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STUDIES OF Ti(IV) AND Zr(IV) CHELATES WITH N_2O_2 SCHIFF BASES OF 2-HYDROXY-1-NAPHTHALDEHYDE WITH AROMATIC DIAMINES

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ABSTRACT

The complexes of Ti(IV) and Zr(IV) with some N_2O_2 Schiff bases derived from 2-hydroxy-1-naphthaldehyde and some aromatic diamines have been prepared and characterized by elemental analysis and conductance measurements as well as TG and DTA. The bonding of the complexes was confirmed from IR and ^1H NMR spectra. Electronic spectra indicated an octahedral arrangement of the groups around the central metal ion.

INTRODUCTION

Interest in the chemistry of metal chelates of tetradentate N_2O_2 Schiff bases (SB) has increased in recent decades [1–7] because of the wide applications of these complexes in various fields. Mn–SB and Ru–SB chelates were found to catalyse the photolysis of water under certain experimental conditions. Also Fe–SB chelates were recently utilised as catalyst for cathodic oxygen reduction with considerable success [8]. Some other SB–metal chelates were utilised as biologically active compounds [1,2,9,10].

The role of the metal–SB complexes in such applications was found to be related to its molecular structure. Thus, it is quite important to have a good understanding of the structure of such metal complexes.

The present investigation is concerned with the preparation and characterization of Ti(IV) and Zr(IV) chelates with Schiff bases derived from 2-hydroxy-1-naphthaldehyde and some aromatic diamines.

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EXPERIMENTAL

All chemicals used were pure products obtained from Aldrich.

The ligands were prepared by condensation of 2-hydroxy-1-naphthaldehyde with *o*-, *m*- or *p*-phenylenediamine and benzidine, or of 2,4-dihydroxybenzaldehyde with benzidine, in the usual way. The ligands are termed *o*-naphphen (**I**), *m*-naphphen (**II**), *p*-naphphen (**III**), naphben (**IV**), naphdiaben (**V**) and dihydroxyben (**VI**).

The chelates were prepared by mixing an alcoholic solution of the ligand (0.01 M) with an alcoholic solution containing 0.01 M (complexes 1–7) or 0.02 M (complexes 8–11) of the metal chloride. The mixture was refluxed on a water bath for ~ 3 h. The solids separated were filtered off, washed several times with ethanol and then dry ether. The complexes thus obtained were stored over dry silica gel.

The complexes were then characterized by elemental analysis, thermal analysis, IR, ^1H NMR and electronic spectra. The working procedure and equipment are the same as previously described [11].

RESULTS AND DISCUSSION

The results of the elemental analyses given in Table 1 are in accordance with the composition suggested for the complexes and reveal that they can have different types of interactions between the metal ion and the ligands.

The data from the thermogravimetric analysis (Table 2) indicate that the thermal degradation of the complexes proceeds in three steps. The first corresponds to removal of water or ethanol molecules and lies within the temperature range 25–160 °C. The second step observed at 250–415 °C is due to the volatilization of the halogens while the third step occuring within the 460–650 °C range represents the final decomposition of the complexes to the metal oxide (MO_2). For some complexes the removal of water or solvent molecules and of the halogen can proceed in one step.

The DTA curves clearly show the main peaks corresponding to the three degradation stages and in addition there are other endothermic peaks observed near 320 °C due to lattice rearrangement of the complexes as well as their melting. The degradation pathway for complexes **1** and **2** can be represented as follows

1st step $[MLCl_2]nH_2O \xrightarrow{25-205\,°C} [MLCl_2]$

$(n = \frac{1}{2}$ for Zr and zero for Ti$)$

2nd step $[MLCl_2] \xrightarrow{250-373\,°C} [ML]^{2+}$

3rd step $[ML]^{2+} \xrightarrow{460-650\,°C} MO_2$

TABLE 1

Analytical data for the Ti^{4+} and Zr^{4+} complexes

Complex	%C		%H		%N		%M		%Cl		Ω [a]	Formula	Ligand
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found			
1	63.04	63.4	3.4	3.9	5.2	5.1	9.0	9.3	13.3	13.0	25.5	$[TiLCl_2]$	**I**
2	57.4	57.6	3.3	4.0	4.8	6.0	15.6	16.8	–	–	25.0	$[ZrLCl_2]\frac{1}{2}H_2O$	**I**
3	62.7	62.8	3.8	4.0	5.04	5.0	–	–	–	12.8	3.0	$[(TiL)_2Cl_4]C_2H_5OH$	**II**
4	57.4	57.6	3.3	3.7	4.74	5.3	15.6	13.8	12.13	11.8	1.9	$[(ZrL)_2Cl_4]H_2O$	**II**
5	49.2	49.4	4.24	4.0	3.95	4.0	12.86	12.7	15.05	14.6	5.6	$[Zr(HL)Cl_3(H_2O)]3H_2O \cdot \frac{1}{2}EtOH$	**III**
6	51.2	50.1	4.5	4.4					15.9	4.9		$[Ti_2LCl_4(OC_2H_5)_2]4H_2O$	**IV**
7	57.0	57.8	3.63	3.7	3.9	3.7	12.7	11.7	14.9	14.4	1.1	$[Zr(HL)Cl_3(H_2O)]\frac{1}{2}H_2O$	**IV**
8	59.1	58.8	3.7	4.1	4.93	5.0	8.45	8.5	–	–	–	$[Ti_2LCl_4]4H_2O$	**V**
9	55.0	54.7	3.43	3.3	4.6	4.5	14.9	16.2	11.6	11.1	–	$[Zr_2LCl_4]4H_2O$	**V**
10	48.12	48.6	4.0	4.2	4.32	4.8	7.39	7.1	–	–	–	$[Ti(H_3L)Cl_3(H_2O)]2H_2O$	**VI**
11	52.42	52.9	3.53	3.60	4.7	4.5	15.32	18.7	11.9	13.9	–	$[Zr_2(H_2L)_2Cl_4]2H_2O$	**VI**

[a] ohm^{-1} mol^{-1} cm^2 (measured in 10^{-3} M solution in DMF).

TABLE 2

Thermal analysis data for some Ti^{4+} and Zr^{4+} Schiff base complexes

Complex	Thermogravimetric analysis			Differential thermal analysis		
	%H_2O or solvent (1)	Halogen elimination (2)	Decomposition to oxide (3)	1	2	3
1	–	12.5 (13.3%) 250 °C	15 (14.8%) 460 °C	Broad endothermic peak at 66 °C	Sharp endothermic peak at 373 °C	Broad endothermic at peak 400–478 °C
2	1.54 (1.53%) 205 °C	12.4 (12.3%) 272 °C	20.6 (21.0%) 503 °C	–	–	–
4	–	–	–	Broad exothermic peak at 55 °C	Strong exothermic peak at 400 °C	Strong exothermic peak at 471 °C
5	11.5 (10.75) H_2O (97 °C) 3.3 (3.25) EtOH (57 °C)	16.4 (17.4%) 379 °C)	13.2 (11.82%) 537 °C	Broad exothermic peak at 47 °C	Broad exothermic peak at 372 °C	Strong exothermic peak at 480 °C
7	3.52 (3.77% H_2O) begin at 60 °C	15.66 (15.46%) 415 °C	up to 790 °C	–	–	–
8	6.25 (6.35% H_2O) 66 °C	13.33 (13.37%) 240 °C	begins at 578 up to 700 °C			
9	5.7 (6.6% H_2O) 94 °C	13.4 (14.1%) 520 °C	begins at 710 °C			
10	4.4 (4.22% H_2O) 150 °C	22.0 (23.2%) 325 °C	10 (12.5% metal) at 550 °C			

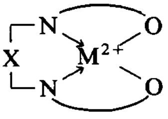

Fig. 1. Bonding in complexes **1**, **2**, **8** and **9**.

The solid state IR spectra of the complexes compared with those of the ligands indicate that the C=N band at 1620–1630 cm^{-1} is shifted to lower values for complexes **1**, **2**, **3**, **4**, **6**, **8**, **9** and **11**, indicating that the ligands coordinate to the metal ions in the dianionic form [12]. This is further supported by the disappearance of the ν_{COH}, at 1290–1325 cm^{-1}, and δ_{OH}, at 1240–1250 cm^{-1}, bands in the spectra of the chelates. This suggests that the SB molecule is behaving as a tetradentate dibasic ligand towards one metal ion. For ligands **I** and **V**, it is clear that one ligand can acquire the metal ion in a tetradentate structure because the two nitrogen atoms are in the *o*-position with respect to each other and, hence, the aromatic ring cannot cause any steric interference. This can be represented as shown in Fig. 1.

For ligands **II** and **VI** forming complexes **3**, **4** and **11** in which the two N atoms are separated from each other, it is not possible for one and the same moleucle to be bonded to one and the same metal ion through four centres. Accordingly, in this case the formation of dimeric chelates is the only way to explain the behaviour of the ligands (Fig. 2).

The spectra of complexes **5**, **7** and **10** show splitting of the C=N band into two peaks, one at lower values and the other at the same position, as well as the decrease in the intensity of the various OH bands. This indicates that the metal ion interacts with one coordination side of the ligand molecule only, the other side remaining unaffected (Fig. 3).

For complex **6**, the IR spectrum shows that the $\nu_{C=N}$ band of the free ligand (1625 cm^{-1}) is shifted to 1630 cm^{-1} while the band of the phenolic C–OH stretching vibration of the free ligand has disappeared. This indicates that the ligand behaves in a dibasic tetradentate manner towards the metal ion. Also the IR spectrum of complex **6** shows bands at 3400 and 2520 cm^{-1} which are attributed to the ν_{OH} of the water molecule and the ethoxy group bonded to the metal ion. Thus, the structure of complex **6** can be formulated as shown in Fig. 4.

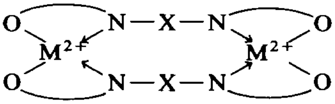

Fig. 2. Bonding in complexes **3**, **4** and **11**.

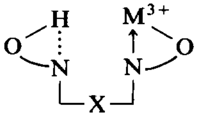

Fig. 3. Bonding in complexes **5**, **7** and **10**.

The far IR spectra of the complexes display the M–N and M–O bands within the ranges 420–430 and 490–530 cm^{-1} respectively. Also the far IR spectra of Zr complexes show bands near 300 cm^{-1} corresponding to the terminal stretching vibration ν_t(Zr–Cl) [13]. For Ti complexes, the far IR spectra display five bands in the region 300–400 cm^{-1} assigned to the terminal Ti–Cl stretching vibration. The total number of bands observed is quite close to the number expected for a *trans* configuration [14–16].

As further support for the mode of bonding suggested, the ^1H NMR spectra of some chelates were recorded in d^6 DMSO. The spectra of complexes **2** and **4** compared to those of the corresponding ligands reveal the disappearance of the signal due to the OH group within the range 9.38–15.15 ppm, while the signal due to the azomethine proton, situated at 9.5 and 8.15 ppm in the spectra of ligands **I** and **II**, is shifted downfield due to the deshielding effect of the metal ion in the chelate ring. On the other hand, the ^1H NMR spectrum of complex **10** shows an obvious decrease in the OH signal intensity, whereas the azomethine proton shows the same behaviour observed for the other complexes although the signal appears more broadened.

Thus, the results of the ^1H NMR spectra are relevant to the bonding suggested for the different complexes.

The electronic absorption spectra in DMF for all the complexes show bands within the range 430–460 and 425–486 nm which can be assigned to the internal and charge transfer transitions respectively. The spectral feature of most complexes under investigation compared to that of their ligands show that the CT band is blue-shifted on complex formation which can be accounted for by the high covalent character of the M–O bond as well as the destruction of the hydrogen-bonded chelate ring. The reflectance or Nujol mull spectra of the complexes show bands within 480–550 and 515–610 nm. The spectra display a red shift in the band positions on going from DMF to Nujol mull or reflectance. From the elemental analysis, IR and ^1H NMR, as well as the electronic spectral data, the proposed structures of the complexes are octahedral. The electronic spectra are listed in Table 3.

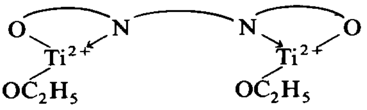

Fig. 4. Bonding in complex **6**.

TABLE 3

The electronic absorption spectra of tetravalent metal chelates in DMF and Nujol mull

Complex	DMF				Nujol mull	
	$\pi-\pi^*$ transition		C.T.		C.T.	
	λ_{max} (nm)	Wavenumber (cm^{-1})	λ_{max} (nm)	Wavenumber (cm^{-1})	λ_{max} (nm)	Wavenumber (cm^{-1})
1	350	28571.428	485	20618.556	610	16393.442
	320	31250.000	455	21978.021	550	18181.818
2	395	25316.455	465	21505.376	550	18181.818
	315	31746.031	450	22222.22	525	19047.619
3	370	27027.027	466	21459.227	515	19417.475
			440	22727.27	480	20833.33
4	385	25974.026	466	21459.227	550	18181.818
			440	22727.27	524	19083.969
					490	20408.163
5	395	25316.456	486	20576.132	570	17543.859
	375	26666.667	460	21739.13	530	18867.924
6	405	24691.358	480	20833.33	560	17857.142
			455	21978.021	520	19230.769
7	405	24641.358	480	20833.33	540	18518.518
			455	21478.021	510	19607.843
			435	22988.505	490	20408.164
8	410	24390.243	465	21505.376	550	18181.818
			445	22371.91	510	19607.843
			430	23255.813		
9	395	25316.456	460	21739.13	545	18348.623
			430	23255.813	505	19801.98
10	375	26666.66	485	20618.556	560	17857.142
			420	23809.523	490	20408.164
11	375	26666.66	425	23529.411	520	19230.764
					490	20408.164

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