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Theoretical calculations of chemical shifts of metal (Hg (II), Pb (II), Ag (I), Zn (II) and Cd (II)) chelates of 1, 2 naphthoquinone 2-oxime,

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ABSTRACT : Five metal chelates of the type M (1,2-naphthoquinone, 2-oxime)$_2$ where M = Ag, Hg, Cd, Zn, Pb, have been synthesized. NMR spectra of proton and carbon 13 have been recorded in CDCl3 of the studied metal chelates and the chemical shifts of proton and carbon 13 are computed by using Gaussian 09 computer code. The Hartree – Fock method was set to calculate the geometry of metal chelates with employing LNNL2DZ basis set. The computed chemical shifts of proton and ^{13}Carbon have been compared with experimental data and found that these values are in good agreement. The chemical shift of nitrogen, oxygen and metals are also reported.

***Key words**: 1-Nitroso-2, naphthol, 1-2 Naphthoquinone-2, Oxime, NMR, Metal chelates*

I. Introduction

The structure and conformational equilibrium of the 1,2-naphthquonone mono oximes have been studied by solid and liquid state NMR and non empirical quantum chemical calculations. The presence of syn and anti oximes of 1,2-naphthquonone 2-oxime in solution is proved by NMR spectroscopy(1). The proton (^{1}H) and carbon (^{13}C) NMR spectra of 2-nitroso, 1-naphthol and the UO_2(IV) complex of it were recorded and analyzed. The quinonide O does not take part in comlexation with UO2 (IV), which is affected by chelation through the oxime O and N (2). Al, Zn, Cu and Ni(II) salts of 1,2-naphthquonone 2-oximewere synthesized. The proton (^{1}H) and carbon (^{13}C) spectral data showed that they exist in the quinine oxime form. Some of them gave rise to metalltropic Z and E isomerism (3). 2-nitroso,1 naphthol has great ability to form metal chelates and it is a sensitive and specific reagent for fluorometric determination of tyrosine residues in proteins and peptides (4). NMR chemical shifts of proton (^{1}H) and carbon (^{13}C). Were calculated by HF method employing 6.31 G level and the data were compared with experimental data by N. R. Gonewar et.al. (5). In this paper we describe
proton (^{1}H) and carbon (^{13}C) NMR of studied metal chelates the observed data was compared with calculated data by Gaussian 09 software code.

II. Materials and Methods

The ligand 1, 2-naphthoquinone 2-oxime is used as it is. A stock solution of Hg (II), Pb (II),Ag (I), Zn (II) and Cd (II) is prepared by using AR grade chemicals. Distilled water is used during synthesis.

2.1 Preparation of metal chelates.

The chelates were prepared by mixing metal salt solution and ligand in 1: 1 proportion for silver and 1:2 for zinc, lead, mercury and cadmium metals. 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. Warm the mixture on water bath for about 15 minutes. On cooling it was filtered and compounds are found to be coloured. These chelates are 1) Ag-2-oximate [Ag(1,2-naphthoquinone, 2-oxime)],
2) Cd-2-oximate [Cd(1,2-naphthoquinone, 2-oxime)$_2$], 3) Pb-2-oximate [Pb(1,2-naphthoquinone, 2-oxime)$_2$], 4) Zn-2-oximate [Zn(1,2-naphthoquinone, 2-oxime)$_2$], and 5) Hg-2-oximate [Hg(1,2-naphthoquinone, 2-oxime)$_2$],

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 recorded in $CDCl_3$ on Varion. 400 MR
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 (6,7). 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.

III. RESULTS AND DISCUSSION

It is reported that the oxime group proton, the chemical shift is predicted at 8.17 and 8.84 ppm in CD2Cl2 & DMSO solvents respectively (5) and the observed chemical shift is 13.6 ppm in DMSO. This chemical shift is reported as 11.0 ppm in solution by A. E. Shehavlev et.al.(1) and 13.7 ppm is observed by T. Shono et.al.(8).

The chemical shift of the remaining protons values are comparable to calculated d values. It suggests that 2- nitroso 1-naphthol exists only in oxime form. The chemical shift of carbon atom in CD_2Cl_2 and DMSO solvents were calculated and experimental data was obtained in $CDCl_3$. It is observed that the chemical shifts of carbon are comparable to each other.

1. Ag- 2-oximate

Fig. 1 shows the structure of Ag 2-oximate and Table: 1 shows chemical shifts of of all atoms present in the studied molecule. The oxime proton is deprotonated hence no chemical shift is predicted. Proton attached to C5 is H12 and its chemical shift is predicted at 9.66 ppm while the observes chemical shift is 8.19 ppm The proton at C_{15} is H_{16} and its predicted value is 7.68 ppm which is comparable to experimental value at 8.22 ppm The chemical shifts of the remaining protons are comparable to predicted values. The chemical shift of C_1 is predicted at 141.51ppm and experimental chemical shift is observed at 131.74.The chemical shift of C_{11} is predicted as 134.54 ppm and the the observed value is 171.71 ppm. This carbon is bonded to oxygen to form C+ O bond. These values are similar to reported data. The nitrogen attached to carbon shows chemical shift at 205.76 ppm. In this silver shows the valence +2 as well as a six member ring formation. The chemical shifts of remaining carbons are within a range of 5-10 ppm which is in good agreement with observed data.

The important bond lengths are presented here as $Ag_{18}O_{20}$ – 1.85979 $A^{0,}$ $Ag_{18}O_{17}$ – 1.855787 A^0, $N_{19}O_{20}$ – 1.41572 A^0, $C_{14}N_{19}$ – 1.43288 A^0, $C_{11}O_{17}$ – 1.28673 A^0. The important angles of the six member ring are as follows

$N_{19}O_{20}Ag_{18}$ – 88.045^{0,} $O_{17}Ag_{18}O_{20}$ – 142.356 ^{0}, $N_{19}C_{14}C_{11}$ – 135.205 ^{0},
$C_{14}C_{11}O_{17}$ – 124.909 ^{0}, $Ag_{18}O_{17}C_{11}$ – 96.575 ^{0} .

Table: 1 Chemical shifts of NMR of Ag-2-oximate in $CDCl_3$

Sr. No.	Atom	δcal.	δExp.
1	12H	9.66	8.19
2	16H	7.68	7.99
3	8H	7.68	7.62
4	9H	7.19	7.42
5	13H	7.17	7.25
6	7H	6.94	6.97
7	14C	205.76	137.32
8	11C	171.71	134.54
9	15C	142.59	132.72
10	1C	141.51	131.74
11	5C	138.15	129.72
12	3C	137.10	128.64
13	2C	124.07	128.44
14	6C	122.90	125.98
15	4C	118.00	122.80
16	10C	113.38	115.91
17	19N	1733.13	--
18	20O	1313.75	--
19	17O	276.40	--
20	18Ag	188.90	--

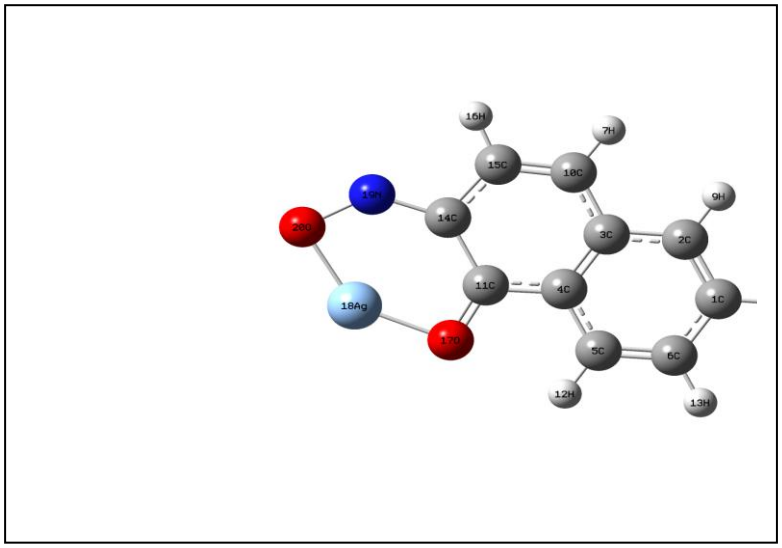

Fig.1 : Molecular structure Ag-2-oximate

2.Cd- 2-oximate

Fig. 2 shows molecular structure Cd-2-oximate and the data of chemical shifts is shown in Table 2. In the case of Cd-2-oximate, after coordination, it is observed that deprotonation is not taking place. Oxime protons H_{41} and H_{39} show chemical shifts at 3.35& 2.50 ppm as against predicted shifts at 3.03 & 2.12 ppm respectively which shows good agreement results. Protons nearer to oxime protons H_{12} and H_{37} shows predicted values 9.07 & 8.54 ppm which is comparable to experimental values 9.14 & 9.11 ppm respectively. Other protons chemical shifts are comparable to calculated values.

^{13}C NMR chemical shift of C_{11} & C_{30} are predicted as 184.11 ppm while the observed values are at 184.37 ppm which is in good agreement with each other. These carbons are involved in to form C=O bonding. The remaining chemical shifts of carbon atoms are comparable to calculated values. Complex is made up of five member ring.

The chemical shift of nitrogen atoms have been predicted as N18 & N_{37} as -31.87 & -41.91 ppm. For oxygen atom, the predicted shifts are O_{17}, O_{36}, and O19 & O_{28} as 516.26, 338.76, 153.75 & 86.60 ppm respectively. The chemical shift for cadmium atom is
predicted at 181.26 ppm.

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

Sr. No.	Atom	δ cal.	δ Exp.	Sr. No.	Atom	δ cal.	δ Exp.
1	12H	9.07	9.14	22	21C	128.25	131.32
2	31H	8.54	9.11	23	20C	127.80	130.54
3	7H	7.44	7.89	24	6C	127.35	129.61
4	16H	7.37	7.57	25	15C	126.86	129.44
5	8H	7.31	7.52	26	2C	126.47	128.86
6	13H	7.18	7.50	27	25C	125.14	126.91
7	26H	7.01	7.13	28	3C	124.15	126.29
8	9H	6.89	7.11	29	34C	120.30	125.58
9	32H	6.88	7.05	30	22C	119.89	122.23
10	28H	6.86	7.02	31	33C	117.90	120.71
11	27H	6.79	6.67	32	23C	117.59	117.49
12	35H	6.74	6.64	33	4C	117.00	117.49
13	41H	3.03	3.35	34	14C	105.69	115.67
14	39H	2.12	2.50	35	18N	-31.87	
15	11C	210.74	184.37	36	37N	-41.91	
16	30C	184.11	184.37	37	17O	516.26	
17	10C	147.08	145.31	38	36O	338.76	
18	29C	136.67	136.62	39	19O	153.75	
19	1C	136.64	134.53	40	28O	86.60	
20	5C	135.79	133.09	41	40Cd	181.26	
21	24C	130.47	132.92				

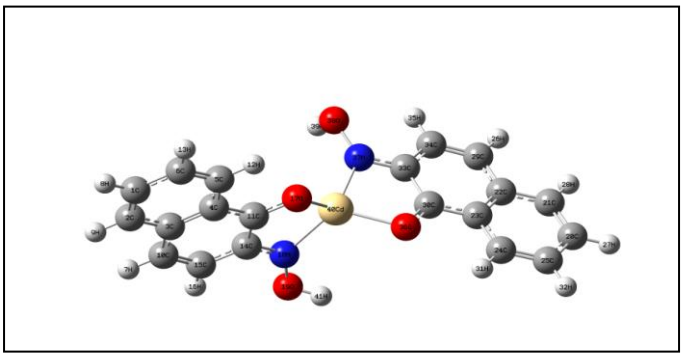

Fig. 2 Molecular structure Cd-2-oximate

3.Pb-2-oximate

Table-3 shows chemical shifts of Pb-2-oximate and Fig. 3 shows the molecular structure. The oxime protons H_{40} & H_{39} show chemical shifts at 6.64 and 1.25 as compared to predicted values at 4.07 and 3.26 ppm respectively. H_{12} and H_{31} protons are nearer to oxime protons and the predicted chemical shifts are at 9.07 & 8.54 pp while the observed values are at 9.14 & 9.11 ppm respectively. Remaining chemical shifts of protons are comparable to predicted values.

^{13}C NMR spectra shows the chemical shifts of carbon at 182.8456 & 147.8693 for C=O bonding while the observed values are 131.32 & 132.72 ppm respectively. The bond between C-N shows the predicted shifts for carbon C14 & C33 as 162.13 & 160.92 ppm while the observed value is 132.77 ppm. It is observed after coordination which demonstrates the strong interaction of the ligand and the central metal atom after coordination.Chemical shift of N_{18} and N_{37} is predicted as 307.93 &370.83 ppm, for oxygen predicted shifts are at 356.38, 314.17, 108.04 & 96.82 ppm for O_{17}, O_{36}, O_{19} and O_{38} respectively. The chemical shift for lead Pb_{41} metal is predicted at 11.68 ppm. These chemical shifts were computed using " gauge-including atomic orbital's" (GIAO) methods (9-11) implemented in Gaussian 09 program.

Table: 3 Chemical shifts of NMR of Pb-2-oximate in $CDCl_3$

Sr. No.	Atom	δ cal.	δ Exp.	Sr. No.	Atom	δ cal.	δ Exp.
1	12H	8.32	8.35	22	6C	126.87	126.35
2	31H	8.18	8.19	23	5C	124.83	125.97
3	16H	7.57	8.16	24	24C	123.37	125.97
4	9H	7.25	8.14	25	20C	122.45	125.27
5	28H	7.25	8.03	26	1C	122.19	125.27
6	35H	7.22	8.02	27	29C	121.93	122.80
7	13H	7.20	8.01	28	10C	120.21	122.80
8	32H	7.18	7.99	29	23C	116.49	77.31
9	26H	7.01	7.72	30	4C	115.67	77.31
10	7H	6.98	7.70	31	22C	114.08	76.99
11	27H	6.82	6.92	32	3C	113.14	76.99
12	8H	6.81	6.67	33	34C	107.20	76.67
13	40H	4.01	6.64	34	15C	106.73	76.67
14	39H	3.26	1.25	35	18N	370.83	--
15	14C	162.13	132.77	36	37N	307.93	--
16	33C	160.92	132.77	37	17O	356.38	--
17	11C	157.67	131.82	38	36O	314.17	--
18	30C	153.55	131.82	39	19O	108.04	--
19	21C	129.43	129.80	40	38O	96.82	--
20	2C	128.87	129.80	41	41Pb	11.68	--
21	25C	127.37	126.35	--	--	--	--

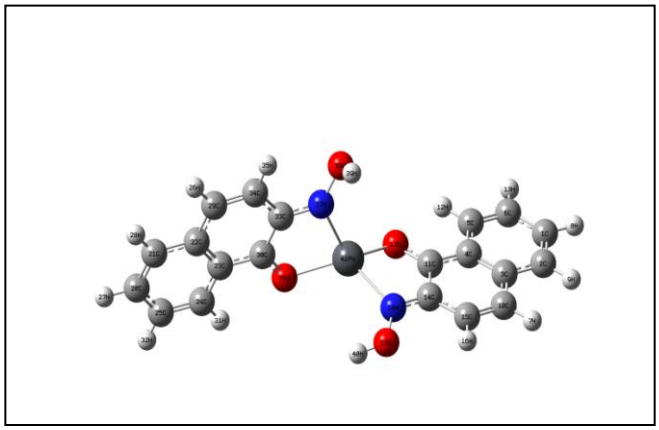

Fig3. : Molecular structure Pb-2-oximate

4.Zn-2-oximate

Molecular structure of Zn-2-oximate is shown in Fig. 4 and table-4 shows chemical shifts of Zn-2-oximate, The oxime protons H_{39} & H_{40} show chemical shifts at 6.64 and 1.55 as compared to predicted values at 3.14 and 2.52 respectively. H_{16} and H_{35} protons are nearer to oxime protons predicted chemical shifts are at 7.43 & 7.73 while the observed values are at 7.56& 7.47 ppm respectively which are in good agreement to each other. Remaining chemical shifts of protons are comparable to predicted values.

The predicted chemical shifts at 225.81 & 216.04 ppm of carbon for C=O carbon bonding while the observed values are as 182.15 & 147.14 ppm respectively. Chemical shift of N_{37} and N_{18} is predicted as 31.50 & -31.33ppm this is may due to trans arragment, For oxygen predicted shifts are at 347.15, 310.17, 87.17 & 87.55 ppp O_{36}, O_{17}, O_{19} and O_{38} respectively. The chemical shift for lead Zn41 metal is predicted at 521.91 ppm. The C=O bond length is predicted as 1.34243 $A^{0,}$ the C=N is 1.34869 A^{0} and Zn = O is 1387672 A0.

Table: 4 Chemical shifts of NMR of Zn 2-oximate in CDCl3

Sr. No.	Atom	δ cal.	δ Exp.	Sr. No.	Atom	δ cal.	δ Exp.
1	31H	8.64	8.37	22	1C	131.09	129.78
2	12H	8.51	8.35	23	21C	130.44	129.09
3	27H	7.55	7.70	24	2C	130.21	128.73
4	26H	7.48	7.58	25	24C	129.91	128.43
5	16H	7.43	7.56	26	25C	128.29	128.19
6	32H	7.40	7.51	27	5C	127.54	127.27
7	28H	7.39	7.49	28	6C	126.70	126.34
8	9H	7.38	7.48	29	22C	125.48	125.98
9	35H	7.33	7.47	30	15C	123.60	125.28
10	7H	7.32	7.46	31	34C	121.92	122.80
11	13H	7.30	7.41	32	3C	121.82	77.31
12	8H	7.27	7.26	33	23C	115.72	77.00
13	39H	3.14	6.64	34	4C	115.08	76.68
14	40H	2.52	1.55	35	37N	31.51	--
15	30C	225.81	182.15	36	18N	-31.33	--
16	11C	216.04	147.14	37	36O	347.15	--
17	33C	149.24	136.06	38	17O	310.17	--
18	29C	145.05	134.90	39	19O	87.55	--
19	10C	138.80	132.75	40	38O	74.94	--
20	14C	137.35	131.81	41	ZN	521.91	--
21	20C	136.70	130.04	--	--	--	--

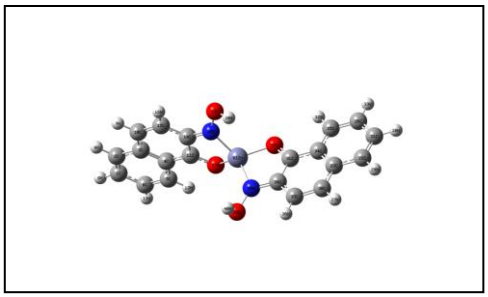

Fig4. : Molecular structure Zn-2-oximate

5.Mercury 2-oximate

Fig5. Shows molecular structure Hg-2-oximate and Table 5 shows the chemical shifts of all atoms present in the studied molecule. In the case of Hg-2-oximate, after coordination, oxime protons H_{39} and H_{40} shows chemical shifts at lower fields at 8.35 for both as against predicted shifts at 1.25 & 8.30 ppm respectively The predicted chemical shifts of protons nearer to oxime proton H_{12} and H_{16} are as 6.38 &1.28 ppm which are compared with experimental values as 8.35 & 8.00 ppm. In this case H12 is nearer but H_{16} is far away in the predicted behavior. Other protons chemical shifts are comparable to calculated values (See Table-5).

^{13}C NMR spectra shows C=O carbons chemical shift as 182.15 &134.94 ppm for C_{11} and C_{30}, while calculated values indicate values as 220.76 & 146.29 ppm respectively. It appears that these chemical shifts are in good agreement. The carbons involving in C-N bonding are C_{14} and C_{33} with chemical shifts as 167.17 &152.33 ppm while the observed values are 147.14 & 137.63 ppm which are found in good agreement. Chemical shift of N_{37} and N_{18} is predicted as 110.98 & 448.71 ppm, for oxygen predicted shifts are at 463.71, 235.19, 62.34 & 57.53 ppm for O_{17}, O_{19}, $O_{36}$and O_{38}. The chemical shift for Hg_{41} metal is predicted at 206.29 ppm.

Table: 5 Chemical shifts of NMR of Hg 2-oximate in $CDCl_3$

Sr. No.	Atom	δ cal.	δ Exp.	Sr. No.	Atom	δ cal.	δ Exp.
1	12H	9.35	8.35	22	3C	135.45	130.04
2	40H	8.330	8.35	23	21C	131.11	129.78
3	8H	8.17	8.26	24	6C	130.71	129.20
4	31H	7.99	8.24	25	2C	128.28	129.10
5	7H	7.67	8.19	26	25C	122.63	128.73
6	13H	7.63	8.17	27	24C	121.78	128.43
7	16H	7.57	8.16	28	23C	118.14	128.19
8	9H	7.39	8.14	29	4C	117.90	127.89
9	28H	7.15	8.00	30	15C	117.60	127.28
10	35H	6.81	6.92	31	29C	116.39	126.35
11	32H	6.74	6.89	32	20C	116.18	126.01
12	26H	6.59	6.67	33	22C	114.63	125.27
13	27H	6.38	6.64	34	34C	110.58	122.79
14	39H	1.28	1.69	35	18N	448.65	--
15	11C	220.76	182.15	36	37N	110.98	--
16	14C	167.17	147.14	37	17O	463.71	--
17	33C	152.33	137.63	38	19O	235.19	--
18	1C	148.60	136.07	39	36O	62.34	--
19	30C	146.29	134.94	40	38O	57.53	--
20	10C	144.53	132.76	41	41Hg	206.29	--
21	5C	136.75	131.79	--	--	--	--

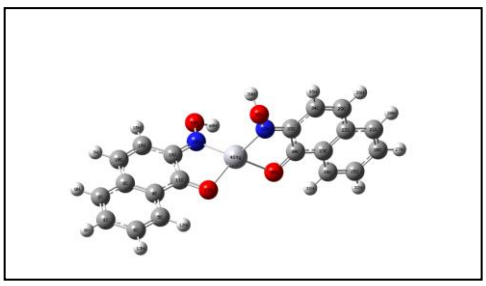

Fig5. : Molecular structure Hg-2-oximate

6. Energy, Dipole moment and point group data of metal chelates have been calculated and shown in Table 6: It is seen from the table that all point group of all metal chelates is same.

Table: 6 Energy, Diople moment and point group Data of chelates

Sr.No.	Name of Chelate	E (RHF) a.u.	Dipole Moment Debye	Point Group
1	Ag -2 oximate	-730.762	2.9288	C1
2	Cd -2 oximate	-1219.868	6.2176	C1
3	Pb -2 oximate	-1176.653	3.5692	C1
4	Zn -2 oximate	-1236.899	7.5792	C1
5	Hg -2 oximate	-1214.599	7.4099	C1

IV. Conclusions

The computed NMR chemical shifts of proton and ^{13}carbon of studied metal chelates i.e. Ag, Cd, Pb, Zn and Hg are compared with experimental data and found most of them are in good agreement. 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 for metals like cadmium , lead , zinc and mercury while silver shows six member ring formation.

V. Acknowledgement

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