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Theoretical Calculations of Chemical Shifts of Zirconium Metal Chelates with 1, 2 Naphthoquinone Oximes

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Abstract: *The chemical shifts of NMR of proton, ^{13}carbon, nitrogen, oxygen and zirconium metal have been computed by using Gaussian 09 soft ware code. The geometries were first determined at the Hartree – Fock level of employing LANL2DZ basis set. Three metal chelates of the type M [NQO] $_2$ where M = Zr, and NQO = 1, 2 napthoquinone, 1-oxime, 1, 2 napthoquinone, 2-oxime and 1, 2 napthoquinone dioxime have been synthesized. Chemical shifts of proton and ^{13}Carbon were experimentally determined and compared with computed chemical shifts. The results were in good agreement.*
Key words*: 1-2 Naphthoquinone oximes, NMR, Zirconium metal chelates*

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I. Introduction

Nuclear magnetic resonance studies in DMSO solvent have shown that 1-nitroso 2- naphthol and 2-nitroso 1- naphthol exist in oxime form (1). NMR chemical shifts of metal chelates of Hg (II), Pb (II), Ag (I), Zn (II) and Cd (II) of 1,2-naphthoquinone-1 oxime have been reported (2) Theoretical calculations of chemical shifts of proton and carbon-13 of 1,2-naphthoquinone 2-xime have been reported by V. B. Jadhav et. al. (3). and that of 1,2-naphthoquinone-2 oximes chelate formed. (4). The chemical shifts of 1, 2 naphthoquinone dioxime for proton and 13carbon were reported (5). The metal chelates formed by dioxime were synthesized and NMR chemical shifts were calculated as well as experimental data were compared (6). Transition metal chelates with ligands containing oxime group have attracted much attention as they exhibit excellent coordination ability and reactivity. In the case of dioxime chelates, the presence of mildly acidic hydroxyl groups and slightly basic nitrogen atom makes dioximes amphoteric ligands which form square planner and octahedral chelates with metal ion as the central atom (7). Owing to the large variety of coordination geometries, coordination numbers and modes of interactions with their ligands, metal complexes give access to a different field of pathways.

This paper describes synthesis and theoretical calculations of chemical shifts of zirconium metal chelates of 1, 2-naphthoquinone, 1-oxime, 1, 2- naphthoquinone, 2-oxime and 1, 2- naphthoquinone dioxime and the data is compared with experimental values.

2. Materials and Methods

1, 2 naphthoquinone, 1-oxime and 1, 2 naphthoquinone, 2-0xime were used of Emerk reagents as it is. Synthesis of 1-2 napthoquinone dioxime was carried as per the reported method (8) which was recrystalized using methanol and dried in vacuum. A stock solution of Zirconium oxy nitrate (II) was prepared by using AR grade quality and deionised water was used in this study.

2.1 Preparation of metal chelates.

The chelates were prepared by mixing metal salt solution and ligand solution in 1: 2 proportions for zirconium metal. The mixture was constantly stirred for one hour on magnetic stirrer. The pH of the mixture was maintained; in between 5.0 – 6.0 by adding ammonia solution to it the mixture was warmed on water bath for about 15 minutes. On cooling it was filtered and compounds were dried in vacuum.

2.2 Instrumental Analysis.

Elemental analysis was carried out with a Perkin Elmer 2400 series for C, H, O & N. The proton and ^{13}C NMR spectra were recorded in $CDCl_3$ on 400-Vnmrs400 instrument in DMSO solvent

2.2.1 Computational details

The entire calculations conducted in the present work were performed at Hartree – Fock (HF/ LANL2DZ) basis set in the Gaussian 09 software code. The geometries were first determined at the Hartree – Fock level of employing LANL2DZ basis set (9-11). The wave number value computed theoretically contains known

systematic error due to the negligence of electron correlation. We have used the scaling factor value of 0.9393 for HF /SDD basic set.

II. Results And Discussion

It is reported that the oxime group proton, the chemical shift is predicted at 8.12 and 8.76 ppm and they observed a doublet in the spectra at 9.24 and 9.22 ppm. (J= 0.122). The chemical shift of the H_2, H_4 and H_6 show doublets and their values are comparable to calculations d values .The remaining δ values of H_1, H_3, H_5 are in good agreement of the calculated values. It suggests that 1- nitroso 2-naphthol exists only in oxime form.

a) Zirconium 1-oximate:

In the case of Zr 1-oximates (see FIG-1.), after coordination, it is observed that deprotonation is not taking place. Oxime protons $H_{20,}$ and H_{39} shows chemical shifts at higher fields at 3.177 and 3.002 ppm as against predicted shifts at 4.81 and 3.65 ppm . Only one proton is observed at 9.06 pp while the predicted proton is at 13.670 ppm. Other protons chemical shifts are comparable to calculated values (See Table-1).

^{13}C NMR spectra shows C=N carbon chemical shift lower fields at 135.656 and 135.61 ppm for C_{31} and C_{14}, while calculated values indicate still lower fields at 147.71 and 144.19 ppm. Remaining chemical shifts of carbon atoms are comparable to calculated values. Complex is made up of six member ring. Chemical shifts of $N_{37 \text{ and }} N_{17,}$ are predicted as 325.89 and 315.71 ppm, for oxygen predicted shifts are at 1006.97, 403.99, 391.06, 181.29 and 170.41 pp for O_{42}, $O_{40,}$ O_{18}, O_{19} and O_{38}. The chemical shift for zirconium metal is predicted at -99.50 ppm.

Table: 1 Chemical shifts of NMR of Zirconium 1-oximate in $CDCl_3$

Sr. No.	Atom	δ cal.	δ Exp	Sr. No.	Atom	δ cal.	δ Exp.
1	11C	162.85	148.27	22	12H	8.72	9.031
2	34C	162.80	148.27	23	13H	7.31	7.97
3	31C	147.71	135.67	24	8H	7.26	7.673
4	14C	144.19	135.67	25	28H	7.18	7.647
5	30C	141.06	134.73	26	33H	7.15	7.572
6	10C	136.16	134.73	27	29H	7.07	7.550
7	1C	134.98	132.88	28	9H	7.05	7.522
8	25C	134.75	131.39	29	27H	7.02	7.333
9	21C	134.75	130.26	30	7H	6.93	7.204
10	22C	133.33	129.80	31	36H	6.85	7.174
11	2C	133.65	129.74	32	16H	5.89	7.089
12	26C	133.65	128.94	33	20H	4.81	3.177
13	6C	133.63	128.94	34	39H	3.65	3.002
14	5C	132.19	126.99	35	37N	325.89	--
15	3C	130.04	125.33	36	17N	315.71	--
16	36C	128.79	120.12	37	42O	1006.97	--
17	23C	127.77	115.92	38	40O	403.99	--
18	4C	123.10	112.91	39	18O	391.06	--
19	24C	117.70	131.39	40	19O	181.29	--
20	15C	109.09	130.26	41	38O	170.41	--
21	32H	11.76	9.060	42	41Zr	-99.50	--

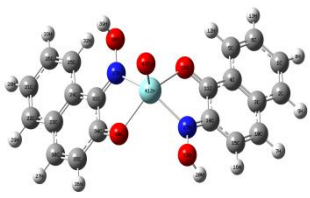

FIG. 1 MOLECULAR STRUCTURE OF ZIRCONIUM 1- OXIMATE

b) Zirconium 2- Oximate

Table-2 shows chemical shifts of Zr 2-oximate, In the case of Zr 2-oximate (see FIG-2), after coordination, Oxime protons $H_{36,}$ and H_{38} shows chemical shifts at higher fields at 3.15 and 2.99 ppm as against predicted shifts at 3.32 and 2.99 ppm . Only two protons are observed at 8.36 and 8.33 pm while the predicted proton is at 9.36 and 9.35 ppm. Other protons chemical shifts are comparable to calculated values.

^{13}C NMR spectra shows C=N carbon chemical shift lower fields at 135.656 and 135.61 ppm for C_{31} and C_{14}, while calculated values indicate still lower fields at 147.71 and 144.19 ppm. Remaining chemical shifts of carbon atoms are comparable to calculated values. Complex is made up of six member ring. Chemical shifts of $N_{37 \text{ and }} N_{17,}$ are predicted as 325.89 and 315.71 ppm, for oxygen predicted shifts are at 1006.97, 403.99, 391.06, 181.29 and 170.41 pp for O_{42}, $O_{40,}$ O_{18}, O_{19} and O_{38}. The chemical shift for zirconium metal is predicted at -99.50 ppm.

Table: 2 Chemical shifts of NMR of Zr2-oximate in $CDCl_3$

Sr. No.	Atom	δ cal.	δ Exp.	Sr. No.	Atom	δ cal.	δ Exp.
1	12-H	9.3660	8.362	24	26-C	136.2456	130.001
2	30-H	9.3530	8.337	25	2-C	135.1379	129.467
3	8-H	7.70410	7.811	26	6-C	135.1092	129.192
4	25-H	7.7006	7.780	27	28-C	134.9538	128.078
5	13-H	7.6095	7.679	28	14-C	134.4880	127.467
6	23-H	7.6085	7.569	29	3-C	133.1279	126.628
7	31-H	7.5275	7.510	30	19-C	131.2656	126.261
8	32-H	7.5258	7.482	31	20-C	124.7303	124.216
9	7-H	7.4686	7.445	32	4-C	122.4963	123.773
10	9-H	7.3085	7.397	33	15-C	121.6620	122.125
11	16-H	6.9902	6.999	34	17-C	116.2621	114.845
12	24-H	6.3413	6.433	35	34-N	273.7459	--
13	36-H	3.3268	3.150	36	33-N	268.0079	--
14	38-H	2.9942	2.992	37	42-O	2078.28	--
15	11C	173.2647	184.337	38	39-O	393.2532	--
16	21-C	153.0311	169.161	39	40-O	306.7837	--
17	10-C	147.3588	152.361	40	35-O	197.3031	--
18	22-C	144.1245	139.494	41	37-O	149.6689	--
19	1-C	142.5595	137.327	42	41-Zr	-82.6223	--
20	5-C	142.0681	137.158	43	--	--	--
21	18-C	141.9981	134.213	44	--	--	--
22	29-C	138.4449	133.252	45	--	--	--
23	27-C	136.271	132.794	--	--	--	--

Fig.2 MOLECULAR STRUCTURE OF ZIRCONIUM 2- OXIMATE

c) ZIRCONIUM DIOXIMATE

Table-3 shows chemical shifts of Zr dioximate (see FIG-3), after coordination, it is observed that deprotonation is not taking place. Oxime protons H_{44} , H_{22}, H_{20} and H_{42} shows chemical shifts at higher fields at 6.705, 6.398, 3.68 and 3.66 ppm as against predicted shifts at 4.55, 4.33, 3.92 and 3.68 ppm respectively. Only two protons are observed at 13.56 and 13.21 ppm while the predicted protons are at 12.04 and 11.46 ppm. Other protons chemical shifts are comparable to calculated values.

^{13}C NMR spectra shows C=N carbon chemical shift lower fields at 140.66, 130.30, 129.36 and 113.97 ppm for $C_{35,}$ C_{32} C_{14} and C_{11} while calculated values indicate still lower fields at 159.89, 143.27, 135.04 and 113.97 ppm. Remaining chemical shifts of carbon atoms are comparable to calculated values. Complex is made up of six member ring. Chemical shift of $N_{39,}$ $N_{38,}$ N_{18} and N_{17} is predicted as 531.64, 470.35, 247.06 and 97.15 ppm. for oxygen predicted shifts are at 175.26, 144.85, 113.28 and 10.13 ppm for O_{41}, O_{40}, O_{19} and O_{21}. The chemical shift for zinc metal is predicted at -236.18 ppm.

Table: 3 Chemical shifts of NMR of Zr dioximate in CDCl3

Sr. No.	Atom	δ cal.	δ Exp.	Sr. No.	Atom	δ cal.	δ Exp.
1	34-H	12.0430	13.56	24	23-C	133.1311	129.802
2	12-H	11.4679	13.21	25	5-C	132.7579	129.741
3	29-H	7.5669	8.078	26	1-C	131.3688	129.741
4	7-H	7.5001	8.057	27	28-C	129.9186	128.948
5	9-H	7.4680	7.98	28	2-C	129.6817	128.948
6	30-H	7.4464	7.665	29	24-C	129.4758	126.994
7	31-H	7.4175	7.566	30	6-C	128.9689	125.238
8	8-H	7.4164	7.520	31	25-C	124.4027	125.238
9	35-H	7.3786	7.499	32	3-C	123.8556	120.126
10	13-H	7.3573	7.412	33	4-C	113.8299	115.826
11	16-H	6.5630	7.032	34	26-C	113.7402	115.826
12	38-H	6.5359	7.006	35	15-C	108.1545	112.921
13	44-H	4.5584	6.705	36	37-C	108.0275	112.921
14	22-H	4.3311	6.398	37	40-N	299.2433	--
15	20-H	3.9269	3.68	38	39-N	295.2234	--
16	42-H	3.6811	3.660	39	18-N	290.7096	--
17	33-C	139.9651	148.271	40	17-N	286.5201	--
18	32-C	137.9530	135.679	41	46-O	652.5761	--
19	36-C	137.6415	134.732	42	19O	124.75	--
20	11-C	136.1002	132.85	43	43O	117.25	--
21	10-C	134.7274	131.390	44	21O	110.64	--
22	14-C	134.4071	130.260	45	41O	110.16	--
23	27-C	133.9241	129.802	46	45Zr	-28.17	--

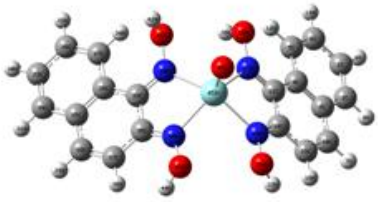

Fig.3 MOLECULAR STRUCTURE OF ZIRCONIUM DIOXIMATE

III. Conclusions

It is observed that zirconium chelates are formed by joining Zr with O-N or N-N and a five member is observed. in all three chelates. The predicted chemical shifts of nitrogen, oxygen and metal atoms are good in aggriment. These values are in reported range. The assignments were confirmed with the help of animation process which is available in Gaussian 09 computer code. The results suggest that it shows the formation of chelates with five member ring.

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