

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

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الخلاصة

حضرت سلسلة جديدة من المعقدات ذوات الصيغة $[RuCl_2L(H_2O)_2]nH_2O$ حيث ان $LH = \alpha$ -2-هيدروكسي-1-نفثاليل-N-(بارا-R-فينيل) نايترين و $n=0-6$ و $R=H, Cl, Br, COCH_3, NHCOCH_3, NH_2, CH_3$ تم تشخيص هذه المعقدات بالتحليل الدقيق للعناصر (CHN) والموصلية والكهربائية المولارية والعزم المغناطيسي وكذلك طيف الأشعة تحت الحمراء والاطياف الالكترونية. اثبتت هذه الدراسات الطيفية بان الليكاند (L) يتناسق بشكل ثنائي السن احادي الشحنة مع ايون الروثينيوم (III) من خلال ذرتي الاوكسجين لمجموعتي النايترين والنفثوليك وبوجود ايوني كلوريد مع جزيئتي ماء ليعطي الشكل الاكثر احتمالا ثماني السطوح حول ايون الروثينيوم في جميع المعقدات. اثبتت دراسة التحليل الدقيق للعناصر في المعقدات اعلاه وكذلك اطياف الاشعة تحت الحمراء لها بوجود جزيئات ماء خارج الكرة التناسقية. اشارت دراسات الموصلية المولارية الى السلوك غير الالكتروليتي للمعقدات.

ABSTRACT

New series of complexes of general $[Ru(Cl)_2(H_2O)_2.L]nH_2O$; where $LH = [\alpha$ -(2-hydroxy-1-naphthyl)-N-(p-R-phenyl nitron)] $n=0-6$ and $R=H, Cl, Br, COCH_3, NHCOCH_3, NH_2$ and CH_3 were formula synthesized and characterized by their elemental analysis(CHN) , molar conductance , magnetic moments , infrared and electronic spectral measurements. The Ligand (L) acted as a bidentate, univalent toward the ruthenium (III) ion via the two oxygen atoms of, the nitron and naphtholic groups, with the presence of two chloride ions and two aqua molecules the most probable octahedral geometry around each ruthenium ion in each complex.

* Presented at the second conference on Chemistry, University of Mosul, college of Education, 17-18 November-2013.

The elemental analysis as well the infrared spectra revealed the presence of lattice water molecules outside the coordination sphere. Their molar conductance measurements revealed the non- electrolytic behavior of the synthesized complexes.

Key words: Ruthenium (III), Nitron, Schiff base complexes.

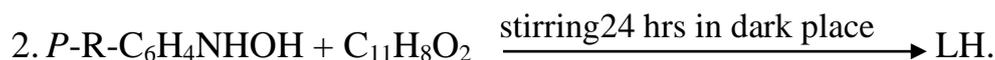
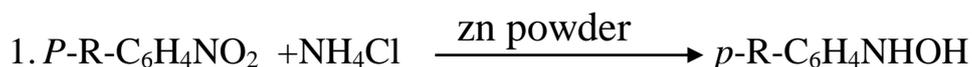
INTRODUCTION

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 nitron 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 nitron 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 4d metal ion complexes with nitrones has prompted us to synthesis and characterize a new series of substituted nitrones with ruthenium (III) chloride.

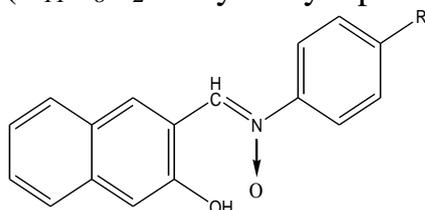
EXPERIMENTAL

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 mol) and ammonium chloride (0.10 mol,5.34g) were dissolved in (100ml) 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 mol) 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).



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



Table(1):The melting points and solvents for the prepared ligands

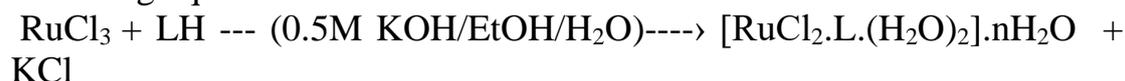
Ligands	R	m.p.°C	Sol.
L ₁	COCH ₃	178	Ethanol
L ₂	Br	65	Ethanol
L ₃	Cl	55	Ethanol
L ₄	CH ₃ CONH	140	Ethanol
L ₅	CH ₃	85	Acetone
L ₆	H	68	Ethanol
L ₇	NH ₂	214	Chloroform

2. Synthesis of the Complexes

A solution of (30 ml, 0.005 mol) of the corresponding ligand in hot ethanol was added to a stirred solution of (20 ml, 0.005 mol) of RuCl₃ in 25 ml of (60%) petroleum ether. A solution of (0.5 M) KOH was added till become alkaline (pH 7-9) then was refluxed for 3hrs and then cooled to room temperature. The solid thus obtained was filtered, washed with ethanol and ether then dried.

RESULT AND DISCUSSION

The synthesized complexes were prepared according to the following equation:



n= 0-6 ; R= H , Cl , Br , COCH₃ , NHCOCH₃ , NH₂ and CH₃

The elemental analysis and some of the physical properties of the prepared complexes are listed in Table (II). They are stable in the solid state and soluble in dimethylformamide (DMF) and dimethylsulfoxide (DMSO) at room temperature. The molar conductivity values in DMF at 10⁻³M are lying in the range (25-48) 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 ruthenium (III) ion has 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 $\nu(\text{C-O})$, $\nu(\text{C=N})$ and $\nu(\text{N}\rightarrow\text{O})$ respectively. The naphtholic (C-O) spectra were shifted to a lower values ($\Delta\nu=15-51$) when compared with the spectra of their complexes .This is interpreted as due to the linkage of the ligand with Ru(III) ion through the oxygen atom of the naphtholic group(14,15). The azomethine (C=N) spectra were found unchanged or very slightly changed ($\Delta\nu=0-2$) 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 (11-22) cm^{-1} in the nitron (N \rightarrow O) group suggesting the involvement of its oxygen atom in the coordination with the ruthenium(III) ion(16). The presence of the coordinated and lattice water molecules in the prepared complexes were indicated by existence of broad bands in the range (3346-3432) 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 (827-849) and (633-694) cm^{-1} respectively(17).The Ru-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 503-531 cm^{-1} attributed to $\nu(\text{M-O})$ stretching(18).

The electronic spectra of the synthesized complexes are tabulated in Table(IV) and showed three bands at (526-623) , (409-460) and (374-397) nm as d-d transition which assigned to ${}^2\text{T}_{2g}\rightarrow{}^4\text{T}_{1g}$, ${}^2\text{T}_{2g}\rightarrow{}^4\text{T}_{2g}$ and ${}^2\text{T}_{2g}\rightarrow{}^2\text{A}_{2g},{}^2\text{T}_{1g}$ in the octahedral environment respectively(19,20). The high intensity bands in the spectra of the synthesized complexes at (268-354) nm were assigned to the charge transfer absorption between the ligands and the ruthenium(III) ion(21).

The magnetic susceptibility measurements of the prepared complexes are lying in the range (1.53-1.91) B.M. are indicative of single electron per Ru(III) ion suggesting their consistency with their octahedral arrangement(21).

In conclusion, the substituted nitron ligands, in the present study, behaved as bidentate, univalent ligands coordinated through the two oxygen atoms of, the naphtholic and nitron groups. The elemental analysis showed the existence of a number of lattice 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 ruthenium (III) ion in each complex as depicted below:

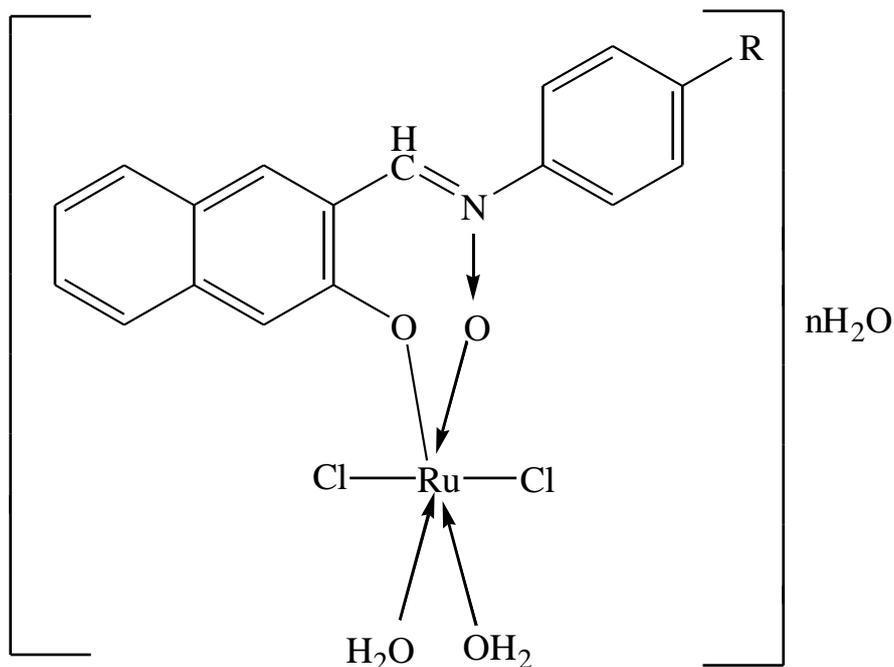


Table (II):Elemental analysis and physical properties of the synthesized complexes

Complexes	Color	m.p. °C	Elemental analysis Calc./(Found)			Yield%	Λ_M (DMF)
			C	H	N		
[RuCl ₂ L ₁ (H ₂ O)]	Light olive	76-78	44.54 (44.00)	3.54 (3.05)	2.73 (2.15)	73	47
[RuCl ₂ L ₂ (H ₂ O) ₂]4H ₂ O	Olive	66-68	32.87 (32.31)	3.73 (3.24)	2.75 (2.10)	64	47
[RuCl ₂ L ₃ (H ₂ O) ₂]2H ₂ O	Olive	140- 142	37.76 (37.12)	3.54 (3.18)	2.59 (2.40)	71	29
[RuCl ₂ L ₄ (H ₂ O) ₂]5H ₂ O	Olive	96-98	57.81 (57.24)	4.17 (4.09)	7.10 (6.96)	90	48
[RuCl ₂ L ₅ (H ₂ O) ₂]3H ₂ O	Olive	160- 162	40.16 (39.79)	4.49 (4.13)	2.60 (2.26)	87	47
[RuCl ₂ L ₆ (H ₂ O) ₂]6H ₂ O	Olive	242d	35.30 (34.89)	4.88 (4.34)	2.42 (2.16)	69	25
[RuCl ₂ L ₇ (H ₂ O) ₂]H ₂ O	Olive	260d	40.57 (40.11)	3.80 (3.43)	5.57 (5.18)	73	44

Table (III):Selected I.R. absorption bands of the ligands and their complexes

Compounds	$\nu_{C=O}$	$\nu_{C=N}$	$\nu_{N\rightarrow O}$	$\nu_{M\rightarrow O}$	Coordinated water		
					$\nu(OH)$	$r(OH)$	$\omega(OH)$
L ₁	1077	1595	1258	-----	-----	-----	-----
[RuCl ₂ L ₁ (H ₂ O) ₂]	1048	1593	1236	506	3432	830	648
L ₂	1105	1599	1356	-----	-----	-----	-----
[RuCl ₂ L ₂ (H ₂ O) ₂]4H ₂ O	1090	1598	1344	530	3421	839	648
L ₃	1139	1597	1255	-----	-----	-----	-----
[RuCl ₂ L ₃ (H ₂ O) ₂]2H ₂ O	1089	1597	1236	519	3423	827	633
L ₄	1163	1598	1346	-----	-----	-----	-----
[RuCl ₂ L ₄ (H ₂ O) ₂]5H ₂ O	1142	1597	1335	531	3382	827	656
L ₅	1170	1599	1261	-----	-----	-----	-----
[RuCl ₂ L ₅ (H ₂ O) ₂]3H ₂ O	1139	1597	1243	531	3346	849	670
L ₆	1163	1599	1253	-----	-----	-----	-----
[RuCl ₂ L ₆ (H ₂ O) ₂]6H ₂ O	1134	1597	1236	531	3422	826	689
L ₇	1215	1598	1283	-----	-----	-----	-----
[RuCl ₂ L ₇ (H ₂ O) ₂]H ₂ O	1164	1599	1264	503	3385	828	694

Table (IV):Electronic spectra and magnetic moments for the synthesized complexes

Complexes	${}^2T_{2g}\rightarrow{}^4T_{1g}$ $\lambda_{max}(nm)$	${}^2T_{2g}\rightarrow{}^4T_{2g}$ $\lambda_{max}(nm)$	${}^2T_{2g}\rightarrow{}^2A_{2g},{}^2T_{1g}$ $\lambda_{max}(nm)$	Charge Transfer	μ_{eff} (B.M.)
[RuCl ₂ L ₁ (H ₂ O) ₂]	560	442	382	302	1.91
[RuCl ₂ L ₂ (H ₂ O) ₂]4H ₂ O	580	429	375	303	1.55
[RuCl ₂ L ₃ (H ₂ O) ₂]2H ₂ O	526	409	374	304	1.57
[RuCl ₂ L ₄ (H ₂ O) ₂]5H ₂ O	613	430	380	268	1.56
[RuCl ₂ L ₅ (H ₂ O) ₂]3H ₂ O	560	428	376	354	1.84
[RuCl ₂ L ₆ (H ₂ O) ₂]6H ₂ O	623	452	397	326	1.53
[RuCl ₂ L ₇ (H ₂ O) ₂]H ₂ O	----	460	387	337	1.74

REFERENCE

- 1) Breuer E., Aurich H.G. and Nielson A., Nitrones, Nitronates and Nitroxides, John Wiley & Sons, New York, 1989.
- 2) Wong E.H.H., Junkers T. and Kowolik C.b., Poly.Chem., 2011, 2, 1008.
- 3) Thiimalaikumar M. and Jegannathan . S., Potugaliae Electrochimica Acta, 2011, 29910, 1.
- 4) Charaborty B., Chhetri .M.S. Chhetri S. Katley and .Samanta A, Ind. J. Chem., 2010, 49B, 209.
- 5) Amutha C., Saravanan .S. Saravanan, .Dhandapani P.S., Muthusbramanian . S. and Sivasubramanian .S, Ind. J. Chem. 2008, 47B, 276.
- 6) Dondas . H.A., Cumins ,J.E., Grigg .R. and. Thornton P, Tetrahedron, 2001, 57, 7951.

- 7) Grigorev I.A., ARKIVOC ,2009,(IV),136.
- 8) Villamena F.A., Dickman .M.H and D.R.Christ , Inorg. Chem.,1998,37,1446.
- 9) Lee J., Twamley .B. and Richter . G.B.Richter Addo,Chem.Comm.,2002,380
- 10) Kannan. S.,Usman A and .Fun H.K,Polyhedron,2002,21(23),2403.
- 11) Yavus S., Ozkan H., Colak N, and Yildirim Y.,Molecules,2011,16,6677.
- 12) West P.R. and Davis .G.C.Davis ,J. Org. Chem.,1989,54,5176.
- 13) Geary W.J.,Chem.Abst.,1974,75.
- 14) Canpolat E, and Kaya M.,Turk . J.Chem.,2005,29,409.
- 15) Mounika K, Anupama B, Pragathi J and Gyanakumari C,J.Sci.Res.,2010,2(3),513.
- 16) Al-Allaf . T.A.K. and .Omer A.O.,Pure and Applied Sciences,1993,20,53.
- 17) Ahmed .A.H, Omran .A.A, and El-Sherbiny G.M.,J .Appl .Sci .Res.,2006,2(1),44.
- 18) Nakamoto K, Infrared Spectra of Inorganic and Coordination Compounds, \5th Ed, John Wiley & Sons,1988,183.
- 19) Sharma.V.K., Srivastava S, and Srivastava A, Bioinorg. Chem. and Appl.,2007, Hindawi Publishing Corporation, Article,10.
- 20) Chitilappilly P.S. and Yusuf K.K.M, Ind .J. Chem.,2008,47A,848.
- 21) El-Hindawy A.M., Al-Madfa .H.A, El-Bindary.A. , Abdul-Ghany S. and Diab .M ,Qatar Univ. Sci .J.,1994,14(C) ,80.