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Synthesis, experimental and theoretical characterizations of a new Cu(II) complex based on 3-hydroxy-2-naphtoic acid

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A new Cu(II) complex was equipped with 3-hydroxy-2-naphtoic acid ligand, which characterized by experimental and theoretical analysis. Structure of the Cu complex was estimated by the X-ray diffraction, FT-IR and atomic absorption spectroscopies. The DFT calculations have been carried out by using the B3LYP functional. The optimized structural parameters such as bond lengths and bond angles have been calculated. Two deprotonated ligands of 3-hydroxy-2-naphtoic acid and four aqua ligands occupy six coordination positions of the octahedral complex. Also, the experimental and theoretical IR spectra of the complex were compared. The calculated vibrational frequencies are in good agreement with the experimental data.

Keywords: 3-hydroxy-2-naphtoic acid; Copper; DFT; XRD; Assignment.

1.INTRODUCTION

3-hydroxy-2-naphtoic acid was applied as a ligand for complexation with metal ions under different conditions [1-4]. The lanthanides were used for the indication of oxygen of hydroxyl group of the acid in 3-hydroxy-2-naphtoic acid [5-6]. Furthermore, the stability constants and thermodynamic study of some ions such as Be+2, Mg+2 and Ca+2 were reported [7]. Also, 3-hydroxy-2-naphtoic acid used with other ligands such as hydrazinehydrate [8] and ethylenediamine [9] for chelating with metal ions.

Transition metal complexes have become increasingly important in synthetic chemistry, coordination chemistry, homogeneous catalysis and biological chemistry [10]. Chemistry of copper complexes is very important, because of the fascinating reactivity exhibited by the resultant complexes and the nature of the ligands that dictates the property of those complexes [11–14]. The copper complexes have the applications in the fields of biochemistry, photochemistry and photophysics [15].

The last few decades have seen an increased interest in copper(II) acetate complexes as building blocks in supra molecular devices due to their favorable excited state and redox properties as well as structural probes for DNA. Copper complexes are also showing promising results in anti-tumor activity and they target a broad spectrum of cancers [16]. These findings promoted us to synthesis and characterization of a copper(II) complex of 3-hydroxy-2-naphtoic acid as ligand.

2.EXPERIMENTAL& COMPUTATIONAL DETAILS

All of the used chemicals and solvents were purchased from Merck, which were used as received. The FT-IR spectra were recorded on a Bruker Tensor 27 as KBr discs.

Melting point (mp) was recorded on a Stuart SMP3 melting point apparatus. X-ray diffraction (XRD) was performed with a Philips PAN analytical X'Pert X-ray diffractometers. The percentage of the Cu2+ ion was measured by using a Hitachi 2-2000 atomic absorption spectrophotometer.

All present calculations have been performed with the Gaussian 03 software package [17] by using the B3LYP [18] functional. The 6-311+G (d,p) basis sets were used excluding for the Cu atom where the LANL2DZ basis sets were used.

First, all geometries were fully optimized. Optimized geometries were confirmed to have no imaginary frequency. Optimized geometries were used to calculate the vibrational frequencies. The DFT-predicted vibrational-frequencies are commonly higher than the experimental frequencies, so they were scaled using a factor of 0.9614 [19]. The structures were visualized by employing the Chemcraft 1.7 program [20].

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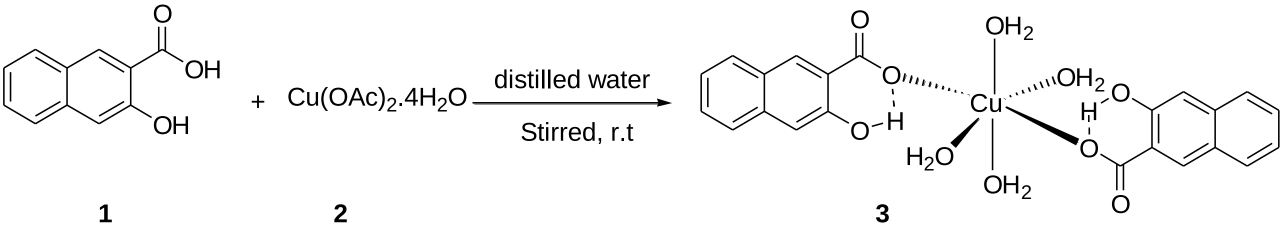
2.1. General procedure for synthesis of the Cu(II) complex 3

3-Hydroxy-2-naphtoicacid (2 mmol) and Cu(OAc)2.4H2O (1 mmol) were added to the distilled water (2 ml) and the solution was stirred for 2 hours. After this time, the precipitation was obtained. The product was filtered, wash with distilled water and dry in 100°C, m.p. (°C) < 300 °C (Scheme 1).



Scheme 1. Synthesis procedure of the Cu complex (3).

3. RESULTS & DISCUSSION

Previously, it has been shown that two molecules of the ligand 1 coordinate to the Mn2+ metal ion together with four H2O molecules as ligand to make an octahedral complex [21]. Herein, a similar formula was proposed for the synthesized Cu complex as [Cu(1)2(H2O)4] in a octahedral geometry. The calculated and experimental percentage of the Cu in the structure of the octahedral complex is 12.46 and 12.61 %, respectively, confirming suitability of the proposed formula for the Cu complex.

3.1. Geometry analysis

Nowadays, computational methods are used as complementary for replacement of experimental methods in identification of the structural and spectral behavior of the chemical compounds. The structural parameters of the Cu(II) complex (species 3) were calculated theoretically. The obtained results are in consistent with the previously reported data for similar compounds [21-28]. Some of the important-calculated structural parameters of the complex 3 are gathered in Table 1. The optimized geometries of the synthesized complex (3) are shown in Fig. 1 with labeling of its atoms.

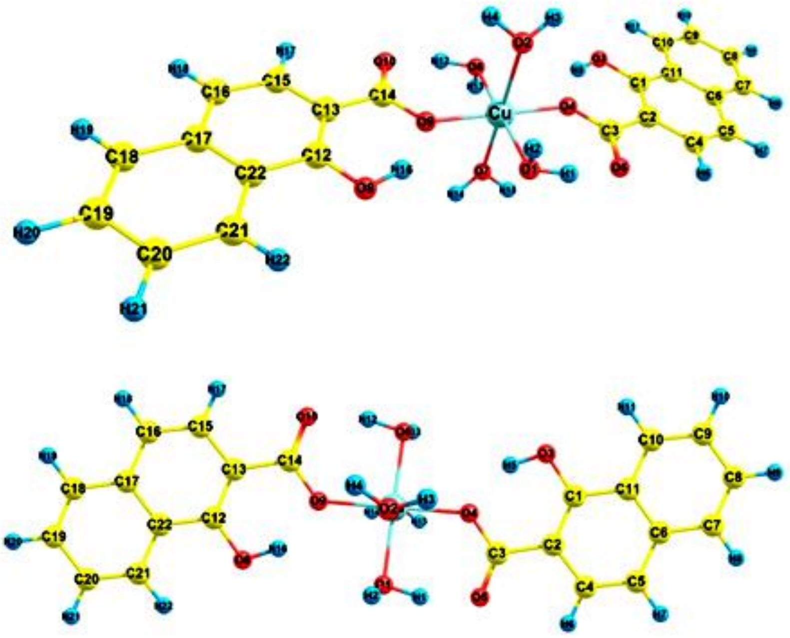


Fig 1. Optimized geometry of the [Cu(1)2(H2O)4] complex in two different views together with its labeling

As seen in Fig. 1, in the optimized geometry of the complex, two anionic ligand of the 3-hydroxy-2-naphtoicacid are bonded to the metal ion, which occupy two position of the complex. The O4 and O9 carboxylic oxygens of two species 1 are coordinated to the Cu(II) metal ion, occupy two equatorial positions of the octahedral complex. Two ligands are planar, which are roughly in a same plane (Table 1). Four other coordination positions are occupied with four H_2O molecules. The Cu-O bond lengths of the axial H_2O ligands are higher than the equatorial ones, confirming occurrence of the Jahn-Teller distortion in structure of the octahedral complex.

For complexation, the ligand 1 was firstly deprotonated. Since, in the optimized geometry of the complex, the C3-O4 and C14-O9 bond lengths are increased, while the C3-O4 and C14-O9 one are decreased in comparison with the optimized geometry of the free ligand 1.

Table 1. Selected structural parameters of the investigated Cu complex 3

Atoms	Bond length (Å)	Atoms	Angle (°)	Atoms	Dihedral angle (°)
Cu-O4	2.00	O1-Cu-O9	87.2	O6-Cu-O9-C14	-8.4
Cu-O9	2.00	O9-C14-O10	123.5	Cu-O9-H16-O8	178.5
Cu-O1	2.05	C13-C14-O10	120.5	O9-H16-O8-C12	0.1
Cu-O6	2.05	C14-O9-Cu	129.5	C13-C12-O8-H16	0.3
C14-O9	1.30	Cu-O9-H16	125.6	O10-C14-C13-C15	-0.9
C14-O10	1.25	O9-H16-O8	147.9	O5-C3-O4-Cu	-1.7
O9-H16	1.66	C12-O8-H16	106.3	C3-O4-H5-O3	0.9
O8-H16	0.99	C12-C13-C14	122.1	C3-C2-C1-O3	-0.1
O8-C12	1.35	O1-Cu-O4	92.8	C10-C11-C1-O3	0.1
C12-C13	1.40	O4-C3-O5	123.5	O5-C3-C2-C4	0.9
C13-C14	1.49	C2-C3-O5	120.5	C3-O4-O9-C14	180.0
C3-O4	1.30	O4-H5-O3	147.9		
C3-O5	1.25	C1-O3-H5	106.3		
O4-H5	1.66	C1-C2-C3	122.1		
O3-H5	0.99				
C1-O3	1.35				
C1-C2	1.40				
C2-C3	1.49				

The X-ray diffraction pattern of the Cu(II) complex was recorded at $2\theta = 0\text{-}60^{\circ}$. The XRD pattern of the Cu(II) complex and its data are shown in Fig. 2 and Table 2, respectively. The obtained data are in agreement with the DFT-calculated structural parameters. Since, the XRD data confirm validity of the optimized geometry for the Cu complex.

Table 2. The Selected XRD data of the Cu complex

Pos. [°2Th.]	d-spacing	Rel. Int. [%]
7.4565	11.85606	47.59
14.6613	6.04204	100.00
19.2826	4.60318	48.38
21.9135	4.05611	13.04
22.8218	3.89669	10.87
24.9048	3.57530	16.87
26.2240	3.39836	38.86
29.3626	3.04186	43.61
31.4406	2.84540	7.99
38.7208	2.32554	8.87
39.6838	2.27130	12.91
40.8965	2.20670	11.60

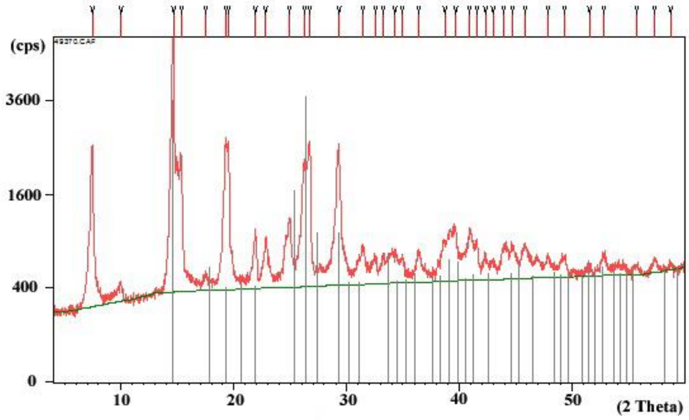


Fig 2. The XRD pattern of the Cu(II) complex.

3.2. Vibrational spectroscopy

For comparison, The FTIR spectra of the free ligand 1 and the Cu complex are shown in Fig. 3. FTIR spectrum of the ligand 1 contains the characteristic vibration bonds –OH and C=O groups at 3282 cm-1 and 1664 cm-1 respectively. The spectrum of the complex 3 is shown the characteristic vibration bonds at 3420 cm-1 and 1663 cm-1 for the stretching and scissoring vibrations of the H_2O ligands, respectively (Fig. 3, Table 3).

In this work, the vibrational modes for the Cu complex 3 were analyzed by comparing the DFT-computed and experimental results of its IR spectrum. Asignments of the selected vibrational frequencies are listed in Table 3. The stretching vibrations of the –CO2 carboxylic groups result in very strong band at about 1450-1550 cm-1 of the spectrum.

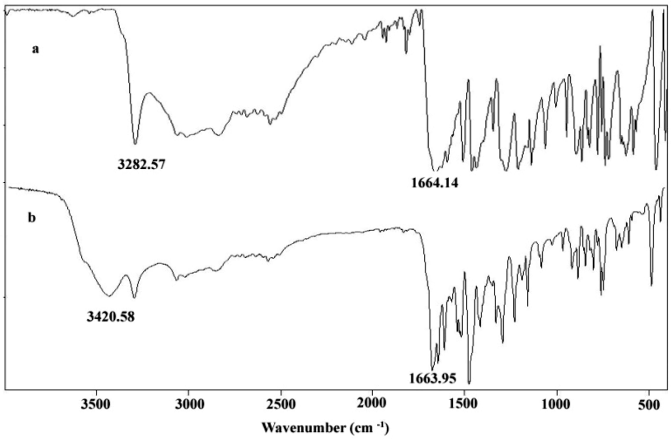


Fig 3. The FT-IR spectrum of a: 3-hydroxy-2-naphtoic acid and b: Cu(II) complex.

Table 3. Selected experimental and calculated IR vibrational frequencies (cm-1) of the investigated complex, species 3

Experimental frequencies	Calculated frequencies	IR Intensity (km.mol-1)	Vibrational assignment
427(m)	403	232	υ(Cu-O) of the H2O ligands
599(w)	614	39	υ(Cu-O4, Cu-O9)
665(w)	671	429	δtwisting(O-H) of the H2O ligands
737(m)	754	134	δout of plane (aromatic hydrogens)
750(m)	762	279	δscissoring (O=C=O)of the carboxylic moieties
790(w)	793	473	δout of plane (H5, H16)
907(w)	894	113	Breathing of the aromatic rings
1072(m)	1025	971	δwagging(O-H) of the H2O ligands
	1119	65	δin plane (aromatic hydrogens)
1147(m)	1142	115	δin plane (aromatic hydrogens) + υ(C2-C3, C13-C14)
	1180	182	υ(C1=O3, C12=O8)
1218(m)	1234	204	δin plane (aromatic hydrogens)
1283(s)	1291	1220	υ(C2-C3, C13-C14)+ υ(C=O) of the carboxylic moieties
	1367	816	υ(C=C) of the aromatic rings + υ(C1=O3, C12=O8)
1404(m)	1413	270	υ(C=C) of the aromatic rings

1466(vs)	1476, 1441	213, 746	υ(C=C) of the aromatic rings + υsym(C=O) of the carboxylic moieties
1507(s)	1514	1708	υ(C3=O5, C14=O10)
1599(s)	1536, 1542	56, 203	υ(C=C) of the aromatic rings
1633(s)	1589, 1553	137, 230	δscissoring of the H2O ligands
1664(vs)	1597	233	υsym(C=C) of the aromatic rings
3053(m, br)	2870	4937	υ(O1-H1 , O6-H12)
	3044-3054	1-40	υasym(C-H) of the benzene rings
	3065-3082	12-69	υsym(C-H) of the benzene rings
3283(m)	3175	2413	υ(O3-H5 , O8-H16)
3421(m, br)	3647	113	υsym(O-H) of the H2O ligands
	3735, 3657	247, 277	υasym(O-H) of the H2O ligands

Overlapping of the O-H and C-H stretching vibrations causes to appear a broad band in the 3600-2000 cm-1 spectral region of the IR spectra [22-26]. Deconvolution of this region of the IR spectrum of the species 3 is given in Table 3, where the strongest band is stretching vibrations of the phenolic O3-H5 and O8-H16 bonds of two ligands (species 1).

4. CONCLUSION

In this work, a copper (II) complex of 3-hydroxy-2-naphtoic acid ligand has been newly synthesized. The complex was characterized by some experimental methods. Also, the optimized geometry, structural parameters and IR vibrational frequencies of the Cu complex have been calculated by using the valuable-DFT methods. The calculated results are in consistent with the experimental data, confirming suitability of the optimized geometry for the complex.

In optimized geometry of the Cu complex, two deprotonated 3-hydroxy-2-naphtoic acid ligands occupy two coordination positions of the octahedral complex. Two other equatorial and two axial positions of the octahedral geometry were occupied by four aqua ligands. The complex involves the Jahn-Teller distortion.

REFERENCES

1. M. N. Desai, *Carr. Sci.*, **34,** 312 (1965).
2. S. L. Gupta, R.N. Soni, *J. Indian Chem. Soc*., **44,** 195 (1967).
3. R. C. Sharma, J. P. Tandon, *Monatsh. Chem*., **106,** 855 (1975).
4. S. S. Sandhu, J. N. Kumaria, R. S. Sandhu, *Thermochim. Acta*., **16,** 246 (1976).
5. Y. H. Deshpande, U. R. Rao, *J. Inorg. Nucl. Chem*., **35,** 3626 (1973).
6. R. P. Aggrawal, R. C. Mehrotra, *J. Less. Common. Metals*, **3,** 398 (1961).
7. R. S. Sandhu, K. Singh, *Therochim. Acta*., **17,** 325 (1976).
8. N. Arunadevi, S. Vairam, *E-J. Chem*., **6,** 413 (2009).
9. W.R. Yin, J.W. Ye, L. Ye, P. Zhang, J.N. Xu, *Acta Crystallogr.*, **63,** 165 (2007).
10. D. Chatterjee, E. Ember, U. Pal, S. Ghosh, R.V. Eldik, *Dalton Trans*., **40,** 10473 (2011).
11. A.Z. El-Sonbati, M.A. Diab, A.A. El-Bindary, G.G. Mohamed, Sh.M. Morgan, *Inorg. Chim. Acta,* **430,** 96 (2015).
12. A.Z. El-Sonbati, M.A. Diab, A.A. El-Bindary, Sh.M. Morgan, *Spectrochim. Acta A***, 127,** 310 (2014).
13. M.A. Diab, A.Z. El-Sonbati, A.A. El-Bindary, A.M. Barakat, *Spectrochim. Acta A***, 116**, 428 (2013).
14. A.Z. El-Sonbati, I.M. El-Deen, M.A. El-Bindary, *J. Mol. Liq*., **215**, 612 (2016).
15. U. McDonnell, M.R. Hicks, M.J. Hannon, A. Rodger, *J. Inorg. Biochem*., **102**, 2052 (2008).
16. M. Shebl, *Spectrochim. Acta A***, 117,** 127 (2014).
17. M.J. Frisch, et al., Gaussian 03, Revision B.03; Gaussian, Inc.: Pittsburgh PA (2003).
18. C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B***, 37**, 785 (1988).

19. D.C. Young, Computational Chemistry: A Practical Guide for Applying Techniques to Real-World Problems, John Wiley & Sons, Inc (2001).
20. G.A. Zhurko, D.A. Zhurko, Chemcraft 1.7, Available at http://www.chemcraftprog.com.
21. H. Eshtiagh-Hosseini, M.R. Housaindokht, S.A. Beyramabadi, S.H. Mir Tabatabaei, A.A. Esmaeili, M. Javan-Khoshkholgh, *J. Struct. Chem*.**78**, 1046 (2011).
22. S.A. Beyramabadi, A. Morsali, M. Javan-Khoshkholgh, A.A. Esmaeili, *J. Struct. Chem*., **53**, 460 (2012).
23. S.A. Beyramabadi, A. Morsali, A.R. Shams, *J. Struct. Chem*., **56**, 243 (2015).
24. S.A. Beyramabadi, H. Eshtiagh-Hosseini, M.R. Housaindokht, S. Shirzadi, A. Morsali, M.A. Naseri, *J. Struct. Chem*., **54**, 1055 (2013).
25. T. Toozandejani, S. A. Beyramabadi, H. Chegini, M. Khashi, A. Morsali, M. Pordel, *J. Mol. Struct.*, **1127**, 15 (2017).
26. N. I. Golovina,G.A. Klitskaya, A.A. Medzhidov, L.O . Atovmyan, *J. Struct. Chem*., **16**, 132 (1975) .
27. S. Saha, A. Sasmal, C. R. Choudhury, C. J. Gómez-Garcia, E. Garribba, S. Mitra, *Polyhedron*, **69**, 262 (2014).
28. F. Heshmatpour, S. Rayati, M. Afghan Hajiabbas, P. Abdolalian, B. Neumüller, *Polyhedron*, **31**, 443 (2012).