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Synthesis and Characterization of Osmium (III) Complexes with Substituted Nitrones

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Abstract: New series of complexes of general formula $[OsL(Cl)_2(H_2O)_2].nH_2O$; where LH=[*alpha*-(2-hydroxy-1-naphthyl)-N-(*para*-R-phenyl nitrone] , n=number of the crystallization water(0-6) and R=H, Cl , Br , $COCH_3$, $NHCOCH_3$, NH_2 and CH_3 were synthesized . The complexes were synthesized from direct reaction of the osmium(III) chloride with ligand (L) in a molar ratio of 1:1 respectively. These complexes were characterized by several physical methods such as melting points, molar conductance and elemental analysis(CHN),magnetic moments as well spectral such as infrared and electronic spectral measurements. These studies revealed that the Ligand (L) was behaved as a bidentate, univalent and coordinated to the osmium(III) ion through the oxygen atoms of both , the hydroxyl and the nitrone groups, as well, the presence of two chloride ions and two aqua molecules to give the most probable octahedral geometry around each osmium ion in each complex. The elemental analysis(CHN) as well the infrared spectra showed the presence crystallization water molecules outside the coordination sphere. Their molar conductance measurements revealed the non-electrolytic behavior of the synthesized complexes.

Keywords: Osmium (III), Nitrone, Schiff base, Complexes

Introduction

Many researchers referred that nitrones have special interest due to the broad spectrum of their applications and their successful use as building blocks in different synthetic strategies. They utilized in organic synthesis(1,2) , their function as inhibitor for corrosion of mild steel in organic acid media(3) and their uses as precursor for synthesizing compounds having antibacterial activities(4,5).As well, their combination with either alkenes or alkynes cyclo-addition were achieved leading to the formation of new C-C and C-O bonds(6).Besides, new methods of nitrone group activation both with nucleophilic reagent by radical cation formation and with electrophilic reagent by generating dipolar stabilized anions were explored(7). The use of nitrones as ligands was also explored by preparing a series of complexes with transition metal ions (8). They are also used as a suitable ligand for heme model as in metalloporphyrine nitrone complex which was characterized by X-ray crystal structure (9). Recent years have witnessed a renewing interest in their chemistry mainly due to the development of the methods of preparation and subsequent applications (10, 11). The shortages of the 5d metal ion complexes with nitrones has prompted us to synthesis and characterize a new series of substituted nitrones with osmium (III) chloride.

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Experimental

1-Preparation of the ligands: The ligands were prepared according to the procedure in two steps (12) and the following procedure was adopted for the preparation of all the ligands in the present study : *Para*-substituted nitrobenzene (0.10 mole) and ammonium chloride (0.10 mole, 5.34 g) were dissolved in (100 ml) of Ethanol, cooled to 10°C and (4.0 g) of zinc powder was added with stirring for 2 hrs. The mixture was filtered to get the hydroxylamine in the filtrate to which (0.07 mole) of 2-hydroxy-1-naphthaldehyde was added. The mixture was stirred for 20 hrs. in a dark place. The precipitate was filtered and washed several times with ether then dried. The following equations represent the methods for the prepared ligands with their melting points and crystallization solvents showed in Table(1).

1. $P\text{-R-}C_6H_4NO_2 + NH_4Cl \xrightarrow{\text{Zn powder}} p\text{-R-}C_6H_4NHOH$
2. $P\text{-R-}C_6H_4NHOH + C_{11}H_8O_2 \xrightarrow{\text{stirring 24 hrs. in dark place}} LH.$

($C_{11}H_8O_2$=2-hydroxynaphthaldehyde) , LH=

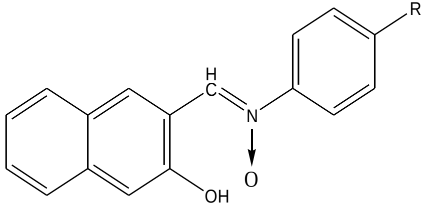


Table 1. The melting points and solvents for the prepared ligands

Ligands	R	M.p.°C	Solvent
L_1	$COCH_3$	178	Ethanol
L_2	Br	65	Ethanol
L_3	Cl	55	Ethanol
L_4	CH_3CONH	140	Ethanol
L_5	CH_3	85	Acetone
L_6	H	68	Ethanol
L_7	NH_2	214	Chloroform

2. Synthesis of the Complexes

A solution of (30 ml, 0.005 mole) of the corresponding ligand in hot ethanol was added to a stirred solution of (20 ml, 0.005 mole) of $OsCl_3$ in 25 ml of (60%) petroleum ether. A solution of (0.5 M) KOH was added till become alkaline (pH 7-9) and refluxed for 3hrs then cooled to the room temperature. The obtained solid was filtered, washed with ethanol and ether then dried.

Result and Discussion

The synthesized complexes were prepared according to the following equation:

$$OsCl_3 + LH \xrightarrow{(0.5M\ KOH/EtOH/H_2O)} [OsCl_2.L.(H_2O)_2].nH_2O + KCl$$

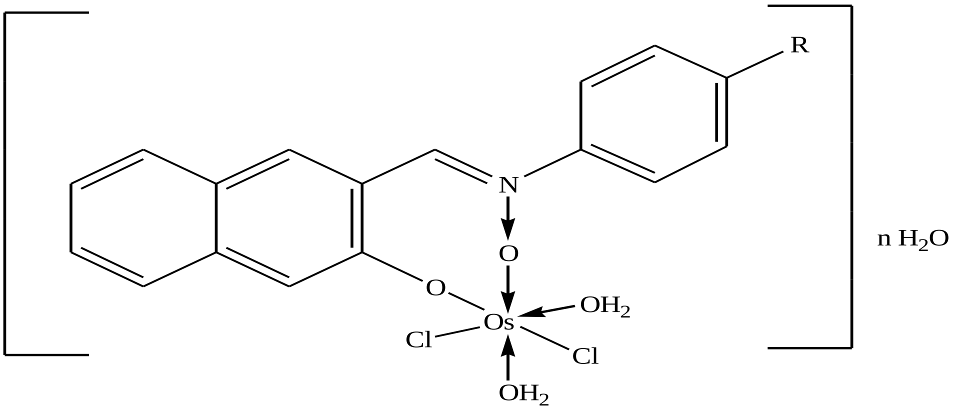
n= 0-6 ; R= $COCH_3$, Br, Cl , CH_3 , H, $NHCOCH_3$ and NH_2.

The elemental analysis and some of the physical properties of the prepared complexes are listed in Table (II). They were stable in the solid state and soluble in dimethylformamide (DMF) and dimethylsulfoxide (DMSO) at room temperature. The molar conductivity values in DMF at 10^{-3}M were lying in the range (19-55) Ω^{-1}. $mol^{1}.cm^{-1}$ indicating the non- electrolytic behavior of all complexes (13) as shown in Table (II).

The coordination sites of the ligands with the osmium (III) ion had been determined by careful comparison of the infrared spectra of the synthesized complexes with that of parent ligands as shown in Table(III). The free ligands showed important spectra in the regions (1077-1215) , (1595-1599) and (1253-1356) attributed to υ(C-O) , υ(C=N) and υ(N→O) respectively. The naphtholic (C-O) spectra were shifted to a lower values ($\Delta\upsilon$=17-52) when compared with the spectra of their complexes .This is interpreted as due to the linkage of the ligand with Os(III) ion through the oxygen atom of the naphtholic group(14,15). The azomethine (C=N) spectra were found unchanged or very slightly changed ($\Delta\upsilon$=1-5) comparing with that of the complexes and hence no indication of the coordination of the azomethine with the metal ion. Moreover, on comparison of the infrared spectra of the ligands and their complexes showed a significant shift toward a lower values by range (7-16) cm^{-1}in the nitrone (N→O) group suggesting the involvement of their oxygen atoms in the coordination with the osmium(III) ion(16). The presence of the coordinated and crystallization water molecules in the prepared complexes were indicated by existence of broad bands in the range (3421-3508) cm^{-1} , as it is not easy to distinguish between both types of water molecules since they appeared as a broad bands. As well, the coordinated water molecules in all complexes is indicated by existence of two somewhat weaker bands assigned as the OH rocking(r) and wagging(ω) vibrations at (814-863) and (633-748) cm^{-1} respectively(17).The Os-Cl bond is usually appeared in the region 200-300 cm^{-1} and this region is beyond the limit of the apparatus. In the low frequency region ,the spectra of the synthesized complexes Table(III) exhibited new bands which were not present in the corresponding ligands ,were located at 435-588 cm^{-1} attributed to υ(Os-O) stretching(18).

The electronic spectra of the synthesized complexes are tabulated in Table(IV) and showed three bands at (451-642) , (402-445) and (362-399) nm as d-d transition which assigned to $^2T_2g\rightarrow{}^4T_1g$, $^2T_2g\rightarrow{}^4T_2g$ and $^2T_2g\rightarrow{}^2A_2g,{}^2T_1g$ in the octahedral environment respectively(19,20). The high intensity bands in the spectra of the synthesized complexes at (270-319) nm were assigned to the charge transfer absorption between the ligands and the osmium(III) ion(21).
The magnetic susceptibility measurements of the prepared complexes were lying in the range (1.54-1.99) B.M. are indicative of single electron per Os(III) ion suggesting their consistency with their octahedral arrangement(21).

In conclusion, the substituted nitrone ligands, in the present study, behaved as bidentate, univalent ligands coordinated through the two oxygen atoms of, the naphtholic and nitrone groups. The elemental analyses showed the existence of a number of crystallization water molecules outside the coordination sphere.The presence of two chloride ions and two coordinated water molecules besides the bidentate ligands gave the most probable octahedral geometry around Os(III) ion in each complex as depicted below :



R=$CH_3C(O)$, Br , Cl , $CH_3C(O)NH$, CH_3 , H , NH_2

Table 2. Elemental analysis and physical properties of the synthesized complexes

Complexes	Color	M.p.°C	Elemental analysis Calc./(Found)			Λ_M (DMF)
			C	H	N	
$[OsCl_2L_1(H_2O)]$	Light olive	76-78	37.92 (38.09)	3.01 (3.68)	3.32 (3.81)	29
$[OsCl_2L_2(H_2O)_2]$	Olive	66-68	31.99 (31.65)	2.37 (2.12)	2.19 (2.01)	42
$[OsCl_2L_3(H_2O)_2]6H_2O$	Olive	140-142	29.09 (27.92)	3.88 (2.16)	2.00 (2.44)	35
$[OsCl_2L_4(H_2O)_2]3H_2O$	Olive	96-98	34.03 (34.18)	3.76 (3.55)	4.18 (4.05)	37
$[OsCl_2L_5(H_2O)_2]2H_2O$	Olive	160-162	35.47 (34.78)	3.64 (3.27)	2.30 (2.09)	55
$[OsCl_2L_6(H_2O)_2]4H_2O$	Olive	242d	32.33 (31.98)	3.83 (3.36)	2.22 (2.11)	39
$[OsCl_2L_7(H_2O)_2]2H_2O$	Olive	260d	33.45 (33.01)	3.47 (3.13)	4.59 (4.31)	19

Table 3. Selected I.R. absorption bands of the ligands and their complexes

Compounds	υ C-O	υ C=N	υ N→O	υ Os→O	Coordinated water		
					ν(OH)	r(OH)	ω(OH)
L_1	1077	1595	1258	------	-----	-----	-----
$[OsCl_2L_1(H_2O)_2]$	1045	1590	1243	475	3445	861	740
L_2	1105	1599	1356	-----	-----	-----	-----
$[OsCl_2L_2(H_2O)_2]$	1071	1596	1345	586	3508	863	676
L_3	1139	1597	1255	-----	-----	-----	-----
$[OsCl_2L_3(H_2O)_2]6H_2O$	1090	1596	1245	586	3421	827	675
L_4	1163	1598	1346	-----	-----	-----	-----
$[OsCl_2L_4(H_2O)_2]3H_2O$	1146	1596	1333	588	34336	827	678
L_5	1170	1599	1261	-----	-----	-----	-----
$[OsCl_2L_5(H_2O)_2]2H_2O$	1136	1594	1245	560	3444	817	645
L_6	1163	1599	1253	-----	-----	-----	-----
$[OsCl_2L_6(H_2O)_2]4H_2O$	1139	1596	1246	435	3443	814	748
L_7	1215	1598	1283	-----	-----	-----	-----
$[OsCl_2L_7(H_2O)_2]2H_2O$	1163	1596	1292	571	3450	829	659

Table 4. Electronic spectra and magnetic moments for the synthesized complexes

Complexes	$^2T_2g\rightarrow{}^4T_1g$ λmax.(nm)	$^2T_2g\rightarrow{}^4T_2g$ λmax(nm)	$^2T_2g\rightarrow{}^2A_2g,{}^2T_1g$ λmax(nm)	Charge Transfer	μ_{eff} (B.M.)
$[OsCl_2L_1(H_2O)_2]$	467	442	395	319	1.71
$[OsCl_2L_2(H_2O)_2]$	460	405	385	316	1.88
$[OsCl_2L_3(H_2O)_2]6H_2O$	---	445	395	337	1.99
$[OsCl_2L_4(H_2O)_2]3H_2O$	538	441	362	316	1.59
$[OsCl_2L_5(H_2O)_2]2H_2O$	620	431	392	288	1.68
$[OsCl_2L_6(H_2O)_2]4H_2O$	509	402	387	307	1.54
$[OsCl_2L_7(H_2O)_2]2H_2O$	529	445	397	270	1.91

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