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Keywords: Cr<sup>+6</sup>, oxo ligand, tetra[benzo]porphyrazine, DFT method.

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**

 $Cr^{+6}$  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  $CrO_3$  and a number of oxo anions,<sup>1,2</sup> in particular  $CrO_4^{2-}$ ,  $Cr_2O_7^{2-}$ ,  $Cr_3O_{10}^{2-}$  and, also, by oxo-fluoro-compounds  $CrOF_4 \mu CrO_2F_2$ .<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 ( $CrF_6$ ) 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  $O^{2-1-3,17,18}$ . 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 3d elements, more adequately predicts the relative energy stabilities of high-spin and lowspin 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 3d-elements with phthalocyanine obtained as a result of various DFT

experiments. quantum-chemical calculations and in 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  $3p^6$ 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 to 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.

OPBE/TZVPB3PW91/TZVFCr1N1199.8199.9Cr1N2199.8199.9Cr1N3199.8199.9Cr1N4199.8199.9Cr1N390.090.0(N1Cr1N2)90.090.0(N3Cr1N4)90.090.0(N4Cr1N1)90.090.0Bond angles sum360.0360.0(N4Cr1N1)90.090.0Bond angles sum360.0360.0(N1N2N3)90.090.0(N1N2N3)90.090.0(N3N4N1)90.090.0(N3N4N1)90.090.0(N3N4N1)90.090.0(N2N3N4)90.090.0(N3N4N1)90.090.0(N2N3N4)90.090.0(N4R5), deg124.1(N2N3N4)125.0124.7(N2C1N8)128.1128.1(N3C1N2)90.090.0(N3C1N2)90.090.0Bond angles in 6-numEvt Tru (TCT2VEVTRCSN3), deg(N2C1N8)128.1128.1(N3C1N2)90.090.0Bond angles sum (BAS*)720.0deg(C2N2C1)106.3106.3(C11C12)106.3106.3(C11C12)106.3106.3(C11C12)105.6135.4N1C3135.6135.4N1C3135.6135.4N1C4136.3135.4N1C5135.4135.4N1C4136.3135.4N1C5 <t< th=""><th>Structural parameter</th><th colspan="2">Calculated by DFT</th></t<>	Structural parameter	Calculated by DFT		
Cr-Nb ond lengths in check a mode, pm           Cr1N1         199.8         199.9           Cr1N2         199.8         199.9           Cr1N3         199.8         199.9           Cr1N3         199.8         199.9           Cr1N3         90.0         90.0           (NICr1N2)         90.0         90.0           (NICr1N1)         90.0         90.0           (NICr1N1)         90.0         90.0           (NICr1N1)         90.0         90.0           (NICr1N1)         90.0         90.0           (NICr1N2)         90.0         90.0           (NICr1N1)         90.0         90.0           (NICr1N2)         90.0         90.0           (NIX2N3)         90.0         90.0           (NIX3N4)         90.0         90.0           (NANN1N2)         90.0         90.0		OPBE/TZVP	B3PW91/TZVP	
Crini         199.8         199.9           Crini         199.0         90.0           (NiCrini)         90.0         90.0           (Nacrini)         90.0         90.0           (Nacrini)         90.0         90.0           (Nacrini)         90.0         90.0           (Nanshai)         90.0         90.0           (Nathini)         124.7         124.7           (Nacrinis)         124.7         124.7           (Nacrinis)         124.7         124.7           (Nacrinis)         124.7         124.	Cr. N hond lon	aths in cholato i	l	
Cr1N2         199.8         199.9           Cr1N3         199.8         199.9           Cr1N4         199.8         199.9           Bond angles in levate node CNA, deg           (N1Cr1N2)         90.0         90.0           (N2Cr1N3)         90.0         90.0           (N3Cr1N4)         90.0         90.0           (N4Cr1N1)         90.0         90.0           Bond angles sum         360.0         360.0           (BAS), deg         90.0         90.0           (N1N2N3)         90.0         90.0           (N3AN1)         90.0         90.0           (N4N1N2)         90.0         90.0           (N4N1N2)         90.0         90.0           (N4N1N2)         90.0         90.0           (N2T1N2)         90.0         90.0           (N2T1N2)         90.0         90.0           (N2T1N2)         90.0         90.0           (N2T1N2)         90.0         90.0           Bond angles sum (BAS <sup>5</sup> ), 720.0         720.0           (N2C1N1)         128.2         128.1           (N2C1N2)         90.0         90.0           Bond angles sum         540.0 <t< td=""><td>Cr1N1</td><td>199.8</td><td>199 9</td></t<>	Cr1N1	199.8	199 9	
CrIN3         199.8         199.9           CrIN4         199.8         199.9           CrIN4         199.8         199.9           Bond angles in believe to the rest of the	Cr1N2	199.8	199.9	
Cr11N3         199.8         199.9           Bond angles is leave on the sector of the sec	Cr1N3	199.8	199.9	
Bond angles in cheate node CrN4, deg           (N1Cr1N2)         90.0         90.0           (N2Cr1N3)         90.0         90.0           (N3Cr1N4)         90.0         90.0           (N4Cr1N1)         90.0         90.0           Bond angles sum         360.0         360.0           Bond angles sum         360.0         90.0           (N1N2N3)         90.0         90.0           (N1N2N3)         90.0         90.0           (N3N4N1)         90.0         90.0           (N4N1N2)         90.0         90.0           Non-bond angles sum         360.0         360.0           Non-bond angles sum         360.0         124.7           (N2C1N8)         128.1         128.1           (C1N2C1)         125.0         124.7           (N3Cr1N2)         90.0         90.0           Bond angles in 5-numbered ring (C2N2CIT1C12), deg         deg           (C2N2C1)         110.3         110.8           (N2C1C11)         108.6         108.3           (C11C12)         106.3         106.3           (C2N2C1)         110.3         110.8           (N2C1C11)         108.5         108.3 <tr< td=""><td>Cr1N4</td><td>199.8</td><td>199.9</td></tr<>	Cr1N4	199.8	199.9	
(N1Cr1N2)         90.0         90.0           (N2Cr1N3)         90.0         90.0           (N3Cr1N4)         90.0         90.0           (N4Cr1N1)         90.0         90.0           Bond angles sum         360.0         360.0           BAS), deg             Non-bond angles between N atoms in N grouping, deg            (N1N2N3)         90.0         90.0           (N3AN1)         90.0         90.0           (N4N1N2)         90.0         90.0           Non-bond angles sum         360.0         360.0           (NBAS), deg             Bond angles in 6-numbered ring (Cr1N2Cl N80           128.1         128.1         128.1           (C1N2Cl)         124.7         124.7           (N3Cr1N2)         90.0         90.0           Bond angles sum (BAS <sup>6</sup> ),         720.0         720.0           dgg           10.8           (N2Cl11)         108.6         108.3           (N2Cl21)         106.3         106.3           (C2N2Cl)         106.3         106.3           (C1Cl12)         106.3         135.4	Bond angles in chelate node CrN <sub>4</sub> , <i>deg</i>			
(N2Cr1N3)         90.0         90.0           (N3Cr1N4)         90.0         90.0           (N4Cr1N1)         90.0         90.0           Bond angles sum         360.0         90.0           (BAS), deg             Non-bond angles between N atoms in V grouping, deg            (N1N2N3)         90.0         90.0           (N2N3N4)         90.0         90.0           (NNAN1N)         90.0         90.0           (Navinna)         90.0         90.0           (NAVIN2)         90.0         90.0           Non-bond angles in 6-number tring (Cr1N2CI)         124.7           (N2CIN8)         128.1         128.1           (CT1N2CI)         124.0         124.4           (N8C8N3)         128.2         128.1           (CRN3Cr1)         124.7         124.7           (N3Cr1N2)         90.0         90.0           Bond angles sum (BAS <sup>6</sup> ),         72.0         72.0           deg          106.3         106.3           (C2N2C1)         106.3         106.3         106.3           (C1C12C2)         106.3         106.3         106.3           (C1C12C2)         <	(N1Cr1N2)	90.0	90.0	
(N3Cr1N4)90.090.0(N4Cr1N1)90.090.0Bond angles sum360.0360.0(BAS), deg <b>Non-bond angles betwern N atoms in V grouping, deg</b> (N1N2N3)90.090.0(N2N3N4)90.090.0(N3N4N1)90.090.0(N4N1N2)90.090.0(N4N1N2)90.090.0(N4N1N2)90.090.0(N4N1N2)90.090.0(N4N1N2)90.0124.7(N2C1N8)128.1128.1(C1N2C1)125.0124.7(N2C1N8)128.2128.1(C1N8C8)124.0124.4(N8C8N3)128.2128.1(C8N3Cr1)124.7124.7(N3Cr1N2)90.090.0Bond angles sum (BAS <sup>6</sup> )72.0deg72.072.0deg106.3106.3(C11C12)106.3106.3(C12C2N2)108.5108.3(C11C122)106.3106.3(C12C2N2)108.5108.3Bond angles sum540.0540.0(BAS <sup>5</sup> ), deg135.4N1C4136.3135.4N2C2136.3135.4N1C4136.3135.4N2C1135.6135.4N1C4136.3135.4N2C2136.3135.4N1C4136.3135.4N2C2136.3135.4N2C3135.4135.4N2C4132.6132.3N7	(N2Cr1N3)	90.0	90.0	
(N4Cr1N1)90.090.0Bond angles sum360.0360.0(BAS), deg360.0360.0(N1N2N3)90.090.0(N2N3N4)90.090.0(N3N4N1)90.090.0(N4N1N2)90.090.0(N4N1N2)90.0360.0(NBAS), deg50.0360.0(N2C1N8)128.1128.1(C1N2C1)125.0124.7(N2C1N8)128.1128.1(C1N8C8)124.0124.4(N3Cr1N2)90.090.0Bond angles sum (BAS <sup>6</sup> ), 720.0720.0Bond angles sum (BAS <sup>6</sup> ), 720.0720.0C2N2C1)106.3106.3(C1C11C12)106.3106.3(C1C11C12)106.3106.3(C11C12C2)106.3106.3(C11C12C2)106.3135.4N1C3135.6135.4N1C3135.6135.4N1C3135.6135.4N1C4136.3135.4N2C2136.3135.4N2C3135.4135.4N2C4132.6132.3N7C4132.6132.3N7C4132.6135.4N2C4136.3135.4N2C5146.8146.8C1C11140.6140.1C12C2146.8146.8C11C12140.61	(N3Cr1N4)	90.0	90.0	
Bond angles sum       360.0         (BAS), deg         Non-bond angles betwern N atoms in K grouping, deg         (N12N3)       90.0       90.0         (N2N3N4)       90.0       90.0         (N3N4N1)       90.0       90.0         (N4N1N2)       90.0       90.0         Non-bond angles sum       360.0       360.0         (NBAS), deg           Bond angles in 6-number tring (CTINECINE NSC8N3), deg         (Cr1N2C1)       125.0       124.7         (N2C1N8)       128.1       128.1         (CR1N8C8)       128.2       128.1         (N8C8N3)       128.2       128.1         (R8C8N3)       128.2       128.1         (S8N3Cr1)       124.7       124.7         (N3Cr1N2)       90.0       90.0         Bond angles sum (BAS <sup>6</sup> ),       720.0       720.0         deg        110.8         (C1C1C12)       106.3       106.3         (C1C1C12)       106.3       106.3         (C1C1C12)       106.3       135.4         (N2C2       136.3       135.4         N1C3       135.6       135.4         N1C4	(N4Cr1N1)	90.0	90.0	
Non-bond angles between N atoms in N₄ grouping, deg         Number Nations in Na grouping, deg         (N1N2N3)       90.0       90.0         (N2N3N4)       90.0       90.0         (N4N1N2)       90.0       90.0         (N4N1N2)       90.0       90.0         (Nambond angles sum       360.0       360.0         (NBAS), deg       124.0       124.7         (N2C1N8)       128.1       128.1         (C1N8C8)       124.0       124.4         (N8SN3)       128.2       128.1         (C8N3Cr1)       124.7       124.7         (N3Cr1N2)       90.0       90.0         Bond angles sum (BAS <sup>6</sup> ),       720.0       720.0         deg       100.3       110.8         (C2N2C1)       110.3       110.8         (N2C1C11)       108.6       108.3         (C11C1C2)       106.3       106.3         (C11C1C2)       106.3       106.3         (BAS <sup>5</sup> ), deg       135.4       135.4         N1C3       135.6       135.4         N1C4       136.3       135.4         N1C4       136.3       135.4         N1C4       136.3       135.4 <td>Bond angles sum</td> <td>360.0</td> <td>360.0</td>	Bond angles sum	360.0	360.0	
Non-bond angles between N atoms in N₄ grouping, deg           (N1N2N3)         90.0         90.0           (N2N3N4)         90.0         90.0           (N3N4N1)         90.0         90.0           (N4N1N2)         90.0         90.0           Non-bond angles sum         360.0         360.0           (NBAS), deg          2           Bond angles in 6-number of ring (Cr1N2C1)         125.0         124.7           (N2C1N8)         128.1         128.1         (24.4)           (N8C8N3)         128.2         128.1         (24.7)           (N3Cr1N2)         90.0         90.0         90.0           Bond angles sum (BAS <sup>6</sup> ),         720.0         720.0           deg          720.0         720.0           (C2N2C1)         110.3         110.8           (N2C1C11)         108.6         108.3           (C11C12C2)         106.3         106.3           (C11C1C2Q)         106.3         135.4           (N2C2         136.3         135.4           N1C3         135.6         135.4           N1C4         136.3         135.4           N2C2         136.3         136.4	(BAS), deg			
(N1N2N3)90.090.0(N2N3N4)90.090.0(N3N4N1)90.090.0(N4N1N2)90.090.0Non-bond angles sum360.0360.0(NBAS), deg360.0360.0Bond angles in 6-number tring (Cr1N2C1)125.0124.7(N2C1N8)128.1128.1128.1(C1N8C8)124.0124.4(N8C8N3)128.2128.1(C8N3Cr1)124.7124.7(N3Cr1N2)90.090.0Bond angles sum (BAS <sup>6</sup> ),720.0720.0deg720.0720.0C2N2C1)(D10.3110.8(N2C1C11)108.6108.3(C121C12)106.3106.3(C12C2N2)108.5108.3Bond angles sum540.0540.0(BAS <sup>5</sup> ), deg135.4NIC3NIC3135.6N1C4136.3135.4N1C4136.3135.4N2C2136.3135.4N2C2136.3135.4N2C4132.6132.3N7C5133.1132.3C-C bond length: jr S-numberet tring, pmC1C11146.9146.8C11C12140.6140.1C12C2168.7 (168.7)167.8 (167.8)Diration (o2Cr1N3)90.0 (90.0)90.0 (90.0)C1C1N1 (02Cr1N1)90.0 (90.0)90.0 (90.0)C1C1N3 (02Cr1N3)90.0 (90.0)90.0 (90.0)O1Cr1N4 (02Cr1N4)<	Non-bond angles between N atoms in N <sub>4</sub> grouping, <i>deg</i>			
(N2N3N4)         90.0         90.0           (N3N4N1)         90.0         90.0           (N4N1N2)         90.0         360.0           Non-bond angles sum         360.0         360.0           (NBAS), deg         200.0         124.7           Bond angles in 6-numberd ring (Cr1N2C1)         125.0         124.7           (N2C1N8)         128.1         128.1         (C1N8C8)           (C1N8C8)         124.0         124.4           (N8C8N3)         128.2         128.1           (C8N3Cr1)         124.7         124.7           (N3Cr1N2)         90.0         90.0           Bond angles in 5-numberd ring (C2N2CT11C12), deg         deg           C2N2C1)         110.3           (N2C1C11)         108.6         108.3           (C1C11C12)         106.3         106.3           (C1C11C2)         106.3         106.3           (C1C11C12)         108.5         108.3           (C1C11C12)         106.3         135.4           (N1C3         135.6         135.4           N1C3         135.6         135.4           N1C4         136.3         135.4           N2C2         136.3	(N1N2N3)	90.0	90.0	
(N3N4N1)         90.0         90.0           (N4N1N2)         90.0         90.0           Non-bond angles sum         360.0         360.0           (NBAS), deg          360.0         360.0           Bond angles in 6-numbered ring (Cr1N2C1)         125.0         124.7           (N2C1N8)         128.1         128.1         (C1N8C8)         124.0           (C1N8C8)         124.0         124.4         (N8C8N3)         124.7           (N3Cr1N2)         90.0         90.0         90.0           Bond angles sum (BAS <sup>6</sup> ),         720.0         720.0           deg           720.0           C2N2C1)         110.3         110.8           (N2C1C11)         108.6         108.3           (C11C12C2)         106.3         106.3           (C11C12C2)         106.3         106.3           (C11C12C2)         106.3         135.4           N1C3         135.6         135.4           N1C4         136.3         135.4           N1C4         136.3         135.4           N1C4         132.6         132.3           N7C4         132.6         132.3	(N2N3N4)	90.0	90.0	
(N4N1N2)       90.0       90.0         Non-bond angles sum       360.0       360.0         (NBAS), deg       360.0       124.7         Bond angles in 6-numbered ring (Cr1N2C1)       125.0       124.7         (N2C1N8)       128.1       128.1         (C1N3C8)       124.0       124.4         (N8C8N3)       128.2       128.1         (C8N3Cr1)       124.7       124.7         (N3C1N2)       90.0       90.0         Bond angles sum (BAS <sup>6</sup> ),       720.0       720.0         deg	(N3N4N1)	90.0	90.0	
Non-bond angles sum         360.0         360.0           (NBAS), deg	(N4N1N2)	90.0	90.0	
Bond angles in 6-numbered ring (Cr1N2C1N8C8N3), deg           (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> ),         720.0         720.0           deg	Non-bond angles sum	360.0	360.0	
Transmit and the function of the problem in the problem in the function of the problem in the probl	Bond angles in 6-numbered ring (Cr1N2C1N8C8N3) deg			
(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> ),       720.0       720.0         deg	(Cr1N2C1)	125.0	124.7	
(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> ),       720.0       720.0         deg	(N2C1N8)	125.0	124.7	
(N8C8N3)       128.2       128.1         (C8N3Cr1)       124.7       124.7         (N3Cr1N2)       90.0       90.0         Bond angles sum (BAS <sup>6</sup> ),       720.0       720.0         deg	(C1N8C8)	124.0	120.1	
(C8N3Cr1)         124.7         124.7           (N3Cr1N2)         90.0         90.0           Bond angles sum (BAS <sup>6</sup> ),         720.0         720.0           deg	(N8C8N3)	128.2	124.4	
(N3Cr1N2)         90.0         90.0           Bond angles sum (BAS <sup>6</sup> ),         720.0           Zender         Zender           Bond angles in 5-numbered ring (C2N2C11C12), deg           (C2N2C1)         110.3           (N2C1C11)         108.6           (N2C1C11)         106.3           (C1C11C12C)         106.3           (C1C11C2C)         106.3           (C1C12C2N2)         108.5           Bond angles sum         540.0           (BAS <sup>5</sup> ), deg         540.0           V           V           NIC3           135.6         135.4           N1C4         136.3         135.4           N2C2         136.3         135.4           N2C2         136.3         135.4           N2C2         136.3         135.4           N7C4         132.6         132.3           N7C5         133.1         132.3           C-C bond lengths in 5-numbered ring, pm           C1C11         146.9         146.8           C11C12         140.6         140.1           C12C2         146.8         146.8           C11C12         140.6	(C8N3Cr1)	124.7	124.7	
Bond angles sum (BAS <sup>6</sup> ),         720.0         720.0           Bond angles in 5-numbered ring (C2N2C1C11)         110.3         110.8           (N2C1C11)         108.6         108.3           (C1C11C12)         106.3         106.3           (C1C2N2C1)         108.5         108.3           (C1C11C12)         106.3         106.3           (C1C12C2N2)         106.3         106.3           Bond angles sum         540.0         540.0           (BAS <sup>5</sup> ), deg         Vertex rings, pm           N1C3         135.6         135.4           N1C4         136.3         135.4           N2C2         136.3         135.4           N2C2         136.3         135.4           N7C4         132.6         132.3           Or-C-bond lengths in 5-numbered ring, pm         Vertex ring, pm           C1C11         146.9         146.8           C11C12         140.6         140.1           C12C2         146.8         146.8           C11C12         140.6         140.1           C12C2         146.8         146.8           C11C12         140.6         140.1           C12C2         167.8 (167.8)         167.8 (167.8)	(N3Cr1N2)	90.0	90.0	
deg           Bond angles in 5-number dring (C2N2CIC11C12), deg           (C2N2C1)         110.3         110.8           (N2C1C11)         108.6         108.3           (C1C11C12)         106.3         106.3           (C1C2C2N2)         106.3         106.3           (C12C2N2)         108.5         108.3           Bond angles sum         540.0         540.0           (BAS <sup>5</sup> ), deg         -         -           NIC3         135.6           N1C4         136.3         135.4           N2C2         136.3         135.4           N2C2         136.3         135.4           N2C2         136.3         135.4           N7C4         132.6         132.3           C-C bond lengths in 5-numbered ring, pm           C1C11         146.9         146.8           C11C12         140.6         140.1           C12C2         146.8         146.8           C1C11         146.9         146.8           C11C12         140.6         140.1           C12C2         146.8         146.8           C11C12         140.6         140.1           C12C2 </td <td>Bond angles sum (BAS<sup>6</sup>),</td> <td>720.0</td> <td>720.0</td>	Bond angles sum (BAS <sup>6</sup> ),	720.0	720.0	
Bond angles in 5-numbered ring (C2N2C1C11C12), deg           (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         540.0         540.0           (BAS <sup>5</sup> ), deg	deg			
(C2N2C1)       110.3       110.8         (N2C1C11)       108.6       108.3         (C1C11C12)       106.3       106.3         (C12C2N2)       108.5       108.3         Bond angles sum       540.0       540.0         (BAS <sup>5</sup> ), deg       540.0       540.0 <b>C-N bond lengths in 6-numbered chet rings, pm</b> N1C3       135.6       135.4         N1C4       136.3       135.4         N2C1       135.6       135.4         N2C2       136.3       135.4         N2C2       136.3       135.4         N7C4       132.6       132.3 <b>C-C bond lengths in 5-numberet ring, pm</b> C1C11       146.9       146.8         C11C12       140.6       140.1         C12C2       146.8       146.8         C11C12       146.8       146.8         Cr-O bond length, pm       V       V         Cr-O bond length, pm       V       V         Cr1O1 (Cr1O2)       168.7 (168.7)       167.8 (167.8)         Bond angles between flue-ime, copper and imegen atoms, deg       O1Cr1N1 (02Cr1N1)         O1Cr1N1 (O2Cr1N2)       90.0 (90.0)       90.0 (90.0)	Bond angles in 5-numb	ered ring (C2N2	2C1C11C12), deg	
(N2C1C11)108.6108.3(C1C11C12)106.3106.3(C11C12C2)106.3106.3(C12C2N2)108.5108.3Bond angles sum540.0540.0(BAS <sup>5</sup> ), deg	(C2N2C1)	110.3	110.8	
(C1C11C12)       106.3       106.3         (C11C12C2)       106.3       106.3         (C12C2N2)       108.5       108.3         Bond angles sum       540.0       540.0         (BAS <sup>5</sup> ), deg	(N2C1C11)	108.6	108.3	
(C11C12C2)       106.3       106.3         (C12C2N2)       108.5       108.3         Bond angles sum       540.0       540.0         (BAS <sup>5</sup> ), deg	(C1C11C12)	106.3	106.3	
(C12C2N2)       108.5       108.3         Bond angles sum       540.0       540.0         (BAS <sup>5</sup> ), deg	(C11C12C2)	106.3	106.3	
Bond angles sum       540.0       540.0         (BAS <sup>5</sup> ), deg       Image: Sum       540.0         C-N bond lengths in 6-numbered chelate rings, pm         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         C-C bond lengths in 5-numbered ring, pm         C1C11       146.9       146.8         C11C12       140.6       140.1         C12C2       146.8       146.8         Cr-O bond length, pm       rero bond length, pm       rero bond length, pm         Cr1O1 (Cr1O2)       168.7 (168.7)       167.8 (167.8)         Bond angles between fluorine, copper and nitrogen atoms, deg       01Cr1N1 (02Cr1N1)         01Cr1N2 (02Cr1N2)       90.0 (90.0)       90.0 (90.0)         01Cr1N3 (02Cr1N3)       90.0 (90.0)       90.0 (90.0)         01Cr1N4 (02Cr1N4)       90.0 (90.0)       90.0 (90.0)	(C12C2N2)	108.5	108.3	
(BAS <sup>-</sup> ), deg           C-N bond lengths in 6-numbered chelate rings, pm           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           C-C bond lengths in 5-numbered ring, pm           C1C11         146.9         146.8           C11C12         140.6         140.1           C12C2         146.8         146.8           Cr-O bond length, pm         V         V           Cr1O1 (Cr1O2)         168.7 (168.7)         167.8 (167.8)           Bond angles between fluorine, copper and nitrogen atoms, deg         01Cr1N1 (02Cr1N1)         90.0 (90.0)         90.0 (90.0)           O1Cr1N3 (02Cr1N3)         90.0 (90.0)         90.0 (90.0)         00.0 (90.0)         01Cr1N4 (02Cr1N4)           O1Cr1N4 (02Cr1N4)         90.0 (90.0)         90.0 (90.0)         90.0 (90.0)	Bond angles sum	540.0	540.0	
C-IN bond lengths in o-numbered cherate rings, pm           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           C-C bond lengths in 5-numbered ring, pm           C1C11         146.9           C1C11         146.9         146.8           C11C12         140.6         140.1           C12C2         146.8         146.8           Cr-O bond length, pm         V         V           Cr1O1 (Cr1O2)         168.7 (168.7)         167.8 (167.8)           Bond angles between fluorine, copper and nitrogen atoms, deg           O1Cr1N1 (O2Cr1N1)         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)           O1Cr1N4 (O2Cr1N4)         90.0 (90.0)         90.0 (90.0)	(BAS <sup>3</sup> ), deg	( numbered of	oloto ninga nun	
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         C-C bond lengths in 5-number of triang, pm         C1C11       146.9       146.8         C11C12       140.6       140.1         C12C2       146.8       146.8         Cr-O bond length, pm       triangen atoms, deg         O1Cr101 (Cr1O2)       168.7 (168.7)       167.8 (167.8)         Bond angles between fluorine, copper and nitrogen atoms, deg       01Cr1N1 (02Cr1N1)       90.0 (90.0)       90.0 (90.0)         O1Cr1N2 (02Cr1N2)       90.0 (90.0)       90.0 (90.0)       00.0 (90.0)         O1Cr1N4 (02Cr1N4)       90.0 (90.0)       90.0 (90.0)       00.0 (90.0)         O1Cr1N4 (02Cr1N4)       90.0 (90.0)       90.0 (90.0)       90.0 (90.0)	NIC2		125 A	
N1C4       130.3       133.4         N2C1       135.6       135.4         N2C2       136.3       135.4         N7C4       132.6       132.3         N7C5       133.1       132.3         C-C bond lengths in 5-numbered ring, pm         C1C11         146.9       146.8         C11C12       140.6       140.1         C12C2       146.8       146.8         Cr-O bond length, pm       roper and ridens, lengen atoms, deg         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)         O1Cr1N4 (O2Cr1N4)       90.0 (90.0)       90.0 (90.0)         O1Cr1N4 (O2Cr1N4)       90.0 (90.0)       90.0 (90.0)	NIC3	135.0	135.4	
N2C1       135.0       135.4         N2C2       136.3       135.4         N7C4       132.6       132.3         N7C5       133.1       132.3         C-C bond lengths in 5-numbered ring, pm         C1C11       146.9         C1C12       140.6       140.1         C12C2       146.8       146.8         Cr-O bond length, pm       rero bond length, pm       rero bond length, pm         Cr1O1 (Cr1O2)       168.7 (168.7)       167.8 (167.8)         Bond angles between fluorine, copper and nitrogen atoms, deg       01Cr1N1 (02Cr1N1)       90.0 (90.0)       90.0 (90.0)         O1Cr1N2 (O2Cr1N2)       90.0 (90.0)       90.0 (90.0)       00.0 (90.0)       00.0 (90.0)         O1Cr1N3 (02Cr1N3)       90.0 (90.0)       90.0 (90.0)       90.0 (90.0)       01Cr1N4 (02Cr1N4)         Bond angles between fluorine, copper and nitrogen atoms, deg       01Cr1N4 (02Cr1N4)       90.0 (90.0)       90.0 (90.0)	NIC4 N2C1	130.5	135.4	
N7C4       132.6       132.3         N7C5       133.1       132.3         C-C bond lengths in 5-numbered ring, pm         C1C11       146.9       146.8         C11C12       140.6       140.1         C12C2       146.8       146.8         C11C12       146.8       146.8         C11C12       146.8       146.8         Cr-O bond length, pm       V       V         Cr1O1 (Cr1O2)       168.7 (168.7)       167.8 (167.8)         Bond angles between fluorine, copper and nitrogen atoms, deg         O1Cr1N1 (O2Cr1N1)       90.0 (90.0)       90.0 (90.0)         O1Cr1N3 (O2Cr1N2)       90.0 (90.0)       90.0 (90.0)         O1Cr1N4 (O2Cr1N4)       90.0 (90.0)       90.0 (90.0)         O1Cr1N4 (O2Cr1N4)       90.0 (90.0)       90.0 (90.0)         Bond angles between fluorine, copper and nitrogen atoms, deg       010	N2C2	136.3	135.4	
N7C5       133.1       132.3         C-C bond lengths in 5-numbered ring, pm         C1C11       146.9       146.8         C11C12       140.6       140.1         C12C2       146.8       146.8         Cr-O bond length, pm       167.8 (167.8)         Bond angles between fluorine, copper and nitrogen atoms, deg         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)         O1Cr1N4 (O2Cr1N4)       90.0 (90.0)       90.0 (90.0)         Bond angles between fluorine, copper and nitrogen atoms, deg       010	N7C4	132.6	132.4	
C-C bond lengths in 5-numbered ring, pm           C1C11         146.9         146.8           C11C12         140.6         140.1           C12C2         146.8         146.8           Cr-O bond length, pm         167.8 (167.8)           Cr1O1 (Cr1O2)         168.7 (168.7)         167.8 (167.8)           Bond angles between fluorine, copper and nitrogen atoms, deg         01Cr1N1 (02Cr1N1)         90.0 (90.0)         90.0 (90.0)           01Cr1N2 (02Cr1N2)         90.0 (90.0)         90.0 (90.0)         00.0 (90.0)         01Cr1N4 (02Cr1N4)           01Cr1N4 (02Cr1N4)         90.0 (90.0)         90.0 (90.0)         90.0 (90.0)         00.0 (90.0)	N7C5	132.0	132.3	
C1C11         146.9         146.8           C11C12         140.6         140.1           C12C2         146.8         146.8           Cr-O bond length, pm             Cr1O1 (Cr1O2)         168.7 (168.7)         167.8 (167.8)           Bond angles between fluorine, copper and nitrogen atoms, deg            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)           Bond angles between fluorine, copper and nitrogen atoms, deg	C–C bond lengths in 5-numbered ring, <i>pm</i>			
C11C12       140.6       140.1         C12C2       146.8       146.8         Cr-O bond length, pm       140.1       140.1         Cr101 (Cr102)       168.7 (168.7)       167.8 (167.8)         Bond angles between fluorine, copper and rogen atoms, deg         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)         Bond angles between fluorine, copper and rivegen atoms, deg       160.000	C1C11	146.9	146.8	
C12C2       146.8       146.8         Cr-O bond length, pm           Cr101 (Cr102)       168.7 (168.7)       167.8 (167.8)         Bond angles between fluorer, copper and rogs at toms, deg         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)         Bond angles between fluoring, copper and troggen at toms, deg	C11C12	140.6	140.1	
Cr–O bond length, pm         Cr1O1 (Cr1O2)       168.7 (168.7)       167.8 (167.8)         Bond angles between fluorer, copper and rusgen atoms, deg         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)         Bond angles between fluorer, copper and rusgen atoms, deg	C12C2	146.8	146.8	
Cr101 (Cr102)         168.7 (168.7)         167.8 (167.8)           Bond angles between fluorine, copper and nitrogen atoms, deg         01Cr1N1 (02Cr1N1)         90.0 (90.0)         90.0 (90.0)           01Cr1N2 (02Cr1N2)         90.0 (90.0)         90.0 (90.0)         00.0 (90.0)         01Cr1N3 (02Cr1N3)         90.0 (90.0)         90.0 (90.0)         01Cr1N4 (02Cr1N4)         90.0 (90.0)         90.0 (90.0)         01Cr1N4 (02Cr1N4)         90.0 (90.0) <td>Cr–O bond length, pm</td> <td></td> <td></td>	Cr–O bond length, pm			
Bond angles between fluorine, copper and nitrogen atoms, deg           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)           Bond angles between fluorine, copper and nitrogen atoms, deg	Cr101 (Cr102)	168.7 (168.7)	167.8 (167.8)	
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)           Bond angles between fluorine, copper and nitrogen atoms, deg	Bond angles between fluorine, copper and nitrogen atoms, deg			
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)           Bond angles between fluorine, copper and nitrogen atoms, deg	O1Cr1N1 (O2Cr1N1)	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)           Bond angles between fluorine, copper and nitrogen atoms, deg	01Cr1N2 (02Cr1N2)	90.0 (90.0)	90.0 (90.0)	
O1Cr1N4 (O2Cr1N4)         90.0 (90.0)         90.0 (90.0)           Bond angles between fluorine, copper and nitrogen atoms, <i>deg</i>	O1Cr1N3 (O2Cr1N3)	90.0 (90.0)	90.0 (90.0)	
Bond angles between fluorine, copper and nitrogen atoms, <i>deg</i>	O1Cr1N4 (O2Cr1N4) 90.0 (90.0) 90.0 (90.0)			
	Bond angles between fluor	rine, copper and	nitrogen atoms, deg	

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  $(BAS^6)$  is exactly 720°, in the 5-membered ones  $(BAS^5)$ , 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]porphyrazine (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  $\Delta H^{0}_{f}$ , 298,  $S^{0}_{f}$ , 298 and  $\Delta G^{0}_{f, 298}$  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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