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Synthesis and Characterization of Some Oxozirconium(IV) Complexes of Semicarbazones and Thiosemicarbazones

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In present studies, oxozirconium(IV) complexes of 4-[N-(2',4'-dichlorobenzalidene)amino]antipyrine semicarbazone (DCBAAPS), 4-[N-(4'-ethlbenzalidene)amino]antipyrine semicarbazone (EBAAPS), 4-[N-(2',4'-dimethylbenzalidene)amino]antipyrine semicarbazone (DMBAAPS), 4-[N-(4'-ethylbenzalidene)amino]antipyrine thiosemicarbazone (EBAAPTS), 4-[N-2',4'-dimethylbenzalidene) amino]antipyrine thiosemicarbazone (DMBAAPTS), with the general composition $ZrO(L)Cl_2.H_2O$ (L = DCBAAPS, EBAAPS, DMBAAPS, EBAAPTS or DMBAAPTS) have been synthesized and characterized. The conductance values of all the ZrO^{2+} complexes are ionic in nature and both the chloro ions are present outside the coordination sphere. The infrared studies reveal the tridentate (N, N, O) nature of semicarbazones and (N, N, S) nature of thiosemicarbazones. The coordination number of zirconium(IV) in these complexes is found to be five.

Key Words: Oxozirconium(IV), Complexes, Semicarbazones, Thiosemicarbazones.

INTRODUCTION

Although, a large numbe of research papers on oxocation metal ocmplexes of Schiff bases are present in literature. Comparatively less work on oxozirconium(IV) complexes of Schiff bases are reported[1,2]. Because of the presence of vacant inner *d*-orbitals, zirconium has all tendency to expand its covalency with corresponding increase in coordination number greater than 4 is achieved by donation of electrons from ligands into the *d*-orbitals of zirconium ions. The coordination number of Zr(IV) in oxozirconium(IV) complexes varies from 5-8, but the coordination number 5, 6 and 7 are quite common[3]. Inpresent studies some *penta*-coordinated complexes of oxozirconium(IV) with 4-[N-(2',4'-dichlorobenzalidene)amino]antipyrine semicarbazone (DCBAAPS), 4-[N-(4'-ethylbenzalidene)antipyrine semicarbazone (EBAAPS), 4-[N-(2',4'-dimethylbenzalidene)amino]antipyrine semicarbazone (DMBAAPS), 4-[N-(4'-ethylbenzalidene)amino]antipyrine thiosemicarbazone (EBAAPTS) and 4-N-(2',4'-dimethylbenzalidene)amino]antipyrine thiosemicarbazone (DMBAAPTS) have been synthesized and characterized.

EXPERIMENTAL

Oxozirconium(IV) chloride was used as received from Reidel. Anhydrous $ZrOCl_2$ was prepared by known method[4,5]. All the 3 semicarbazones were synthesized from 4-amino antipyrine as reported earlier[6,7], while thiosemicarbazones were synthesized in the laboratory by Agarwal *et al.*[8] method.

All the complexes of oxozirconium(IV) with semicarbazones/thiosemicarbazones were prepared as follows. To the corresponding semicarbazone/thiosemicarbazone solution in methanal (1.1 mmol), a methanolic solution of oxozirconium(IV) chloride (1 mmol) has added. The reaction mixture was refluxed on a water bath for *ca.* 2-3 h and then colled at room temperature. The reparated product was reaction filtered, washed with methanol, followed by diethyl ether and dried in vaccum desicator occer P_4O_{10}.

Infrares spectra (in KBr pellets) were recorded on a Perkin-Elmer 5998 (4000-200 cm^{-1}) spectrophotometer and all other physico-chemical measurements were done as reported earlier[1] and zirconium was estimated as ZrO_2.

RESULTS AND DISCUSSION

The reaction $ZrOCl_2$ in methanol with DCBAAPS, EBAAPS, DMBAAPS, EBAAPTS and DMBAAPTS resulted in the formation of the complexes of the general composition $ZrO(L)Cl_2.H_2O$ (L = DCBAAPS, EBAAPS, DMBAAPS, EBAAPTS or DMBAAPTS). The analytical data of these complexes are given in Table-1. All the complexes are generally soluble in common organic solvents and can be stored for long period at room temperature. The molar conducatance of these complexes in nitrobenzene reveals the ionic nature and both the chloro ions are present outside the coordination sphere. The molecular weight of these complexes as determine eryosiopically in freezing nitrobenzene are in good agreement with the conductance value (Table-1). The present complexes of oxozirconium(IV) are weakly diamagnetic. Since the ground state of oxozirconium(IV) compounds contain no unpaired electrons, the compounds are therefore weakly diamagnetic, as observed by others[9,10].

All the 3 semicarbazones (DCBAAPS, EBAAPS and DMBAAPS) are expected to act as tridentate coordinating through the carbonyl-O, hydrozinic-N and azomethinic-N atoms. The key unfrared bands (cm^{-1}) of these complexes are presented in Table-2. The characteristic absorption of the carbonyl group in DCBAAPS, EBAAPS and DMBAAPS is observed in 1705-1700 cm^{-1} region[11]. In the complexes, this band is shifted towards lower energy in 1652-1642 cm^{-1} region (Table-2). The amide-II band in free ligands has been observed in 1565-1560 cm^{-1} region. In all the present ZrO^{2+} complexes, this band is also shifted toward lower wave numbers by *ca.* 30 cm^{-1}. This observation suggests coordination through the carbonyl oxygen atom. The strong band at *ca.* 1600 cm^{-1} in these semicarbazones apparently has a large contribution from the ν(C=N) mode of semicarbazone moiety[12]. This has been observed as a blud shift in the position of the (C=N) band in all the compelxes to the free ligands. Another strong band was observed in 1620-1615 cm^{-1} region due to azomethine (C=N) absorption. On complexation this band is shifted towards the lower frequency region clearly indicating the coordination through the azomethine N-atom[13,14]. In far infrared region the bands due to ν(Zr-N)/ν(Zr=O) are also observed[1,2]. In $ZrOCl_2(L).H_2O$ (L = DCBAAPS, EBAAPS or DMBAAPS, the presence of coordinated water was suggested by the very broad absorption centred around 3450 cm^{-1} in the infrared spectra. Bands at *ca.* 930 and 770 cm^{-1} may be attributed to rocking and wagging modes of the coordinated water[15].

TABLE-1
ANALYTICAL, CONDUCTIVITY AND MOLECULAR WEIGHT DATA OF OXOZIRCONIUM(IV) COMPLEXES OF SEMICARBAZONE AND THIOSEMICARBAZONE

Complex	Colour (yield %)	Analysis: found (calcd.) (%)				m.w. found (calcd.)	Λ_m (ohm^{-1} cm^2 mol^{-1})	Electrolytic nature
		Zr	N	S	Cl			
$ZrOCl_2 \cdot (DCBAAPS) \cdot H_2O$	Yellow (70)	14.73 (14.84)	13.59 (13.70)	–	11.48 (11.58)	202 (613)	53.9	1:2
$ZrOCl_2 \cdot (EBAAPS) \cdot H_2O$	Yellow (72)	15.76 (15.90)	14.55 (14.68)	–	12.32 (12.41)	188 (572)	52.4	1:2
$ZrOCl_2 \cdot (DMBAAPS) \cdot H_2O$	Yellow (70)	15.75 (15.90)	14.56 (14.68)	–	12.32 (12.41)	189 (572)	52.1	1:2
$ZrOCl_2 \cdot (EBAAPTS) \cdot H_2O$	Yellowish brown (70)	15.32 (15.47)	14.18 (14.28)	5.39 5.44	11.98 (12.07)	194 (588)	52.7	1:2
$ZrOCl_2 \cdot (DMBAAPTS) \cdot H_2O$	Yellowish brown (72)	15.33 (15.47)	14.16 (14.28)	5.40 5.44	11.57 (12.07)	194 (588)	53.8	1:2

TABLE-2
INFRARED ABSORPTION FREQUENCIES (cm^{-1}) OF ZrO(IV) COMPLEXES OF DCBAAPS, EBAAPS AND DMBAAPS

Complex	ν(OH)	ν(C=N) azomethinic	ν(C=N) hydrazinic	ν(C=O)			ν(V-N)/ ν(V-O)
				I	II	III	
DCBAAPS	–	1610 m	1600 m	1705 s	1562 m	1355 m	–
$ZrOCl_2(DCBAAPS).H_2O$	3400 s, br	1592 s	1622 s	1648 s	1530 m	1332 m	450 m, 390 w
EBAAPS	–	1615 m	1605 m	1705 s	1570 s	1350 m	–
$ZrOCl(EBAAPS).H_2O$	3405 s, br	1590 m	1628 m	1645 s	1537 m	1332 m	445 m, 387 w
DMBAAPS	–	1608 m	1600 m	1702 m	1565 s	1342 s	–
$ZrOCl_2(DMBAAPS).H_2O$	3410 s, br	1582 m	1628 m	1650 s	1532 m	1322 m	440 m, 390 w

A study and comparision of infrared spectra of both thiosemicarbazones (EBAAPTS and DMBAAPTS) and their ZrO^{2+} complexes (Table-3) imply that these ligands he have as neutral tridentate (N, N, S). The strong bands observed in 3440-3270 region in the free ligands have been observed to ν(N-H) vibrations practically no effect on these frequencies after complexation preclude the possibility of complexation of this group. The absorptions at *ca.* 1600 cm^{-1} in the free ligands can be attributed to ν(C=N) vibrations of imine nitrogen, which is in agreement with the observations of previous workers[16].

TABLE-3
INFRARED ABSORPTION FREQUENCIES (CM^{-1}) OF OXOZIRCONIUM(IV) COMPLEXES OF EBAAPTS AND DMBAAPTS

Assignments	EBAAPTS	$ZrOCl_2$ (EBAAPTS)H_2O	DMBAAPTS	$ZrOCl_2$ (DMBAAPTS)H_2O
ν(N-H)	3440 s	3435 m	3360 s	3345 m
	3270 s	3265 m	3330 s	3315 m
ν(C=N)	1600 vs	1570 m	1600 vs	1565 m
ν(C=S)+	1330 s	1380 s	1310 m	1370 m
ν(C=N)+	1305 s	1330 m	1290 m	1330 m
ν(C-N)				
ν(NCS)+	1120 m	1160 m	1115 m	1170 m
CS bonding	1095 m	1130 m	1095 w	1130 m
ν(N-N)	1050 m	1062 m	1050 m	1065 m
ν(C=S)	820 s	790 s	830 s	780 m
	760 vs	700 m	730 m	710 m
ν(Zr-N)/ν(Zr-S)	–	380 m	–	375 m
	–	340 w	–	342 w

On complexation, these frequencies were observed to the shifted to lower wave number (Table-3) suggesting involvement of unsaturated nitrogen atoms of the azomethine groups in bonding with the ZrO^{2+}. In substituted thiourias, the (C=S) stretching vibrations combine with some other vibrations as (C-N) stretching and bonding as well as (N-C-S) bending modes[17]. In the spectra of present thiosemicarbazones, the bands observed in 1300-1125 cm^{-1}, 1120-1095 and 840-730 cm^{-1}, 1120-1095 and 840-730 cm^{-1} are assigned to [(C=S) + ν(C=N) + ν(C-N)], [δ(N-C-S), + δ(C=S)] bending and ν(C=S) stretching, respectively, following the observations of some other workers[18]. Coordination of sulphur with the metal in would result in displacement of electrons toward the latter, thus resulting in the weakening of (C=S) bond. Hence on complexation (C=S) stretching vibrations should decrease and that of (C-N) should increase[18]. In both the complexes of ZrO^{2+} with EBAAPTS and DMBAAPTS, the frequencies in the ragne 1300-1125 cm^{-1} are increased by nearly 50-60 cm^{-1}.

Similarly bending modes of (N-C-S) and (C=S) also increase but to a lesser amount. On the othe hand, on complexation the frequencies in 840-760 cm^{-1} are shifted to lower wave numbers and intensity of the bands are reduced. All these peculiar changes on complexation unequivocally support Zr-S coordination. The possibility of thione-thiol tautomerism (H-N-C=S) $\rightleftharpoons$ (C=N-SH) in these ligands has been ruled out for no bands around 2700-2500 cm^{-1} characteristics of thiol group is displayed in the infrared absorption[19]. In far infrared region ν(Zr-N)/ν(Zr-S) also observed[1,2]. The presence of coordinated water was suggested by the very broad absorption centered around 3450 cm^{-1} in the infrared spectra. Bands at *ca.* 930 and 770 cm^{-1} may be attributed to locking and wagging modes of the coordinated water.

In past a nubme of workers have isolated the oxozirconium(IV) complexes of azomethines and tried to locate the ν(Zr=O) stretching. But this assignment is not unambiguous. In present complexes, a weak band at 830-820 cm^{-1} is assigned to ν(Zr=O) vibration[22]. However, there is no reliable evidence for the existence of the (Zr=O) moiety in zirconyl complexes. The structure determination of $ZrOCl_2.8H_2O$ by Clearfield and Vaughen[23] was a great step forward, since it showed that this salt contained $[Zr(OH)_2]^{2+}$ or $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ ions in aqueous solution.

In the present studies, the author describes the thermal properties of ZrO^{2+} complexes of DCBAAPS, EBAAPS and DMBAAPS thermal decomposition data of these complexes are presented in Table-4 the careful analysis of thermal curves suggested that these complexes contain one water molecule in coordination sphere, which is clar by loss in weight *ca.* 3.3 % at *ca.* 140 ºC. There is no change upto *ca.* 215 ºC, after that there is a break in the curves due to evaporation of one molecule of DCBAAPS/EBAAPS. Finally at *ca.* 650 ºC, ZrO_2 is formed as DMBAAPS end product.

TABLE-4
THERMAL DATA OF ZrO^{2+} COMPLEXES OF SEMICARBAZONES OF 4-aminoantipyrine

Complex	Decomposition temp. (ºC)		Decomposition product	Weight loss (%)	
	Initial	Final		Exp.	Theor.
	75	120	$ZrOCl_2$(DCBAAPS)	3.43	3.30
$ZrOCl_2$(DCBAAPS).H_2O	210	350	$ZrOCl_2$	65.27	63.97
	415	630	ZrO_2	79.11	77.38
	75	120	$ZrOCl_2$(EBAAPS)	3.20	3.06
$ZrOCl_2$(EBAAPS).H_2O	205	340	$ZrOCl_2$	67.32	66.60
	420	635	ZrO_2	81.11	79.04
	80	125	$ZrOCl_2$(DMBAAPS)	3.21	3.05
$ZrOCl_2$(DMBAAPS).H_2O	230	355	$ZrOCl_2$	68.19	66.77
	420	635	ZrO_2	81.32	79.15
	75	120	$ZrOCl_2$(EBAAPTS)	3.43	3.30
$ZrOCl_2$(EBAAPTS).H_2O	210	350	$ZrOCl_2$	65.27	63.97
	415	630	ZrO_2	79.11	77.38
	75	120	$ZrOCl_2$(DMBAAPTS)	3.20	3.06
$ZrOCl_2$(DMBAAPTS).H_2O	205	340	$ZrOCl_2$	67.32	66.60
	420	635	ZrO_2	81.11	79.04

In case of thiosemicarbazone complexes of $ZrOCl_2$, *i.e.*, $ZrOCl_2(EBAAPTS)\cdot H_2O$ and $ZrOCl_2(DMBAAPTS)\cdot H_2O$, the T.G. curves show that these complexes complete their thermal processes in there steps. In the first step the coordinated water molecule is lost in temperature region 90-135 ºC (*ca.* 3 % loss in weight), while in temperature region 200-260 ºC, the thiosemicarbazone EBAAPTS/DMBAAPTs evaporated off and finally at *ca.* 630 ºC, ZrO_2 is formed as final product (Table-4). These changes can be shown as:

$$ZrOCl_2.L.H_2O \rightarrow ZrOCl_2.L \rightarrow ZrOCl_2 \rightarrow ZrO_2$$

(L = EBAAPTS or DMBAAPTS)

In the present work the data on stiochemistry of oxozirconium(IV) complexes and their physico-chemical studies indicate that the probable coordination number for zirconium in the complexes is found to be five. The conductance measurements indicate the ionic nature of these complexes and behave as 1:2 electrolytes, with this view, the zirconyl complexes have the compositioni $[Zr(OH)_2L]Cl_2$. The infrared spectral data reveal that all the three semicarbazones used are N, N, O-donors while thiosemicarbazone are N, N, S-donors. Thus in $[Zr(OH)_2.L.Cl_2]$ L = DCBAAPS, EBAAAS, DMBAAPS, EBAAPTS or DMBAAATS the coordination number of zirconium is found to the five.

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