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Natural Bond Population Analysis of Dichlorobis (Benzimidazole) Co(II) Complex

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Abstract

The structure of dichlorobis(benzimidazole)Co(II) complex was calculated by Density Functional Theory (DFT) method, with Becke's three parameter exchange-functional of Lee, Yang and Paar and 6-31G(d,p) basis set. The electronic properties and the bond orders of the molecule were calculated. The natural bond orbitals calculations were performed in order to understand second-order interactions between the filled and vacant orbitals, which is a measure of the inter-molecular delocalization or hyper conjugation. The strongest electron donation become from a lone pair orbital on the nitrogen atoms, LP(1)N to the antibonding acceptor LP*(6;8)Co orbitals and from a lone pair orbital on the chlorine atoms, LP(2;4)Cl to the antibonding acceptor LP*(5;6;7)Co orbitals. The electronic properties, such as HOMO/LUMO energies were performed.

Keywords:* *Dichlorobis(benzimidazole)Co(II) complex; Density functional theory; Natural bond orbital; Electronic properties.

Introduction

Benzimidazole is a bicyclic heterocycle system consisting of two nitrogen atoms and fused phenyl ring shows wide range of biological activities. Benzimidazole possess wide spectrum of biological activities like including antibacterial, antifungal, antiviral, anti-inflammatory, anticonvulsant, antidepressant, antihypertensive, analgesic, and hypoglycemic properties. Benzimidazole derivatives exhibit a wide variety of pharmacological properties including antitumor activity [1] and inhibition of nucleic acid synthesis [2]. Due to their parasitic and antiviral activities, they were investigated in medical industrial fields.

The complexes of transition metal salts with benzimidazole derivatives are important biological molecules [3]. Metal complexes of biologically important ligands are more effective than free ones [4]. The complexe of [Co(benzimidazole)$_2$Cl$_2$] was reported from several authors [5-7].

The aim of the present work is by using natural bond orbital analysis to investigate the nature of bonding in dichlorobis(benzimidazole)Co(II) complex. The results from NBO calculations can provide the detailed insight into the electronic structure of the title compound.

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Computational Methods

The calculations were carried out at density functional level using Gaussian 03 software [8]. It was used B3LYP [9-11] with added polarization functions – 6-31G(d,p). Vibrational analysis was performed at each stationary point found, that confirm its identity as an energy minimum. The population analysis was done by the natural bond orbital method. The population analysis has also been performed by the natural bond orbital method [12] at the same level of theory using NBO 3.1 program as implemented in the Gaussian 03W package [13]. The software package GaussView, Version 5 [14] was used for data preparation and visualization of the results.

Natural bond orbital analysis stresses the role of intermolecular orbital interaction in the complex. For each donor (Φ_i) and acceptor (Φ_j), the stabilization energy ($\Delta E_{ij}^{(2)}$) associated with electron delocalization between donor and acceptors estimated as Eq. 1 [15]:

$$\Delta E_{iJ}^{(2)} = q_i \frac{\left\langle \phi_i \middle| F_{ij} \middle| \phi_j \right\rangle^2}{\varepsilon_j - \varepsilon_i} \qquad (1)$$

where q_i is the orbital occupancy, ε_i and ε_j are diagonal elements and F_{ij} is Fock matrix element [12].

Results and Discussion

The optimized equilibrium geometry was performed by the energy minimization. The optimized geometrical structure and atomic labeling of [Co(benzimidazole)$_2$Cl$_2$] are presented in FIG. 1.

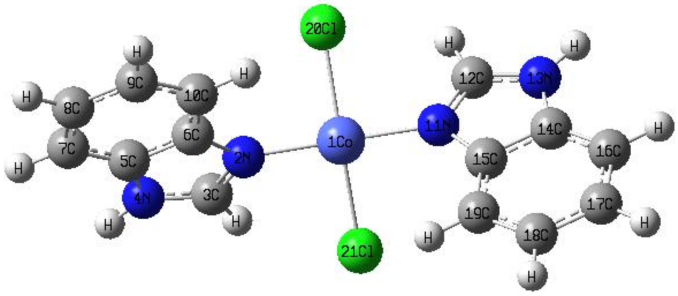


FIG. 1. **The optimized structure and atomic labeling of [Co(benzimidazole)$_2$Cl$_2$].**

The natural bond orbital analysis was provided to investigate the nature of electronic conjugation between the bonds in this molecule. The natural charges on atoms and the order of the bonds in the title compound are presented in the TABLE 1. The largest negative charges (−0.565 e) are located on two nitrogen atoms, N^4 and N^{13}. The larges positive charge (0.782) is located on Co atom.

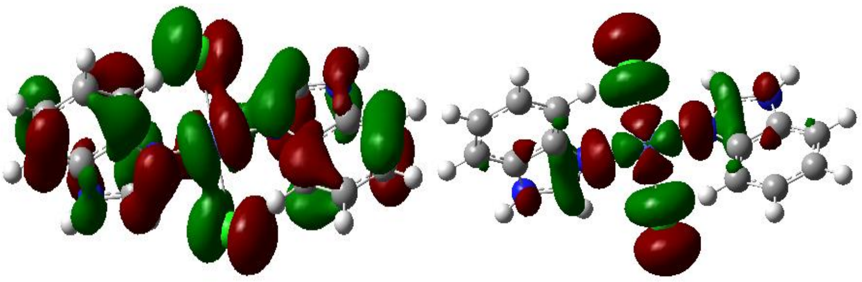
The natural bond population analysis provides a convenient basis for investigation charge transfer and conjugative interactions in the molecule. It is a method for investigation the intra- and inter-molecular bonding and interactions among bonds. This analysis provides the study of filled orbitals and empty orbitals and their interactions with the stabilization energy $E^{(2)}$ resulting from the second-order perturbation theory. Delocalization of electron density between occupied Lewis type orbitals and formally unoccupied orbitals corresponds to a stabling donor-acceptor interaction. NBO analysis was performed on the molecule at the DFT/B3LYP/6-31G(d,p) level in order to elucidate the intra molecular delocalization of electron density within the molecule. In TABLE 2 the perturbation energies of donor-acceptor interactions are presented.

TABLE 1. **The NBO atomic charges and bond orders of [Co(benzimidazole)$_2$Cl$_2$], calculated by the B3LYP/6-31G(d,p).**

Atom	Natural charges	Bond	Bond order
Co	0.782	Co–N$^{2(11)}$	0.718
Cl$^{20(21)}$	−0.563	Co–Cl$^{20(21)}$	1.052
N$^{2(11)}$	−0.537	N$^{2(11)}$–C$^{3(12)}$	1.616
N$^{4(13)}$	−0.565	C$^{3(12)}$–N$^{4(13)}$	1.373
C$^{3(12)}$	0.264	N$^{4(13)}$–C$^{5(14)}$	1.220
C$^{6(15)}$	0.130	C$^{5(14)}$–C$^{6(15)}$	1.273
C$^{5(14)}$	0.127	C$^{6(15)}$–N$^{2(11)}$	1.237
C$^{7(16)}$	−0.267	C$^{5(14)}$–C$^{7(16)}$	1.381
C$^{8(17)}$	−0.232	C$^{7(16)}$–C$^{8(17)}$	1.523
C$^{9(18)}$	−0.246	C$^{8(17)}$–C$^{9(18)}$	1.421
C$^{10(19)}$	−0.217	C$^{9(18)}$–C$^{10(19)}$	1.532
		C$^{10(19)}$–C$^{6(15)}$	1.357

The strongest interactions are the electron donations from a lone pair orbital on the nitrogen atoms, LP(1)N$^{2(11)}$ to the antibonding acceptors LP(6)*Co and LP(8)*Co orbitals which result in stabilization of the system. These interactions increases ED(0.092, 0.048 e) (LP(6)*Co and LP(8)*Co) that weakens LP(1)N$^{2(11)}$ ED(0.878) leading to stabilization of 33.97 kcal/mol and 14.02 kcal/mol. There occurs a strong intramolecular conjugative interaction of N$^{2(11)}$-C$^{3(12)}$ from N$^{4(13)}$ of LP(1)N$^{4(13)}$ $\rightarrow \pi^*$N$^{2(11)}$-C^{12} which increases ED(0.197 e) that weakens LP(1)N$^{4(13)}$ ED(0.801e) leading to stabilization of 29.72 kcal/mol. Also there occurs a strong inter molecular conjugative interaction of C$^{9(18)}$–C$^{10(19)}$ from C$^{5(14)}$–C$^{6(15)}$ of π^*C$^{5(14)}$-C$^{6(15)}$ $\rightarrow \pi^*$C$^{9(18)}$-C$^{10(19)}$ which increases ED(0.145 e) that weakens the respective bonds C$^{5(14)}$-C$^{6(15)}$ ED(0.233 e) leading to stabilization of 76.18 kcal/mol and also the conjugative interaction of π^*C$^{7(16)}$-C$^{8(17)}$ $\rightarrow \pi^*$C$^{9(18)}$-C$^{10(19)}$ leading to stabilization of 107.33 kcal/mol. The conjugative interaction of LP(4)Cl^{20} → LP(5,6,7)*Co; LP(4)Cl^{21} → LP(5,6,7)*Co leading to stabilization of 22.94, 27.02 and 29.44 kcal/mol respectively.

The HOMO and LUMO molecular orbitals are known as Frontier, which played an important role for evaluating molecular chemical stability and reactivity. The HOMO acts as an electron donor, while the LUMO is an electron acceptor. The energy gap ($\Delta E_{\mathrm{LUMO-HOMO}}$) represents the chemical reactivity of the compounds. The HOMO and LUMO plots of the title compound are shown in FIG. 2.



1 **2**

$\psi_{\text{Homo}} = 28.7\%\ \boldsymbol{6d_{xz}}(\text{Co}) + 14.0\%\ \boldsymbol{7d_{xz}}(\text{Co}) + 4.8\%\ \boldsymbol{6d_{yz}}(\text{Co}) + 4.1\%\ \boldsymbol{3p_{x}}(\text{Cl}^{21}) + 4.1\%\ \boldsymbol{3\ p_{x}}(\ (\text{Cl}^{20}) + 2.0\%\ \boldsymbol{7d_{yz}}(\text{Co})$

$\psi_{\text{Lumo}} = 38.0\%\ \boldsymbol{6d_{x^2-y^2}}(\text{Co}) + 13.6\%\ \boldsymbol{7d_{x^2-y^2}}(\text{Co}) + 9.1\%\ \boldsymbol{6d_{xy}}(\text{Co}) - 5.3\%\ \boldsymbol{3\ p_{y}}(\ (\text{Cl}^{20}) + 5.3\%\ \boldsymbol{3\ p_{y}}(\ (\text{Cl}^{21}) + 3.2\%\ \boldsymbol{7d_{xy}}(\text{Co})$

FIG. 2. **HOMO (1) and LUMO (2) for [Co(benzimidazole)$_2$Cl$_2$].**

TABLE 2. **Second-order perturbation theory analysis of Fock matrix in NBO basis.**

Donor NBO (i)	ED (i)/e	Acceptor NBO (j)	ED (j)/e	$E^{(2)}$ kcal/mol	E(j) – E(i) a.u.	F(i,j) a.u.
n1 N^{11}	0.878	n6* Co	0.092	33.97	0.52	0.171
n1 N^{11}	0.878	n8* Co	0.048	14.02	0.73	0.132
n1 N^{13}	0.801	$\pi^*N^{11}–C^{12}$	0.197	29.72	0.26	0.112
n1 N^{13}	0.801	$\pi^*C^{14}–C^{15}$	0.233	15.92	0.31	0.090
$\pi^*N^{11}–C^{12}$	0.197	$\pi^*C^{14}–C^{15}$	0.233	16.41	0.05	0.053
$\pi^*C^{14}–C^{15}$	0.233	$\pi^*C^{18}–C^{19}$	0.145	76.18	0.02	0.082
$\pi^*C^{16}–C^{17}$	0.161	$\pi^*C^{18}–C^{19}$	0.145	107.33	0.01	0.080
n2 Cl^{20}	0.983	n7* Co	0.064	16.83	0.97	0.168
n4 Cl^{20}	0.854	n5* Co	0.163	22.94	0.26	0.106
n4 Cl^{20}	0.854	n6* Co	0.093	27.02	0.48	0.143
n4 Cl^{20}	0.854	n7* Co	0.064	29.44	0.60	0.174
n2 Cl^{21}	0.983	n7* Co	0.064	16.84	0.97	0.168
n4 Cl^{21}	0.854	n5* Co	0.163	22.94	0.26	0.106
n4 Cl^{21}	0.854	n6* Co	0.092	27.02	0.48	0.143
n4 Cl^{21}	0.854	n7* Co	0.064	29.44	0.60	0.174
n1 N^{2}	0.878	n6* Co	0.093	33.97	0.52	0.171
n1 N^{2}	0.878	n8* Co	0.048	14.02	0.73	0.132
n1 N^{4}	0.801	$\pi^*N^{2}–C^{3}$	0.197	29.72	0.26	0.112
n1 N^{4}	0.801	$\pi^*C^{5}–C^{6}$	0.233	15.92	0.31	0.090
$\pi^*N^{2}–C^{3}$	0.197	$\pi^*C^{5}–C^{6}$	0.233	16.41	0.05	0.053
$\pi^*C^{5}–C^{6}$	0.233	$\pi^*C^{9}–C^{10}$	0.145	76.24	0.02	0.082
$\pi^*C^{7}\text{-}C^{8}$	0.161	$\pi^*C^{9}\text{-}C^{10}$	0.145	107.40	0.01	0.080

In TABLE 3 energies of frontier orbitals and energy of the gap for [Co(benzimidazole)$_2$Cl$_2$] are presented. For a system, a lower value of $\Delta E_{\text{LUMO–HOMO}}$ makes it more reactive or less stable and higher value represents more hardness or less softness of a compound. The energy of HOMO is related to the ionization potential and LUMO energy is related to the electron affinity and explains types of reaction in conjugated system. By application of the Koopmans' theorem [16] the frontier orbital energies are given by: $I=-E_{\text{HOMO}}=571.8684$ kJ/mol; $A=-E_{\text{LUMO}}=97.9326$ 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 [Co(benzimidazole)$_2$Cl$_2$] are: $\chi=-\mu=(I+A)/2=334.9005$ kJ/mol ; $\eta=(I-A)/2=236.9679$ kJ/mol.

TABLE 3. **Energies of frontier orbitals and energy of the gap for [Co(benzimidazole)$_2$Cl$_2$].**

Energy	**[kJ/mol]**
E_{HOMO}	–571.8684
E_{LUMO}	–97.9326
$\Delta E_{\text{LUMO–HOMO}}$	473.9358

Conclusion

The geometry of [Co(benzimidazole)$_2$Cl$_2$] was optimized with DFT/B3LYP methods using 6-31G(d,p) basis se. HOMO–LUMO studies reveal the intramolecular charge transfer through conjugated system. The natural orbital charges obtained by B3LYP/6-31G(d,p) method were presented. The transactions give stabilization to the structure were identified by second order perturbation energy calculations. Using NBO analysis the stability of the molecule arising from conjugative interaction and charge delocalization was analyzed. The strongest electron donation become from a lone pair orbital on the nitrogen atoms, LP(1)$N^{2(11)}$ to the antibonding acceptor LP*(6;8)Co orbitals and from a lone pair orbital on the chlorine atoms, LP(2;4)$Cl^{20(21)}$ to the antibonding acceptor LP*(5;6;7)Co orbitals. The present quantum chemical study may lead to the understanding of properties and activity of [Co(benzimidazole)$_2$Cl$_2$].

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