

Research Article

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Natural Bond Orbitals (NBO) for The Nanostructural Complex Diethylditiosemicarbazidediaquo Cr (III), [Cr (DDTC)₂(OH₂)₂]

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Abstract

The concept of natural orbital was first introduced by Per-Olov Löwdin in 1955 to describe the exclusive set of orthonormal functions of 1 electron which are intrinsic to the wave function of n electrons, for n > 1. An extensive treatment of the Natural Bond Orbitals (NBOs) is performed nowadays by the research group led by Professor Dr. Weinhold from the University of Wisconsin (USA). The model is based on the description of the atomic orbitals (AO), which form the characteristic bonds in the molecules. In principle, the model that describes the bonds is based on Lewis' model that describes bonds as simple, double, or triple, according to the presence of one, two, or three pairs of electrons participating in the bonds, respectively. The rigidity of the Lewis' model does not appear in the NBO model, in which electrons can achieve Rydberg energetic levels. In this work, we provide information about the constitution of the wave functions of the chemical bonds presented by the complex [Cr (DDTC)₂(OH₂)₂], as well as about the processes of charge transference. Both results are useful to electronic spectroscopy interpretation.

Key Words: Natural Bond Orbitals (NBOs); [Cr (DDTC)₂(OH₂)₂]; Wave functions;

Introduction

NBO analysis provides valuable information concerning the location of the natural atomic orbitals (NAOs), the degree of relocation of the electronic structure, the charge balance, and the order of the bonds, among other information about the electronic structure of a given complex. This study is based on a method for the optimized transformation of a given wave function in a localized form, corresponding to the elements of one center (isolated pair) and of two centers (bond) of its Lewis structure. We apply NBO analysis in order to elucidate some of the characteristics mentioned above for the chromium complex [Cr (DDTC)₂(OH₂)₂].

Materials and Methods

In order to perform the analysis of the natural bond orbitals

for the complex [Cr (DDTC)₂(OH₂)₂], it is necessary to obtain its geometric structure. We used the quantum mechanical method B3LYP (Becke's three-parameter Lee-Yang-Parr) based on the functional density theory. The calculations were performed using the Gaussian computer program (Gaussian, 2003) [1] in an Intel@ CoreTM i5 (1.80 GHz) machine with 4GB of RAM.

Results and Discussion

Structural geometry of the complex [Cr (DDTC)₂(OH₂)₂]

In Figure 1, we show the geometry obtained for [Cr (DDTC)₂(OH₂)₂].

We used the visualization program Chemcraft (Chemcraft, 2019) [7].

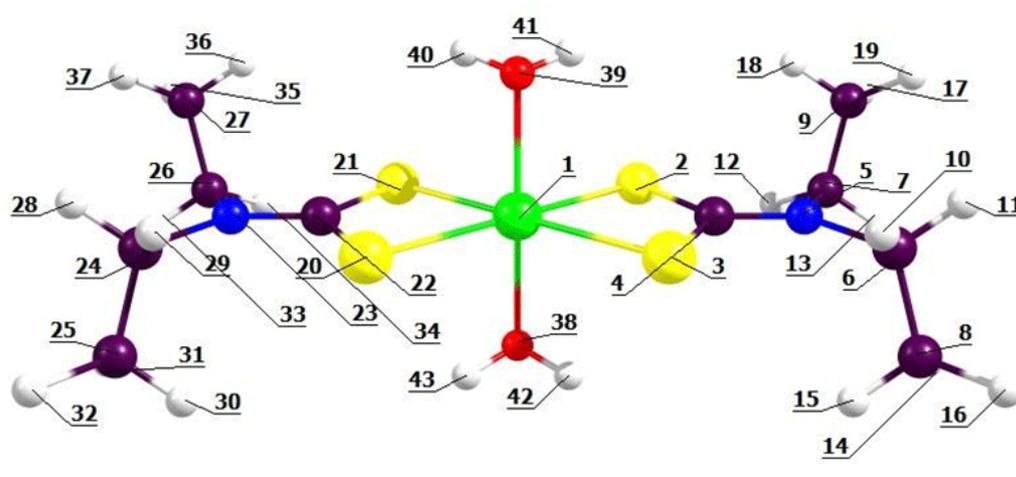


Figure 1: Structure of the complex $[\text{Cr}(\text{DDTC})_2(\text{OH}_2)_2]$ obtained using the B3LYP/6-311G(d, p) procedure

Analysis of the natural bond orbitals. Natural Lewis structures

Each type of NBO A-B decomposes into its constituent natural hybrid orbitals (NHOs) hA and hB over the atoms A and B, $\Psi_{AB} = c_A h_A + c_B h_B$, with polarization coefficients c_A and c_B that satisfy the equation $|c_A|^2 + |c_B|^2 = 1$.

The bond hybrids hA and hB are built from the natural atomic orbitals (NAOs) over the atoms A and B resembling the classic Pauling hybridization framework. In this case, however, all details of the hybridization by hybrid natural orbitals (NHOs) and the polarizations were numerically optimized in order to provide the best possible description of the electronic density.

The valence hybrids hA and hB define the two-layer valence NBOs: one orbital "in phase" of the Lewis type $\Psi_{AB} = c_A h_A + c_B h_B$ and the correspondent NBO out of phase (not occupied), not of the Lewis type: $\Psi^*_{AB} = c_B h_A - c_A h_B$.

Density matrices and orbitals

The set of NBOs of the Lewis type usually includes a central nucleus (labeled as "CR" in the output of the NBO program) and a lone valence pair ("LP"), as well as bond orbitals with two centers ("BD"). The Lewis set also includes the unoccupied valence without bond ("LP*") and the extra valence layer of Rydberg orbitals ("RY*"), as well as the antibonding valence ("BD*") from the equation $\Psi^*_{AB} = c_B h_A - c_A h_B$. Hence, the NBOs constitute a set of chemical bases of the Lewis type (without star) and orbitals that do not correspond to the Lewis type (starred). Each member is closely related to the localized Lewis structure diagram or its ability to undergo chemical change [2-6].

Considering the interactions of the alpha and beta electrons, the

Cr-S (Cr1-S20 and Cr1-S21) bonds are formed by the interaction between $\sigma_{\text{CrS}} = 0.3291(\text{sp}^0.07\text{d}^2.05)\text{Cr} + 0.9446(\text{sp}^{14.50}\text{d}^0.01)\text{S}$ with 32.05% s, 2.13% p, and 65.81% d, with the orbital centered on the Cr atom, with 6.44% s and 93.81% d, with the orbital centered on the S atom. The electronic occupancy in this bond was 1.94285 (alpha and beta electrons). The polarization coefficients to form the bond were of 10.77% for the Cr atom and of 89.23% for the S atom, presenting a high polarization on the S atom. This indicates a high ionic character for the Cr-S bond. To the alpha electrons, the S-C bonds can be represented as $\sigma_{\text{S-C}} = 0.6577(\text{sp}^{4.51}\text{d}^{0.04})\text{S} + 0.7533(\text{sp}^{2.04}\text{d}^{0.0})\text{C}$, and to the beta electrons as $\sigma_{\text{S-C}} = 0.6583(\text{sp}^{4.52}\text{d}^{0.04})\text{S} + 0.7528(\text{sp}^{2.04}\text{d}^{0.0})\text{C}$. The total electronic occupancy was 1.98275 electrons. This depicts a simple bond, with the polarization directed to the C atom with a mean value of 56.70%. Then, this bond is more covalent than ionic. The same representation of the wave function was obtained for the S3-C4 bond. As for the S20-C22 and S21-C22 bonds, the orbital wave functions are represented as follows: for the alpha electrons, $\sigma_{\text{S-C}} = 0.6577(\text{sp}^{4.51}\text{d}^{0.04})\text{S} + 0.7533(\text{sp}^{2.04}\text{d}^{0.0})\text{C}$; and for the beta electrons, as $\sigma_{\text{S-C}} = 0.6583(\text{sp}^{4.52}\text{d}^{0.04})\text{S} + 0.7528(\text{sp}^{2.04}\text{d}^{0.0})\text{C}$, with a total electronic occupancy of 1.98275. We have the same representation of the orbital wave function for the S3-C4 bond. For the S20-C22 and S21-C22 bonds, the orbital wave functions are represented as follows: to the alpha electrons, $\sigma_{\text{S-C}} = 0.6577(\text{sp}^{4.51}\text{d}^{0.04})\text{S} + 0.7533(\text{sp}^{2.04}\text{d}^{0.0})\text{C}$; and to the beta electrons, as $\sigma_{\text{S-C}} = 0.6583(\text{sp}^{4.52}\text{d}^{0.04})\text{S} + 0.7528(\text{sp}^{2.04}\text{d}^{0.0})\text{C}$, with a total electronic occupancy of 1.98275. These results also show the symmetry of the bonds in the equatorial plane of the molecular structure.

The double bond C=N for the alpha electrons is represented as $\pi_{\text{CN}} = 0.6036(\text{sp}^{1.91}\text{d}^0.0)\text{C} + 0.7973(\text{sp}^{1.61}\text{d}^0.0)\text{N}$, and $\pi_{\text{CN}} = 0.5126(\text{sp}^{1.90}\text{d}^0.0)\text{C} + 0.8587(\text{sp}^{1.60}\text{d}^0.0)\text{N}$, and for the beta electrons as: $\pi_{\text{CN}} = 0.6031(\text{sp}^{1.91}\text{d}^0.0)\text{C} + 0.7977(\text{sp}^{1.61}\text{d}^0.0)\text{N}$ and $\pi_{\text{CN}} = 0.5126(\text{sp}^{1.92}\text{d}^0.0)\text{C} + 0.7937(\text{sp}^{1.61}\text{d}^0.0)\text{N}$. The electronic

occupancy of the bond was of 1.97399 alpha electrons and 1.97391 beta electrons, with a total presence of 3.9379 in the bond. This characterizes a double bond, with a mean value of 31.40% for the polarization over the C atom, and a mean value of 68.5% for the N atom. Those values are justified by the electronegativity difference between the C and the N atom.

The molecular orbitals that contain the C atoms in the bonds of the -CH₂ and -CH₃ groups are as follows: orbitals of alpha spin: C6-C8 bonds equivalent to C7-C9, C24-C25, and C26-C27 (see the structure depicted in Figure 1).

Spin alpha orbitals

(0.99219) BD (1) C 6 - C 8

(50.59%) 0.7113* C 6 s (29.76%) p 2.36(70.20%) d 0.00(0.04%)

(49.41%) 0.7029* C 8 s (29.51%) p 2.39(70.45%) d 0.00(0.04%),

Spin beta orbitals

(0.99210) BD (1) C 6 - C 8

(50.61%) 0.7114* C 6 s (29.75%) p 2.36(70.21%) d 0.00(0.04%)

(49.39%) 0.7028* C 8 s (29.51%) p 2.39(70.45%) d 0.00(0.04%)

The C atoms with hybrid orbitals sp^{2.36} and sp^{2.39} are intermediaries in terms of Lewis for the sp² and sp³ hybridizations, with an approximate decrease of 30% of the sp³ character, and with an enhancement of the sp² character. Hence, the C-C bonds present higher force constants. We assume this as being one of the reasons for the frequency shift to the blue presented by the C-H stretch vibrations in the complex's vibrational spectrum.

Charge transference between the orbitals

Donor and acceptor interactions: analysis of the Fox matrix according to the second order perturbation theory with the NBOs as the basis. Table 1 shows the donor and acceptor orbitals and the energy in Kcal/mol. In the table, the most representative interactions are shown in the NBO/B3LYP calculations for the complex [Cr(DDTC)₂(OH₂)₂].

Molecular orbitals of the complex [Cr (DDTC)₂ (OH₂)₂]

The fundamental state of the complex presents several occupied molecular orbitals distributed between -215.66 and -0.15 a.u. in the vacuum. In Figure 2, we present the graphs of the border orbitals for [Cr (DDTC)₂(OH₂)₂] in the fundamental state.

As expressed before, the energy gaps between the unoccupied orbitals of low energy (LUMO) and the occupied orbitals of higher energy (HOMO), obtained by the B3LYP method, are: Alpha MO 102 (O) - Beta 110 MO (U) = 0.50430319 a.u.; -1.372289685004 eV.

Table 1: B3LYP/6-311G (d, p) donor-acceptor interactions between orbitals and stabilization energy (values over 25 kcal/mol)

Donor NBO (alpha electrons)	NBO acceptor	E (2) kcal/mol
89. LP*(6)Cr1	88. LP*(5)C 1	138.86
91. LP (2) S2	88. LP*(5)Cr1	28.35
94. LP (2) S3	88. LP*(5)Cr1	28.35
92. LP (3) S2	510. BD*(2) C 4 - N 5	25.31
(beta electrons)		
87. LP*(4)Cr1	85. LP*(2)Cr 1	60.18
91. LP (2) S2	85. LP*(2)Cr 1	20
94. LP (2) S 3	85. LP*(2)Cr 1	27.08
97. LP (2) S 20	85. LP*(2)Cr 1	27.08
100. LP (2) S 21	85. LP*(2)Cr 1	27.08
97. LP (2) S 20	528. BD*(2) C22 - N23	24.97

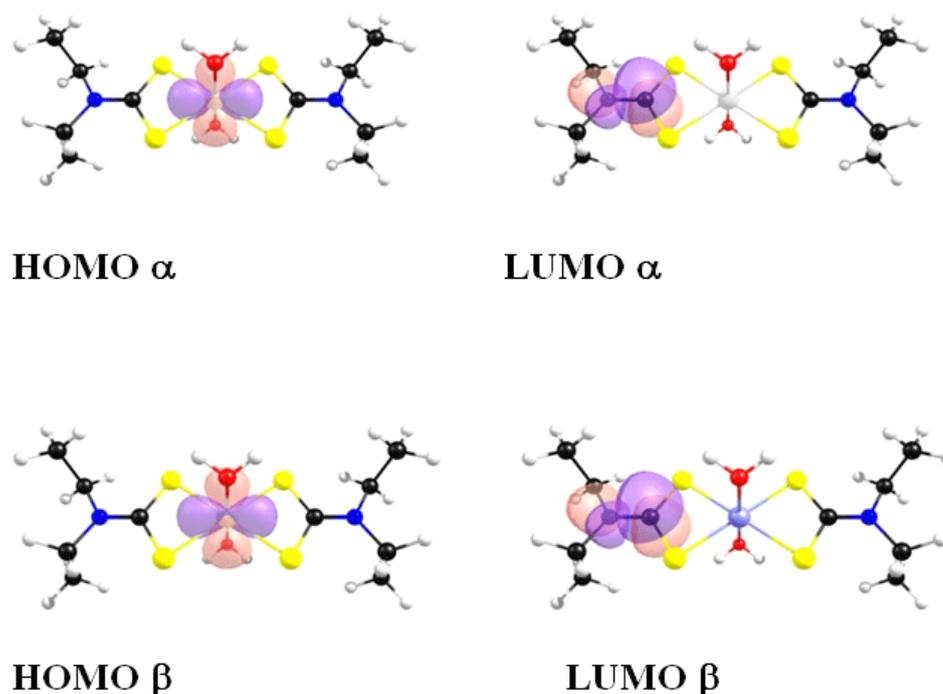


Figure 2: Representations of the HOMO (α), HOMO (β), LUMO (β), and LUMO (β) orbitals, using the B3LYP method, for the complex $[\text{Cr}(\text{DDTC})_2(\text{OH}_2)_2]$.

Conclusions

We described the natural bond orbitals for the complex $[\text{Cr}(\text{DDTC})_2(\text{OH}_2)_2]$. We discussed the constitution of the molecular orbitals that form the central bonds of the complex: N=C, C-S, Cr-S, and C-C. We also reported the polarization of the bonds as a percentage of the participant atoms, as well as the electronic occupancy of the bonds.

The processes of charge transference were analyzed in the context of the chemical bonds, considering the different types of atomic orbitals and including the most distant ones.

The $sp^{2.36}$ and $sp^{2.39}$ between the C-C atoms of the $-\text{CH}_2$ and $-\text{CH}_3$ groups, with approximate decrease of 30% of the sp^3 character, and with an enhancement of the sp^2 character, is one of the reasons for the frequency shift to the blue of the C-H stretch vibrations in the vibrational spectrum of the $[\text{Cr}(\text{DDTC})_2(\text{OH}_2)_2]$ nanostructured complex.

Declaration of Interest Statement

The authors declare that the article is original and that they have no conflict of interest.

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