivity of 4×10^{-9} A.

Results and Discussions

1. Elemental Analysis

The results of analysis are given in Table I. The data obtained by microanalysis showed that the stoichiometry of the isolated metal complexes was

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TABLE I. Analytical Data for Zincon Complexes.

Complex	Microanalysis Results[a]										Colour
	C		H		N		Cl		M		
	F	C	F	C	F	C	F	C	F	C	
$ZrL_2 \cdot 2H_2O$	45.50	45.83	2.55	2.86	10.40	10.69	–	–	8.50	8.70	pink
$InL \cdot H_2OCl$	37.90	38.19	2.40	2.70	8.65	8.91	5.30	5.65	18.00	18.27	violet
$LaL \cdot H_2OCl$	36.40	36.78	2.30	2.60	8.30	8.35	5.10	5.44	20.90	21.25	blue
$CeL \cdot H_2OCl$	36.45	36.71	2.30	2.60	8.25	8.56	5.10	5.43	21.1	21.43	pink
$UO_2L \cdot 2H_2O$	31.00	31.29	2.00	2.21	7.00	7.30	–	–	30.95	31.14	blue

[a] F (%found), C (%calculated).

TABLE II. IR and Eletronic Spectral Data for Zincon and its Metal Complexes.

Compound	IR (cm^{-1})								Visible		
	νOH	νNH	νC=O	νC=N	νN=N	δH_2O	$\nu M \leftarrow N$	$\nu M \leftarrow O$	λ_{max}	$\epsilon \times 10^5$	p*K*
Zincon	3440	3220	1710	1600	1400	–	–	–	510, 560	8, 7.5	
$ZrL_2 \cdot 2H_2O$	3400	3220	1694	1595	1395	–	405	478	525	6.1	10.22
$InL \cdot Cl \cdot H_2O$	3410	3180	1680	1600	1385	1610	405	480	535, 660	5, 4.2	6.42
$LaL \cdot ClH_2O$	3410	3100	1700	1600	1380	1610	405	482	565, 645	9.6	10.30
$CeL \cdot ClH_2O$	3420	3180	1695	1600	1375	1608	405	480	520, 570	5.7, 4	6.70
$UO_2L \cdot ClH_2O$	3420	3200	1685	1595	1395	–	403	482	610	5.5	6.96

[a] ϵ mol^{-1} cm^{-1} $\times 10^5$ M solution in DMF.

($ML \cdot ClH_2O$), where M = In(III), La(III) and Ce(III), but for the UO_2(II) was ($ML \cdot 2H_2O$). The composition of Zr(IV) complexes was ($ML_2 \cdot 2H_2O$).

For zirconium and uranyl ions the complexes crystallized with two water molecules, while for indium, lanthanium and cerium ions the complexes have one water molecule coordinated to the central metal atom (this conclusion is derived from the results of IR spectra).

2. *The IR Spectra*

The mode of bonding of the metal ion to the ligand was investigated by analysing the IR spectra. The important infrared bands are depicted in Table II. The comparison shows that the band at 1600 cm^{-1} in the spectra of the free ligand (attributed to the νC=N of the hydrazon moiety) is not influenced by coordination. This indicates that this group would not take part in complex formation. Also the band corresponding to νN–H at 3220 cm^{-1} in the spectra of the ligand is shifted to lower frequency in all complexes, except in the zirconium complex, due to coordination with the metal ions. The two bands at 1400 cm^{-1} and 1700 cm^{-1} in the free ligand attributed to the νN=N and νC=O groups respectively are shifted to lower wavenumbers in the spectra of complexes. This shift shows that N=N and C=O groups are involved in chelate formation of the complexes [11].

The band observed at 1325 cm^{-1} can be assigned to δOH of the phenolic group in the free ligand (absent in the spectra of complexes). The disappearance of this band is apparently due to the displacement of the hydrogen ion from the OH group through the interaction of the ligand with the metal ions.

The spectra of the complexes show a broad absorption band in the 3400–3440 cm^{-1} region characteristic of the presence of water molecules in the chelates. The appearance of δOH of water at 1610 cm^{-1} for In^{3+}, La^{3+} and Ce^{3+} complexes after heating the complexes at 120 ℃ suggest that water molecules are held strongly in these three complexes [12].

Bands are exhibited at 405 and 480 cm^{-1} in the spectra of chelates which are assigned to the $\nu M \leftarrow N$ and $\nu M \leftarrow O$ vibration [13] respectively, providing proof of chelate formation.

3. *Electronic Absorption Spectra*

The visible spectrum of zincon in dimethylformamide has absorption maxima at 510 and 560 nm, wavelengths, which are different from thoese observed in case of other complexes when dissolved in DMF. The absorption spectra are shown in Fig. 1. The bands correspond to the metal–ligand complexes

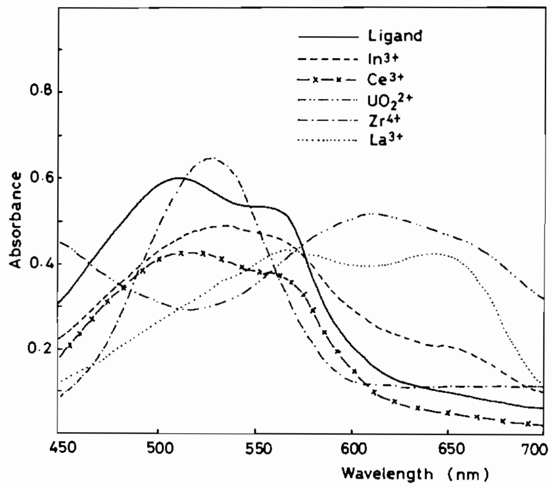


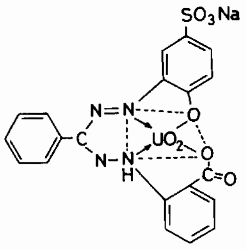
Fig. 1. Absorption spectra.

have λ_{max} at 525 nm for the zirconium complex, 535 and 660 nm for the indium complex, 565 and 645 nm for the lanthanium complex, 520 and 570 nm for the cerium complex and 610 nm for the uranyl complex. This red shift in λ_{max} in the case of metal complexes refer to the difference of perturbing effect of metal ions. The change in colour with the shift of the bands support complex formation. The position of λ_{max} (Table II) and the shape of the bands suggests an octahedral structure for In^{3+}, La^{3+}, and Ce^{3+} complexes, square planar geometry for the $UO_2{}^{2+}$ complex and tetrahedral bipyramidal for Zr^{4+} complex [14].

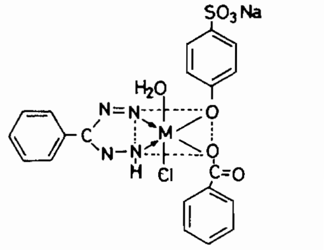
4. *Nuclear Magnetic Resonance*

The proton NMR spectra in DMSO (d_6) for the complexes show shifts of varying magnitude towards a lower field by 0.4–0.8 ppm for the signals of aromatic proton (7.5–8.5 ppm). Also the signal of the NH group (12.5 ppm) exhibits a shift towards a lower field. These shifts of the signals corresponding to aromatic proton and NH proton downfield may be attributed to the perturbing effect of the metal ion on the ligand as a result of its coordination with the lone pair of the nitrogen atom of the azo-group. The absence of the signals corresponding to the protons of the OH and COOH groups, which are observed at 8.8 and 6.3 ppm respectively in the spectra of the free ligand, indicates that complex formation takes place through a proton displacement from the phenolic OH and carboxylic groups by the metal ion.

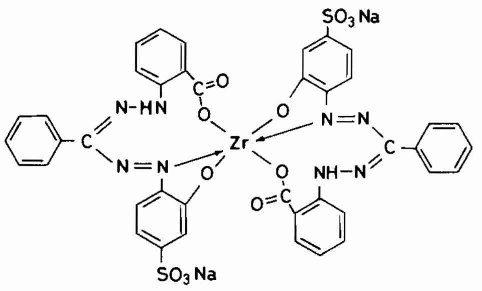
Accordingly, the structure of zincon with the metal ions complexes may be formulated as follows:



For UO_2^{2+} Complex



For In^{3+}, La^{3+}, and Ce^{3+} Complexes



For Zr^{4+} Complex

5. *The Electrical Measurements of Metal Complexes*

The electrical resistivities in ohm × cm and the activation energies in electron volts (ev) of zincon and its investigated complexes, obtained from the equation [$\rho = \rho^{\circ}$ EXP (E/KT)] and studied at different temperatures ranging from 400–700 K, are depicted in Table III. The resistivities varied from 2.2×10^5–2.7×10^7 ohm cm, which are in the range of typical semiconductor resistivities [15].

The plot of log σ *vs.* 1/T as shown in Fig. 2 is more effectively linear for the free ligand, but an inflection

TABLE III. The Activation Energies and the Resistivities at Different Temperature of Zincon Complexes.

Compound	Temperature (K)					E_1 (ev)	E_2 (ev)	Transition Temp.
	433 K	473 K	533 K	573 K	633 K			
Zincon	3.3×10^6	4.6×10^5	–	–	–	0.344	–	–
In-Complex	7.9×10^6	2.1×10^6	5.0×10^5	3.5×10^5	2.2×10^5	0.215	0.094	543 K
Ce-Complex	1.7×10^7	2.5×10^6	6.5×10^5	5.3×10^5	4.4×10^5	0.232	0.096	533 K
UO_2-Complex	1.9×10^7	6.4×10^6	1.9×10^6	9.9×10^5	5.0×10^5	0.216	0.120	600 K
Zr-Complex	3.0×10^7	1.1×10^7	2.8×10^6	1.4×10^6	6.8×10^5	0.275	0.163	553 K
La-Complex	–	2.0×10^8	2.7×10^7	1.1×10^7	2.2×10^6	0.327	0.224	643 K

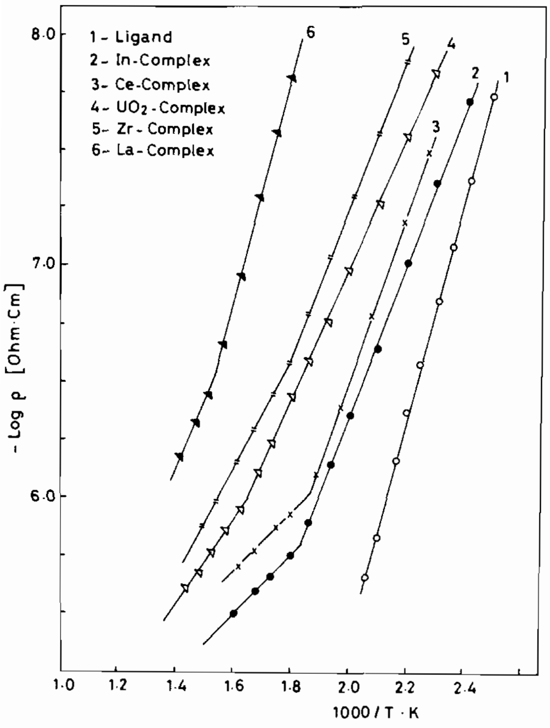


Fig. 2. Plot of log σ *vs.* 1/T.

is observed in case of metal–ligand complexes. It can be concluded that the inflection may be attributed to the change of dominance in mechanism as the temperature passes from one regime to another. The transition temperatures are 643, 600, 553, 543, 533 K for La^{3+}, UO_2^{2+}, Zr^{4+}, In^{3+} and Ce^{3+} complexes, respectively. From the slope of the linear parts in Fig. 2 the activation energies were calculated and are given in Table III.

The resistivities of the metal complexes are higher than those of the pure ligand, while the corresponding activation energies are lower. This may be due to the increase of electron delocalization. The observed resistivities at any temperature and the activation energies of the studied zincon complexes follow the order $La^{3+} > Zr^{4+} > Ce^{3+} > UO_2^{2+} > In^{3+}$. Here the trend depends on the ionic radius of the cation and its ligand field strength. Theoretically, an increase of the resistivity will decrease the number of delocalized electrons, so the stability of the complex must be increased [16]. Accordingly, the order of stability of the investigated zincon complexes is $La^{3+} > Zr^{4+} > Ce^{3+} > UO_2^{2+} > In^{3+}$. This agrees with the trend of the K values of the complexes, given in Table II, calculated using a limiting absorbance method [17].

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