



# STABILIZATION OF DIOXOCHROMIUM(VI) IN THE COMPLEX WITH TETRA[BENZO]PORPHYRAZINE AND TWO OXO LIGANDS: DFT QUANTUM-CHEMICAL CONSIDERATION

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Based on the results of a quantum chemical consideration in the framework of DFT OPBE/TZVP and B3PW91/TZVP methods, the possibility of the self-existence of a chromium heteroligand complex with (NNNN)-donor macrocyclic ligand – tetra[benzo]porphyrazine and two oxo ligands where chromium oxidation degree is (+6), have been shown. The data on the key structural parameters and also, on multiplicity of the ground state of the given macrocyclic metal complex have also been presented.

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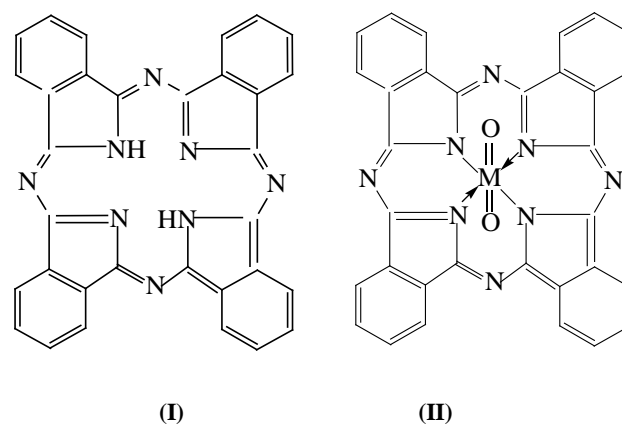
## INTRODUCTION

Cr<sup>+6</sup> oxidation degree is known to be highest theoretically possible oxidation degree of the given 3*d*-element, however, chromium compounds with such a degree of oxidation are represented only by chromium trioxide CrO<sub>3</sub> and a number of oxo anions,<sup>1,2</sup> in particular CrO<sub>4</sub><sup>2-</sup>, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, Cr<sub>3</sub>O<sub>10</sub><sup>2-</sup> and, also, by oxo-fluoro-compounds CrOF<sub>4</sub> and CrO<sub>2</sub>F<sub>2</sub>.<sup>3-11</sup> Besides, judging by the data of the review,<sup>3</sup> so far there is no information on either simple or coordination Cr(VI) compounds, which would contain other chemical elements besides oxygen and fluorine. Moreover, even the possibility of the existence of chromium(VI) fluoride (CrF<sub>6</sub>) has not been confirmed. Nevertheless, there is no reason to believe that Cr(VI) complexes cannot exist, and, in this connection, it seems interesting to find such coordination compounds.

It has long been established that a (NNNN)-donor macrocyclic ligand as tetra[benzo]porphyrazine or phthalocyanine having structural formula **I** (Figure 1) capable to stabilize a wide variety of oxidation states of *d*-elements-both low and high (see, for example, review articles<sup>12-14</sup> and the books<sup>15,16</sup>). Another ligand which is capable of stabilizing high oxidation states, is the oxo anion O<sup>2-</sup>.<sup>1-3,17,18</sup> By taking into account the aforesaid, it seems appropriate to use for Cr(VI) stabilization the combination of the given two ligands that occurs in the macrocyclic metal chelates with structural formula **II** shown in figure 1.

As it was indicated above, there is no information on such a metal complex in the current literature; nonetheless, at the present time, a possibility of its existence can be evaluated using modern quantum chemical calculation methods. In

this connection, this article has been devoted to consideration of the given problem.



**Figure 1.** The NNNN ligand (**I**) and complex (**II**) (M=Cr(VI))

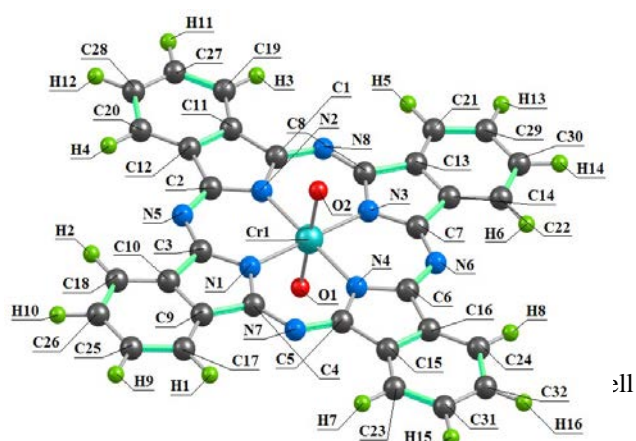
## CALCULATION METHOD

Quantum-chemical consideration of the chromium complex having formula **II** was done by using the two versions of DFT method, namely OPBE/TZVP and B3PW91/TZVP as it was done already in our earlier articles.<sup>19,20</sup> First of them combines the common TZVP extended triple zeta split-valence basis set<sup>21,22</sup> with the OPBE non-hybrid functional,<sup>23,24</sup> which as reported earlier,<sup>24-28</sup> in the case of 3*d* elements, more adequately predicts the relative energy stabilities of high-spin and low-spin states and reliably characterizes key geometric parameters of corresponding molecular structures. The other DFT calculation method combines the common TZVP and B3PW91 functional,<sup>29,30</sup> and according to data,<sup>31</sup> has minimal value of so-called "normal error" in comparison with other DFT methods. Such a conclusion is in full harmony with the data of structural parameters of macrocyclic complexes of various 3*d*-elements with phthalocyanine obtained as a result of various DFT

quantum-chemical calculations and in experiments. Calculations were done by using the Gaussian09 program package.<sup>32</sup> The correspondence of the found stationary points to energy minima was proved in all cases by the calculation of second derivatives of energy with respect to atom coordinates. All equilibrium structures corresponding to minima of the potential energy surfaces had only real positive frequency values. Chromium in the oxidation degree +6 has 3p<sup>6</sup> electronic configuration; in this connection, spin multiplicities 1, 3 and 5 were considered in calculation. Among the structures optimized at these multiplicities, the lowest-lying structure was selected. Parameters of molecular structures with the given multiplicities were calculated by the unrestricted methods (*UOPBE* and *UB3PW91*, respectively). The standard thermodynamic parameters of formation of this complex were calculated according to procedure described in literature.<sup>33</sup>

## RESULTS AND DISCUSSION

By judging to the data obtained by us as a result of our calculation carried out using the OPBE/TZVP as well as the B3PW91/TZVP, the chromium macrocyclic complex having structural formula **II** is capable of self-existence, at least in the gas phase. Molecular structure of the given complex obtained by B3PW91/TZVP method is shown in figure 2, molecular structure obtained by the OPBE/TZVP method, looks similarly. The calculated chemical bond lengths between atoms and bond angles for this macrocyclic metal complex presented in table 1. As it may be seen from these data, both methods used by us, give practically identical data for all structural parameters indicated above. A little difference between the results of these methods occurs only in the case of bond lengths Cr1O1 (Cr1O2). As it can be seen from figure 2, and table 1, the chromium complex under examination has in general a structure of regular tetragonal bipyramid or flattened octahedron (since here, the lengths of the Cr–O bonds are noticeably less rather than the lengths of the Cr–N bonds). CrN<sub>4</sub> chelate node in this macrocyclic compound has the structure of regular quadrangle (square) because the Cr–N bond lengths, distances between adjacent nitrogen atoms (N1 and N2, N2 and N3, N3 and N4, N4 and N1) absolutely identical (according to OPBE/ TZVP, 199.8 and 282.5 pm; according to B3PW91/TZVP, 199.9 and 282.7 pm, respectively), and both (NCrN) bond angles and (NNN) non-bond ones are equal to 90.0 °.



**Figure 2.** Structure of the complex obtained by B3PW91/TZVP method.

**Table 1.** Bond lengths and bond angles in the chromium complex with tetra[benzo]porphyrazine and two oxo ligands of type **II**.

Structural parameter	Calculated by DFT	
	OPBE/TZVP	B3PW91/TZVP
<b>Cr–N bond lengths in chelate node, pm</b>		
Cr1N1	199.8	199.9
Cr1N2	199.8	199.9
Cr1N3	199.8	199.9
Cr1N4	199.8	199.9
<b>Bond angles in chelate node CrN<sub>4</sub>, deg</b>		
(N1Cr1N2)	90.0	90.0
(N2Cr1N3)	90.0	90.0
(N3Cr1N4)	90.0	90.0
(N4Cr1N1)	90.0	90.0
Bond angles sum (BAS), deg	360.0	360.0
<b>Non-bond angles between N atoms in N<sub>4</sub> grouping, deg</b>		
(N1N2N3)	90.0	90.0
(N2N3N4)	90.0	90.0
(N3N4N1)	90.0	90.0
(N4N1N2)	90.0	90.0
Non-bond angles sum (NBAS), deg	360.0	360.0
<b>Bond angles in 6-numbered ring (Cr1N2C1N8C8N3), deg</b>		
(Cr1N2C1)	125.0	124.7
(N2C1N8)	128.1	128.1
(C1N8C8)	124.0	124.4
(N8C8N3)	128.2	128.1
(C8N3Cr1)	124.7	124.7
(N3Cr1N2)	90.0	90.0
Bond angles sum (BAS <sup>6</sup> ), deg	720.0	720.0
<b>Bond angles in 5-numbered ring (C2N2C1C11C12), deg</b>		
(C2N2C1)	110.3	110.8
(N2C1C11)	108.6	108.3
(C1C11C12)	106.3	106.3
(C11C12C2)	106.3	106.3
(C12C2N2)	108.5	108.3
Bond angles sum (BAS <sup>5</sup> ), deg	540.0	540.0
<b>C–N bond lengths in 6-numbered chelate rings, pm</b>		
N1C3	135.6	135.4
N1C4	136.3	135.4
N2C1	135.6	135.4
N2C2	136.3	135.4
N7C4	132.6	132.3
N7C5	133.1	132.3
<b>C–C bond lengths in 5-numbered ring, pm</b>		
C1C11	146.9	146.8
C11C12	140.6	140.1
C12C2	146.8	146.8
<b>Cr–O bond length, pm</b>		
Cr1O1 (Cr1O2)	168.7 (168.7)	167.8 (167.8)
<b>Bond angles between fluorine, copper and nitrogen atoms, deg</b>		
O1Cr1N1 (O2Cr1N1)	90.0 (90.0)	90.0 (90.0)
O1Cr1N2 (O2Cr1N2)	90.0 (90.0)	90.0 (90.0)
O1Cr1N3 (O2Cr1N3)	90.0 (90.0)	90.0 (90.0)
O1Cr1N4 (O2Cr1N4)	90.0 (90.0)	90.0 (90.0)
<b>Bond angles between fluorine, copper and nitrogen atoms, deg</b>		
O1CrO2	180.0	180.0

As may be seen from Fig. 3, Cr atom is oriented in the center of square formed by four donor nitrogen atoms N1, N2, N3 and N4. Both four 6-membered metal-chelate rings and four 5-membered non-chelate one with one nitrogen atom and four carbon atoms adjoining to 6-membered metal-chelate rings, as in the range of bond angles in them. Besides, all they are strictly coplanar since the sum of the internal bond angles in each of the 6-membered cycles (BAS<sup>6</sup>) is exactly 720°, in the 5-membered ones (BAS<sup>5</sup>), is exactly 540°, which coincides with the sums of the internal angles in a flat hexagon and pentagon, respectively. The given complex has a center of symmetry and therefore for it a priori one can expect that value of the electric moment of the dipole will be zero. The data for calculating this parameter (0.00 Debye units according to both OPBE/TZVP and B3PW91/TZVP method) are in full accordance with such a forecast.

The ground state of the chromium complex considered by us, according to both calculation methods used here, is a spin triplet ( $M_S = 3$ ) that is a little unusually for such an electron configuration as  $3p^6$ . However, according to the data obtained as a result of using these methods, the nearest excited singlet state in the case of OPBE/TZVP method has only a little higher energy (12.0 kJ mol<sup>-1</sup>) whereas in the case of B3PW91/TZVP method, much more significant one (97.1 kJ mol<sup>-1</sup>). By taking into account that, as it was indicated in the section Calculation Method, that OPBE/TZVP method more adequately predicts the relative energy stabilities of high-spin and low-spin states than B3PW91/TZVP method, the first value must be more reliable. Such a conclusion is favored by NBO analysis of the given complex according to which, the values of spin square operator ( $\langle S^2 \rangle$ ) of the given compound are 2.0554 and 2.1008, respectively, that correspond of availability of namely two unpaired electrons in it and  $M_S = 3$ .

## CONCLUSION

From the data presented above, it clearly follows that both variants of the DFT method, used in the given article (OPBE/TZVP and B3PW91/TZVP), quite definitely showed about the possibility of the existence of chromium complex of composition [CrL(O)<sub>2</sub>] containing double deprotonated form (L<sup>2-</sup>) of tetra[benzo]porphyrzine (H<sub>2</sub>L) and two oxo ligands (O<sup>2-</sup>). In this complex, as expected, donor nitrogen atoms occupy four positions of the "equatorial plane" of the tetragonal bipyramid, oxygen atoms occupy its two axial positions (Figure 2). The Cr–N and Cr–O atom interatomic distances (Table 1) in this compound correspond in their size to single bonds chromium – nitrogen (Cr–N) and to double chromium – oxygen (Cr=O), and, hence, the oxidation degree of the given 3d-element in the given macrocyclic metal complex is namely +6. It should be noted in this connection that, according to our calculations of standard thermodynamic parameters  $\Delta H_{f, 298}^0$ ,  $S_{f, 298}^0$  and  $\Delta G_{f, 298}^0$  of the complex under study using method described in<sup>33</sup>, all they are positive (369.7 kJ mol<sup>-1</sup>, 1152.4 J mol<sup>-1</sup> K and 632.9 kJ mol<sup>-1</sup>, respectively by OPBE/TZVP method), and, hence, the given compound cannot be obtained from simple substances formed by chemical elements containing in its composition (Cr, O, N, C and H). Nevertheless, both variants of the DFT method used by us, predict the possibility of the existence of this complex, and there is

every reason to believe that this compound sooner or later will be obtained experimentally also.

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## CONFLICT OF INTEREST

The authors declare that they have no conflict of interest, financial or otherwise.

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