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NMR Studies On Metal (Hg (II), Pb (II), Ag (I), Zn (II) And Cd (II)) Chelates Of 1, 2 Naphthoquinone 1-Oxime,

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Abstract: *NMR chemical shifts of proton, [13]carbon, nitrogen , oxygen and metal i.e. Ag, Cd, Pb, Zn and Hg have been computed by using Gaussian 09 code. The geometries were first determined at the Hartree – Fock level of employing LANL2DZ basis set. Five metal chelates of the type M [NQO]$_2$ where M = Hg, Cd, Zn, Pb: NQO = 1, 2 napthoquinone-1-oxime and Ag (NQO) have been synthesized. Chemical shifts of proton and [13]Carbon were determined and compared with computed chemical shifts. 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.*

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

I. Introduction

The ^{1}H and ^{13}C NMR spectra of 1-nitroso-2-naphthol with dioxouranium (VI) were recorded and analysed. The results show the nitrosonaphthols exist predominantly in the oxime form, and that the 1-nitroso compounds have a preferred structure. The quinonoid oxygen does not take part in the complexation with dioxouranium (VI), which is effected by chelation through the oxime oxygen and nitrogen (1). Nyholm and coworkers (2, 3) have described the formation of adducts of the type ML, by mixing the metal hydroxide or ethoxide with the ligand in a medium of low dielectric constant (usually absolute ethanol), (where M = alkali metal and HL = 1-nitroso-2-naphthol. Potassium, rubidium caesium derivatives behave similarly while there are considerable differences amongst potassium, sodium and lithium compounds. All the ligands were found to chelate the metal, forming six membered ring **which** actually forms an acid salt. Increase in radius (or decrease in ionisation potential) of the metal appears to facilitate the isolation of adducts in the solid state whereas ion pairing in solution is naturally stronger for smaller cations. It was also found that hydrogen bonding is not essential for the formation of adducts between the chelating ligand and the alkali metal salt of the chelate anion. Some metal ion complexes of 1, 2-naphthoquinone 1-oxime have been reported (4). The complexe Co $(nqo)_3$ (nqoH= 1-nitroso-2-naphthol) have seen prepared by the interaction of the nitrosonaphthol with cobalt (II) chloride in air and under nitrogen (5).

In this paper, we describe proton NMR and carbon ^{13}NMR of the studied complexes. We have calculated chemical shifts and compared with experimental results.

II. Materials And Methods

The ligand 1, 2-naphthoquinone 1-oxime is used as it is. A stock solutions of Hg (II), Pb (II), Ag (I), Zn (II) and Cd (II) were 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

.

2.2 Instrumental Analysis.

Elemental analysis was carried out with a Perkin Elmer 2400 series for C, H, and O & N. The proton and ^{13}C NMR spectra were 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 8.12 and 8.76 ppm (8) 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 calculated d values .The remaining δ □ □ values of H_1, H_3, H_5 are in good aggreement of the calculated values. It suggested that 1- nitroso 2-naphthol exists only in oxime form (9).The chemical shift of carbon atom in CD_2Cl_2 and DMSO solvents were calculated and experimental data was obtained in $CDCl_3$.

1. Silver 1-oximate

Table: 1 shows chemical shifts of NMR of Ag 1-oximate in $CDCl_3$ the number of carbon atoms is according to Fig. 1. The chemical shift of C_1 is predicted at 138.36 ppm and 147.74 ppm .The chemical shift of C_2 is predicted as 171.2 ppm and 174.3 ppm in CD_2Cl_2 and DMSO which is comparable to observed value 184.6 ppm in $CDCl_3$ as well as C_2 is having C=O bonding. These results are similar to reported data (1). NMR spectra in solution of ^{13}C shows chemical shifts for (C=O) at 184.6ppm and (C=N) 147.74ppm. Elizabeth et.al. (10) reported the NMR of silver complex of 1-nitroso 2- naphthol and suggested a structure consisting N-Ag-O bonding. We have calculated NMR chemical shifts considering O-Ag-O bonding i.e. six member rings. The oxime proton (H_7) shows chemical shift at 8.3526 ppm and DFT calculations predicted at 8.3045 ppm. The chemical shifts of other proton nuclei are in good agreement with calculated values.The chemical shifts of C_3-C_{10} are predicted within a range 5 – 10 ppm which is in good agreement with experimental data. Fig. 1 shows structure of silver 1-oximate.

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

Sr. No.	Atom	δcal.	δExp.	δExp. Ref. (10)
1	7H	8.3045	8.3526	7.82
2	16H	7.6141	7.7199	6.6
3	9H	7.2193	7.5571	7.55
4	8H	7.0714	7.4949	7.55
5	13H	7.0184	7.2624	7.55
6	12H	6.6446	6.5935	9.30
7	11C	202.0712	147.9017	--
8	14C	180.1865	144.8848	--
9	10C	163.4130	131.0471	--
10	6C	133.2251	130.7965	--
11	2C	130.6948	129.7111	--
12	4C	127.2367	129.6750	--
13	1C	125.9551	125.7970	--
14	5C	123.3950	123.1670	--
15	15C	123.395	77.3179	--
16	3C	111.5653	76.6820	--
17	17N	1739.4933		
18	18-O	1330.0807		
19	19-O	299.8914		
20	20Ag	188.5528		

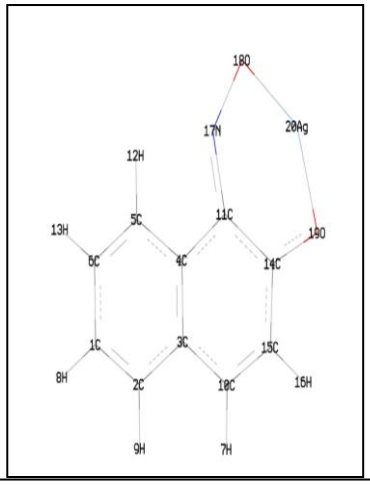

Fig. 1 Structure of Ag 1-oximate

1.2. Cadmium 1-Oximate

In the case of Cd-1-oximate, after coordination, it is observed that deprotonation is not taking place. Oxime protons H_{19} and H_{39} shows chemical shifts at lower fields at 14.1690 as against predicted shifts at 7.0971. Protons nearer to oxime protons H_{12} and H_{32} shows shifts at 8.9718 as against calculated value at 7.5896. Other protons chemical shifts are comparable to calculated values (See Table-2).

^{13}C NMR spectra shows C=O carbon chemical shift lower fields at 145.0546 for C_{34} and C_{14}, while calculated values indicate still lower fields at 195.6087. Remaining chemical shifts of carbon atoms are comparable to calculated values. Complex is made up of five member ring. $C_{11}N_{17}$ and $C_{31}N_{37}$ bonds show elongation length by 0.03368A^o because of reduced electron density after metal coordination which is well supported by Stefen Wirth et.al (11). The observed bond length pattern is comparable to that of only other structure of characterized iridium complex with 1, 2-naphthoquinone -1-oximato ligand (12). Chemical shift of N_{37} and $N_{17}$is predicted as 101.99, for oxygen predicted shifts are at 352.33, &161.33 as doublates for O_{40}, O_{38}, O_{20} and O_{18}. The chemical shift for cadmium metal is predicted at 195.03 ppm.

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

Sr. No.	Atom	δ cal.	δ Exp.	Sr. No.	Atom	δ cal.	δ Exp.
1	19H	7.6971	14.1690	22	11C	130.2581	130.5467
2	39H	7.6971	14.1690	23	26C	127.0492	129.4490
3	12H	7.5896	8.9718	24	6C	127.0491	129.4490
4	32H	7.5896	8.9718	25	21C	125.9885	128.8664
5	16H	7.4433	7.7920	26	1C	125.9884	128.8664
6	36H	7.4433	7.6324	27	35C	125.0914	126.9114
7	9H	7.3044	7.6151	28	15C	125.0913	126.9114
8	29H	7.3044	7.5583	29	5C	124.9592	126.3006
9	8H	7.0022	7.5404	30	25C	124.9591	126.3006
10	28H	7.0022	7.5255	31	3C	124.3379	125.5867
11	13H	6.9039	6.4860	32	23C	124.3378	125.5867
12	33H	6.9039	6.4860	33	4C	123.0372	122.2324
13	7H	6.8969	6.4860	34	24C	123.0372	122.2324
14	27H	6.8968	6.4860	35	37N	101.9971	--
15	14C	195.6087	145.0546	36	17N	101.9959	--
16	34C	195.6087	145.0546	37	20-O	352.3351	--
17	22C	136.1803	134.5400	38	40-O	352.3350	--
18	2C	136.1802	134.5400	39	38-O	161.3356	--
19	30C	132.7651	132.9243	40	18-O	161.3352	--
20	10C	132.7649	132.9243	41	41Cd	195.0325	--
21	31C	130.2583	130.5467				

3. Lead 1-Oximate

Table-3 shows chemical shifts of Pb-1-oximate, the oxime protons H19 & H39 show chemical shifts at 8.3326 and 7.5634 as compared to predicted values at 7.5127 and 7.4240 respectively. H_{12} and H_{32} protons are nearer to oxime protons predicted chemical shifts are at 7.4381 & 7.084 while the observed values are at 7.5702 & 7.550 respectively. Remaining chemical shifts of protons are comparable to predicted values.

^{13}C NMR spectra shows chemical shifts at 182.8456 & 147.8693 for C=O carbon bonding. The predicted chemical shift for C_{34} is at higher field 154.0582 while C_{14} is at 146.61. Other protons chemical shifts are comparable to calculated values. $C_{11}N_{17}$ and $C_{31}N_{37}$ bonds show elongation length by 0.03597A^o because of reduced electron density after metal coordination which is well supported by Stefen Wirth et.al (11). Chemical shift of N_{37} and $N_{17}$is predicted as 184.4751 & 172.0818, for oxygen predicted shifts are at 190.0239, 169.8742, 114.0519 & 98.8897for O_{40}, O_{38}, O_{20} and O_{18} respectively. The chemical shift for lead Pb_{41} metal is predicted at 10.1271 ppm. These chemical shifts were computed using " gauge-including atomic orbitals" (GIAO) methods (13-15) implemented in Gaussian 09 program.

Table: 3 Chemical shifts of NMR of Pb1-oximate in $CDCl_3$

Sr. No.	Atom	δ cal.	δ Exp.	Sr. No.	Atom	δ cal.	δ Exp.
1	16H	7.8135	9.3028	22	6C	125.5525	129.6929
2	36H	7.6512	8.3520	23	15C	125.3073	129.6576
3	19H	7.5127	8.3326	24	1C	124.7592	129.6576
4	9H	7.4680	7.7172	25	35C	124.0154	128.5792
5	29H	7.4571	7.6927	26	21C	121.7592	128.5792
6	12H	7.4381	7.5702	27	3C	121.427	125.7801
7	39H	7.4240	7.5634	28	30C	120.9936	125.7801
8	32H	7.0848	7.5550	29	5C	118.9404	123.1381
9	8H	7.0219	7.5487	30	23C	117.9821	123.1381
10	13H	6.9007	7.5362	31	25C	116.7508	77.3173
11	27H	6.8774	7.5288	32	10C	116.5800	77.3173
12	28H	6.8535	7.5183	33	4C	111.9825	77.0000
13	33H	6.8383	6.5964	34	24C	111.5864	77.8818
14	7H	6.7599	6.5719	35	17N	186.4571	--
15	34C	154.0582	182.8456	36	37N	172.0818	--
16	14C	146.6178	147.8693	37	40-O	190.0239	--
17	11C	142.2985	147.8693	38	20-O	169.8742	--
18	22C	135.6442	144.8388	39	18-O	114.0559	--
19	2C	134.3967	131.0216	40	38-O	98.8897	--
20	31C	133.8542	131.0216	41	41Pb	10.1271	--
21	26C	126.0958	129.6929				

4. Zinc 1-Oximate

Table-4 shows chemical shifts of Zn-1-oximate, the oxime protons H_{19} & H_{39} show chemical shifts at 8.3528 and 7.7178 as compared to predicted values at 7.2903 and 7.2712 respectively. H_{12} and H_{32} protons are

nearer to oxime protons predicted chemical shifts are at 6.8834 & 6.9271while the observed values are at 6.5471& 7.4867 respectively. Remaining chemical shifts of protons are comparable to predicted values.

^{13}C NMR spectra shows chemical shifts at 182.83 & 147.86 for C=O carbon bonding. The predicted chemical shift for C_{34} is at higher field 171.9752 while C_{14} is at 170.7577. Other protons chemical shifts are comparable to calculated values. Chemical shift of N_{37} and $N_{17}$is predicted as 277.1146 & 274.9659, for oxygen predicted shifts are at 268.1979, 266.3975, 161.5988 & 158.5886 for O_{40}, O_{38}, O_{20} and O_{18} respectively. The chemical shift for lead Zn41 metal is predicted at -150.402 ppm.

Table: 4 Chemical shifts of NMR of Zn 1-oximate in CDCl3

Sr. No.	Atom	δ cal.	δ Exp.	Sr. No.	Atom	δ cal.	δ Exp.
1	36H	7.2903	8.3528	22	2C	134.4523	130.7554
2	16H	7.2712	7.7178	23	26C	127.9134	129.6918
3	29H	7.2196	7.5639	24	6C	127.7587	129.6473
4	9H	7.2151	7.5555	25	21C	126.3882	128.5650
5	27H	7.0178	7.5495	26	1C	126.0806	125.7649
6	7H	6.9983	7.5370	27	35C	123.3546	123.1148
7	28H	6.9863	7.5245	28	15C	123.2052	123.1148
8	8H	6.9616	7.5141	29	25C	122.9066	77.3179
9	33H	6.9571	7.5003	30	5C	122.5987	77.3179
10	13H	6.9418	7.4932	31	23C	121.4975	77.0000
11	32H	6.9271	7.4867	32	3C	121.4645	77.0000
12	39H	6.9089	7.2599	33	24C	112.7304	76.6824
13	12H	6.8834	6.5471	34	4C	112.476	76.6824
14	19H	6.7242	6.5726	35	37N	277.1146	--
15	34C	171.9752	182.83	36	17N	274.9659	--
16	14C	170.7577	147.86	37	40-O	268.1979	--
17	30C	137.373	--	38	20-O	266.3975	--
18	31C	137.0605	--	39	38-O	161.5988	--
19	10C	136.7541	--	40	18-O	158.5886	--
20	11C	136.6087	144.82	41	41Zn	-150.402	--
21	22C	134.492	131.00				

5. Mercury 1-oximate

In the case of Hg-1-oximate, after coordination, oxime protons H_{19} and H_{39} shows chemical shifts at lower fields at 9.2837 |& 9.2641 as against predicted shifts at 7.8704. Protons nearer to oxime protons H_{12} and H_{32} shows shifts at 8.3334 & 7.7177 as against calculated value at 7.4442. Other protons chemical shifts are comparable to calculated values (See Table-5).

^{13}C NMR spectra shows C=O carbon chemical shift higher fields at 147.8653& 182.8446 for C_{34} and C_{14}, while calculated values indicate still lower fields at 193.6606. Chemical shift of N_{37} and N_{17} is predicted as 14.3338 & 14.3339, for oxygen predicted shifts are at 424.1048, &163.2626 as doublates for O_{40}, O_{38}, O_{20} and O_{18}. The chemical shift for Hg_{41} metal is predicted at 171.4929 ppm.

Table: 5 Chemical shifts of NMR of Hg 1-oximate in $CDCl_3$

Sr. No.	Atom	δ cal.	δ Exp.	Sr. No.	Atom	δ cal.	δ Exp.
1	19H	7.8704	9.2837	22	25C	127.2655	130.7720
2	39H	7.8704	9.2641	23	3C	126.9309	129.6951
3	12H	7.4442	8.3334	24	23C	126.9309	129.6951
4	32H	7.4442	7.7177	25	6C	126.779	129.6529
5	16H	7.3756	7.6932	26	26C	126.7789	129.6529
6	36H	7.3756	7.5639	27	4C	125.3698	128.5765
7	9H	7.3252	7.5558	28	24C	125.3698	128.5765
8	29H	7.3252	7.5493	29	1C	125.1591	125.7785
9	8H	6.9985	7.5443	30	21C	125.1591	125.7785
10	28H	6.9985	7.4933	31	15C	124.3378	123.1316
11	13H	6.9403	7.4871	32	35C	124.3378	123.1316
12	33H	6.9403	7.2599	33	11C	114.2511	77.3177
13	7H	6.8458	6.5970	34	31C	114.2511	76.6822
14	27H	6.8458	6.5725	35	17N	14.3339	--
15	14C	193.6606	182.8446	36	37N	14.3338	--
16	34C	193.6606	147.8653	37	20-O	424.1048	--
17	2C	136.4994	147.8653	38	40-O	424.1048	--
18	22C	136.4993	144.8364	39	18-O	163.2627	--
19	10C	130.8818	131.0184	40	38-O	163.2626	--
20	30C	130.8818	131.0184	41	41Hg	171.4929	--
21	5C	127.2655	130.7720				

Fig. 2 shows symbol and numbering of atoms in a molecules where Hg can be replaced by metal atoms such as Pb, Zn and Cd which is considered for theoretical calculations.

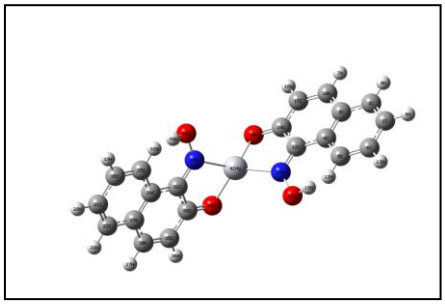

Fig. 2 Molecular structure of metal chelate

IV. Conclusions

The calculated NMR chemical shifts of proton ^{13}carbon, nitrogen, oxygen and metal i.e. Ag, Cd, Pb, Zn and Hg were computed and chemical shifts of proton and of ^{13}carbon were 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.

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