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Theoretical calculations of chemical shifts of metal chelates of 1, 2 naphthoquinone dioxime

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ABSTRACT

Theoretical calculations of chemical shifts of NMR 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 $M = Ag, Hg, Cd, Zn$ and Pb , and $NQO = 1, 2$ naphthoquinone dioxime have been synthesized. Chemical shifts of proton and 13 Carbon were determined and compared with computed chemical shifts.

Key words: 1-2 Naphthoquinone dioxime, NMR, Metal chelates

INTRODUCTION

Our nuclear magnetic resonance studies on 1,2-naphthoquinone-1 oxime (1) and the metal chelates formed by them (2), 1,2-naphthoquinone-2 oxime (3) and the metal chelates formed by them (4), have led us to investigate the vicinal dioxime compounds derived from 1,2-naphthoquinone. It is well known that the complex or chelate formation ability of the $-C(=NOH) - C(=NOH) -$ group is greatly influenced by the arrangement of the two oxime groups. The dioxime chelates are biologically active. (5). The role of complexes of vicinal dioximes in coordination chemistry has been studied (6, 7). The substitution pattern of vicinal dioxime moiety affects the structure and stability of the complexes (8-10). Transition metal chelates with ligands containing oxime group have attracted much attention as they exhibit excellent coordination ability and reactivity. The presence of mildly acidic hydroxyl groups and slightly basic nitrogen atom makes dioximes amphoteric ligands which form square planar and octahedral chelates with metal ion as the central atom (11). 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 metal (Hg (II), BP (II), Ag (I), Zn (II) and Cd (II)) chelates of 1, 2 naphthoquinone dioxime and the data is compared with experimental data.

MATERIALS AND METHODS

Synthesis of 1-2 naphthoquinone dioxime was carried as per the reported method (12) which was recrystallized using methanol and dried in vacuum. A stock solution of Hg (II), Pb (II), Ag (II), Zn (II) and Cd (II) was prepared by using AR grade chemicals and deionised water.

2.1 Preparation of metal chelates.

The chelates were prepared by mixing metal salt solution and ligand solution 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. Warmed the mixture 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 Varian. 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 (13, 14). 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.

RESULTS AND DISCUSSION

The NMR chemical shifts of proton and carbon 13 of 1-2 naphthoquinone dioxime were reported (15). The oxime proton of C10 and C9 i.e. H7, H8 have predicted chemical shift at 8.47 and 8.53 ppm but the observed values were at down field indicates at 13.28 and 13.62 ppm. The chemical shifts of H1 to H6 which were attached to naphthalene skeleton were observed in good agreement to the calculated data and in the range of ± 0.5 ppm. The chemical shifts of ^{13}C NMR of vicinal dioxime i.e. 1-2 naphthoquinone dioxime were given for predicted and observed δ ppm values. The chemical shift of C9 and G10 were calculated as 137.3 and 135.5 ppm but the observed values of δ ppm were downfield at 145.2 and 136.37 ppm. Here C9 and G10 is a cause of $\text{C}=\text{N}$ bonding of oxime group which is a most indicative of the quinonide structure. The chemical shifts of C1 to C8 are observed higher i.e. lower field by a range of ± 10 -15 ppm as compared to calculated data. The DEPT data of ^{13}C was also given. It gave an anti form of vicinal dioxime.

Table: 1 Chemical shifts of NMR of Ag dioximate in CDCl_3

Sr. No.	Atom	$\delta_{\text{cal.}}$	$\delta_{\text{cal.Exp.}}$
1	7H	8.09	8.77
2	12H	8.09	8.75
3	16H	7.93	7.87
4	8H	7.50	7.17
5	9H	7.27	7.02
6	13H	7.14	6.87
7	10C	144.02	140.62
8	14C	140.75	133.94
9	11C	138.58	129.68
10	5C	137.54	129.31
11	15C	136.52	128.79
12	1C	136.19	122.47
13	3C	129.47	114.00
14	6C	128.12	40.12
15	2C	126.61	39.70
16	4C	120.65	38.87
17	17N	1112.39	--
18	18N	1058.33	--
19	20O	1118.79	--
20	19O	962.83	--
21	Ag	200.85	--

Silver dioximate ($\text{C}_{20}\text{H}_{16}\text{AgN}_4\text{O}_4$)

Table: 1 shows chemical shifts of NMR of Ag dioximate in CDCl_3 . The chemical shifts of C_{14} and C_{11} are predicted at 140.75 ppm and 138.58 ppm while the experimental chemical shifts are observed at 133.94 and 129.68 ppm respectively. In this, both the carbon atoms are involved bonding with nitrogen. The calculated chemical shifts of nitrogen are at 1112.39 and 1058.33 ppm which are nearly equal. It shows the formation of Ag^{2+} ion. We have calculated NMR chemical shifts considering O-Ag-O bonding i.e. seven member ring. The oxime proton is absent in

calculated and experimental data. The chemical shifts of other proton nuclei are in good agreement with calculated values. The chemical shifts of C₃-C₁₀ are predicted within a range 5 – 10 ppm which is in good agreement with experimental data. Fig. 1 shows structure of silver dioximate.

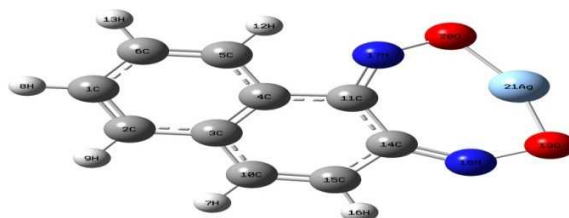


Fig.1 MOLECULAR STRUCTURE OF SILVER DIOXIMATE

2. Cadmium dioximate (C₂₀H₁₆CdN₄O₄)

In the case of Cd-dioximate, after coordination, it is observed that deprotonation is not taking place. Oxime protons H₄₂, H₄₃, H₂₀ and H₄₄ shows chemical shifts at higher fields at 3.32, 2.50, 2.49 and 1.21 ppm as against predicted shifts at 4.317, 3.207, 1.087 and 0.8071 ppm. Only one proton is observed at 14.32 ppm while the predicted proton is at 13.670 ppm. Other protons chemical shifts are comparable to calculated values (See Table-2).

¹³C NMR spectra shows C=N carbon chemical shift lower fields at 146.31, 141.26, 135.83 and 135.43 ppm 145.0546 for C₃₅, C₃₂, C₁₁ and C₁₄, while calculated values indicate still lower fields at 159.69, 153.86, 150.476 and 148.601 ppm. Remaining chemical shifts of carbon atoms are comparable to calculated values. Complex is made up of six member ring. Chemical shift of N₃₈, N₁₈, N₃₉ and N₁₇ is predicted as 458.76, 350.009, 298.042 and 219.607 ppm, for oxygen predicted shifts are at 170.47, 136.165, 85.82 and 32.814 ppm for O₄₁, O₁₉, O₄₀ and O₂₁. The chemical shift for cadmium metal is predicted at 231.084 ppm.

Table: 2 Chemical shifts of NMR of Cd dioximate in CDCl₃

Sr. No.	Atom	δ cal.	δ Exp.	Sr. No.	Atom	δ cal.	δ Exp.
1	12H	13.67	14.32	24	26C	129.32	129.65
2	33H	8.70	9.13	25	2C	128.73	129.29
3	37H	7.67	9.11	26	23C	128.00	128.96
4	29H	7.19	8.09	27	27C	127.56	128.56
5	28H	7.06	7.40	28	1C	125.32	128.05
6	34H	6.93	7.17	29	10C	124.76	126.94
7	30H	6.92	7.10	30	24C	124.47	126.58
8	16H	6.78	7.07	31	6C	124.07	126.35
9	9H	6.71	6.98	32	36C	118.04	121.35
10	7H	6.56	6.88	33	15C	117.97	114.01
11	8H	6.51	6.85	34	3C	115.88	113.84
12	13H	6.45	6.63	35	4C	114.67	113.46
13	42H	4.31	3.32	36	25C	113.99	112.95
14	43H	3.20	2.50	37	38N	458.76	--
15	20H	1.08	2.49	38	18N	350.00	--
16	44H	0.80	1.21	39	39N	298.04	--
17	35C	159.69	146.31	40	17N	219.60	--
18	32C	159.86	141.26	41	41O	170.47	--
19	11C	150.47	135.85	42	19O	136.16	--
20	14C	148.60	135.43	43	40O	85.82	--
21	31C	135.21	133.89	44	21O	32.814	--
22	5C	132.08	133.89	45	45Cd	231.08	--
23	22C	131.97	130.75	--	--	--	--

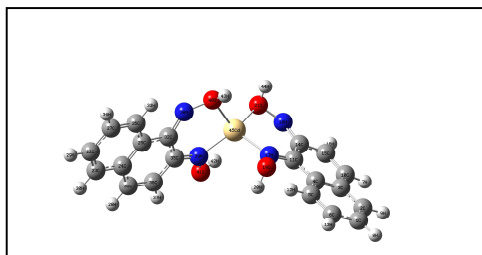


Fig.2 MOLECULAR STRUCTURE OF CADMIUM DIOXIMATE

3. Lead dioximate (C₂₀H₁₆PbN₄O₄)

Table-3 shows chemical shifts of Pb dioximate, In the case of Pb-dioximate, after coordination, it is observed that deprotonation is not taking place. Oxime protons H₄₃, H₄₂, H₂₀ and H₄₄ shows chemical shifts at higher fields at 7.49, 7.04, 0.79 and 0.77 ppm as against predicted shifts at 6.84, 6.71, 1.42 and 0.18 ppm respectively. Only one proton is observed at 14.32 pp while the predicted proton is at 15.46 ppm. Other protons chemical shifts are comparable to calculated values (See Table-2).

¹³C NMR spectra shows C=N carbon chemical shift lower fields at 147.94, 140.61, 134.32 and 130.25 ppm for C₃₂, C₃₅, C₁₄ and C₁₁ while calculated values indicate still lower fields at 153.65, 147.57, 144.08 and 130.30 ppm. Remaining chemical shifts of carbon atoms are comparable to calculated values. Complex is made up of six member ring. Chemical shift of N₃₉, N₃₈, N₁₇ and N₁₈ is predicted as 530.87, 455.88, 380.21 and 256.25 ppm. for oxygen predicted shifts are at 277.91, 197.72, 158.65 and 117.32 ppm for O₄₀, O₄₁, O₁₉ and O₂₁. The chemical shift for cadmium metal is predicted at 13.59 ppm.

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

Sr. No.	Atom	δ cal.	δ Exp.	Sr. No.	Atom	δ cal.	δ Exp.
1	12H	15.46	14.32	24	27C	129.94	129.69
2	33H	8.98	12.94	25	23C	128.70	129.29
3	37H	7.63	8.67	26	2C	128.52	129.22
4	16H	7.32	8.11	27	26C	127.91	128.77
5	29H	7.29	7.97	28	10C	124.09	128.77
6	28H	7.18	7.87	29	6C	124.07	128.55
7	34H	7.17	7.42	30	1C	123.65	126.78
8	30H	6.90	7.37	31	24C	123.28	122.95
9	43H	6.84	7.19	32	15C	123.22	115.47
10	9H	6.71	7.17	33	25C	117.79	114.01
11	42H	6.71	7.04	34	4C	117.05	113.21
12	7H	6.67	6.95	35	3C	115.60	113.06
13	8H	6.38	6.90	36	36C	114.95	112.65
14	13H	6.35	6.68	37	39N	530.87	--
15	20H	1.42	0.79	38	38N	455.88	--
16	44H	0.18	0.77	39	17N	380.21	--
17	32C	153.65	147.94	40	18N	256.25	--
18	25C	147.57	140.61	41	40O	277.91	--
19	14C	144.08	134.32	42	41O	197.72	--
20	31C	139.18	134.32	43	19O	158.65	--
21	22C	134.11	133.89	44	21O	117.32	--
22	5C	133.54	133.89	45	45Pb	13.59	--
23	11C	130.30	130.25	--	--	--	--

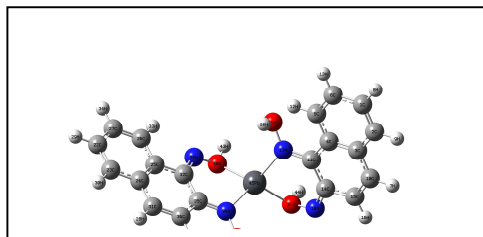


Fig.3 MOLECULAR STRUCTURE OF LEAD DIOXIMATE

4. Zinc dioximate (C₂₀H₁₆ZnN₄O₄)

Table-4 shows chemical shifts of Zn dioximate, after coordination, it is observed that deprotonation is not taking place. Oxime protons H₄₂, H₄₃, H₄₄ and H₂₀ shows chemical shifts at higher fields at 8.86, 7.51, 3.36 and 2.49 ppm as against predicted shifts at 8.89, 7.40, 0.74 and 0.51 ppm respectively. Only one proton is observed at 11.94 ppm while the predicted proton is at 11.50 ppm. Other protons chemical shifts are comparable to calculated values.

¹³C NMR spectra shows C=N carbon chemical shift lower fields at 140.66, 130.30, 129.36 and 113.97 ppm for C₃₅, C₃₂, C₁₄ and C₁₁ 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 N₃₉, N₃₈, N₁₈ and N₁₇ 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 O₄₁, O₄₀, O₁₉ and O₂₁. The chemical shift for zinc metal is predicted at -236.18 ppm.

Table: 4 Chemical shifts of NMR of Zn dioximate in CDCl₃

Sr. No.	Atom	δ cal.	δ Exp.	Sr. No.	Atom	δ cal.	δ Exp.
1	12H	11.50	11.94	24	26C	130.20	128.94
2	42H	8.89	8.86	25	23C	128.28	123.00
3	33H	8.66	8.64	26	36C	127.57	114.06
4	28H	7.54	8.13	27	5C	127.56	40.12
5	29H	7.46	7.70	28	24C	124.04	39.91
6	43H	7.40	7.51	29	6C	121.57	39.70
7	34H	7.27	7.50	30	10C	118.91	39.50
8	30H	6.95	7.49	31	4C	118.38	39.29
9	37H	6.77	7.42	32	25C	117.70	39.08
10	9H	6.74	7.40	33	1C	116.16	38.87
11	16H	6.45	7.22	34	3C	114.88	38.56
12	7H	6.32	7.17	35	15C	114.42	38.24
13	13H	6.04	7.06	36	11C	113.97	36.51
14	8H	6.00	6.68	37	39N	531.64	--
15	44H	0.74	3.36	38	38N	470.35	--
16	20H	0.51	2.49	39	18N	247.06	--
17	35C	159.89	140.66	40	17N	97.15	--
18	31C	145.79	133.95	41	41O	175.26	--
19	32C	143.27	130.30	42	40O	144.85	--
20	22C	136.84	129.73	43	19O	113.28	--
21	14C	135.04	129.36	44	21O	10.13	--
22	27C	131.45	129.28	45	45Zn	-236.18	--
23	2C	131.22	128.84	--	--	--	--

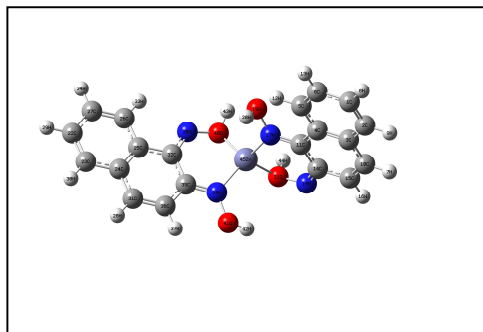


Fig.4 MOLECULAR STRUCTURE OF ZINC DIOXIMATE

5. Mercury dioximate (C₂₀H₁₆HgN₄O₄)

Table-5 shows chemical shifts of Hg-dioximate, after coordination, it is observed that deprotonation is not taking place. Oxime protons H₄₂, H₄₃, H₂₀ and H₄₄ shows chemical shifts at higher fields at 3.31, 3.31, 2.50 and 2.49 ppm as against predicted shifts at 4.88, 4.35, 1.68 and -0.079 ppm respectively. Only one proton is observed at 14.31 ppm while the predicted proton is at 14.905 ppm. Other protons chemical shifts are comparable to calculated values.

¹³C NMR spectra shows C=N carbon chemical shift lower fields at 147.99, 140.62, 133.24 and 129.68 ppm for C₃₅, C₃₂, C₁₁ and C₁₄ while calculated values indicate still lower fields at 163.34, 154.85, 149.26 and 144.85 ppm. Remaining chemical shifts of carbon atoms are comparable to calculated values. Complex is made up of six member ring. Chemical shift of N₃₈, N₁₈, N₃₉ and N₁₇ is predicted as 487.63, 356.16, 313.17 and 200.55 ppm. for oxygen predicted shifts are at 169.82, 163.41, 111.70 and 23.23 ppm for O₄₁, O₁₉, O₄₀ and O₂₁. The chemical shift for mercury metal is predicted at 200.91 ppm.

Table: 5 Chemical shifts of NMR of Hg dioximate in CDCl₃

Sr. No.	Atom	δ cal.	δ Exp.	Sr. No.	Atom	δ cal.	δ Exp.
1	12H	14.90	14.31	24	2C	129.38	113.98
2	33H	8.75	8.67	25	27C	129.18	113.98
3	37H	7.85	8.15	26	26C	128.92	40.12
4	29H	7.22	8.12	27	23C	128.66	39.91
5	34H	7.07	7.72	28	1C	124.72	39.70
6	28H	6.97	7.60	29	6C	124.01	39.50
7	30H	6.93	7.40	30	10C	122.82	39.50
8	9H	6.81	7.38	31	24C	122.41	39.29
9	16H	6.75	7.11	32	15C	118.64	39.08
10	7H	6.55	7.09	33	4C	115.98	38.87
11	8H	6.52	6.98	34	3C	115.42	38.75
12	13H	6.47	6.88	35	36C	114.68	38.12
13	42H	4.88	3.31	36	25C	113.52	37.95
14	43H	4.35	3.31	37	38N	487.63	--
15	20H	1.68	2.50	38	18N	356.16	--
16	44H	-0.07	2.49	39	39N	313.17	--
17	35C	163.34	147.99	40	17N	200.55	--
18	32C	154.85	140.60	41	41O	169.72	--
19	11C	149.26	133.24	42	19O	163.41	--
20	14C	144.84	129.68	43	40O	111.70	--
21	31C	136.56	129.30	44	21O	23.239	--
22	22	22C	133.40	45	Hg	200.91	--
23	23	5C	132.25	--	--	--	--

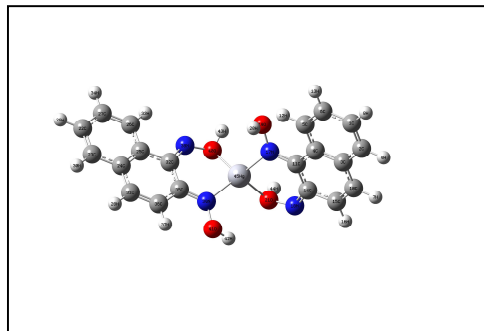


Fig.5 MOLECULAR STRUCTURE OF MERCURY DIOXIMATE

CONCLUSION

It is observed that silver chelate is made up of seven atom ring and the valence of silver is two. The chelates of cadmium, lead, zinc and mercury with 1-2 naphthoquinone dioxime are formed with six member ring and deprotonation is not taking place which is confirmed the chemical shifts calculated and experimental values. The predicted chemical shifts of nitrogen, oxygen and metal atoms are good in agreement. 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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