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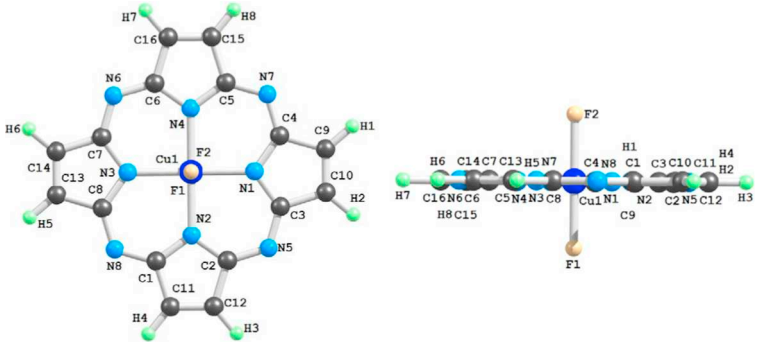
Short communication

About possibility of stabilization of unusual copper(IV) oxidation state in complexes with porphyrazine and two fluorine ligands: Quantum-chemical design

Oleg V. Mikhailov*, Denis V. Chachkov

Kazan National Research Technological University, K. Marx Street 68, 420015 Kazan, Russia
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", Lobachevskii Street 2/31, 420111 Kazan, Russia

GRAPHICAL ABSTRACT



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ABSTRACT

Based on the results of a quantum chemical calculation using the DFT method, the possibility of the existence of a copper heteroligand complex with porphyrazine and two fluoride ions with an oxidation state of **IV** that is unusual for this element has been shown. Also, data on the structural parameters and multiplicity of the ground state of this complex have been presented.

1. Introduction

As early as 1973, in the work [1], the coordination compound of copper – cesium hexafluorocuprate(IV) having $Cs_2[CuF_6]$ composition, in which copper is in an abnormally for this 3*d*-element high oxidation state IV, had been described for the first time. This complex was produced according to reaction $2CsCuCl_3 + 2CsF + 5F_2 \rightarrow 2Cs_2[CuF_6] + 3Cl_2$ proceeding by mixing $CsCuCl_3$, cesium fluoride, and fluorine together at high pressure. This compound was also mentioned in some later works, in particular [2–9]. Also, perovskite-type lanthanum, strontium and copper mixed oxide containing Cu(III) and Cu (IV), is known from [8,9]. The review [6] mentions copper(IV) complexes with biguanides having $[Cu(RBig)_2(OH)_4]$ and $[Cu(RBig)X_3]X$ composition, where RBig is substituted biguanide RNHC(=NH)NHC(=NH)NH_2, R is phenyl, 4-chlorophenyl or 2-methylphenyl, X = F, Cl. Information on any other Cu(IV) coordination compounds obtained

* Corresponding author.
E-mail address: olegmkhlv@yandex.ru (O.V. Mikhailov).

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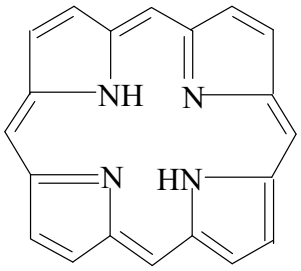
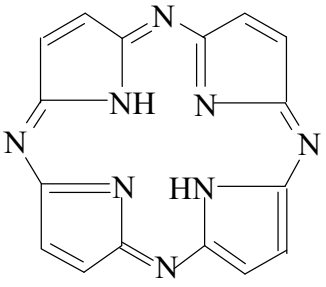
after the publication of the article [6] is currently absent [10], although it is unlikely that the ONLY above complexes are the Cu(IV) compounds. In this regard, it is of interest to find out whether other coordination compounds of copper in which this 3*d*-element is in the oxidation state of IV, can exist in any conditions.

It has been well known for a long time that porphine **I** and its various analogs, in particular, 5,10,15,20-tetraazaporphine (porphyrazine) **II**, are capable of stabilizing the most diverse oxidation states of *d*-elements – low as well as high (see, f.e. [11–14]). The other ligand capable of stabilizing namely high oxidation states, is the fluoride anion F^- [5–7]. In connection with this circumstance, it seems appropriate

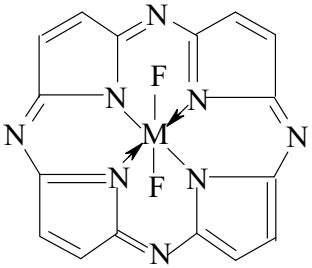


I



II

to use for the stabilization of the above oxidation state of Cu(IV) namely the combination of these two ligands, which occurs in complexes of type **III** (M is the



III

atom of the *d*-element, and, in particular, Cu). There is currently no information about such coordination compounds in the literature, but at present time, it is possible to estimate the possibility of their existence using modern quantum chemical calculation methods. This paper has been devoted to decision of the given question.

2. Method

Quantum-chemical calculations were performed by the two versions of DFT method. In the first of them (OPBE/TZVP), combining the common TZVP extended triple zeta split-valence basis set [15,16] and the OPBE non-hybrid functional [17,18], which, as shown in [18–22], in the case of 3*d* elements most adequately predicts the relative energy stabilities of high-spin and low-spin states, and reliably characterizes key geometric parameters of corresponding molecular structures. In the second, B3PW91/TZVP, combining the common TZVP and B3PW91 functional [23,24] which, according to data [25], has minimal value of so-called "normal error" in comparison with other variants of DFT method. This 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 (see *Supplemental material*). Calculations were performed with the Gaussian09 program package [26]. 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. Cu(IV) has $3d^7$ electronic configuration, and, 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 always calculated by the unrestricted (UOPBE) method. The possibility of the existence of radical cationic forms that can be isostructural Cu(IV) complex considered in this paper, was also taken into account in the calculation. And both in the framework of the DFT OPBE/TZVP method and in the framework of the DFT

Table 1
Bond lengths and bond angles in the Cu(IV) complex of type **III**.

Structural parameter	Calculated to DFT OPBE/TZVP method	Calculated to DFT B3PW91/TZVP method
Cu—N bond lengths in chelate node, *pm*		
Cu1N1	192.8	195.3
Cu1N2	192.6	195.3
Cu1N3	192.8	195.3
Cu1N4	192.6	195.3
Bond angles in chelate node CuN_4, *deg*		
(N1Cu1N2)	90.0	90.0
(N2Cu1N3)	90.0	90.0
(N3Cu1N4)	90.0	90.0
(N4Cu1N1)	90.0	90.0
Bond angles sum (BAS), *deg*	360.0	360.0
Non-bond angles between N atoms in N_4 grouping, *deg*		
(N1N2N3)	90.1	90.0
(N2N3N4)	89.9	90.0
(N3N4N1)	90.1	90.0
(N4N1N2)	89.9	90.0
Non-bond angles sum (NBAS), *deg*	360.0	360.0
Bond angles in 6-numbered chelate ring (Cu1N1C4N7C5N4), *deg*		
(Cu1N1C4)	125.9	125.6
(N1C4N7)	128.8	128.1
(C4N7C5)	120.6	122.6
(N7C5N4)	128.8	128.1
(C5N4Cu1)	125.9	125.6
(N4Cu1N1)	90.0	90.0
Bond angles sum (BAS^6), *deg*	720.0	720.0
Bond angles in 5-numbered ring (C3N1C4C9C10), *deg*		
(C3N1C4)	108.2	108.7
(N1C4C9)	108.9	108.9
(C4C9C10)	107.0	106.7
(C9C10C3)	107.0	106.7
(C10C3N1)	108.9	108.9
Bond angles sum (BAS^5), *deg*	540.0	540.0
C—N bond lengths in 6-numbered chelate rings, *pm*		
N1C3	136.1	134.7
N1C4	136.1	134.7
N7C4	132.2	132.5
N7C5	132.2	132.5
C—C bond lengths in 5-numbered ring, *pm*		
C4C9	145.4	147.5
C9C10	135.5	134.1
C10C3	145.4	147.5
Bond angle between fluorine and copper atoms, *deg*		
(F1Cu1F2)	180.0	180.0
Cu—F bond lengths, *pm*		
Cu1F1	198.0	191.4
Cu1F2	198.0	191.4
Bond angles between fluorine, copper and nitrogen atoms, *deg*		
F1Cu1N1	90.0	90.0
F1Cu1N2	90.0	90.0
F1Cu1N3	90.0	90.0
F1Cu1N4	90.0	90.0

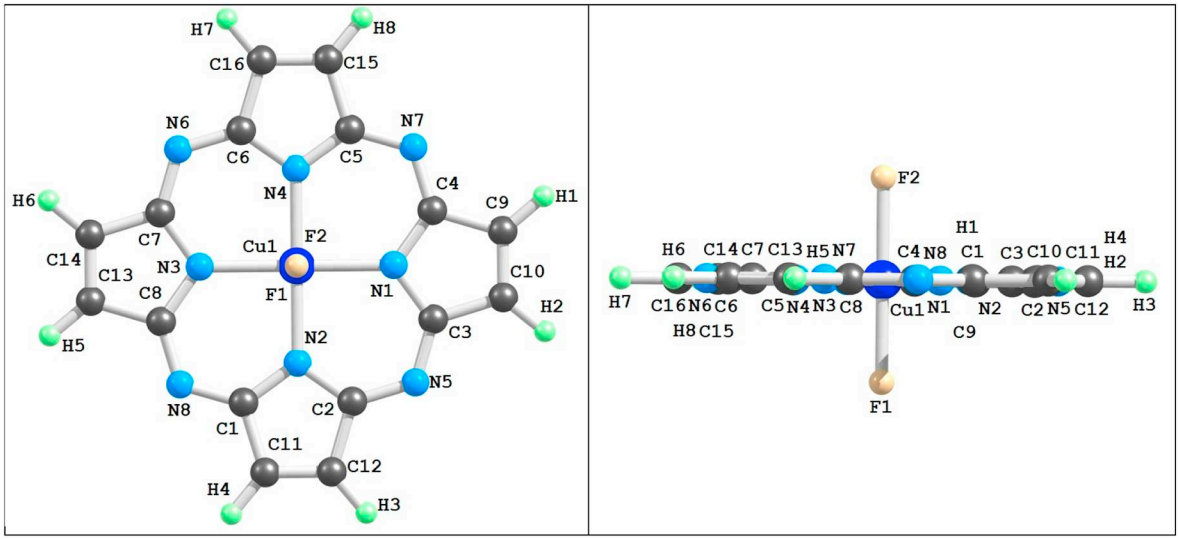


Fig. 1. Molecular structure of Cu(IV) complex of type **III** obtained as a result of DFT B3PW91/TZVP quantum-chemical calculation: view from above (*left*), side view (*right*).

B3PW91/TZVP one, if these forms appeared, they had always higher total energy values compared to the Cu(IV) complex.

3. Results and discussion

According to the data obtained by us as a result of the quantum-chemical calculation carried out using both the DFT OPBE/TZVP method and the DFT method B3PW91/TZVP, the above Cu(IV) complex of type **III** having $[CuL]^{2+}2F^{-}$ composition (**L** is a deprotonated form of porphyrazine **II**) is capable to self-existence, at least in the gas phase. The calculated chemical bond lengths between atoms and bond angles for this compound are presented in Table 1. As it is easy to see from these data, both of methods used by us, give almost identical data for all structural parameters indicated above. Molecular structure of this complex obtained by DFT B3PW91/TZVP method, is shown in Fig. 1; its molecular structure obtained by the DFT OPBE/TZVP method, looks similarly.

As can be seen from this Figure, chelate node CuN_4 and all four 6-membered metal chelate rings, as well as all four 5-membered non-chelate rings containing one nitrogen atom and four carbon atoms and adjacent to 6-membered metal chelate rings in this complex have a strong planar structure. Exactly the same conclusion can be made if we take into account the sum of the bond angles in each of these structural fragments (360.0°, 720.0° and 540.0°, respectively) (Table 1). Each of the DFT methods that we used, gives its own individual (although slightly different) sets of bond angles in chelate node, metal chelate rings, and in non-chelate 5-membered rings, formed by one nitrogen atom and four carbon atoms.

However, the sums of these angles in each of these calculation methods are absolutely the same. The fluorine and copper atoms in this complex form between themselves an angle of 180° (Table 1) and, therefore, are located on the same straight line; on the other hand, all bond angles formed by fluorine, copper atoms and donor nitrogen atoms of the chelate node, are equal to 90°. Besides, copper – donor nitrogen and copper – fluorine interatomic distances (Table 1) correspond in their size to single Cu—N and Cu—F bonds. The noted facts, as well as the fact that the Cu—N and Cu—F bond lengths are different among themselves, make it possible to assign the Cu(IV) compound under study to the number of pseudo-octahedral complexes with tetragonal distortion. It should be noted in this connection that the values of the dipole electric moments for this complex calculated using each of the above used DFT method variants are 0.00 Debye units that is in full accordance with its strong planar structure with a center of symmetry.

According to the data of our calculations, the ground state of the Cu (IV) heteroligand complex $[CuL]^{2+}2F^{-}$ under study in the framework of the DFT OPBE/TZVP method (which, as we mentioned above in paragraph Method, in the case of 3*d*-elements most adequately predicts the relative energy stabilities of high-spin and low-spin states) is a spin doublet. Such a situation is quite expected for tetragonal copper complexes with a high degree of oxidation, a $3d^7$ configuration, and a coordination number of a metal ion equal to 6; besides, according to the data of this method, the nearest excited quartet state has much higher energy (142.7 kJ/mol). This circumstance makes impossible an availability a spin crossover for it. It should be noted in this connection that DFT B3PW91/TZVP method, however, gives an inverse relationship: the ground state is a spin quartet, while the nearest doublet state has an energy 193.5 kJ/mol higher. However, testing the wave functions of the ground state for stability within each of these methods using the STABLE = OPT procedure showed that the wave function of ground state for $M_S = 2$ is stable under the perturbations considered whereas the wave function of ground state for $M_S = 4$ has an internal instability.

The given circumstance, and, also, the fact that even the Cu(IV) complex with fluoride ions alone, which are ligands of a weak field, namely, $Cs_2[CuF_6]$ mentioned above, has the spin doublet as the ground state and μ_{eff} value equal to 1.55 μB, the spin doublet should be considered the most probable ground state of the complex under consideration. According to our calculation by the DFT OPBE/TZVP method, for the $[CuF_6]^{2-}$ complex, where the oxidation state of Cu(IV) is beyond doubt, the effective charge (NBO) on the Cu atom is +1.21 ē in the ground state ($M_S = 2$) and +1.24 ē in the nearest excited ($M_S = 4$). According to data of our calculation by the same method, the NBO on Cu atom in the $[CuL]^{2+}2F^{-}$ complex in its ground state ($M_S = 2$) is +0.80 ē, in the nearest excited one ($M_S = 4$), is +0.79 ē. (In [CuL] complex, they are +0.76 ē and + 0.44 ē, respectively). As can be seen from these values, the difference between these values is quite noticeably. Nevertheless, since the fluorine atom has a much higher electronegativity compared to the nitrogen atom, and the degree of covalence of the Cu—N bond is significantly higher than the degree of covalence of the Cu—F bond, this difference in the values of effective charges on the copper atoms in $[CuL]^{2+}2F^{-}$ and $[CuF_6]^{2-}$ seems to be quite natural. On the other hand, part of the electron density is transferred from the central Cu atom to the d_π-electron system of the

porphyrazine macrocycle that also contributes to decrease of the effective charge on the copper atom in comparison to effective charge on the same atom in the $[CuF_6]^{2-}$ complex.

Note at the end of this paragraph that the chemical oxidation of axial ligands with the possible transition of the Cu(IV) complex into a radical form with a lower oxidation state of this element, can be considered practically excluded here owing to the high electronegativity of fluorine atoms. (Indirect confirmation of this, the fact of the existence of the $[CuF_6]^{2-}$ anion containing Cu(IV), can serve). Taking into account all the above, we can assert that our opinion about the existence of Cu(IV) complexes of the $[Cu\mathbf{L}]^{2+}2F^-$ composition does not contradict the known experimental data.

4. Conclusion

As can be seen from the above data, both variants of the DFT method used by us, namely OPBE/TZVP and B3PW91/TZVP, predict the possibility of the existence of at least one more Cu(IV) complex, namely $[Cu\mathbf{L}]^{2+}2F^-$, where **L** is double deprotonated form of porphyrazine. The point is now to find it in the experiment.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.inoche.2019.05.025.

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