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Preparation of Manganese (II) Complexed with 2-hydroxy-1,4-naphthoquinone, Identification of Molecular Structure with the Help the Infrared and Raman Spectra and Theoretical Calculations of Vibration Bands

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ABSTRACT: Manganese(II) complex of 2-hydroxy-1,4-naphthoquinone ($(2HNQ)_2Mn$) (Mn: Manganese) have been prepared for the first time, elemental analysis of this complex prepared was obtained, infrared and Raman spectra were recorded in 4000-30 cm^{-1} range and molecular structure were estimated. However, the experimentally observed vibrational bands and intensity was calculated at HF using the 6-31G (dp) basic function. The obtained experimental and theoretical values were compared one-to-one.

Keywords: Hf, infrared, raman, 2-hydroxy-1,4-naphthoquinone

Mangan(II) ile 2-hydroxy-1,4-naphthoquinone Kompleksinin Hazırlanması, Infrard ve Raman Spektrumları Yardımıyla Moleküler Yapının Aydınlatılması ve Titreşim Bantlarının Teorik Olarak Hesaplaması

ÖZET: 2-hydroxy-1,4-naphthoquinone molekülü ile Mn(II) kompleksi ($(2HNQ)_2Mn$) ilk kez hazırlandı. Hazırlanan bu kompleksin elemental analizleri yapıldı, infrared ve Raman spektrumları 4000-30 cm^{-1} aralığında kaydedildi ve yapısı hakkında tahminde bulunuldu. Yine Deneysel olarak gözlenen titreşim bantları ve şiddetleri, teorik olarak, HF metoduyla 6-31G(dp) temel fonksiyonu kullanılarak hesaplandı. Deneysel ve teorik olarak elde edilen değerler bire-bir karşılaştırıldı.

Anahtar kelimeler: Hf, infrared, raman, 2-hydroxy-1,4-naphthoquinone

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INTRODUCTION

Naphthoquinones which have been widely used in diverse cultures such as colorants for cosmetics, foods, and for medicinal purposes, including antitumor, anti-inflammatory, and antimicrobial agents are largely found in plants, microorganisms and some animals (Thomson, 1971; Masuda et al., 1987; Papageorgiou et al., 1999). It is well-known that the much of the compound where the quinine functionality is present possesses important biological activities, involving mechanism where the reduced species play role as an electron transfer mediator (González et al., 1991; Ferraz et al., 2001). The oxine ligand plays an important role in some biological systems, and its function is related at least in part to its chelating ability with metals (Chabereck and Martell 1959). The detailed crystal data of 2-hydroxy-1,4-naphthoquinone were reported by Dekkers, et al.(1996) and Todkary et al. (2004). Copper complex, structural, spectroscopic and magnetic properties of 2-hydroxy-1,4-naphthoquinone were reported (Salunke-Gawali et al., 2004) and also iron(II) complex and structural properties of 2-hydroxy-1,4-naphthoquinone were studied (Garge et al., 1990). Ab initio and semi empirical study of structure and electronic spectra of hydroxy substituted naphthoquinones were reported by Khan and Khan (2005). The structures and harmonic force fields of 1,4-naphthoquinone and naphthalene were calculated with DFT theory (Nonella 1996). Up to our best literature survey, there is no report on the transition $(2HNQ)_2Mn$ compound of 2-hydroxy-1,4-naphthoquinone and its HF calculation. In the present study, the spectroscopic and structural properties of synthesized $(2HNQ)_2Mn$ complex with 2-hydroxy-1,4-naphthoquinone were reported and furthermore, the infrared and Raman vibrations of $(2HNQ)_2Mn$ complex were calculated with HF

MATERIAL AND METHODS

Experimental

All chemicals were reagent grade and were used without further purification. Manganese Mn(AcO)2 (1 mmol) was dissolved in absolute ethyl alcohol (10 ml). To this, solution (2 mmol) of 2-hydroxy-1,4-naphthoquinone(2HNQ) solution in 25 ml ethanol was added. The mixture was stirred magnetically at room temperature at 2 hours. The precipitated complex was filtered, washed with ether and dried.

The freshly prepared compound was analyzed for C and H by a Leco CHNS-932 and for Mn by a ICPS-OES analyzer (Table 1.) but single crystal of the $(2HNQ)_2Mn$ compound could not be obtained.

Table 1. Analytical data for the compound prepared

Compound	Calculation/Found (%C)	Calculation/Found (%H)	Calculation/Found (% Mn)
$(2HNQ)_2Mn$	57.02 56.03	2.51 2.65	13.65 13.02

Infrared spectra of 2-hydroxy-1,4-naphthoquinone and the compound prepared were recorded between 4000-400 cm^{-1} and 700-30 cm^{-1} with ATR technical by Perkin Elmer Spectrum 400 FT-IR/FT-FIR spectrometer. Also, Raman spectra of the compound prepared were analyzed and recorded between 4000-450cm^{-1} with Bruker FRA 106/S spectrometer at Middle East Technical University lab.)

Computational Details

We have performed quantum mechanical calculations of the optimize parameters of compound $(2HNQ)_2Mn$ by using the HF/6-31G(dp) basis set to provide complete information regarding the structural characteristic and the fundamental vibrational modes. We have used the optimized parameters to calculate the vibrational spectra of the compound by taking the same basis set and computational methods.

Thus, our calculations make sure that there are not imaginary frequencies at the lowest energy state. The incomplete incorporation of electron correlation and the use of finite basis set in the HF calculations lead to some systematic errors. Therefore, all the calculated vibrational frequencies are scaled by 0.9024 for HF/6-31G(dp) basis set (Kral et al., 2005) in order to determine the vibrational spectra of the molecule accurately.

Molecular structure was optimized at C_1 symmetry (no symmetry constraint) and was not restricted. All the calculations were performed by using Gauss View molecular visualization program (Frisch et al., 2009) and GAUSSIAN09 program package on the personal computer (Gaussian 09 and Revision 2009).

The values of the vibrational modes corresponding to the optimized geometry of the compound $(2HNQ)_2Mn$ by performing based on HF method with the basis set of 6-31G(dp) are given in Table 2., along with the available experimental data.

RESULTS AND DISCUSSION

The ligand molecule 2HNQ consists of 19 atoms, suggesting that it has 51 normal vibrational modes. The geometry of the molecule is planar and belongs to point group Cs. In this case, OH molecule group as point mass is present within the molecular plane. The 51 fundamental modes of vibrations are distributed into the irreducible representations under Cs symmetry as 34 in-plane vibrations of a' species and 17 out of plane vibrations of a'' species. All vibrations are active in both IR and Raman spectra. All the frequencies are assigned in terms of fundamental, overtone and combination bands. The molecular structure and numbering of the atoms of 2HNQ is shown in Figure 1.

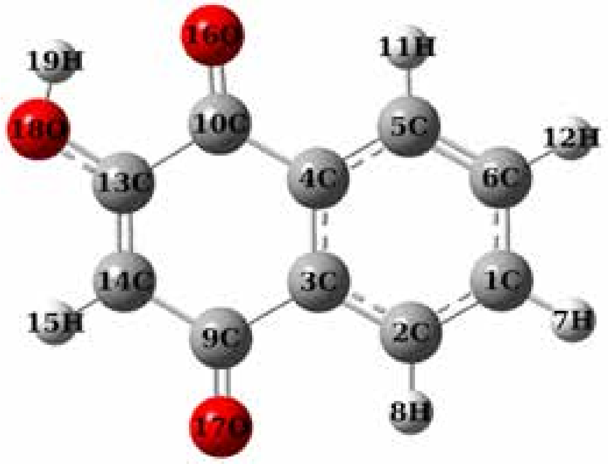

Figure 1. The molecular structure and numbering of the atoms of 2M8Q

The characteristic vibrations and assignments of 2M8Q ligand are described in Table 2. The spectrum of 2M8Q exhibited broad at 3153 cm^{-1} and weak at 3074 cm^{-1} band, this could be attributed to (O-H) stretch band and (C-H) stretch band in aromatic ring respectively. While the strong band at 1676 cm^{-1} which belongs to C=O asymmetric stretch band and the other strong bands belong to the (C=C) and (C-O) stretch band were found at 1458 cm^{-1} and 1283 cm^{-1} respectively (Figure 4).

X-ray diffraction studies were performed on the type $(2M8Q)_2Cu(H_2O)_2$ and $(2M8Q)_2Fe(H_2O)_2$ compounds. The results of these compounds exhibited that one half on the molecule generated the other half to give a monomeric unit whit the Cu(II) or Fe(II) ions lying on the center of inversion. The Cu(II) or Fe(II) ions are hexa-coordinated with two bidentate 2HNQ ligands and two water molecules (Salunke-Gawali et al., 2004; Garge et al., 1990). In that case, molecule has a center of symmetry. In such molecules, the vibrations observed in the infrared spectrum are not observed in the Raman spectrum and vice versa.

For the compound prepared, comparison of the calculated and observed infrared and Raman spectra are shown in Figure 2-3, respectively.

$(2HNQ)_2Mn$ compound was determined to have the center of symmetry (Figure 2-3, Table 2.), suggesting that one half of the molecule generates the other half to give a unit with the Mn ion lying on the center of inversion. The Mn atom is tetra-coordinated with two bidentate 2HNQ ligands. According to the analytical results of C, H and Mn, the compound was found to consist of two ligands (2HNQ) and one metal (Mn) atoms (Table 1.).

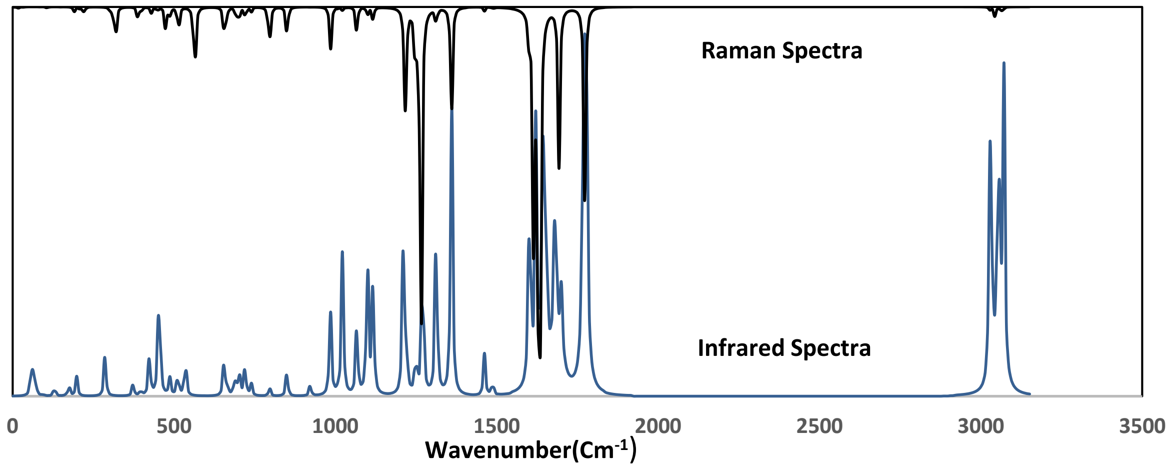

Figure 2. Comparison of calculated infrared and Raman spectrum of prepared compound ($(2HNQ)_2Mn$)

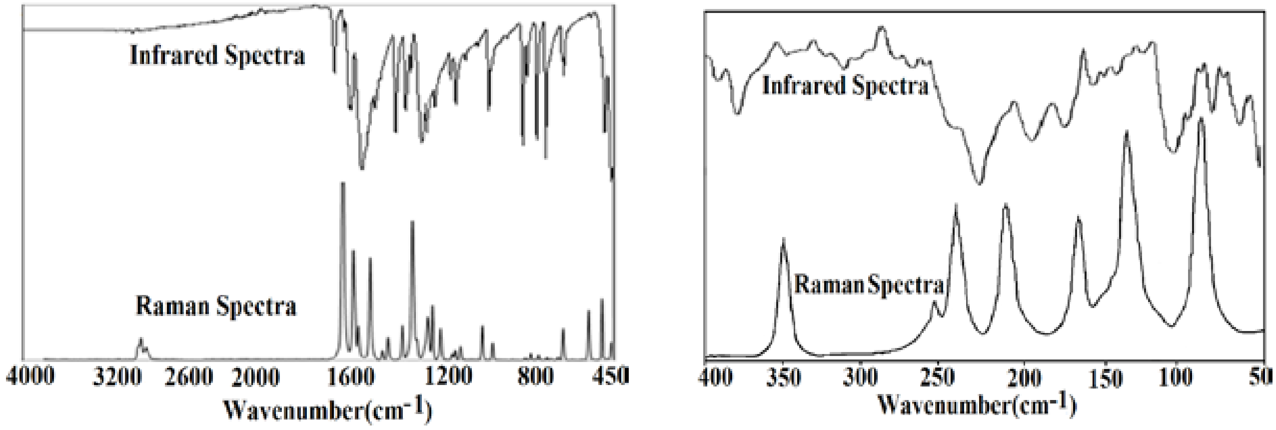

Figure 3. Comparison of observed infrared and Raman spectrum of prepared compound ($(2HNQ)_2Mn$)

A comparison of the IR spectra at the free ligand 2HNQ and prepared $(2HNQ)_2Mn$ compound was represented in Figure 4. Figure 4. exhibits the OH band appearing at 3158 cm^{-1} as broad in the free ligand 2HNQ molecule which does not appear in the $(2HNQ)_2Mn$ compound, suggesting that the water molecule is not found in the prepared $(2HNQ)_2Mn$ compound but indicating the presence of Mn-O bond in the prepared compound. The very weak intensity the C-H band appear at 3068 and 3016 cm^{-1} in the free ligand 2HNQ molecule. The 3068 cm^{-1} band shifted to low band 3064 cm^{-1} at IR spectra and the 3062 cm^{-1} at Ra spectra. The 3016 cm^{-1} band does not appear in the $(2HNQ)_2Mn$ compound. The bands 3064 cm^{-1} at IR spectra and the 3062 cm^{-1} at Ra spectra were calculated at 3063.672 cm^{-1} and 3063.666 cm^{-1}. The infrared spectra of the prepared complexes exhibited (C-O) in the IR (1273 cm^{-1}) and Ra (1280 cm^{-1}) which show a shifting to the lower frequencies by 10-13 cm^{-1} in comparison with ligand (2M8Q), indicating the coordination of ligands with metal ions through the oxygen atoms. The C-O bands in the $(2HNQ)_2Mn$ compound were calculated at 1265.252 cm^{-1} and 1248.990 cm^{-1}, respectively. In addition, the C=O band appeared at 1676 cm^{-1} as medium in the free ligand 2HNQ molecule which shifted to low band 1654 cm^{-1} at IR spectra and the 1653 cm^{-1} at Ra spectra in the $(2HNQ)_2Mn$ compound and thereby suggesting that the oxygen atom of ligand 2HNQ molecule are coordinated to the metal ion. The bands 1654 cm^{-1} at Ir spectra and the 1653 cm^{-1} at Ra spectra in the $(2HNQ)_2Mn$ compound were calculated at 1692.858 cm^{-1} and 1688.069 cm^{-1} respectively.

As presented in Table 2., most vibration modes of coordinated 2-hydroxy-1,4-naphthoquinone shifted to higher frequency when compared with the free 2-hydroxy-1,4-naphthoquinone values. Analogous shifts upon coordination were observed in pyridine (Lee and Boo 1996), and quinoline complexes (Johnson et al., 1993). In the current study, a few split bands in the vibrational spectra of $(2HNQ)_2Mn$ compound were observed. The general trend for distorted complexes was ascertained to have a far greater number of split bands in the IR spectra than the non-distorted ones.

The metal ligand bands are helpful for determining the local structure around metal ions. Without metal isotope labeling and X-ray analysis, it is difficult to do this. According to X-ray diffraction studies on transition metal $(2M8Q)_2Cu(H_2O)_2$ and $(2M8Q)_2Fe(H_2O)_2$ compounds, two bidentate 2HNQ ligands coordinate to the metal by forming a trans-planar structure and two water molecules occupy the axial position (Salunke-Gawali et al., 2004; Garge et al., 1990).

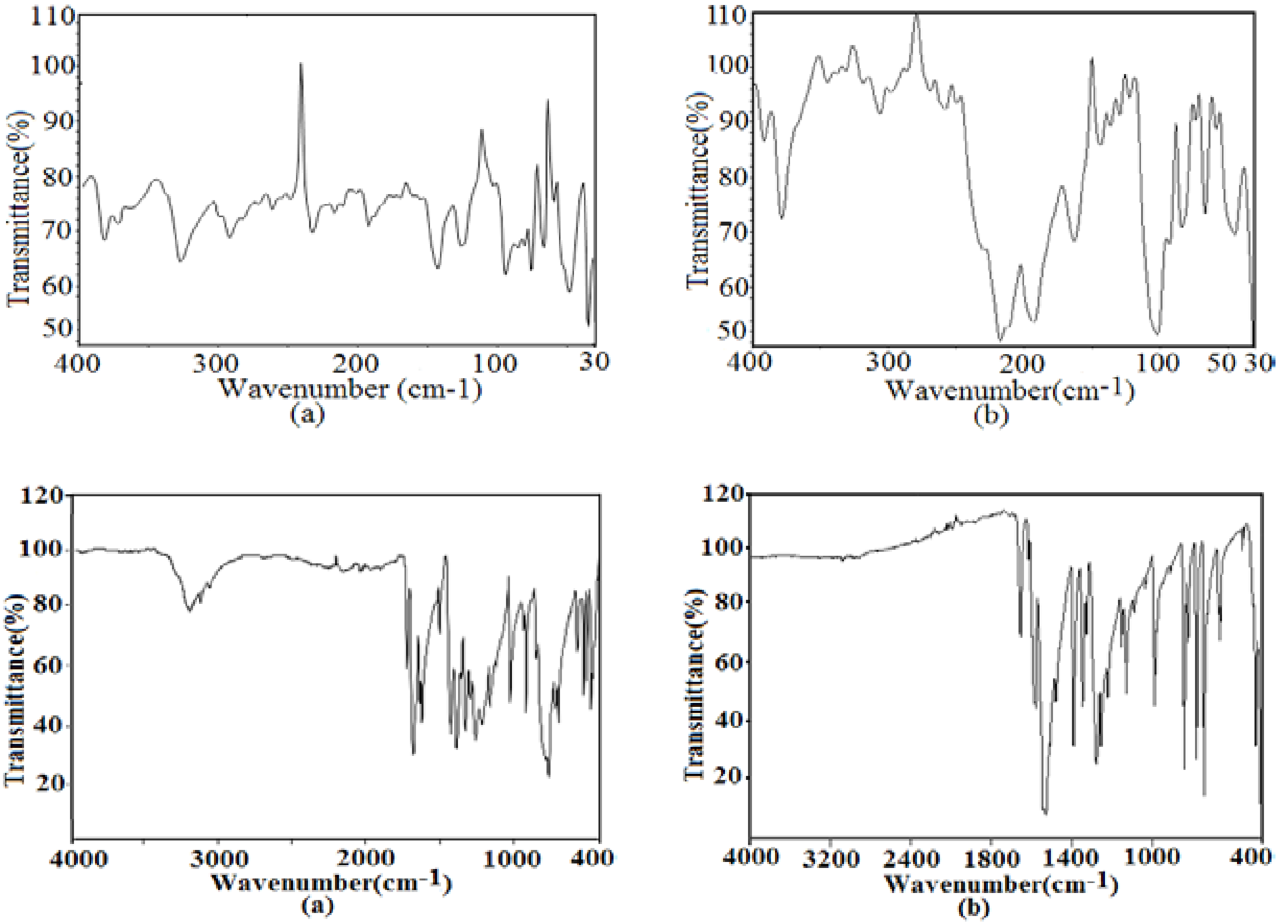

Figure 4. (a) Infrared spectra of free 2HNQ ligand and (b) $(2HNQ)_2Mn$ compound

Table 2. The observed IR, Raman and calculated frequencies using the HF/6-31G(dp) with scaled frequencies, their intensities and probable assignments for $Mn(2HNQ)_2$ and 2HNQ

Compound (2HNQ)$_2$Mn						Ligand 2HNQ	Assigned by theoretical calculation
	Calculated HF/6-31G(dp)			Observed		Observed	Approx. Assig.
No: Scl*(cm$^-$)		Ir. int.	Ra. int.	Ir.	Ra.	Ir.	
1	7.356	2.3905	0	-----	-----	-----	Molecule Butterfly
2	19.110	4.3881	0	-----	-----	-----	Molecule Torsion
3	34.287	1.4665	0	-----	-----	-----	Molecule twist
4	58.633	0	12.6123	-----	-----	-----	Molecule fluctuation
5	70.507	0	5.3193	-----	87 m	-----	γ (CCO)
6	84.743	0.265	0	84 m	-----	-----	γ (CCC)
7	94.004	0	0.3816	-----	108 m	-----	γ (CCC)
8	106.725	4.0188	0	102 vs	-----	-----	Molecule stress
9	129.717	0	2.9979	-----	-----	-----	γ (CCC)
10	149.273	0.4794	0	164 s	-----	-----	γ (CCC)
11	164.626	0	0.1652	-----	-----	-----	γ (CCC)
12	174.654	0	3.5547	-----	175 m	-----	Sym. υ(O-O)
13	190.396	16.7188	0	191 vs	-----	-----	Asym. υ(O-O)
14	198.406	0.0002	6.642	-----	198 w	-----	δ ring
15	209.409	10.4387	0	-----	------	-----	γ (CCC)
16	222.006	18.8052	0	218 vs	-----	-----	γ (CCC) + γ (O-Mn)
17	286.176	0	14.4331	-----	-----	-----	γ (CCC) + γ (O-Mn)
18	304.016	18.5255	0	-----	298 w	-----	δ(CCC)
19	318.516	128.645	0	-----	-----	-----	δ(CCC)
20	373.232	0	4.2885	-----	381 vw	-----	γ (CCC) + γ (C-O)
21	388.434	43.9937	0	379 s	-----	-----	γ (CCC) + γ (C-O)
22	396.844	0	1.8079	-----	387 w	-----	γ (CCC)
23	399.241	9.349	0	394 m	-----	-----	γ (CCC)
24	423.803	0	14.7777	-----	-----	-----	γ (CCC)
25	429.537	19.9319	0	412 br	-----	-----	γ (CCC)
26	446.814	0	0.9922	-----	437 vw	-----	δ(CCC)
27	448.229	12.4205	0	452 s	-----	433 s	δ(CCC))
28	453.902	0	43.7338	-----	459 m	-----	δ(CCC)
29	474.275	81.0044	0	-----	-----	461 s	δ(CCC)
30	486.788	0	6.4329	-----	-----	-----	δ(CCC)
31	488.332	25.5071	0	484s	-----	485 s	δ(CCC)
32	511.790	0	8.2241	-----	509 m	-----	Sym. υ(Mn-O)
33	513.672	85.4172	0	518 w	-----	-----	Asym. υ(Mn-O)
34	535.159	0	13.9776	-----	-----	-----	δ(CCC)
35	564.128	250.618	0	-----	-----	-----	δ(CCC)
36	654.068	0	11.3847	-----	550 m	-----	γ (CCC)
37	656.115	108.446	0	659 m	-----	655 s	γ (CCC)
38	663.615	0.0091	5.2711	-----	-----	-----	δ(CCC)
39	663.697	18.073	0.0026	667 m	-----	675 m	δ(CCC)
40	687.136	0	6.3336	-----	679 m	-----	γ (CCC)
41	693.579	45.1379	0	-----	-----	-----	γ (CCC)
42	701.365	0	10.6573	-----	701vw	-----	δ(CCC)+ δ(C=O)
43	703.415	24.5212	0	-----	-----	-----	δ(CCC)+ δ(C=O)
44	720.086	0.0008	11.7531	-----	-----	-----	δ(CCC)
45	720.969	36.2521	0.0003	723 w	-----	720 s	δ(CCC)
46	739.481	15.2272	0.0001	739 vs	-----	734 s	γ (CCC)
47	739.649	0.0003	4.5324	-----	-----	-----	γ (CCC)
48	794.753	0	0.7389	-----	-----	-----	γ(C-H)
49	794.972	115.64	0	779 s	-----	-----	γ(C-H)
50	796.614	0	2.5292	-----	-----	-----	γ(C-H)
51	798.840	28.3203	0	819 m	-----	805 m	γ(C-H)

52	849.743	0.0001	9.7407	-----	-----	-----	δ(CCC)
53	850.168	102.311	0	840 s	-----	873 s	δ(CCC)
54	922.034	0.4558	0	-----	-----	890 s	γ(C-H)
55	922.055	0	4.5256	-----	-----	-----	γ(C-H)
56	984.441	0	36.1681	-----	989 w	-----	γ(C-H)
57	985.041	142.400	0	986 s	-----	981	γ(C-H)
58	1005.858	2.3859	0.0009	-----	-----	-----	γ(C-H)
59	1005.865	0.0019	1.1965	-----	-----	-----	γ(C-H)
60	1021.899	0	59.549	-----	-----	-----	δ(CCC)
61	1022.133	10.2923	0	-----	-----	-----	δ(CCC)
62	1033.785	0.7561	0.0011	1038 w	-----	-----	δ(CCC)
63	1033.786	0.0044	0.1972	-----	1034 m	-----	δ(CCC)
64	1066.140	87.4029	0	-----	-----	-----	δ(CCC)
65	1066.357	0	30.5141	-----	-----	-----	δ(CCC)
66	1099.201	27.704	0.0001	1087 w	-----	1077 w	δ(C-H)
67	1099.221	0	61.4697	-----	-----	-----	Ring breathing
68	1116.611	44.2496	0	1127 m	-----	1118 s	Ring breathing
69	1116.627	0	48.4454	-----	-----	-----	δ(C-H)
70	1209.750	0	60.1825	-----	-----	-----	δ(C-H)
71	1210.456	27.4029	0	-----	-----	1172 s	δ(C-H)
72	1217.411	355.196	0	1219 m	-----	1214 s	δ(C-H)
73	1219.073	0	27.0687	-----	1221 w	-----	δ(C-H)
74	1248.272	205.128	0	1253 s	-----	1252 m	υ ring(C-C)
75	1248.990	0	18.0111	-----	1270 w	-----	υ ring(C-C)+ υ(C-O)
76	1265.252	1285.55	0	1273 s	-----	1284 s	υ(C-O)
77	1270.133	0	66.3061	-----	----	-----	υ ring(C-C)
78	1312.258	0	80.0853	-----	1346 s	-----	υ ring(C-C)
79	1312.550	51.1633	0	1322 s	-----	1338 s	υ ring(C-C)
80	1359.837	363.547	0	1343 m	-----	-----	υ ring(C-C)
81	1360.055	0.0001	135.389	1388 s	-----	1381 s	υ ring(C-C)+υ(C-H)
82	1461.664	0	19.6122	-----	1458 w	------	υ ring(C-C)+δ(C-H)
83	1461.755	13.9585	0	1477 m	-----	1458 w	υring(C=C)+δ(C-H)
84	1487.263	0	6.3848	-----	1536 m	-----	υ ring(C-C)
85	1487.435	4.6485	0	1533 vs	-----	1578 m	υ ring(C-C)
86	1599.400	0	57.9001	-----	1590 w	-----	υ ring(C-C)
87	1599.607	81.1417	0	1580 s	-----	1592 m	υ ring(C-C)
88	1614.847	858.865	0	1611 w	-----	-----	υ ring(C-C)
89	1616.154	0	330.904	-----	1611 m	-----	υ ring(C-C)
90	1631.738	2144.82	0	-----	-----	1638 s	υ ring(C-C)
91	1647.611	0	353.998	-----	-----	-----	υ ring(C-C)
92	1688.069	0	634.061	-----	1653vs	-----	Sym. υ(C=O)
93	1692.858	530.029	0	1654 m	-----	1676 m	Asym. υ (C=O)
94	1772.523	648.014	0	-----	-----	-----	υ ring(C-C)
95	1773.222	0	605.604	-----	-----	-----	υ ring(C-C)
96	3027.723	10.0437	0.0811	-----	-----	3016 vw	υ(C-H)
97	3043.386	0.005	163.368	-----	-----	-----	υ(C-H)
98	3043.386	32.1053	0.0009	-----	-----	-----	υ(C-H)
99	3043.386	0.0001	316.180	-----	-----	-----	υ(C-H)
100	3061.518	8.3749	0.0008	-----	-----	-----	υ(C-H)
101	3061.525	0	143.735	-----	-----	-----	υ(C-H)
102	3063.666	0.0001	218.449	-----	3062 w	-----	υ(C-H)
103	3063.672	5.2484	0.006	3064 vw	-----	3068 vw	υ(C-H)
104	3069.823	6.9309	0.0141	-----	-----	-----	υ(C-H)
105	3069.829	0.0004	232.163	-----	-----	-----	υ(C-H)
				-----	-----	3153 br υ(O-H)	-----

(s.f.): Scaling factor, *s.f.: 0.9024., Scl.: Scaled., int.: intensity, m.: medium, Ir.:infrared, Ra.: Raman, s.: strong, w.: weak, v.: very, br: broad, ν:stretching, δ:in-plane bending, γ:out-of plane bending, Scs: scissoring, Assig.: assignment

But the compound is considered to be trans-structured due to lack of OH group. For this structure, four Mn-O in quinone carbonyl group stretches are expected. These Mn-O bands have been identified at 518 cm^{-1} in infrared spectra to be asymmetric stretch and 509 cm^{-1} in Raman spectra to be symmetric stretch. The Mn-O band assigned at 540 cm^{-1} (Kindell and Dawood 2013) and at (510-535 cm^{-1}) range (Tarek 2005). The bands at 518 cm^{-1} and 509 cm^{-1} were calculated at 513.672 cm^{-1} and 511.790 cm^{-1}. Also, the 218 cm^{-1} band at infrared spectra assigned the combination of the γ (O-Mn) and γ (CCC) vibrations.

Based on the data presented in Figure 4, the structure of $(2HNQ)_2Mn$ compound is planar and the two 2HNQ ligands are coordinated in trans- geometry and it might be conformationally distorted trans structure. Indeed, it is worthy to note that the X-ray crystal structure analysis is perquisite for the certain results

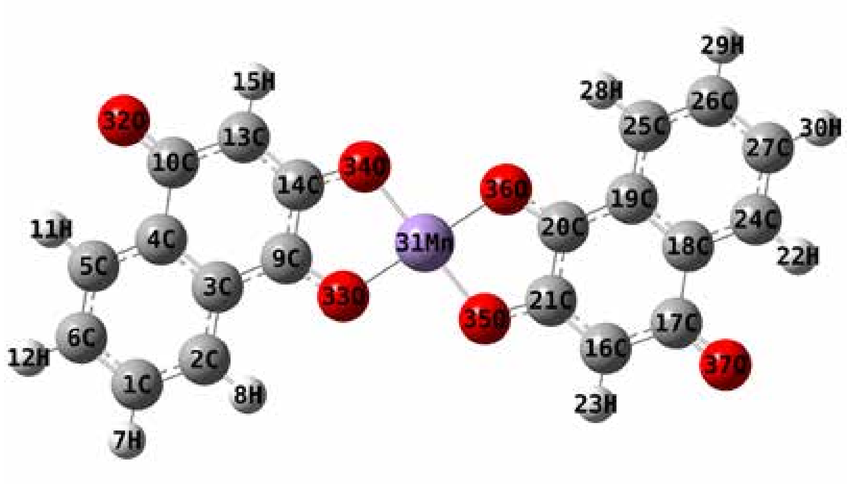

Figure 5. The proposed structure of $(2HNQ)_2Mn$ compound

In order to compare the theoretical data with the experimental data, correlation graphics of the frequencies for the proposed structure of $(2HNQ)_2Mn$ compound and ligand (2HNQ) based on the calculations were presented (Figure 6.). Accordingly, the experimental fundamentals were ascertained to be in good agreement with the scaled fundamentals and to possess good correlation with structure of $(2HNQ)_2Mn$ compound and ligand (2HNQ) (Figure 6.)

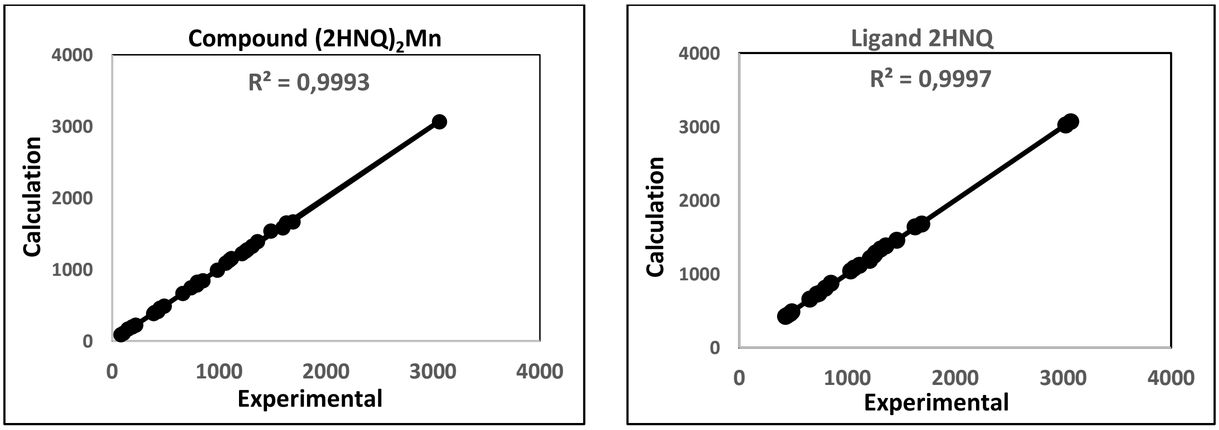

Figure 6. Correlations graphics of frequencies for compound $(2HNQ)_2Mn$ and ligand (2HNQ)

CONCLUSION

The structure of 2-hydroxy-1,4-naphthoquinone complex with Mn(II) was determined with the help of analyzed for C and H, the observed infrared and Raman spectra. The geometry of ligand and complex were optimized using the HF method with 6-31G(dp) basis set. The metal–ligand binding mode in the complex was confirmed from the calculations. In complex, Mn(II) coordinates through the ring oxygen atom. The HF/6-31+G(dp) was also used for predicting IR and Raman spectra for the complexes.

The 105 fundamentals were assigned in the present work. The HF/6-31G(dp) method gave good results, comparable with the experimental data from the literature for similar compounds.

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REFERENCES

Ashwini VT, Rupali TD, Salunke-Gawali S, Linares J, Varret F, Marrot J, Yakima JV, Bhadbhade M, Srinivas D, Shridhar PG, Rane Y, 2006. SOM assembly of hydroxynaphthoquinone and its oxime: Polymorphic X-ray structures and EPR studies. Spectrochimica Acta, 63: 130–138.

Chabereck S, Martell AE, 1959. Organic Sequestering Agents, John Wiley and Sons, Inc., New York, USA. 325 p.

Dekkers J, Kooıjman H, Kroon J, Grech E, 1996. 2-hydroxy-1,4-naphthoquinone. Acta Crystallographica, 52: 2896-2899.

Ferraz PAL, Abreu FC, Pinto AB, Glezer V, Tonholo J, Goulart MOF, 2001. Antimicrobial activities of the henna extract and some synthetic naphthoquinones derivatives. Journal Electroanalytical Chemistry, 507: 275.

Frisch A, Frisch MJ, Clemente FR, Trucks GW, 2009. Gaussian09 User's Reference, Gaussian Inc., 340 Quinnipiac St., Bldg. 40 Wallinford, CT 06492 USA.

Garge P, Chikate R, Padhye S, Savariault JM, de Loth P, Tuchangues JP, 1990. Iron(II) complexes of ortho functionalized para-naphtoquinones and molecular structure of bis(aqua) bis(lawsone)iron(II) and intermolecular magnetic exchange interactions in bis(3-aminolawsone)iron(II). Inorganic Chemistry, 29: 3315-3320.

Gaussian 09, Revision 2009. Gaussian, Inc., 40 Wallingford, CT 06492 USA.

González FJ, Aceves JM, Miranda R, González I, 9991. The electrochemical reduction of perezone in the presence of benzoic acid in aceto nitrile. Journal Electroanalytical Chemistry, 310: 293-303.

Johnson BG, Gill PM, Pople JA, 1993. The performance of a family of density functional methods. Journal Chemical Physics, 98: 5612.

Khan MS, Khan ZH, 2005. Ab initio and semiempirical study of structure and electronic spectra of hydroxy substituted naphthoquinones. Spectrochimica Acta, 61: 777–790.

Kindell AS, Dawood IJ, Aziz MR, 2013. Synthesis and Characterization of some Mixed Ligand Complexes Containing (8-hy droxyquinoline) and (2-picoline) with some Metal Ions. Journal Baghdad for Science, 10: 396-403.

Kral IK, Johnson DR, Kacker NR, 2005. Uncertainties in Scaling Factors for ab Initio Vibrational Frequencies. Journal of Physical Chemistry A, 37: 8430-8437.

Lee SY, Boo BH, 1996. Molecular structures and vibrational spectra of pyrrole and carbazole by density functional theory and conventional ab Initio calculations. Journal of Physical Chemistry, 100: 15073-15078.

Masuda K, Funayama S, Komiyama K, Umezawa I, Ito K, 1987. ITO, K. Constituents of Tritonia crocosmaeflora, I. Tricizarin A, a novel antimicrobial naphthazarin derivative. Journal of natural products, 50: 418-421.

Nonella M, 1996. Structures and harmonic force fields of 1,4-naphthoquinone and naphthalene: a density functional study. Journal of Molecular Structure (Theochem), 362: 7-21.

Papageorgiou VP, Assimopoulou AN, Couladouros EA, Hepworth D, Nicolaou KC, 1999. The chemistry and biology of alkannins, shikonins and related naphthazarin natural products. Angewdte Chemie International, 38: 270-300.

Salunke-Gawali S, Rane SY, Puranik VG, Guyard-Duhayon C, Varret F, 2004. Three dimensional hydrogen-bonding network in a copper complex of 2-hydroxy-1,4-naphthoquinone: structural, spectroscopic and magnetic properties. Polyhedron, 3: 2541–2547.

Tarek Ismail MA, 2005. Mononuclear and binuclear Co(II), Ni(II), Cu(II), Zn(II) and complexes of Schiff-base lands derived from 7-formyl-8-hydroxyquinoline and diaminonaphthalenes. Journal of Coordination Chemistry, 58: 141-151.

Thomson RH, 1971 Naturally Occurring Quinones. Academic Press, London, 732 p.