



Cu^{IV} OXIDATION STATE STABILIZATION IN THE MACROCYCLIC COMPOUND WITH PHTHALOCYANINE AND TWO FLUORO LIGANDS: DFT QUANTUM-CHEMICAL RESEARCH

Denis V. Chachkov^[a] and Oleg V. Mikhailov^{[b]*}

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Based on the results of a quantum chemical calculation using two variants of the DFT method, and namely DFT OPBE/TZVP and DFT B3PW91/TZVP, the possibility of the existence of a copper heteroligand complex with phthalocyanine, two F⁻ ions and an oxidation state of copper (+4) which is non-traditional for this 3*d* element, have been shown. The data on the key structural parameters and also, on multiplicity of the ground state of such a complex have also been presented.

*Corresponding Authors

E-Mail: olegmkhlv@gmail.com

- [a] Kazan Department of Joint Supercomputer Center of Russian Academy of Sciences – Branch of Federal Scientific Center “Scientific Research Institute for System Analysis of the RAS”, Lobachevski Street 2/31, 420111 Kazan, Russia
 [b] Kazan National Research Technological University, K. Marx Street 68, 420015 Kazan, Russia

INTRODUCTION

As has long been well known, the most typical for copper in its stable compounds is the oxidation state equal to +2 and, accordingly, oxidation state II. Compounds with a higher oxidation state of copper, namely +3, in particular tripotassium hexafluorocuprate(III) K₃[CuF₆] and heptapotassium di[hexaaxoiodato(VII)]cuprate(III) K₇[Cu(IO₆)₂], although are quite stable but uncharacteristic for the given 3*d*-element.¹ Even less characteristic for copper is the oxidation state +4, although the first of such Cu compounds, namely of dicaesium hexafluorocuprate(IV) Cs₂[CuF₆], was obtained almost 50 years ago by Harnischmacher and Hoppe.² The given metal complex was also studied in later works, in particular.³⁻⁹ Along with this fluoro-complex, compounds with a copper oxidation state of +4 that contain chemical elements with lower electronegativity, namely oxygen, for example, heteronuclear mixed oxide of lanthanum, strontium and perovskite type copper with Cu(III) and Cu(IV),^{8,9} and nitrogen, like complexes of Cu(IV) with substituted biguanides (RBig = RNHC(=NH)NHC(=NH)NH₂), namely [Cu(RBig)₂(OH)₄] and [Cu(RBig)₃]₃X, where R is phenyl, 4-chlorophenyl, 2-methylphenyl, X = F, Cl,^{1,10,11} are also known. After the publication of the two reviews,^{1,6} information on any new coordination compounds containing Cu(IV) did not appear in the literature. Nevertheless, there is no reason to believe that there can be no other Cu(IV) complexes.

In this connection, it seems interesting to find out whether, in principle, other copper coordination compounds in which this 3*d*-element has an oxidation state of +4, can exist under any conditions.

It has long been established that phthalocyanine (**I**) capable to stabilize a wide variety of oxidation states of *d*-elements - both low and high (see, in particular, review connection that the copper(II) complex with the such a macrocyclic ligand was accidentally obtained way back in 1927 as a by-product in the synthesis of 1,2-dicyanobenzene from 1,2-dibromobenzene in the presence of copper(I) cyanide CuCN,¹⁷) and turned out to be actually the first macrocyclic metal complex that became known to chemical science.

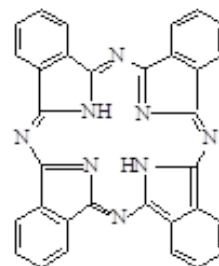


Figure 1. Structure of phthalocyanine (**I**).

Another ligand which capable of stabilizing high oxidation states, is the fluoride anion.⁴⁻⁷ In connection with this circumstance, it seems appropriate to use precisely the combination of these two ligands that takes place in the complexes having structural formula **II** to stabilize the oxidation state of Cu⁴⁺ (M is *d*-element atom, and, in particular, Cu).

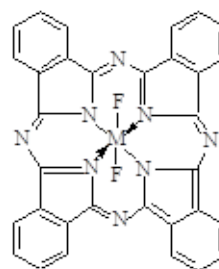


Figure 2. Proposed structure of Cu(IV) complex (**II**).

There is currently no information on such a metal complex in the literature, but nevertheless, at present, it is possible to assess the possibility of its existence using modern quantum chemical calculation methods which are now widely used for studying the structure of molecules. This is what the given investigation is devoted.

CALCULATION METHOD

Quantum-chemical calculation of the copper complex of type **II** was done by using the two versions of DFT method, namely DFT OPBE/TZVP and DFT B3PW91/TZVP. First of these methods, combining the common TZVP extended triple zeta split-valence basis set^{18,19} and the OPBE non-hybrid functional,^{20,21} as shown in the literature,^{21–25} 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. Second one, combining the common TZVP and B3PW91 functional,^{26,27} according to data,²⁸ has minimal value of so-called “normal error” in comparison with other variants of DFT method. 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 experiment.

Calculations were done by using the Gaussian09 program package.²⁹ 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. Copper in the oxidation state +4 has 3*d*⁷ electronic configuration; in this connection, spin multiplicities 2, 4 and 6 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 earlier.³⁰

RESULTS AND DISCUSSION

According to the data obtained by us as a result of the quantum-chemical calculation carried out using the both DFT OPBE/TZVP method and the DFT method B3PW91/TZVP, the copper complex having structural formula **II** is capable to self-existence, at least in the gas phase. Molecular structure of the given complex obtained by DFT OPBE/TZV method, is shown in Figure 3. Molecular structure obtained by the DFT B3PW91/TZVP method, looks similar. The calculated chemical bond lengths between atoms and bond angles for this macrocyclic metal complex presented in Table 1. These data show that both methods used by us, give almost identical data for all structural parameters indicated above. Some difference between the results of these methods is noted only in the case of bond lengths Cu1F1 (Cu1F2).

Table 1. Bond lengths and bond angles in the copper complex with phthalocyanine and two fluoro ligands of type **II**.

Structural parameter	Calculated by DFT	
	OPBE/TZVP	B3PW91/TZVP
Cu–N bond lengths in chelate node, pm		
Cu1N1	198.1	197.8
Cu1N2	198.1	197.8
Cu1N3	198.1	197.8
Cu1N4	198.1	197.8
Bond angles in chelate node CuN ₄ , °		
(N1Cu1N2)	90.0	90.0
(N2Cu1N3)	90.0	90.0
(N3Cu1N4)	90.0	90.0
(N4Cu1N1)	90.0	90.0
Bond angles sum, °	360.0	360.0
Non-bond angles between N atoms in N ₄ grouping, °		
(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
Bond angles in 6-numbered ring (Cu1N2C1N8C8N3), °		
(Cu1N2C1)	125.0	125.0
(N2C1N8)	128.5	128.3
(C1N8C8)	123.0	123.4
(N8C8N3)	128.5	128.3
(C8N3Cu1)	125.0	125.0
(N3Cu1N2)	90.0	90.0
Bond angles sum ⁶ , °	720.0	720.0
Bond angles in 5-numbered ring (C2N2C1C11C12), °		
(C2N2C1)	109.8	110.0
(N2C1C11)	108.9	108.8
(C1C11C12)	106.2	106.2
(C11C12C2)	106.2	106.2
(C12C2N2)	108.9	108.8
Bond angles sum ⁵ , °	540.0	540.0
C–N bond lengths in 6-numbered chelate rings, pm		
N1C3	135.7	135.3
N1C4	135.7	135.3
N2C1	135.7	135.3
N2C2	135.7	135.3
N7C4	132.7	132.1
N7C5	132.7	132.1
C–C bond lengths in 5-numbered ring, pm		
C1C11	146.9	146.7
C11C12	140.4	139.8
C12C2	146.9	146.7
Cu–F bond length, pm		
Cu1F1 (Cu1F2)	195.1	190.7
Bond angles between fluorine, copper and nitrogen atoms, °		
F1Cu1N1 (F2Cu1N1)	90.0	90.0
F1Cu1N2 (F2Cu1N2)	90.0	90.0
F1Cu1N3 (F2Cu1N3)	90.0	90.0
F1Cu1N4 (F2Cu1N4)	90.0	90.0

As it can be seen from Figure 3, and Table 1, the complex under consideration has, on the whole, a structure of regular tetragonal bipyramid or slightly flattened octahedron (since here, the lengths of the Cu–F bonds are somewhat shorter than the lengths of the Cu–N bonds). CuN₄ chelate node of this complex has the structure of regular quadrangle (square) because the Cu–N bond lengths, distances between adjacent nitrogen atoms (N1 and N2, N2 and N3, N3 and N4, N4 and N1) absolutely identical (according to DFT OPBE/ TZVP, 198.1 and 280.1 pm and according to DFT B3PW91/TZVP, 197.8 and 279.7 pm, respectively) and all (NCuN) bond angles as well as (NNN) non-bond angles are equal to 90.0°. Copper atom is in the center of square formed by four nitrogen atoms N1, N2, N3 and N4 (Figure 3). All four 6-membered metal-chelate rings as well as all four 5-membered non-chelate rings with one nitrogen atom and four carbon atoms adjoining to 6-membered metal-chelate rings, are completely identically between themselves in the lengths of bonds between the corresponding atoms as well as in the range of bond angles in them. Both of them are strictly coplanar, because the sum of the internal bond angles in each of the 6-membered cycles (BAS⁶) is 720°, in the 5-membered ones (BAS⁵), is 540°, which coincides with the sums of the internal angles in a flat hexagon and pentagon, respectively.

This 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 DFT OPBE/TZVP and DFT B3PW91/TZVP method) are in full accordance with such an expectation.

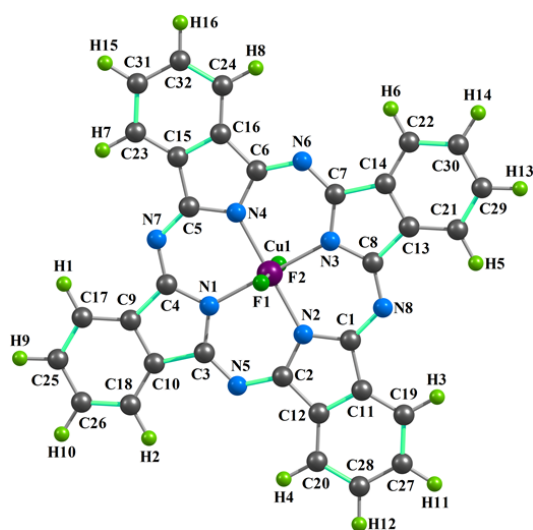


Figure 3. Molecular structure of Cu(IV) complex of type II obtained by means of DFT OPBE/TZVP quantum-chemical calculation.

The ground state of the copper complex under study, according to both calculation methods used here, is a spin doublet. It is quite expected for tetragonal-bipyramidal complexes with $3d^7$ configuration, and a coordination number of a metal ion equal to 6. Besides, according to the data of each of these methods, the nearest excited quartet state has only a little higher energy (by 1.4 kJ mol⁻¹ in the case of DFT OPBE/TZVP and 2.1 kJ mol⁻¹ in the case of DFT B3PW91/TZVP), which, apparently, makes spin-crossover in this complex a very, very likely phenomenon.

CONCLUSION

As can be seen from the data presented above, both variants of the DFT method used by us in this work, namely OPBE/TZVP and B3PW91/TZVP, quite definitely gave evidence about the possibility of the existence of copper complex [CuLF₂] containing fluoride anion (F⁻) and double deprotonated form (L²⁻) of phthalocyanine (H₂L). The copper–donor nitrogen atom and copper–fluorine interatomic distances (Table 1) in this compound correspond in their size to single bonds Cu–N and Cu–F, and, hence, the oxidation state of copper in it is namely +4. It should be noted in this connection that, according to our calculations of standard thermodynamic parameters $\Delta H_{f,298}^0$, $\Delta S_{f,298}^0$ and $\Delta G_{f,298}^0$ of the complex under study using method described in³⁰, all they are positive (339.8 kJ mol⁻¹, 1180.3 J mole⁻¹ K⁻¹ and 596.0 kJ mol⁻¹, respectively), and, hence, the given compound cannot be obtained from simple substances formed by chemical elements containing in its composition (copper, fluorine, nitrogen, carbon and hydrogen). Nevertheless, both variants of the DFT method used by us, namely OPBE/TZVP and B3PW91/TZVP, predict the possibility of the existence of this complex, and the point is now to find it in the experiment.

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CONFLICT OF INTEREST

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

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