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On the vibrational spectrum of thorium chelate of 1, 2-naphthoquinone, 2-oxime

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Abstract: The vibrational spectrum of thorium chelate of 1,2-naphthoquinone, 2-oxime was recorded and analyzed. The vibrational wavenumbers have been calculated using Gaussian 09 software code, employing RHF / SDD basis set and compared with experimental values. The fundamental modes are assigned by using animation software. The predicted infrared intensities and Raman activities are reported. The calculated frequencies are in good agreement with the experimental values. The calculated geometrical parameters are also given. The study is extended to calculate the HOMO-LUMO energy gap, Ionization potential (I), Electron affinity (A), Global hardness (η), chemical potential (μ) and global electrophilicity (ω). The calculated HOMO-LUMO energies show the charge transfer occurs in the molecule. Optimized geometrical parameters of the title compound are in agreement with similar reported structures.

Keywords: 1-2 naphthoquinone, 2-oxime, IR, HF, Energy gap, Thoriummonoximate

I. INTRODUCTION

The chemistry of coordination compounds has shown a rapid development in diverse disciplines as a result of the possible use of these new compounds in biological applications. Rare earth metal complexes with potential biological activity are the focus of extensive investigations.

Oximes have often been used as chelating ligands in the field of coordination chemistry and their metal complexes have been of great interest for many years. Oxime metal chelates are biologically active (1). Quinones and naphthoquinones are widely distributed in nature and play a vital role in certain cellular functions. Owing to the large variety of coordination geometries, coordination numbers, and modes of interactions with their ligands, metal complexes or mostly chelates give access to a different field of pathways in cancer treatment than do organic compounds. The discovery of the anticancer properties of cisplatin was a breakthrough event as far as interest in metal complexes was concerned (2). The structure of 1-2 naphthoquinone 2-oxime is examined by use of the HF (6-31 G* level), density functional theory DFT (6-31 G* level) & hybrid functional B3LYP. Using the optimized structure of the titled compound IR, NMR, and ultraviolet data is calculated and compared with experimental data. It shows good relation between theoretically calculated IR wave numbers & observed values for Mid – Far IR data (3). The polarographic behavior of the 1, 2-naphthoquinone has been investigated in the pH range 3 to 14. All of the compounds produce well defined polarographic reduction waves which can be used for analytical purposes. Polarographic evidence indicates that the monoximes and the dioximes exhibit tautomerism (4). Ab initio, Hartree- Fock and Density Functional Theoretical study of vibrational spectra of zirconium chelate of 1, 2- naphthoquinone-2, oxime have been reported by G. S. Jagtap et.al. (5).

This paper describes synthesis and vibrational spectra of thorium chelate of 1, 2-naphthoquinone 2-oxime calculated by HF basis set, the data is compared with experimental values. Geometrical parameters, Mulliken atomic charges and HOMO – LUMO energy gap of the chelates is reported.

II. Materials and Methods

The ligand 1, 2-naphthoquinone 2-oxime or 2-nitroso 1- naphthol is used as it is supplied by (Fluka, chemicals). A stock solution of thorium nitrate [$\text{Th}(\text{NO}_3)_4$] is prepared by using AR grade chemicals. Deionised water is used during synthesis.

A. Preparation of metal chelates

The chelates were prepared by mixing metal salt solution and ligand in 1: 1 proportion for silver chelate and 1: 2 for other 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 found to be coloured.

B. Instrumental Analysis

Elemental analysis was carried out with a Perkin Elmer 2400 series for C, H, and O & N. The IR spectra are recorded on a Thermo Fischer FTIR spectrophotometer iS5 model in a KBr matrix and in the range of 4000 – 400 cm^{-1} as well as in the range of 1000 – 300 cm^{-1} .

1. Computational details

The entire calculations conducted in the present work were performed at Hartree – Fock (HF/ SDD) basis set in the Gaussian 09 software code. The geometries were first determined at the Hartree – Fock level of employing SDD 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. The absence of imaginary wave number on the calculated Vibrating Spectrum conform that the structure corresponds to minimum energy. HOMO-LUMO energy gap and other related molecular parameters are calculated.

III. Results and Discussion

The infra red frequencies of Th (NQO) 2 are analysed on the basic of the characteristics vibration of hydroxyl, Carbonyl, C=N, N-O and Th-N modes. The computed vibrational wave numbers of IR with intensity are used for identifying modes unambiguously. The harmonics vibrational frequencies calculated for Th (NQO)2 at HF using the SDD basis set have been summarized Table -1. It can be noted that calculated results are harmonics frequencies while the observed contains unharmonic contribution also. The value of the wave number is lower than the former due to anharmonicity. Comparison between the calculated and the observed vibration spectra help us to understand the observed spectral frequency.

Table 1: Wave numbers of Thorium2-oximate by HF

SR.NO	frequency	INT.	Raman Activity	EXP CM ⁻¹	INT.	Assignment
1.	67.80683	10.825	6.2689	--	--	O-H Bending
2.	81.82536	8.78	2.48	--	--	O-H Bending
3.	111.4875	21.394	2.165	--	--	O-H Bending
4.	121.5683	6.628	1.321	--	--	N-O bending
5.	136.319	8.104	4.842	--	--	N-O bending
6.	146.5606	15.837	6.989	--	--	Th-O bending
7.	184.6249	45.841	1.052	--	--	Th-N bending
8.	189.2859	11.513	11.413	--	--	N-O bending
9.	194.3933	13.47	10.451	--	--	C-H Bending o.p.
10.	199.3042	55.143	14.413	--	--	Th-N stretching
11.	215.8764	28.597	44.604	--	--	Th-O stretching
12.	226.493	0.094	13.359	--	--	N-O Bending
13.	247.7976	35.71	1.871	--	--	O-H Bending.
14.	324.6852	86.083	7.906	--	--	Th-O Stretching
15.	332.6767	127.643	8.608	--	--	C-O Stretching
16.	347.2131	66.068	14.922	--	--	Th-O Stretching
17.	352.5794	66.41	7.739	352.23	36.2	O-H Bending.
18.	369.1159	26.482	15.653	--	--	C=N Bending.
19.	405.3052	11.466	5.069	396.47	32.0	C-H Bending o.p.
20.	407.7606	5.829	3.902	423.79	31.1	C-H Bending o.p.
21.	486.7376	86.966	1.344	484.6	57.24	Th-N bending
22.	492.0058	12.155	2.389	490.1	61.85	Th-N bending
23.	500.8812	18.324	10.898	--	--	Th-N bending
24.	505.1225	38.66	20.032	501.7	79.26	C-O Stretching
25.	511.2656	68.922	4.284	--	--	C-O Stretching
26.	517.5784	10.516	100.058	517.3	79.26	Th-O Stretching
27.	557.0625	15.143	7.393	--	--	C-H Bending o.p.
28.	558.5	20.738	12.644	561.2	96.03	C-H Bending o.p.
29.	582.7423	10.449	7.72	589.8	93.92	C=O Stretching
30.	638.8967	0.911	3.417	623.9	91.33	C=O Stretching
31.	640.12	9.068	2.397	640.3	20.75	C-H Bending I.p.
32.	663.8622	9.401	0.957	669.0	93.91	C-H Bending I.p.
33.	668.4071	6.824	0.558	674.1	97.56	C-H Bending o.p.
34.	725.6598	16.97	17.714	721.5	75.08	C-H Bending o.p.
35.	726.6867	6.259	74.399	731.6	88.32	C-O Stretching
36.	766.9475	15.583	1.55	758.1	31.51	C-H Bending I.p.
37.	769.2244	38.421	0.669	--	--	C-H Bending o.p.
38.	785.0645	105.239	29.985	787.5	74.39	C-H Bending o.p.
39.	792.8327	17.333	11.362	796.75	35.5	C-H Bending o.p.
40.	797.8062	16.334	6.289	797.2	98.08	C=N bending
41.	798.5651	20.751	16.412	--	--	M-N Stretching
42.	821.5751	132.821	3.97	817.61	31.3	C-H Bending o.p.
43.	841.7725	107.092	4.872	841.3	25.63	C-H Bending o.p.
44.	877.81	1.202	3.621	--	--	C-H Bending o.p.
45.	878.9529	1.234	3.032	--	--	C-H Bending I.p.
46.	898.1681	0.478	2.681	--	--	C-H Bending I.p.
47.	899.5342	3.82	3.726	913.8	98.64	C-H Bending o.p.
48.	960.1889	141.806	11.721	959.43	45.8	C-H Bending o.p.
49.	964.9838	64.062	14.921	--	--	C-H Bending I.p.
50.	971.7877	0.462	6.825	971.2	60.68	C-H Bending I.p.
51.	991.0654	0.694	6.547	981.8	58.72	C-H Bending o.p.
52.	1012.808	2.554	2.547	1004.2	82.25	C-H Bending o.p.
53.	1013.272	2.405	2.467	--	--	C-H Bending o.p.
54.	1033.166	4.223	17.038	1032.9	62.54	C-H Bending o.p.
55.	1033.362	1.538	31.235	--	--	C-H Bending I.p.
56.	1034.585	1.552	14.801	--	--	C-H Bending I.p.

57.	1035.389	1.163	7.909	--	--	C-H Bending I.p.
58.	1100.49	25.903	49.219	1104.7	67.95	C-H Bending I.p.
59.	1131.304	223.026	24.857	1137.6	32.85	C-H Bending I.p.
60.	1133.42	29.112	170.39	1143.5	39.43	C-H Bending I.p.
61.	1156.109	5.057	19.749	1154.0	17.75	C-H Bending i.p.
62.	1162.547	27.634	83.982	1165.0	33.71	C=C Stretching
63.	1180.905	70.203	52.194	1173.4	25.65	C-H Bending i.p.
64.	1187.218	67.336	154.103	1192.2	56.95	N-O Stretching
65.	1198.066	38.87	6.991	--	--	N-O Stretching
66.	1203.611	10.125	19.08	--	--	N-O Stretching
67.	1257.864	1.675	21.944	1253.0	43.52	C-H Bending I.p.
68.	1261.812	6.328	90.534	1260.8	36.21	C-H Bending I.p.
69.	1272.891	29.727	111.024	1260.8	36.21	C-H Bending I.p.
70.	1278.419	40.738	98.764	1275.5	56.41	C=O Stretching
71.	1305.188	78.743	115.934	--	--	C=O Stretching
72.	1307.92	39.167	330.368	1309.9	19.42	C=C Stretching
73.	1341.975	69.229	99.288	1344.	15.24	C-H Bending I.p.
74.	1391.067	78.001	51.945	1391.4	16.84	C=O Stretching
75.	1430.685	6.753	10.745	1404.1	11.91	O-H Bending
76.	1435.355	76.803	1.397	--	--	O-H Bending
77.	1436.355	23.381	11.461	1445.6	51.59	N-O Stretching
78.	1442.275	35.525	25.138	1455.4	37.81	C-H Bending i.p.
79.	1475.419	135.981	696.556	1468.9	47.43	C-H Bending i.p.
80.	1478.839	53.043	1548.536	1478.0	28.71	C-H Bending i.p.
81.	1492.643	92.652	73.442	--	--	C=O Stretching
82.	1495.268	15.533	84.316	1503.6	54.87	C=C Stretching
83.	1564.718	189.308	190.443	1557.8	6.86	C=C Stretching
84.	1569.924	99.466	551.659	--	--	C=O Stretching
85.	1580.299	123.287	91.273	--	--	C=O Stretching
86.	1581.978	15.93	433.081	1581.1	33.60	C=O Stretching
87.	1646.293	322.878	443.63	1650.4	57.44	C=O Stretching
88.	1651.535	114.279	1620.977	1654.0	83.49	C-N Stretching
89.	1681.402	19.869	33.41	1681.6	89.82	C-H Stretching
90.	1681.768	10.873	48.946	1684.3	84.21	C=N Stretching
91.	1701.287	47.155	553.238	1693.8	93.74	C=N Stretching
92.	1704.626	108.002	245.4	1700.2	88.56	C-C Stretching
93.	3029.047	13.581	53.393	--	--	C-H Stretching
94.	3029.253	1.486	33.382	--	--	C-H Stretching
95.	3030.333	6.573	13.986	--	--	C-H Stretching
96.	3035.985	6.071	18.132	--	--	C-H Stretching
97.	3041.467	13.47	118.585	--	--	C-H Stretching
98.	3041.592	11.553	102.638	--	--	C-H Stretching
99.	3053.191	23.159	87.459	--	--	C-H Stretching
100.	3054.798	34.855	76.165	--	--	C-H Stretching
101.	3056.147	64.075	92.974	--	--	C-H Stretching
102.	3058.941	47.115	97.87	--	--	C-H Stretching
103.	3066.531	46.819	194.449	--	--	C-H Stretching
104.	3066.808	50.03	359.222	--	--	C-H Stretching
105.	3517.579	21.224	197.9	3547.3	46.13	O-H Stretching
106.	3522.919	19.304	175.232	3561.8	50.94	O-H Stretching

O-H vibrations

The hydroxyl OH group provides four normal vibrations, ν OH, δ OH and γ OH, of which not only the stretching vibration but also the out-of-plane deformation is good group vibrations (8).HF level calculations give the ν OH mode at 3517.579 and 3522.919 cm^{-1} . We observed these values at 3547.3and 3561.8 cm^{-1} . The moderate to strong absorption at $1350 \pm 40 \text{ cm}^{-1}$ in the spectrum of phenol is assigned to δ OH mode (9). In the FTIR spectrum of title compound, the vibration at 1404.1 is observed for δ OH mode. This band is predicted by HF at1430.685 and 1435.355 cm^{-1} . The γ OH mode is observed in the FTIR spectrum at 352.23 cm^{-1} . The vibration for γ OH are predicted by HF at 352.5794 cm^{-1} .

C-H vibration

The Naphthalene structure shows the presence of structural vibration in the region 3250-2950 cm^{-1} which is characteristics for the zero identification of C-H stretching vibration .The region 3250-3100 cm^{-1} is for symmetric stretching. and 3100-2950 cm^{-1} for are asymmetric stretching modes of vibration.(10). For most cases, the naphtholic C-H vibration absorption bands are usually weak and it is too weak for detection. In the present work, for the Th(NQO)₂ the FTIR band is observed at 3241.64, 3058.7 and 3136.7 cm^{-1} have been assigned to C-H stretching vibration. The HF level predicted absorption at3066.808, 3066.531, 3058.941, 3056.147, 3054.798, 3053.191, 3041.592, 3041.467, 3035.985, 3030.333, 3029.253 and 3029.047 cm^{-1} .

The title compound has both C-H out of plane and in plane bending vibration. The out of plane bending mode of C-H vibration of $\text{Th}(\text{NQO})_2$ is predicted at 405-558, 769-877 and 849-1033 cm^{-1} and in experimental values found at 396-561, 787-841 and 913-1032 cm^{-1} . These frequencies are well in agreement with the experimental and predicted data. HF level and SDD basis shows this region which gives number of vibration and are comparable with experimental results as shown in Fig 1. In plane bending vibration, the regions are predicted at 640-766, 1033-1156 and 1257-1478 in the region 1095-617 cm^{-1} and 562-254 cm^{-1} which are comparable with the experimental recorded data at 640-758, 1104-1173 and 1253-1478 in the region 1095-617 cm^{-1} and 562-254 cm^{-1} .

C=N Vibrations.

The stretching frequency of C=N bond is observed at 1700.2 and 1693.8 cm^{-1} in the FTIR spectra of $\text{Th}(\text{NQO})_2$ while these are predicted by HF/ SDD at 1701.287 and 1681.768 cm^{-1} . The bending frequency of C=N is found in the FTIR spectrum at 797.2 cm^{-1} while HF / SDD predicted at 797.8062 and 369.1159 cm^{-1} . The $\nu(\text{C}=\text{N})$ in chelates shows lower frequency owing to elongation of these bonds on co-ordination.

N-O Bending Vibration. The observation of $\gamma(\text{N}-\text{O})$ wave number is not observed in the FTIR spectrum. HF/SDD level predicted IR frequencies at 226.493, 189.2859, 136.319 and 121.5683 cm^{-1} . The absorption of this $\gamma(\text{N}-\text{O})$ at higher wave number indicates that this bond is significantly shorter in the chelates. The higher wave length of the N-O indicates that nitrosoatoms of the oxime group coordinate to the centre (11,12).

N-O Stretching Vibration. The observation of (N-O) stretching vibration is found at 1192.2 cm^{-1} while HF/SDD level predicted IR frequencies at 1187.218, 1198.066 and 1203.611 cm^{-1} .

Th-N Stretching. The frequencies of Th-N stretching are not observed in the FTIR spectrum but the predicted IR values are at 199.304 cm^{-1} by HF level.

Th-N bending vibration

The IR absorption frequencies of Th- N bending are predicted at 184.624, 486.737, 492.005 and 500.851 cm^{-1} with HF level. Experimental values are recorded at 484.6 and 490.1 cm^{-1} only. Only later two values are in good agreement.

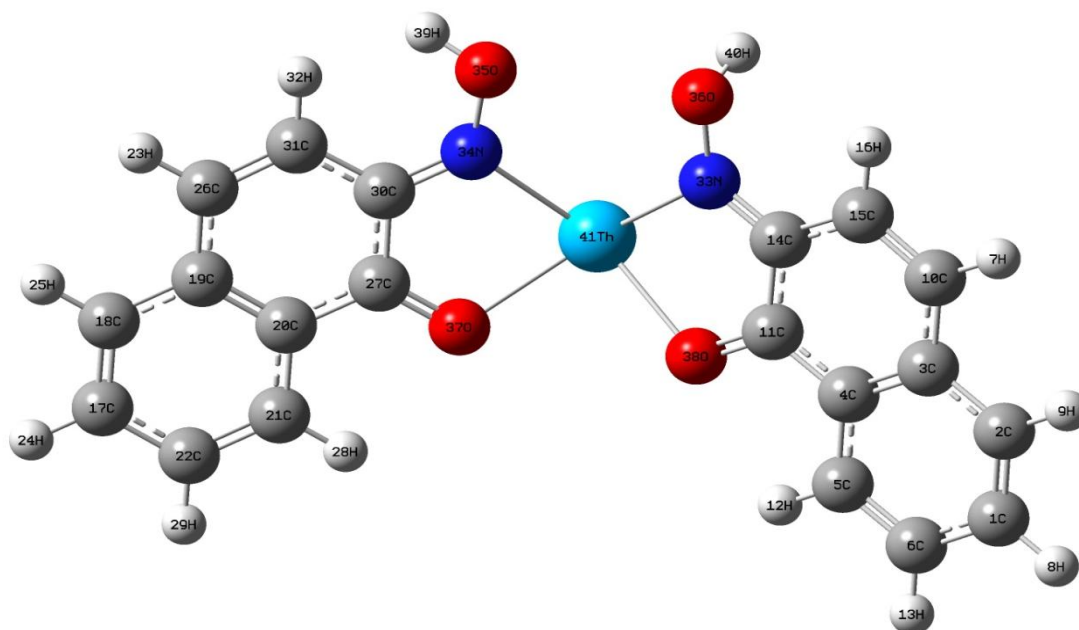


Fig.1 Molecular structure of thorium2-oximate

Molecular geometry.

The optimized structure parameters of $\text{Th}(\text{NQO})_2$ calculated by ab initio, HF/SDD basis set are listed in Table 2 in accordance with the atom numbering scheme given in Fig -1. The values of bond length in $\text{\AA}$, bond angles and dihedral angles in degree are given in Table 2.

Table No:-2 Bond Length and Bond Angle and Dihedral Angle of Th_2 -oximate

Bond length	$\text{\AA}$	Bond angle	($^\circ$)	Dihedral angle	($^\circ$)
Th41-O38	2.272	Th41-O38-C11	113.219	Th41-O38-C11-C4	-170.519
H40-O36	0.96	H40-O36-N33	109.471	H40-O36-N33-C14	90.207
H39-O35	0.96	H39-O35-N34	109.471	H39-O35-N34-C30	-30.207
O38-C11	1.287	O38-C11-C4	120.562	O38-C11-C4-C3	-179.020
O37-C27	1.287	O37-C27-C20	120.562	O37-C27-C20-C19	179.020

O36-N33	1.360	O36-N33-C14	123.708	O36-N33-C14-C11	170.628
O35-N34	1.360	O35-N34-C30	123.708	O35-N34-C30-C27	-170.627
O34-C30	1.305	N34-C30-C27	119.008	N34-C30-C27-C20	-179.940
N33-C14	1.305	N33-C14-C11	119.008	N33-C14-C11-C4	179.939
Th41-N34	2.297	Th41-N34-C30	112.563	Th41-N34-C30-C31	-171.685
H32-C31	1.070	H32-C31-C26	120.111	H32-C31-C26-C19	-179.870
C31-C26	1.358	C31-C26-C19	120.831	C31-C26-C19-C18	-179.826
C30-C27	1.436	C30-C27-C20	118.951	C30-C27-C20-C19	-0.354
H29-C22	1.070	H29-C22-C21	120.001	H29-C22-C21-C20	179.828
H28-C21	1.070	H28-C21-C20	119.986	H28-C21-C20-C19	-179.925
C27-C20	1.398	C27-C20-C19	119.972	C27-C20-C19-C18	179.929
C26-C19	1.408	C26-C19-C18	119.437	C26-C19-C18-C17	-179.897
C2-C1	1.355	C2-C1-C6	120.058	C20-C19-C18-C17	0.062
C3-C2	1.401	C3-C2-C1	120.141	C22-C21-C20-C19	0.082
C4-C3	1.360	C4-C3-C2	119.689	C4-C3-C2-C1	-0.062
C5-C4	1.401	C5-C4-C3	120.094	C5-C4-C3-C2	0.107
H9-C2	1.07	H9-C2-C1	119.929	H9-C2-C1-C6	179.983
C10-C3	1.408	10C-C3-C2	119.437	10C-C3-C2-C1	179.897
C11-C4	1.398	C11-C4-C3	119.972	C11-C4-C3-C2	-179.93
H13-C6	1.070	H13-C6-C5	120.001	H13-C6-C5-C4	-179.988
C15-C10	1.358	C15-C10-C3	120.831	C15-C10-C3-C2	179.827

The CNO angle in typical oximes is relatively constant around 112-113° (13, 14). In the present chelate the C34-N38-O40 angle is opened up by about 10° from the expected value and found constant for all four angles. The naphthalene carbon ring is relatively planar, the largest deviation from the mean plane being 0.023 Å° for the C1 carbon atom. The N and O atoms lie approximately in the naphthalene mean plane. A further interesting finding is that the outside angle C35-C34-N38 [121.27°] is significantly larger than the inside angle C31-C35-N38 [119.41°]. It may be noted that almost the same differences are predicted. It is obvious that the only marked distortions of the geometry and orientation of the present 1,2-oxime groups are associated with the oxime groups on the carbon atom. Fig.2 shows atomic charges of atoms.

Mulliken Atomic Charges

Mulliken charges arise from the Mulliken population analysis (15,16) and provide a means of estimating partial atomic charges from calculations carried out by the methods of computational chemistry, particularly those based on the linear combination of atomic orbitals molecular orbital method, and are routinely used as variables in linear regression QSAR procedures(17).

In the application of quantum mechanical calculation to molecular system, the calculation of effective atomic charges plays an important role. The electron distribution of Th (NQO)₂ is compared in the two different mechanical methods and the sensitivity of the calculated charges to charge in choice of methods is studied. By determining electron population of each atom in the defined basis function, the Mulliken charges are calculated by HF/SDD. The results are presented in Table-3 which the values of atomic charges of each atom of the concerned molecule. Fig. 2 shows Atomic charge against atoms of the said molecule.

Table-3:- Mulliken Atomic Charges of Th (NQO)₂

Sr. No.	Atom	Atomic charge	Sr. No.	Atom	Atomic charge
1	1C	-0.26472	22	22C	-0.25491
2	2C	-0.38572	23	23H	0.214617
3	3C	0.358505	24	24H	0.212747
4	4C	0.209589	25	25H	0.214792
5	5C	-0.35184	26	26C	-0.481580
6	6C	-0.25736	27	27C	0.260265
7	7H	0.213023	28	28H	0.254321
8	8H	0.211189	29	29H	0.211210
9	9H	0.214110	30	30C	0.457239
10	10C	-0.43449	31	31C	-0.444091
11	11C	0.262521	32	32H	0.165906
12	12H	0.251841	33	33N	-0.661854
13	13H	0.209456	34	34N	-0.701957
14	14C	0.365666	35	35O	-0.475932
15	15C	-0.44979	36	36O	-0.487222
16	16H	0.233436	37	37O	-0.752002
17	17C	-0.26527	38	38O	-0.754313
18	18C	-0.38427	39	39H	0.388956
19	19C	0.358408	40	40H	0.401860
20	20C	0.208704	41	41Th	2.280946
21	21C	-0.35195			

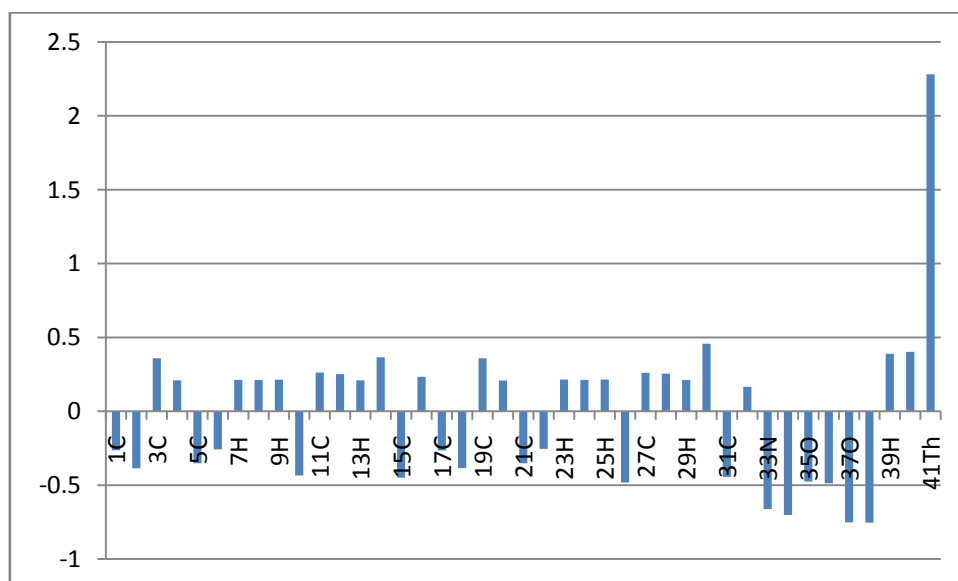


Fig.2 Atomic charge on each atom

HOMO-LUMO energy gap and related molecular properties.

The HOMO-LUMO energy gap of the molecule $\text{Th}(\text{NQO})_2$ in the HF and SDD basis set has been calculated. The HOMO-LUMO energy gap is constant in both methods. It is known that the value of E_{HOMO} is often associated with the electron donating ability of inhibitor molecule, higher values of E_{HOMO} is an indication of the greater ease of donating electrons to the unoccupied d orbital of the receptor. The value of E_{LUMO} is related to the ability of the molecule to accept electrons, lower values of E_{LUMO} shows the receptor would accept electrons. Consequently, the value of E_{gap} provides a measure for the stability of the formed complex on the metal surface. The frame work of SCF MO theory, the ionization energy and electron affinity can be expressed through HOMO and LUMO energies AS $I = -E_{\text{HOMO}}$, $A = -E_{\text{LUMO}}$. The hardness compounds to the gap between the HOMO and LUMO orbital energies. If the gap energy is higher than the Hardness is also larger. The global hardness $\eta = \frac{1}{2} (E_{\text{HOMO}} - E_{\text{LUMO}})$. The hardness is associated with the stability of chemical potential (μ) can be expressed in combination of electron affinity and ionization potential. The global electrophilicity index (ω) is also calculated and listed in table- 4.

Table No: - 4 Comparison of HOMO-LUMO, Energy gap and related Molecular Properties of $\text{Th}(\text{NQO})_2$

Molecular Properties	HF/SDD
HOMO eV	-0.22805
LUMO eV	0.02583
Energy gap	0.20222
Ionisation Potential (I)	0.22805
Electron Affinity(A)	-0.02583
Global Hardness (η)	0.10111
Chemical Potential (μ)	0.10111
Global Electrophilicity (ω)	0.05055

Thermodynamic properties

On the basis of vibrational analysis at B3LYP / SDD and HF / SDD level, several thermodynamic parameters are calculated and are presented in Tabl-5. The zero point vibration energy (ZPVE) and the entropy, $S_{\text{vib}}(T)$ are calculated to the extent of accuracy and the variations in ZPVE seem to be insignificant. The total energy and the change in total entropy of $\text{ZrO}(\text{NQO})_2$ at room temperature at different methods is only marginal.

Table 5 Theoretically computed Energies (a.u.), Zero point Energy (Kcal / mol) Rotational Constants (GHz),Entropy (cal $\text{mlo}^{-1}\text{K}^{-1}$) and Dipole moment D (Kcal. $\text{mlo}^{-1}\text{K}^{-1}$)

Parameter	HF/SDD
Total Energy e.u.	-1579.545
Zero Point Energy	204.307

Rotational constants	0.30855
	0.08456
	0.07204
Entropy Total	128.406
Translational	44.928
Rotational	36.390
vibrational	47.067
Dipole movement (D)	9.7675

IV. Conclusions

The experimental vibration frequencies are compared with HF level calculation 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. The molecular geometry of Th (NQO)₂ is best at the HF/ SDD level. The HOMO- LUMO energy was calculated and other related molecular properties were also discussed. The Mulliken atomic charges were calculated and the results were discussed. Thermodynamic parameters were calculated.

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