STRUCTURAL AND ELECTRONIC PROPERTIES OF [Cd(BENZIMIDAZOLE)$_2$Cl$_2$]

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ABSTRACT

The complexes of transition metal salts with benzimidazole derivatives were studied as models of some important biological molecules. Metal complexes of biologically important ligands are more effective than free ones. The dichlorobis(benzimidazole)Cd(II) complex was obtained. The equilibrium geometry, harmonic vibrational frequencies and infrared intensities were calculated by density functional B3LYP method with the 6-31G(d,p) basis set and LANL2DZ for cadmium. The experimental infrared spectrum was compared with calculated and complete vibrational assignment was provided. The scaled theoretical wavenumbers showed very good agreement with the experimental values. The bond orders and the electronic properties of the complex were calculated. The calculated highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) with frontier orbital gap were presented. The electrostatic potential was calculated in order to investigate the reaction properties of the molecule.

Key words: dichlorobis(benzimidazole)Cd(II) complex, quantum chemical calculations, geometry optimization, electronic properties

INTRODUCTION

Benzimidazole is a typical heterocyclic ligand with nitrogen as the donor atom. Benzimidazole derivatives have attracted great deal of interests because of their application in the area of drugs and pharmaceuticals such as antitumor, antiviral, anticancer and antimicrobial activities [4,6,8,17]. The biological activity and pharmacological properties of the benzimidazole derivatives, have led researchers to investigate the coordination behavior of benzimidazole derivatives towards transition metal ions.

Density functional theory calculations are reported to provide excellent vibrational frequencies of organic compounds if the calculated frequencies are scaled to compensate for the approximate treatment of electron correlation, for basis set deficiencies and for the anharmonicity [2,9,10,15,16,27].

The aims of the present work is using Density functional theory calculations to determine the geometric structure of [Cd(benzimidazole)$_2$Cl$_2$], to provide complete vibrational assignment for the IR spectra and to investigate quantum chemical parameters, such as highest occupied, lowest unoccupied molecular orbital energy levels, energy gap, electrostatic potential, atomic charges.

EXPERIMENTAL

The [Cd(benzimidazole)$_2$Cl$_2$] complex was prepared according to the method outlined by Goodgame [7]. The infrared spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer in the $4000 - 400$ cm^{-1} range, with the samples embedded in KBr matrixes. The thermogravimetric analysis was performed on an apparatus STA 449 F3 JUPITER (Netzsch) for TG-DTG/DSC at heating rate $10°C$ min^{-1} from room temperature to $950°C$ under flowing air (20 cm^3 min^{-1}).

COMPUTATIONAL METHODS

The full optimization of [Cd(benzimidazole)$_2$Cl$_2$] complex was carried out by Density Functional Theories (DFT) method using Gaussian 03 software [5]. It was used Becke's three parameter hybrid exchange functional with Lee–Yang–Parr correlation functional (B3LYP) [1,14,21] with added polarization functions – 6-31G(d,p) and LANL2DZ [11,12,28] for cadmium. All calculations were converged to 10^{-8} a.u. The vibration frequencies were also calculated to the structure with optimized geometry and no imaginary frequency were obtained, so the stationary

point correspond to the minima of the potential energy surface. In order to characterize the electronic population on each atomic centre a Mulliken population analysis [18] was carried out for [Cd(benzimidazole)$_2$Cl$_2$].

An effective method for studying the reaction behavior of the molecules is the measuring of their electrostatic potential [22]. The electrostatic potential of [Cd(benzimidazole)$_2$Cl$_2$] was calculated by DFT method.

RESULTS AND DISCUSSION

1. Geometry Optimization

It is well known that DFT methods work better for systems containing transition metal atoms. For these reasons it is used the B3LYP level for analysis of dichlorobis(benzimidazole)Cd(II) complex.

The visualization of the optimized geometrical structure and atomic labeling of the title molecule are presented in Figure 1. The optimized geometry is shown in Table 1.
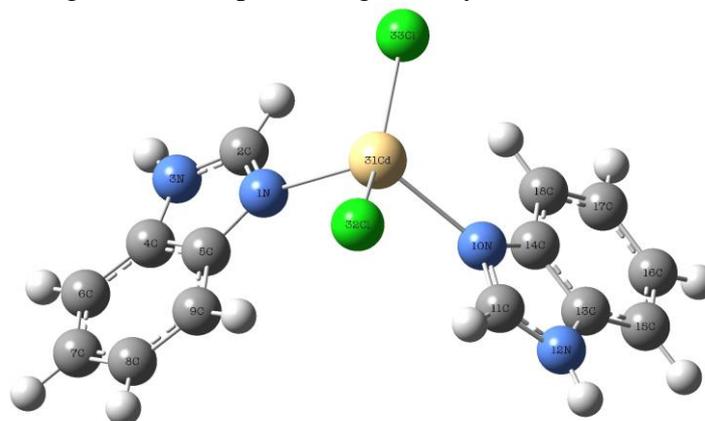

Figure 1. Optimized geometrical structure and atomic labeling of [Cd(benzimidazole)$_2$Cl$_2$]

Table 1. Some optimized geometrical parameters of [Cd(benzimidazole)$_2$Cl$_2$]

Parameters		Parameters	
Bond length (Å)		**Bond angle (degree)**	
Cd^{31}–N$^{1(10)}$	2.374	N$^{1(10)}$–C$^{2(11)}$–N$^{3(12)}$	112.2
Cd–Cl$^{32(33)}$	2.469	C$^{2(11)}$–N$^{3(12)}$–C$^{4(13)}$	107.8
N$^{1(10)}$–C$^{2(11)}$	1.317	N$^{3(12)}$–C$^{4(13)}$–C$^{5(14)}$	104.8
C$^{2(11)}$–N$^{3(12)}$	1.361	C$^{4(13)}$–C$^{5(14)}$–N$^{1(10)}$	109.1
N$^{3(12)}$–C$^{4(13)}$	1.390	C$^{5(14)}$–N$^{1(10)}$–C$^{2(11)}$	106.1
N$^{1(10)}$–C$^{5(14)}$	1.394	C$^{4(13)}$–C$^{6(15)}$–C$^{7(16)}$	116.5
C$^{4(13)}$–C$^{5(14)}$	1.412	C$^{6(15)}$–C$^{7(16)}$–C$^{8(17)}$	121.7
C$^{4(13)}$–C$^{6(15)}$	1.396	C$^{7(16)}$–C$^{8(17)}$–C$^{9(18)}$	121.7
C$^{6(15)}$–C$^{7(16)}$	1.392	C$^{8(17)}$–C$^{9(18)}$–C$^{5(14)}$	117.3
C$^{7(16)}$–C$^{8(17)}$	1.410	C$^{9(18)}$–C$^{5(14)}$–C$^{4(13)}$	120.6
C$^{8(17)}$–C$^{9(18)}$	1.391	C$^{5(14)}$–C$^{4(13)}$–C$^{6(15)}$	122.3
C$^{9(18)}$–C$^{5(14)}$	1.400	N^{1}–Cl^{32}–N^{10}–Cl^{33}	56.3
Bond angle (degree)		C$^{2(11)}$– N$^{1(10)}$–Cd^{31}–N$^{10(1)}$	-99.5
Cl^{32}–Cd^{31}–Cl^{33}	146.2	C$^{9(18)}$– C$^{5(14)}$–N$^{1(10)}$–Cd^{31}	0.3
N^{1}–Cd^{31}–N^{10}	107.6	C^{5}– N^{1}–N^{10}–C^{14}	111.5
Cd^{31}–N$^{1(10)}$–C$^{5(14)}$	133.2	C^{5}– N^{1}–N^{10}–C^{11}	-21.8

Since the crystal structure of the title compound is not available till now, the optimized structure can only be compared with other similar systems for which the crystal structures have been solved. For example, the optimized bond lengths of C–C in phenyl ring fall in the range from

1.391 to 1.412 Å for B3LYP/6-31G(d,p) method which are in good agreement with those in crystal structure of aniline (1.380 – 1.403 Å) [20] and dibromobis(benzimidazole)Zn(II) (1.323 – 1.393 Å) [23].

As can be seen from Figure 1, the Cd atom is coordinated tetrahedral by two Cl⁻ anions and two benzimidazole ligands. The optimized bond length of Cd–Cl is 2.469 Å is in good agreement with this in crystal structure of similar complex (2.451 Å) [29] and Cd–N distance of 2.374 Å is in good agreement with this in crystal structure of of similar complex (2.268 – 2.306 Å) [29,30]. Also the bond distances and angles within the benzimidazole molecules are comparable to those obtained earlier for the free benzimidazole [3].

Quantum chemical calculations provide the ability to calculate the net atomic charges (q), which are localized at the corresponding atoms as a result of the redistribution of the electrons in the molecule. Though they are not connected with physical properties and cannot be observed experimentally, they allow the understanding of the distribution of the electronic density in a system of connected atoms and predict some chemical properties of the molecules.

The nitrogen atoms exhibit their electro negative nature as expected. The net atomic charges, calculated by Mulliken and the order of the bonds in the investigated compound are presented in Table 2.

Table 2. Mulliken atomic charges and bond orders of [Cd(benzimidazole)$_2$Cl$_2$]

Atom	Charges	Bond	Bond order
Cd^{31}	11.701	Cd^{31}–N$^{1(10)}$	0.216
Cl$^{32(33)}$	−2.295	Cd–Cl$^{32(33)}$	0.543
N$^{1(10)}$	−4.233	N$^{1(10)}$–C$^{2(11)}$	1.329
N$^{3(12)}$	−0.397	C$^{2(11)}$–N$^{3(12)}$	1.120
C$^{2(11)}$	−0.141	N$^{3(12)}$–C$^{4(13)}$	1.307
C$^{5(14)}$	0.444	N$^{1(10)}$–C$^{5(14)}$	1.101
C$^{4(13)}$	0.518	C$^{4(13)}$–C$^{5(14)}$	1.224
C$^{6(15)}$	−0.137	C$^{4(13)}$–C$^{6(15)}$	1.354
C$^{7(16)}$	−0.078	C$^{6(15)}$–C$^{7(16)}$	1.514
C$^{8(17)}$	−0.108	C$^{7(16)}$–C$^{8(17)}$	1.442
C$^{9(18)}$	−0.181	C$^{8(17)}$–C$^{9(18)}$	1.420
		C$^{9(18)}$–C$^{5(14)}$	1.501

2. HOMO-LUMO Analysis

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are the main orbitals that plays an important role in chemical stability. The HOMO exhibits the ability to donate an electron and LUMO as an electron acceptor serves the ability to obtain an electron. The HOMO and LUMO energy calculated by B3LYP/6-31G (d,p) level of theory show the energy gap which reflects the chemical activity of the molecule.

Figure 2. Homo MO – (1) and Lumo MO – (2) of [Cd(benzimidazole)$_2$Cl$_2$]

Energy of frontier orbitals and energy of the gap are:
$$E_{\text{HOMO}} = -641.856 \text{ kJ/mol}$$

$$E_{LUMO} = -97.196 \text{ kJ/mol}$$
$$\Delta E_{LUMO-HOMO} = 544.660 \text{ kJ/mol}$$

High values of E_{HOMO} have a tendency of the molecule to donate electrons to appropriate acceptor molecules with low energy, empty molecular orbitals. The energy of the lowest un-occupied molecular orbital indicates the ability of the molecule to accept electrons. The lower value of E_{LUMO}, the more probable it is that the molecule would accept electrons. Consequently, concerning the value of the energy of the gap $\Delta E_{LUMO-HOMO}$, larger values of the energy difference will provide low reactivity to a chemical species. The results for the calculations of the ionization potential (I) and the electron affinity (A) by application of the Koopman's theorem [24] are shown. According to the Hartree–Fock theorem, the frontier orbital energies are given by: $I = -E_{HOMO} = 641.856$ kJ/ mol; $A = -E_{LUMO} = 97.196$ kJ/mol. This theorem establishes a relation between the energies of the HOMO and the LUMO and the ionization potential and the electron affinity, respectively. Although no formal proof of this theorem exists within DFT, its validity is generally accepted. Electronegativity (χ), chemical potential (μ) and global hardness (η), their operational and approximate definitions for [Cd(benzimidazole)$_2$Cl$_2$] are: $\chi = -\mu = (I + A)/2 = 369.526$ kJ/mol; $\eta = (I - A)/2 = 1272.33$ kJ/mol.

3. *Molecular Electrostatic Potential Analysis*

The molecular electrostatic potential surface (MEP) which is a method of mapping electrostatic potential onto the iso-electron density surface simultaneously displays electrostatic potential distribution, molecular shape, size, charge density and dipole moments of the molecule and it provides a visual method to understand the relative polarity [25].
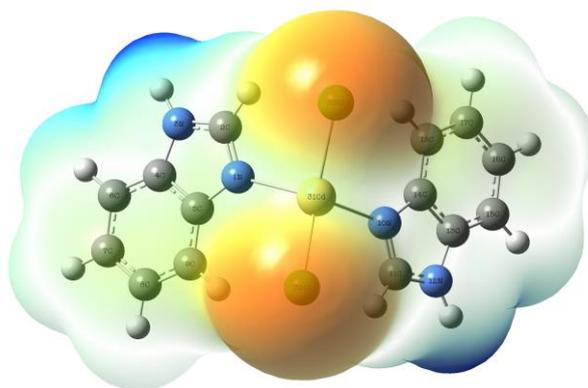

Figure 3. Molecular electrostatic potential 3D map of [Cd(benzimidazole)$_2$Cl$_2$]

The electron density isosurface for [Cd(benzimidazole)$_2$Cl$_2$] onto which the electrostatic potential surface was mapped is shown in Figure 3. The regions with negative electrostatic potential, correspond to the areas of high electron density representing a strong attraction between the proton and the points. On this molecular surface these regions are over the Cl^{32} and Cl^{33} – V_{min} = −0.06067 a.u. The positive valued regions, areas of lowest electron density, have deep blue color indicating the regions of maximum repulsion. The regions of most positive electrostatic potential are over the N^3 and N^{12} – V_{max} = 0.07737 a.u. The molecular electrostatic potential is widely used as a reactivity map displaying most probable regions for the electrophilic attack of charged point – like reagents on organic molecules. The MEP is a useful feature to study reactivity given that an approaching electrophile will be attracted to negative regions (where the electron distribution effect is dominant) [19,26].

4. *Vibrational Spectral Analysis*

The vibrational spectra of [Cd(benzimidazole)$_2$Cl$_2$] was calculated by DFT with B3LYP

functional having extended basis sets 6-31G(d,p) and LANL2DZ for cadmium. Frequencies recorded experimentally for [Cd(benzimidazole)$_2$Cl$_2$] are compared with the calculated obtained by DFT (Figure 4).

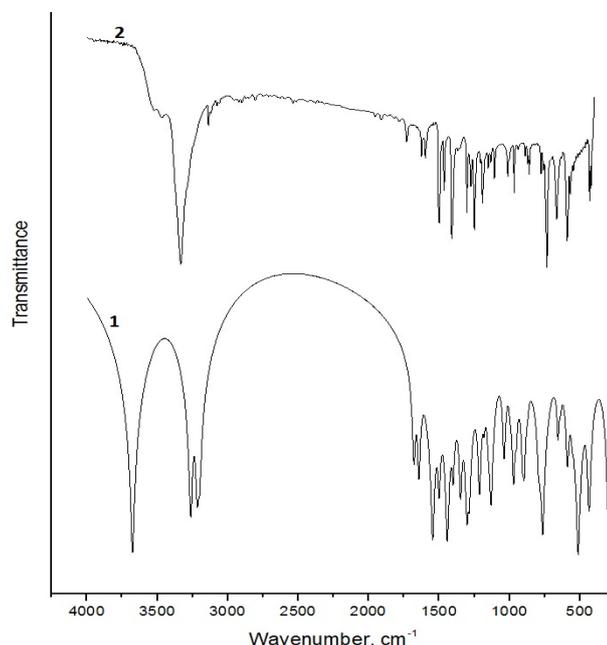**Figure 4.** IR spectrum of [Cd(benzimidazole)$_2$Cl$_2$]**,** 1 – calculated, 2 – experimental

It is well known that the harmonic frequencies by DFT calculations are usually higher than the corresponding experimental quantities due to the facts of the electron correlation approximate treatment, the anharmonicity effect and basis set deficiency, etc. [13]. In order to improve the calculated values in agreement with the experimental values, it is necessary to scale down the calculated harmonic frequencies. After scaling, the theoretical frequencies match well with the experimental ones. The experimental assigments of IR for vibrations, IR theoretical and relative intensities were reported in Table 3.

Table 3. Some experimental and calculated characteristic frequencies (cm^{-1}), IR intensity and probable assignments of [Cd(benzimidazole)$_2$Cl$_2$]

Calculated frequencies	I_{Abs}	Experimental frequencies	Assignments	Calculated frequencies	I_{Abs}	Experimental frequencies	Assignments
3675	168	3543 *w*	$\nu_{(N-H)}$ *ipb*	1131	37	1107 *s*	$\nu_{(C-H)}$ *ipb*
3262	43	3333 *s*	$\nu_{(C-H)}$ *ipb*	971	17	967 *s*	*Rband*
3201	20	3139 *w*	$\nu_{(C-H)}$ *ipb*	896	11	860 *m*	$\nu_{(C-H)}$ *ipb, Rband*
1677	12	1629 *m*	$\nu_{(C=C)}$, *Rband*	765	68	735 *s*	$\nu_{(C-H)}$ *opb*
1643	15	1597 *m*	$\nu_{(C=C)}$, *Rband*	655	3	666 *m*	$\nu_{(C-H)}$ *opb, Rband*
1545	94	1510 *s*	$\nu_{(C=N)}$, *Rband*	588	9	590 *s*	$\nu_{(C-H)}$ *opb, Rband*
1500	32	1497 *m*	$\nu_{(N-H)}$ *ipb*	513	122	570 *w*	$\nu_{(N-H)}$ *opb*
1442	90	1465 *s*	*Rband*	436	26	432 *s*	*Rband ipb*
1401	15	1410 *s*	*Rband*	435	17	422 *s*	*Rband opb*
1302	52	1303 *s*	$\nu_{(C-N)}$	299	59	–	$\nu_{as(Cd-Cl)}$
1286	35	1275 *s*	$\nu_{(C-H)}$ *ipb*	273	5	–	$\nu_{s(Cd-N)}$
1213	22	1249 *s*	$\nu_{(C-H)}$ *ipb*	269	3	–	$\nu_{as(Cd-N)}$
1147	6	1191 *m*	$\nu_{(C-H)}$ *ipb*	254	17	–	$\nu_{s(Cd-Cl)}$

Scale factors of 0.9613 for calculated frequencies with B3LYP/6-31G(d,p)
s - strong; *m* - medium; *w* - weak; *vw* - very weak
ν - stretching; *Rband* – ring deformation; *ipb* – in-plane bending; *opb* – out-of-plane bending
I_{Abs}-Theoretical infrared intensities

These assignments are important to understand the molecular structure of the title molecule. Any discrepancies noted between the observed and the calculated wavenumbers due to the fact that

the calculations were actually performed on single (isolated) molecules in the gaseous state. Thus some reasonable deviations from the experimental values seem to be justified.

CONCLUSION

The equilibrium geometries and harmonic frequencies of dichlorobis(benzimidazole)Cd(II) complex were determined and analysed at DFT level of theory utilizing 6-31G(d,p) basis set and LANL2DZ for cadmium. The difference between the observed and scaled wavenumber values of most of the fundamentals is very small. Any discrepancy noted between the observed and the calculated frequencies may be due to the fact that the calculations were done on a single molecule in the gaseous state contrary to the experimental values recorded in the presence of intermolecular interactions. Therefore, the assignments made at higher levels of theory with only resonable deviations from the experimental values, seem to be correct. HOMO-LUMO analysis may serve as a useful quantity to explain reactivity and structure–activity relationship of molecule. Information about the size, charge density distribution and structure–activity relationship of dichlorobis(benzimidazole)Cd(II) complex was obtained by mapping electron density isosurface with electrostatic potential. The present quantum chemical study may lead to the understanding of properties and activity of $[Cd(benzimidazole)_2Cl_2]$.

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