Available online at www.pelagiaresearchlibrary.com

Pelagia Research Library

Der Chemica Sinica, 2012, 3(3): 766-769

Pelagia Research Library
ISSN: 0976-8505
CODEN (USA) CSHIA5

Synthesis and Theoretical studies of a Cobalt Complex with 1,3-thiazole derivatives

Masume Maleki, Farshid Salimi*, Ali Shafaghat, Mohmmad Khodadadi-Moghaddam

Department of Chemistry, Faculty of Science, Ardabil Branch, Islamic Azad University, Ardabil, Iran

---

ABSTRACT

The synthesis and characterization of cobalt(II) complex with 1,3-thiazole derivativeis described. In this work, we will report a combined experimental and theoretical study on molecular structure, vibrational spectra and energies of N,N'-Bis(1,3-thiazol-2-yl)methylenediamine cobalt(II).The molecular geometry, vibrational frequencies andenergiesin the ground state are calculated by using HF and DFT (B3LYP) levels of theory with complete relaxation in the potential energy surface using 6-31G(d,p) basis sets. The harmonic vibrational frequencies were calculated and the scaled values have been compared with experimental FTIR and FT-Raman spectra. The observed and the calculated frequencies are found to be in good agreement. The experimental spectra also coincide satisfactorily with those of theoretically constructed bar type spectrograms.

Key words: Co(II), Complex,HF, DFT, IR.

INTRODUCTION

Thiazole and its derivatives have biological significance, e.g. it is fonud in the vitamin B1 molecule and in the coenzyme cocarboxylase as thiazole. The penicillin molecule also contains a thiazolidine ring.

2-Aminothiazoles are known mainly as biologically active compounds with a broad range of activity and as intermediates in the synthesis of antibiotics and dyes. It is also known that heterocyclic compounds with free amino groups may exhibit teratogenic and mutagenic properties because of their ability to form non-covalent complexes with DNA [5,6]. The importance of such derivatives is due to their biological properties; for example, some of them show significant bacteriostatic [7], tuberculostatic [8], hypoglycemic, anti-inflammatory, diuretic and fungicidal activities [9], and some of them are useful for treating of asthma [10].Derivatives of thiazole have anti-inflammatory activity [11] antituberculosis [12], antioxidant activity [13] and antibacterial [14] properties.

We report here the synthesis and study of complex of Co(II) with ligand derived from 2-Aminothiazole.

However, the detailed HF/DFT (B3LYP) at 6-31G(d,p)comparative studies on the complete FTIR spectra of N,N'-Bis(1,3-thiazol-2-yl)methylenediamine cobalt(II) have not been reported so far.

In this study, molecular geometry, optimized parameters and vibrational frequencies, energies are computed and the performance of the computational methods for ab initio (HF) and DFT (B3LYP)at 6-31G(d,p)basis sets are compared.

MATERIALS AND METHODS

Complex N,N'-Bis(1,3-thiazol-2-yl)methylenediamine cobalt(II)(1)

Cobalt chloride (1 mmol) was dissolved in absolute acetonitrile (5 ml). To this, (3mmol) N,N'-Bis(1,3-thiazol-2-yl)methylenediamine (L^1) in THF (10 mL) was added. The mixture was stirred magnetically at room temperature. The precipitated complex were filtered, washed with ether and dried.

Computational Details

All calculations were performed using the Gaussian 98package of program [15] on a Windows-XP operating PC. The molecular structure of the title compound in the ground state is computed by performing both HF and DFT (B3LYP) with 6-31G* basis set.

RESULTS AND DISCUSSION

The optimized molecular structure of title molecule is obtained from Gaussian 98 and GaussView3.0 programs are shown in the Figure 1.

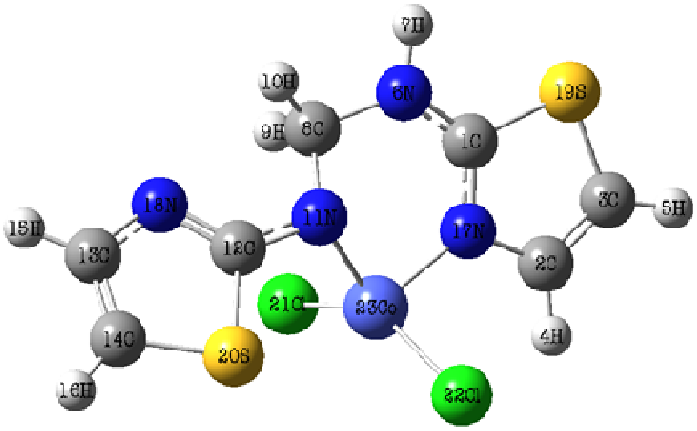

Fig. 1. Numbering system adopted in the study for (1) by using DFT (B3LYP)/6-31G(d, p)

Computational (theoretical) calculations energy differences for the compound (1) were determined by optimizing the geometry at various computational levels. Comparison of the energies at the HF/6-31G(d, p) level listed in Table 1 shows the differences in the energies.

Table 1. Theoretically computed energies (a.u.), zero-point vibrational energies (kcal mol^{-1}), rotational constants (GHz), entropies (cal mol^{-1} K^{-1}) for compound of (1) at the HF/B3LYP/6-31G(d, p)

Parameters	HF/6-31G(d,p)	B3LYP/6-31G(d,p)
Total energy	-3582.1123	-3589.4348
Zero-point energy	99.8695	91.8890
Rotational constants	0.5687	0.6004
	0.2266	0.2316
	0.2053	0.2058
Entropy total	130.086	135.289
Translational	43.365	43.365
Rotational	33.762	33.684
Vibrational	52.959	58.240

The optimized structural parameters of compound (1) calculated by ab initio-HF and DFT (B3LYP) levels with the standard 6-31G(d, p) basis set are listed in Table 2.

Table 2.Geometrical parameters optimized of compound (1), bond length (Å) and angle (˚) at the HF//B3LYP/6-31G(d, p)

Angle lengths	HF	B3LYP	Bond lengths	HF	B3LYP
	6-31G(d,p)			6-31G(d,p)	
C(1)-S(19)-C(3)	88.40	89.55	C(2)-C(3)	1.3245	1.3481
S(19)-C(3)-C(2)	110.13	110.27	S(19)-C(3)	1.7494	1.7545
C(3)-C(2)-N(17)	115.28	115.00	C(2)-N(17)	1.3939	1.3913
C(2)-N(17)-C(1)	112.14	112.60	C(1)-S(19)	1.7371	1.7533
N(17)-C(1)-N(6)	124.46	124.67	C(1)-N(17)	1.3073	1.3267
N(17)-C(1)-S(19)	113.06	112.57	C(1)-N(6)	1.3209	1.3439
S(19)-C(1)-N(6)	122.48	122.75	N(6)-C(8)	1.4622	1.4657
C(1)-N(6)-C(8)	123.62	123.00	C(8)-N(11)	1.4415	1.4529
N(6)-C(8)-N(11)	110.40	109.50	N(11)-C(12)	1.3710	1.3654
C(8)-N(11)-C(12)	113.12	112.93	C(12)-S(20)	1.7536	1.7833
N(11)-C(12)-N(18)	124.76	126.58	C(12)-N(18)	1.2836	1.3145
N(18)-C(12)-S(20)	114.36	114.20	N(18)-C(13)	1.3772	1.3689
N(11)-C(12)-S(20)	120.87	119.19	S(20)-C(14)	1.7384	1.7349
C(12)-N(18)-C(13)	111.02	110.66	C(14)-C(13)	1.3354	1.3676
C(12)-S(20)-C(14)	88.48	88.18	N(17)-Co(23)	1.9078	1.8677
N(18)-C(13)-C(14)	116.63	116.73	N(11)-Co(23)	1.8697	1.8701
S(20)-C(14)-C(13)	109.46	110.15	Co(23)-Cl(21)	2.1754	2.1695
Cl(21)-Co(23)-Cl(22)	141.73	143.95	Co(23)-Cl(22)	2.1979	2.1819
Cl(21)-Co(23)-N(11)	102.26	99.14			
Cl(21)-Co(23)-N(17)	100.96	98.45			
Cl(22)-Co(23)-N(11)	108.98	111.58			
Cl(22)-Co(23)-N(17)	98.56	97.50			
Co(23)-N(11)-C(8)	115.59	115.29			
Co(23)-N(11)-C(12)	117.92	110.21			
Co(23)-N(17)-C(1)	124.71	124.80			
Co(23)-N(17)-C(2)	122.58	122.48			

Table 3. Theoretical and experimental IR spectral data (cm^{-1}) of compound (1)

Experimental	HF/6-31G(d,p)	DFT/6-31G(d,p)	Vibration
3194	3901	3670	$\upsilon_{N-H\ (stre.)}$
-	3459	3299	$\upsilon_{C-H(ring\ thiazal)\ (stre.)}$
-	3444	3277	$\upsilon_{C-H(ring\ thiazal)\ (stre.)}$
-	3429	3272	$\upsilon_{C-H(ring\ thiazal)\ (stre.)}$
-	3396	3225	$\upsilon_{C-H(ring\ thiazal)\ (stre.)}$
-	3329	3121	$\upsilon_{C-H\ (stre.)}$
2912	3221	3040	$\upsilon_{C-H\ (stre.)}$
1582	1794	1609	$\upsilon_{C-C\ (stre.)}+\upsilon_{N-H\ (ben.)}+\upsilon_{C-H\ (ben.)}$
1492	1738	1619	$\upsilon_{C-N(ring\ thiazal)\ (stre.)}+\upsilon_{C-C\ (stre.)}+\upsilon_{C-H\ (ben.)}$
1458	1729	1538	$\upsilon_{C-N\ (stre.)}+\upsilon_{C-C\ (stre.)}+\upsilon_{C-H(ben.)}+\upsilon_{N-H\ (ben.)}$
1381	1677	1518	$\upsilon_{N-H}+\upsilon_{C-H\ (ben.)}$
1342	1663	1463	$\nu_{C-H\ (ben.)}$
1265	1647	1500	$\upsilon_{C-N(ring\ thiazal)\ (stre.)}+\upsilon_{N-H\ (ben.)}$
-	1528	1387	$\upsilon_{C-H(ben.)}$
-	1472	1343	$\upsilon_{C-H(ring\ thiazal)\ (ben.)}+\upsilon_{C-H(ben.)}$
-	1469	1358	$\upsilon_{C-H(ring\ thiazal)\ (ben.)}$
-	1436	1307	$\upsilon_{C-H(ring\ thiazal)\ (ben.)}+\upsilon_{C-N}$
-	1392	1343	$\upsilon_{C-H(ring\ thiazal)\ (ben.)}+\upsilon_{C-H\ (ben.)}$
1125	1184	1114	$\upsilon_{C-H(ring\ thiazal)}$
1187	1152	1271	υ_{N-H}
1072	1043	904	$\upsilon_{C-H(ring\ thiazal)}$
1050	1030	871	$\upsilon_{C-H(ring\ thiazal)}$
1012	917	847	Ring brething
864	906	825	$\upsilon_{C-H(ring\ thiazal)+}$ Ringbrething
754	821	762	υ_{C-S}
734	802	687	$\upsilon_{C-H(ring\ thiazal)}$
688	726	642	$\upsilon_{C-H(ring\ thiazal)}$

Vibrational spectroscopy is extensively used in organic chemistry for the identification of functional groups of organic compounds, the study of molecular conformations, reaction kinetics, *etc.* The observed and calculated data of the vibrational spectrum of compound **1** are given in Table 3.

CONCLUSION

Ab initio and DFT levels at 6-31G (d,p) basis sets calculations were carried out on cobalt(II) complex with N,N'-bis(2-Thiazol-yl)methylenediamin. The HF and DFT method with the 6-31G (d,p) basis set have been used to determine the ground state geometries, vibrational spectra and energies of compound (1).

REFERENCES

[1] H. A. Kirst, E. F. Szymanki, D. E. Dorman, J. C. Occolowitz, N. D. Jones, M. O. Chaney, R. L. Hamil and M. M. Hoehn, *J. Antibiot.*, **1975,** 28, 286.
[2] P. Brookes, A. T. Fuller and J. Walker, *J. Chem. Soc.*, **1957**,689.
[3] M. N.G. James and K. J. Watson, *J. Chem. Soc.*, **1966**, 1361.
[4] J.C. Eriks, H. Vandergoot, G.J. Sterk, H. Timmerman, *J. Med. Chem*., **1992**, 35, 3239.
[5] C.E. Voogd, J.J. Van der Stel, H.W. Verharen, *Mutat. Res.*,**1983**, 118,153.
[6] J.C. Greenaway, A.G. Fantel, M.R. Juchau, *ToxicolApplPharmacol*., **1986**, 82, 307.
[7] A.L. Mndzhoyan, V.G. Afrikyan, Izv. *AN Armyan.SSR Ser. Khim.Nauk*, **1957**, 10, 143.
[8] A.L. Mndzhoyan, N.A. Apoyan, L.D. Zhuruli, Yu. Zh. Ter-Zakharyan, *Biol. SvoistvaKhim. Soedin.,Akad. Nauk Arm. SSR, Inst. Tonkoi Organ. Khim.*,**1962**, 219.
[9] V.P. Chernykh, V.I. Kabachnyi, V.A. Shapovalova, L.A. Porokhnyak, V.N. Savchenko, *Khim.-pharm. Zh.*, **1989**, 23, 825.
[10] H. Cousse, G. Mouzin, U. S. Patent, **1981**, 4246271.
[11] SrinivasAmpati, RajuJukanti, VidyaSagar, Rama Ganta, SarangapaniManda, *Der ChemicaSinica*, **2010**, 1, 157.
[12]DinkarMundhe, A. V. Chandewar, Mahendra R. Shiradkar, *Der ChemicaSinica*, **2011**, 2, 137.
[13] KuntalHazra, L.V.G. Nargund, P. Rashmi, J.N. NarendrSharath Chandra and B. Nandha,*Der ChemicaSinica*, **2011**, 2, 149.
[14] JitendraShukla, KuntalHazra, P. Rashmi, L.V.G. Nargund, *Der ChemicaSinica*, **2011**, 2, 4.
[15] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr, R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelti, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. MoroKuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, M. Head-Gordon, E.S. Replogle, J.A. Pople, GAUSSIAN 98 (Revision A. 3) Gaussian Inc., Pittsburgh, PA, USA (1998).