

**A GRADIENT-CORRECTED HYBRID HF–DFT STUDY
OF STRUCTURE AND VIBRATIONAL SPECTROSCOPIC
PROPERTIES OF THE DICHLORODIOXOCHROMIUM(VI)
COMPLEX WITH 1,10-PHENANTHROLINE**

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Abstract: In order to get a more exact basis for the band assignments in the case of dichlorodioxochromium(VI) complex with 1,10-phenanthroline (especially regarding the order of appearance of the antisymmetric and symmetric CrO₂ stretching bands) a quantum chemical study of this system was carried out. Two levels of theory were employed – the HF/6-31++G(*d,p*) and the density-functional-theory-based (DFT) method B3–LYP/6-31++G(*d,p*). Full geometry optimizations of the title complex were carried out, employing Schlegel's gradient optimization algorithm. Harmonic vibrational analyses of the stationary points located on both potential energy hypersurfaces were subsequently carried out in order to test their character and to compute the harmonic vibrational frequencies of the complex. Predictions of the *ab initio* and DFT quantum chemical approaches regarding the order of appearance of the antisymmetric and symmetric CrO₂ stretching bands in the case of the studied complex were compared to the cases of analogous 2,2'-bipyridine and 2,2'-biquinoline complexes containing the CrO₂ group, which were previously studied by us [1–6].

Key words: vibrational spectra; hybrid HF-DFT methodology; dichlorodioxochromium(VI) complex; 1,10-phenanthroline; CrO₂ stretching vibrations

1. INTRODUCTION

Some time ago, while spectroscopically studying the MO_2Cl_2 ($M \in \{\text{Cr}, \text{Mo}, \text{W}\}$) complexes with 2,2'-bipyridine [1], a clear trend was observed concerning the separation between the bands originating from the essentially pure $\text{O}=\text{M}=\text{O}$ stretching modes (groups of bands rather than single ones were observed). The separation was largest in the case of the tungsten compound and smallest in that of chromium (it should be borne in mind that the W atom has the largest and the Cr one the smallest mass). If the OMO group is likened to a triatomic *molecule*, if its vibrations are treated classically (and independent of the rest of the molecule) and if the OMO angle is 90° , the symmetric stretching frequency should not depend on the mass of M. Although the above-mentioned angle is not (and is not expected to be) 90° , the antisymmetric OMO stretching frequency should be more mass-dependent than the symmetric one. The preliminary *ab initio* calculations (performed at the HF SCF level of theory) showed that the symmetric stretching frequency in the case of the tungsten compound is *higher* than the antisymmetric one and an analogous situation was encountered in $\text{WO}_2(\text{H}_2\text{N}-\text{CH}_2-\text{NH}_2)\text{Cl}_2$ and $\text{WO}_2(\text{NH}_3)_2\text{Cl}_2$ – two hypothetical compounds modelling the experimentally studied $\text{WO}_2(\text{bpy})\text{Cl}_2$. However, our later work (at a higher level of theory) [5] showed that for both $\text{CrO}_2(\text{bpy})\text{Cl}_2$ and $\text{CrO}_2(\text{H}_2\text{N}-\text{CH}_2-\text{NH}_2)\text{Cl}_2$ the calculated value of the symmetric stretching OCrO frequency is *lower* than that of the antisymmetric stretch. Thus it appeared to be advantageous to check whether the situation would be analogous in the case of the CrO_2Cl_2 complex with 1,10-phenanthroline – a ligand similar to 2,2'-bipyridine but larger than it. This was done by performing a gradient-corrected hybrid HF–DFT study of $\text{CrO}_2(\text{phen})\text{Cl}_2$. An additional gain from such a study would be to have a complete set of assignments for the ligand vibrations although the exact frequency values may not be extremely precise, a feature characteristic for all DFT computations and rectified by scaling with an appropriate factor. In order for such a scaling to be meaningful, however, a set of *experimental* frequencies must be available. Unfortunately, our attempts to synthesize the complex were not entirely successful so that at this point a comparison between the calculated and experimental frequencies could not be made. To circumvent this obstacle, the calculated frequencies were compared with the experimentally available frequencies for other 1,10-phenanthroline complexes [7, 8] and with the data for free phenanthroline [9].

As for the choice of the quantum chemical approach, we believed that for the problem in hand the most efficient way is to employ not the simple DFT method but a gradient-corrected hybrid HF–DFT one. The reasoning behind

such a choice was that pure DFT methodologies do not account properly for the exchange interaction component of the functional.

2. COMPUTATIONAL DETAILS

The present theoretical study was performed employing two levels of theory to treat the electronic structure problem. The first approach was the single-determinantal Hartree–Fock (HF) one, with the 6-31++G(*d,p*) basis set used for orbital expansion. However, it has been shown that the HF theory systematically neglects the dynamical electron correlation effects in multi-electronic systems, which leads to systematic overestimation of the values of the harmonic vibrational frequencies computed from the Hessian matrices corresponding to minima of the studied potential energy hypersurfaces (PEHs). Therefore in the present study we have also adopted a second methodology, which circumvents the previously elaborated problem with respect to both the dynamical electron correlation effects and the exchange component of the overall energy for a many-body fermionic system. This methodology was based on the Kohn–Sham variant of the gradient-corrected hybrid HF–DFT approach. For the purpose of this study, Becke’s three-parameter adiabatic connection exchange functional (B3 [10]) was used in combination with the Lee–Yang–Parr correlation functional (LYP [11]) – the methodology known under the acronym B3–LYP, often written simply as B3LYP), with the same basis set as in the case of HF approach. Full geometry optimizations of the dichlorodioxochromium(VI) complex with 1,10-phenanthroline were performed with the Schlegel’s gradient optimization technique (computing analytically the second derivatives of energy with respect to the nuclear coordinates [12]). The characters of the stationary points located at the molecular PEHs were tested with harmonic vibrational analyses. The absence of imaginary frequencies (negative eigenvalues of the second-derivative matrix) confirmed that both of them correspond to real minima (rather than to saddle points). Within the density functional calculations, the Kohn–Sham equations [13] were solved self-consistently using the previously mentioned basis sets for orbital expansions, and the (99,590) grid for numerical integration (99 radial and 590 angular integration points).

All quantum chemical calculations were carried out with the Gaussian 98 series of programs [14].

3. RESULTS AND DISCUSSION

Due to its potential relevance to the spectroscopic problems which are still open, the first task of this computational work was to determine the optimized geometry of the CrO_2 fragment and its closest neighborhood in the studied system.

Although no symmetry restrictions were imposed during the geometry optimizations, the minima located at molecular PEHs corresponded to C_{2v} symmetry. The calculated relevant geometric parameters for the studied complex are summarized in Table 1. The main geometrical features are the non-linearity of the CrO_2 group, the OCrO angles exceeding considerably the 90° value and being, instead, closer to the tetrahedral one. It should be noted that the calculated value of the OCrO angle in the present case is slightly larger than the value of the OWO one derived in [2]. Thus, accounting for our previous results in this field, a general conclusion may be derived for the structure around the central Cr atom. Namely, the inclusion of a more massive aromatic system as a complexing agent leads to an *increase* of the Cr–O distances, and a simultaneous *decrease* of the Cr–Cl and Cr–N distances, accompanied by a slight *increase* of the OCrO angle. Since the mass of the ligand in the presently studied complex is even higher than that of 2,2'-bipyridine, the effects are expected to be even larger in the case of $\text{CrO}_2(\text{biq})\text{Cl}_2$.

The optimized geometry of $\text{CrO}_2\text{Cl}_2(\text{phenanthroline})$ calculated at the B3–LYP/6-31++G(*d,p*) level of theory (*i.e.* the geometry corresponding to the minimum on the studied PEHs) is presented in Fig. 1.

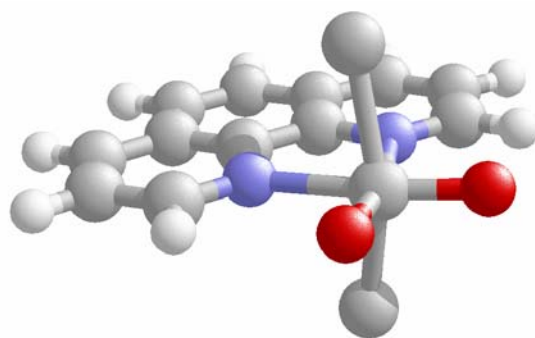


Fig. 1. The optimized geometry of $\text{CrO}_2\text{Cl}_2(\text{phenanthroline})$ at the B3–LYP/6-31++G(*d, p*) level of theory

Table 1

Optimized geometry parameters of the studied system calculated at B3-LYP/6-31++G(d,p) level of theory (all distances in angstroms, angles in degrees)

Parameter	HF	B3-LYP
$r(\text{Cr-O})$	1.582	1.579
$r(\text{Cr-Cl})$	2.368	2.355
$r(\text{Cr-N})$	2.232	2.189
$r(\text{N-C})$	1.483	1.358
$r(\text{C-C})$	–	1.476
$r(\text{N-H})$	1.022	–
$r(\text{C-H})$	1.089	–
$\angle(\text{OCrO})$	111.8	110.3
$\angle(\text{ClCrCl})$	157.2	152.4
$\angle(\text{NCrN})$	63.1	72.9
$\angle(\text{NCN})$	102.4	–
$\angle(\text{CNCr})$	–	117.8
$\angle(\text{NCC})$	–	115.6

To address the spectroscopic problems related to the title species, we have performed a harmonic vibrational analysis of the minima located on the studied PEHs. The frequencies of the most relevant modes connected to the CrO_2Cl_2 fragment for the studied system are given in Table II (the presented values have been obtained without any empirical scaling). Comparisons with our previously published data for other similar systems of this type [5] imply that upon the increase of the ligand mass and/or size, the antisymmetric and symmetric $\nu(\text{OCrO})$ modes shift to lower frequencies, while the $\delta(\text{OCrO})$ mode shifts to higher frequencies. It is important to note that, contrary to our previous results regarding the $\text{WO}_2(\text{bpy})\text{Cl}_2$ system, in the present case the antisymmetric $\nu(\text{OCrO})$ mode appears at *higher* frequencies than the symmetric one, an order which is more frequently observed in molecular spectroscopy. Data on two phenanthroline modes (to be discussed later) are also included in Table 2.

Table 2

Harmonic vibrational frequencies and IR intensities for the most relevant modes involving the OCrO group within the studied system (all calculations were carried out with the 6-31++G(d,p) basis set)

Mode	HF		B3-LYP	
	Wavenumber cm ⁻¹	I km mol ⁻¹	Wavenumber cm ⁻¹	I km mol ⁻¹
$\nu_{\text{as}}(\text{OCrO})$	1033.2	155.8	1165.8	120.3
$\nu_{\text{s}}(\text{OCrO})$	1020.1	110.4	1140.2	98.3
$\delta(\text{OCrO})$	459.3	4.7	520.4	3.2
$\nu_{\text{Kekulé}}(\text{CC})$	1090.8	8.2	1112.3	7.5
$\nu(\text{CC})$	1048.7	8.0	1089.5	6.5

In Table 3 the harmonic vibrational frequencies of selected other relevant modes, primarily those localized in the phenanthroline aromatic part of the complex, are presented. In this Table, the experimental IR spectroscopic data for phenanthroline taken from Ref. [9] are also shown.

As can be seen, the agreement between the harmonic vibrational frequencies obtained by the two methodologies in the present study and those obtained by other DFT-based methodologies [9] is very good. This may be attributed to the fact that most of the localized vibrational motions within the phenanthroline unit are only slightly affected by complexation, due to the rather rigid structure of this chelate ligand. The complexation effects on these modes are comparable to the solid state effects on this molecular system [9].

In our previous studies of various benzene ring-containing systems, we have paid particular attention to the reminiscent of the mode known as “Kekulé-type vibration” within this ring [15, 16]. This particular vibration (the ν_{14} mode of B_{2u} symmetry in benzene according to Wilson’s notation [15, 16]) has long been recognized as a multiconfigurational problem within the language of the electronic structure theory [15, 16]. Therefore it has been especially interesting to test the performances of various methods based on the density – functional theory with respect to the prediction of the exact position of this mode in the vibrational spectrum.

Table 3

Harmonic vibrational frequencies of selected relevant modes, primarily those localized in the phenanthroline aromatic part of the studied complex, together with the experimental IR spectroscopic data for phenanthroline taken from Ref. [14] (all calculations were carried out with the 6-31++G(d,p) basis set). The presented values were scaled by standard scaling factors for the corresponding levels of theory

Mode no. ^a	Symmetry	Wavenumber / cm ⁻¹		
		HF	B3-LYP	Experimental ^a
52	A ₁	1600.2	1622.1	1616
51	B ₁	1584.1	1603.8	1599
50	A ₁	1580.0	1599.3	1586
49	B ₁	1544.2	1571.2	1560
48	B ₁	1478.3	1498.5	1493
47	A ₁	1495.6	1512.3	1503
46	A ₁	1427.2	1455.2	1447
45	B ₁	1400.0	1428.3	1422
44	B ₁	1395.6	1412.8	1405
43	A ₁	1375.8	1395.8	–
42	A ₁	1322.1	1355.6	1345
41	B ₁	1300.8	1325.2	1312
40	A ₁	1278.3	1301.3	1295
39	B ₁	1254.3	1296.3	1268
38	B ₁	1201.2	1224.9	1217
37	A ₁	1190.7	1212.9	1204
33 ^b	A ₁	1090.8	1112.3	1096
31	A ₁	1048.7	1089.5	1034

^aData taken from Ref. [9]; ^bReminiscent of the $\nu_{\text{Kekule}}(\text{CC})$ mode.

Besides the "Kekulé" mode, the ν_4 (B_{2g}) vibration (the ring puckering mode), corresponding to a ring torsional motion, has also been shown to be particularly sensitive to electron correlation effects and to the basis set size [15, 16]. It has been demonstrated that even the MP2 methodology with the 6-31G(d,p) basis set fails to describe these modes correctly, and much larger basis sets of TZ2P + f quality are required for the successful treatment of this problem. On the other hand, the BLYP methodology has proven to be capable of handling both of these vibrations with sufficient accuracy, implying a correct description of the correlated density provided by this gradient-corrected DFT method [15, 16]. In the present case, on the basis of the B3-LYP/6-31++G(d,p) vibrational analysis, the "Kekulé-type" vibration in the studied system appears at significantly higher frequencies than in the free benzene molecule. As the frequency of this mode is not expected to be significantly affected by mono- and disubstitution in the benzene ring [15, 16], one is left with the conclusion that the presently employed method does not describe properly this multiconfigurational mode.

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Резиме

ИЗУЧУВАЊЕ СО ГРАДИЕНТНО КОРИГИРАНА ХИБРИДНА HF-DFT МЕТОДОЛОГИЈА НА СТРУКТУРАТА И ВИБРАЦИОНИТЕ СПЕКТРОСКОПСКИ КАРАКТЕРИСТИКИ НА КОМПЛЕКСОТ НА ДИХЛОРОДИОКСОХРОМ(VI) СО 1,10-ФЕНАНТРОЛИН

Во обид да се дојде до поточна основа за асигнација на лентите во инфрацрвениот спектар на дихлородиоксохром(VI) комплексот со 1,10-фенантролин (особено во однос на редоследот на појавување на лентите од антисиметричната и симетричната CrO₂ валентни вибрации), извршено е квантнохемиско изучување на овој систем. Беа користени две нивоа на теорија: HF/6-31++G(d,p) и методата базирана на теоријата за функционал на густината (DFT) B3-LYP/6-31++G(d,p). Извршена беше целосна оптимизација на изучуваниот комплекс, користејќи го Шлегеловиот градиентен оптимизационен алгоритам. Потоа беа извршени хармониски вибрациони анализи за стационарните точки на двете хиперповршини на потенцијалната енергија. Ова беше сторено за да се тестира карактерот на овие точки и да се пресметаат хармониските вибрациони фреквенции на комплексот. Предвидувањата за редоследот на појавување на лентите од двете валентни вибрации на CrO₂ фрагментот добиени врз основа на *ab initio* и DFT квантнохемиските приоди беа споредени со резултатите добиени за аналогните комплекси со 2,2'-бипиридин и 2,2'-бихинолин.

Клучни зборови: вибрациони спектри; хибридна HF-DFT методологија; комплекс на дихлородиоксохром(VI); 1,10-фенантролин; CrO₂ валентни вибрации

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