DFT Study on the Fe, Cu and Zn Complexes of 4-(2-Thiazolylazo) Resorcinol

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In this work, the Fe(II), Cu(II) and Zn(II) complexes of the 4-(2-thiazolylazo) resorcinol (TAR) ligand were characterized theoretically. Their optimized geometries and theoretical vibrational frequencies were computed using the density functional theory (DFT), where the B3LYP functional was employed. In the structures of octahedral complexes, the deprotonated TAR (TAR^-) acts as an anionic tridentate ligand *via* azo nitrogen, thiazolyl nitrogen and phenolic O^-. In the octahedral complexes, the two TAR^- ligands are roughly perpendicular to each other. The $Cu(TAR)_2$ complex is predicted to exhibit the Jahn-Teller distortion.

Keywords: Density functional theory; IR Assignment; Azo-compound; 4-(2-Thiazolylazo) resorcinol; Geometry optimization

1. INTRODUCTION

Due to interesting applications in optical data storage, photoswitching, photochromic materials, dyes and pharmaceuticals, the azo compounds have attracted much attention [1-5]. Among the azo compounds, 4-(2-thiazolylazo) resorcinol (TAR) is a well-known chelating reagent in acid-base titrations [6], separation of trace metal ions from food and environmental samples [7,8], and spectrophotometric determination of metal ions [9].

Now, theoretical investigations are applicable in many areas of chemistry, such as kinetics and mechanism investigations of the reactions, spectroscopic assignments, characterization of molecular structures, and so on [10-17]. They could, at the same time, be considered as complementary to or replacing experimental methods.

Many metal complexes of TAR have been synthesized [7,9,18-20]. Recently, Karipcin *et* al. [21], have synthesized the $M(TAR)_2$ complexes of TAR, where M is Fe(II), Cu(II) and Zn(II). But as we know, no crystal structure has been reported for these complexes. In this work, we have theoretically investigated the geometrical structures of the complexes. Comparison of the theoretical and experimental vibrational frequencies was used as an evidence for the suitability of the optimized geometries. This method is frequently used for identification of chemical compounds [16,17,22]. The assignment of the IR bands of the studied complexes can be useful in identification of similar compounds.

2. THEORETICAL METHODS

All calculations were performed with the Gaussian 03 software package [23] by using the B3LYP hybrid functional [24] and the 6-31+G(d,p) basis set. First, all degrees of freedom were optimized for all the geometries.

The optimized geometries of the complexes were confirmed to have no imaginary frequency of the Hessian. Then, the gas phase optimized geometries were used to compute their vibrational frequencies. The DFT vibrational frequencies are higher than the experimental ones [17,22], which can be corrected by applying the scaling of frequencies. Here, the scale factor of 0.9614 was used for the calculated frequencies [22].

3. RESULTS AND DISCUSSION

3.1. Geometry optimization

Here, geometries of the deprotonated TAR (TAR^-) ligand and its $M(TAR)_2$ complexes (M= Fe^{II}, Cu^{II} and Zn^{II}) were fully optimized in the gas phase. In Table 1, some of the calculated structural parameters are listed, which are in good agreement with the corresponding values reported for similar compounds [7,9,18-20].

The TAR first loses its phenolic proton, which is bonded to the O2 atom. The optimized geometry of the obtained anionic TAR^- species is shown in Fig. 1. As seen, the geometry of TAR^- is not planar, but the benzene and thiazolyl rings make a dihedral angle of approximately 50° with each other. Although, each of the benzene and thiazolyl rings is planar. For example, the C2-C6-C9-C8 dihedral angle is 49.1° (Fig. 1 and Table 1).

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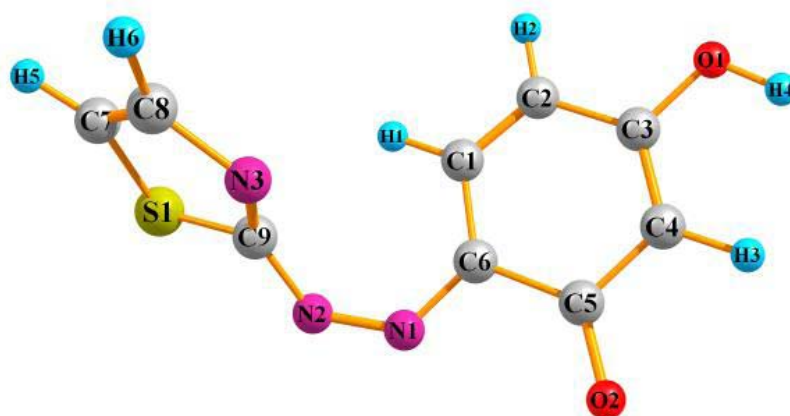E-mail: beiramabadi@yahoo.com

Fig. 1. The B3LYP/6-31+G(d,p) optimized structures of the TAR⁻ ligand.

Fig. 2. The B3LYP/6-31+G(d,p) optimized structures of the M(TAR)$_2$ complexes, where M=Fe(II), Cu(II) and Zn(II).

In the structures of the complexes, the TAR⁻ species acts as a tridentate anionic ligand, which has an N,N,O⁻ binding mode. The optimized geometries of the Fe, Cu and Zn complexes are shown in Fig. 2 and their structural parameters are gathered in Table 1. In the optimized geometries of the complexes, the coordinated TAR⁻ is more planar than its free form. The dihedral angles N2-C9-S1-C7 and C2-C6- C9-C8 confirm this conclusion (Table 1).

The two TAR⁻ ligands, bonded to the central metal, fill six coordination positions of the octahedral complex. In the optimized geometries of the complexes, the TAR⁻ ligands are roughly perpendicular to each other, and form a dihedral angle of approximately 80.0° with each other.

The calculated structural parameters (Table 1) provide confirmation of the Jahn-Teller effect in the octahedral Cu(II) complex, which lengthens the equatorial bonds (Cu-N6 and Cu-O4) and shortens the axial bonds of a tetragonally distorted Cu(II) complex in comparison with the Fe and Zn complexes. In this way, the Cu-O4 bond is longer than the Cu-O2 bond, while the Cu-N3 bond is shorter than the Cu-N6 one.

As expected, the C3-O1 and C12-O2 bond lengths are 136 pm, which corresponds to a single C-O bond. The C5-O2 and C14-O4 bond lengths are 127 pm, corresponding to a C=O double bond.

3.2. Vibrational spectroscopy

Theoretical description of vibrational spectra is of practical importance for the identification of compounds. Here, the IR spectra of the M(TAR)$_2$ complexes were characterized theoretically. In Table 2, the selected vibrational wavenumbers computed by the B3LYP/6-31+G(d,p) approach are listed.

Overlapping of stretching vibrations of the O-H bonds with the C-H stretching modes leads to band broadening in the 3600-2000 cm⁻¹ spectral region of the IR spectra [17, 25-29]. The deconvolution of this region is given in Table 2. In all IR spectra, the most intensive band is related to the stretching vibrations of the phenolic O-H bonds.

An important diagnostic for coordination of the azo and Schiff-base ligands is the energy value of the very intensive band in the 1660-1500 cm⁻¹ region of the IR spectra [17,21,25-28]. By coordination, the symmetrical stretching modes of

C=N bonds shift to lower energy by 33 cm^{-1} in   comparison with the free TAR ligand (1513 cm^{-1})

Table 1. Selected structural parameters of the TAR$^-$ ligand and its M(TAR)$_2$ complexes.

	TAR$^-$	M		
		Fe	Cu	Zn
Bond length (PM)				
O1-H4	96.6	96.7	96.7	96.7
O1-C3	138.3	136.2	136.1	136.1
C3-C4	136.8	138.3	137.8	137.9
C5-C6	148.9	145.2	146.5	146.9
C6-N1	135.6	135.5	134.7	134.3
N1-N2	129.5	130.8	129.6	129.6
C9-N2	136.8	136.7	137.2	137.8
C9-N3	132.1	133.5	132.4	132.5
C8-N3	136.9	137.1	136.9	137.2
C7-C8	136.9	136.6	136.8	136.7
C7-S1	174.6	174.4	174.0	174.0
C5-O2	124.7	128.4	127.1	127.5
O2-N1	277.8	258.4	266.1	266.1
M- O2	-	215.9	213.7	212.5
M- O4	-	215.9	218.0	212.5
M- N1	-	215.5	202.0	220.5
M- N3	-	225.6	225.7	230.3
M- N4		215.4	202.9	220.5
M- N6	-	227.2	232.0	230.3
M- N2	-	306.8	292.5	310.5
Angle (°)				
C1-C2-C3	118.8	119.5	119.5	119.3
O2-C5-C6	124.1	119.6	120.9	121.3
C1-C6-N1	125.2	127.0	125.2	125.9
C5-C6-N1	115.1	111.4	113.6	113.0
C6-N1-N2	126.7	122.6	122.3	122.6
N1-N2-C9	126.4	107.5	111.2	110.1
N2-C9-N3	130.3	123.4	125.9	126.5
N2-C9-S1	115.7	122.9	120.1	119.5
C9-S1-C7	88.9	89.2	88.9	89.1
C7-C8-N3	117.4	115.1	115.6	115.6
O2-M-O4	-	91.0	96.7	99.1
O2-M-N1	-	82.8	79.5	75.8
O2-M-N3	-	148.2	154.5	146.6
O2-M-N4	-	162.0	99.1	108.7
O2-M-N6	-	90.9	91.3	93.5
N1-M-N4	-	177.6	178.0	173.4
N1-M-N3	-	79.2	75.3	70.9
N1-M-N6	-	102.5	106.8	104.4
N1-M-O4	-	102.3	102.1	108.6
Dihedral angle (°)				
O1-C3-C4-C5	179.8	-179.8	-179.9	-179.8
O2-C5-C6-N1	-9.2	-0.2	-0.5	-0.3
C6-N1-N2-C9	-28.5	178.1	-179.9	-179.9
N2-C9-S1-C7	170.1	179.8	180.0	179.9
S1-C7-C8-N3	0.7	0.1	0.2	0.2
C2-C6- C9-C8	-49.1	177.0	179.8	179.9
M-O2-N1-N3	-	0.2	3.4	2.0
O2- M-N4-N6	-	89.9	88.9	87.3
N3-O2- M-N4		178.9	-172.6	-171.1
C6-C9-C15-C18	-	80.8	-86.9	80.0
C3-C6-C15-C12	-	-74.0	-76.0	-79.6
C7-C9-C16-C18	-	80.2	87.8	81.2

Table 2. Some calculated IR vibrational frequencies (cm^{-1}) of the Fe, Cu and Zn complexes of TAR.

TAR	Fe	Cu	Zn	Vibrational assignment
418(89)	422(94)	428(77)	429(95)	$\delta op(-OH)$
-	496(30)	500(14)	496(11)	$\upsilon(M-N)$
-	516(58)	513(43)	519(56)	$\upsilon_{asym}(M-O)$
-	527(34)	516(55)	520(52)	$\upsilon_{sym}(M-O)$
1016(33)	-	-	-	$\delta_{op}(N1-H5)$
1140(376)	1135(467)	1136(428)	1136(468)	$\upsilon(C9-S1)$
1186(243)	1199(202)	1198(218)	1198(291)	$\upsilon(C-O)phenolic$
1338(112)	1340(616)	1349(842)	1345(751)	$\upsilon_{asym}(N2-C9-N3) + \upsilon_{asym}(C7-C8-N3)$
1452(945)	1405(271)	1405(274)	1409(359)	$\upsilon(N-N)$
1513(60)	1476(76)	1472(232)	1479(194)	$\upsilon(C-N)$
1617(324)	1521(135)	1528(34)	1524**(337)**	$\upsilon(C5-O2)$
1569(177)	1592(486)	1589(935)	1591(1024)	$\upsilon(C-C)$ benzene
3053-3078(11,3)	3069-3104(14,6)	3068-3106(14,8)	3068-3103(14,7)	$\upsilon(C-H)$ benzene
3080(12)	3113(8)	3113(8)	3112(10)	$\upsilon(C-H)$ thiazolyl ring
3100(115)	-	-	-	$\upsilon(N1-H5)$
3660(133)	3667(126)	3666(125)	3666(122)	$\upsilon(O-H)$ phenolic

The intensity of each absorption is shown in parentheses in front of its computed frequency.

$\delta_{op}=$ out-of-plane-rotational vibration.

Computed values suggested that the stretching C5-O2 and C14-O4 vibrations appear as a strong band in the IR spectra at 1550-1500 cm^{-1}, while the C3-O1 and C12-O3 stretching vibrations appear as a strong band at energies lower by 250 cm^{-1}. This is in agreement with their C=O double bond and C-O single bond characteristics, respectively. By complexation, the $\upsilon(C5-O2)$ and $\upsilon(C14-O4)$ bands shift to lower energies in comparison with the free TAR ligand.

An intensive band at about 1140 cm^{-1} in the IR spectra of the ligand and complexes is attributed to the stretching vibration of the C-S bonds (Table 2). The presented vibrational assignments can be used for analysis of similar compounds, helping to explain their vibrational behaviour.

4. CONCLUSIONS

In this work, the optimized geometries and IR vibrational frequencies of the Fe(II), Cu(II) and Zn(II) complexes of the TAR ligand were calculated by the DFT method. All complexes are octahedral, where the two TAR$^-$ act as anionic tridentate ligands. The ligands coordinate to the metal ions *via* the thiazolyl N atom, azo N atom and the deprotonated phenolic O$^-$.

The free TAR$^-$ ligand is not planar. However, it is more planar in the coordinated form. The two TAR$^-$ ligands are roughly perpendicular to each other. The Cu(II) complex exhibits Jahn-Teller distortion.

The important vibrational modes of the TAR ligand and its complexes were assigned theoretically, which can be used for identification of similar compounds.

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DFT-ИЗСЛЕДВАНЕ НА КОМПЛЕКСИТЕ НА ЖЕЛЯЗОТО, МЕДТА И ЦИНКА С 4-(2-ТИАЗОЛИЛАЗО)РЕЗОРЦИНОЛ

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(Резюме)

В настоящата работа са охарактеризирани теоретично комплексите на Fe(II), Cu(II) и Zn(II) с лиганди от 4-(2-тиазолилазо) резорцинол (TAR). Изчислени са тяхните оптимизирани геометрии и теоретичните вибрационни честоти с помощта на DFT-теорията при използването на B3LYP-функционал. В структурите на октаедричните комплекси депротонирания TAR (TAR⁻) действа като анионен тридентатен лигандчрез азо-азотния атом, тиазолил-азотния атом и фенолния кислороден атом. В октаедричните комплекси двата TAR⁻ лиганди са почти взаимно перпендикулярни. Предполага се комплексът Cu(TAR)₂ да проявява Jahn-Teller отместване.