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Electronic Structure of 1,5-Cyclooctadiene-copper(I)-hexafluoroacetylacetonate

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The valence electronic structure of the compound 1,5-cyclooctadiene-copper(I)-hexafluoroacetylacetonate [(1,5-COD)Cu(hfac)], a prospective precursor for creation of thin copper films for microelectronics, has been investigated by ultraviolet photoelectron (He I) and X-ray emission spectroscopy. Electronic interactions of the 1,5-COD ligand with the copper atom were revealed by comparing spectra of the complex and of free 1,5-COD. C Kα spectra indicated a significant decrease of π electron density in the double bonds of 1,5-COD with the coordination of this molecule to the copper atom. The spectral changes and features were interpreted using the results of density functional calculation on the molecules. The detailed analysis of the highest occupied molecular orbitals of (1,5-COD)Cu(hfac) was carried out to explain the relatively low values of first ionization potential and decomposition temperature for the complex.

Introduction

Although copper (I) hexafluoroacetylacetonate Cu(hfac) cannot be isolated,[1] its complexes with various π-donor ligands are found to be stable prospective precursors for the chemical vapor deposition (CVD) of thin copper films[2−4] used in the microelectronic devices. One of the most promising compounds among them is an adduct of Cu(hfac) with 1,5-cyclooctadiene, with the composition (1,5-COD)Cu(hfac).[5−9] The synthesis of thin copper films by CVD-method consists of thermolysis (sometimes under additional photostimulation) of the precursor molecules. Some authors have proposed mechanisms of this process for (1,5-COD)Cu(hfac),[10,11] but the electronic structure of this compound, needed to clarify various aspects of its reactivity, still remains to be investigated.

Photoelectron (He I) and X-ray emission spectroscopy methods are used to probe the valence electronic structure by measuring the energy and density. Each of these methods has been used with support of semiempirical or ab initio calculations to establish the electronic structure of some β-diketonate complexes of metals (see, e.g., refs 12−14). Complexes of copper (I) β-diketonates with additional ligands coordinated by π-electrons of double bond or free electron pair of heteroatom were also investigated by means of the ultraviolet (UV) photoelectron spectra excited by He I and He II lines.[15] Simultaneous application of UV photoelectron and X-ray emission spectroscopy obtains information concerning the energies and localization of molecular orbitals. The nature of the interaction between molecular fragments of the considered complex compound is revealed. The first method provides data on the total density of occupied states, and the second one measures the local partial density of occupied states, using dipole selection rules.

Our purpose is to examine the electronic structure and chemical bonding in the compound (1,5-COD)Cu(hfac), to reveal the reasons of its thermolytical decomposition at relatively low temperature. UV (He I) photoelectron and X-ray fluorescence (C Kα spectra) spectroscopy were used. The interpretation of spectral data and the analysis of chemical bonding in the considered complex and 1,5-COD molecule as free ligand were performed on the basis of density functional calculations.

Experimental Section

The compound (1,5-COD)Cu(hfac) was obtained by the method described elsewhere.[16] The yellow crystals were purified by vacuum sublimation (2×10^{-2} Torr) at 65° C.

He I spectrum of the complex was recorded on Perkin-Elmer PS-18 spectrometer. The spectrum was calibrated by Xe $^2P_{1/2}$ and Xe $^2P_{3/2}$ lines at 12.13 and 13.43 eV, respectively. The residual pressure in the spectrometer chamber was equal to 2×10^{-5} Torr.

C Kα spectra of the complex (1,5-COD)Cu(hfac) and the ligand 1,5-COD were recorded on a laboratory X-ray spectrometer "Stearate". Samples were deposited on the copper substrate and cooled to the liquid nitrogen temperature in a vacuum chamber of X-ray tube. The parameters of operating regime for the X-ray tube with copper anode were: $U = 6$ kV, $I = 0.5$ A. The single-crystal of ammonium biphthalate (NH_4AP) was used as a crystal analyzer. The technique for application of this crystal analyzer to obtain C Kα spectra is described in ref 17. The resolution of spectra was equal to ~0.5 eV, the energy of X-ray bands was determined with ± 0.15 eV accuracy.

Calculation Details. Density functional theory (DFT) calculations of the molecules (1,5-COD)Cu(hfac) and 1,5-COD were performed by Becke's three parameter hybrid method using the gradient-corrected correlation potential of Lee, Yang, and Parr (B3LYP method)[18,19] within the Jaguar program.[20] The calculations were done with 6-31G** basis set for all atoms except for Cu where the effective core potential with LACVP basis[21] was employed. The geometries of both molecules were optimized in C_{2v} point-group symmetry by analytical method to the value less than 5×10^{-5} hartree/bohr for the largest Cartesian energy gradient component.

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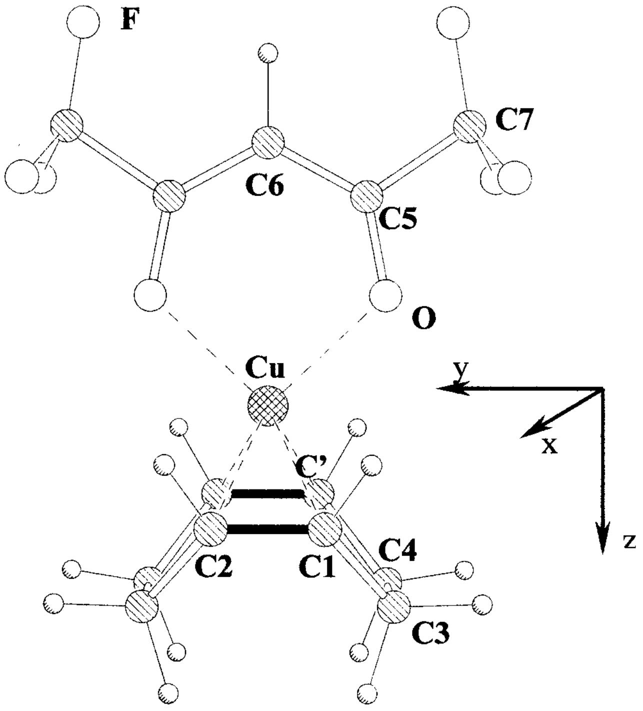

Figure 1. Molecular structure of (1,5-COD)Cu(hfac) calculated in the given coordinate system.

TABLE 1: Calculated and Measured Bond Lengths (in Å) for (1,5-COD)Cu(hfac)

bond	C_{2v} symmetry calculation	X-ray diffraction[a]
C1−C2	1.338	1.331; 1.367
C1−C3	1.511	1.503; 1.504; 1.506; 1.522
C3−C4	1.583	1.520; 1.536
Cu−C1	2.070	2.049; 2.089; 2.466; 2.550
Cu−O	2.000	1.999; 2.001
O−C5	1.244	1.241; 1.247
C5−C6	1.382	1.371; 1.393
C5−C7	1.522	1.518; 1.525
C7−F	1.280	1.269; 1.283; 1.299

[a] Experimental data from ref 16.

TABLE 2: Calculated and Measured Bond Angles (in degree) for (1,5-COD)Cu(hfac)

angle	C_{2v} symmetry calculation	X-ray diffraction[a]
C1−Cu−C2	37.7	30.7; 38.6
C1−Cu−C′	89.4	80.8; 82.5
C1−Cu−O	101.6	94.0; 115.4
O−Cu−O	93.0	93.3
Cu−O−C5	122.5	122.4; 122.6
O−C5−C6	129.6	128.4
O−C5−C7	113.5	113.4; 113.7

[a] Experimental data from ref 16.

Theoretical C Kα spectra were built in the framework of the frozen orbital approximation (Koopman's theorem) on the basis of calculation on the ground state of molecules. X-ray emission arises as a result of electron transitions from valence shell of a compound to the previously created core vacancies. The energy of X-ray transition was computed as the difference between the eigenvalues of valence (i) and core (j) orbitals:

$$E_{ij} = \epsilon_i - \epsilon_j \tag{1}$$

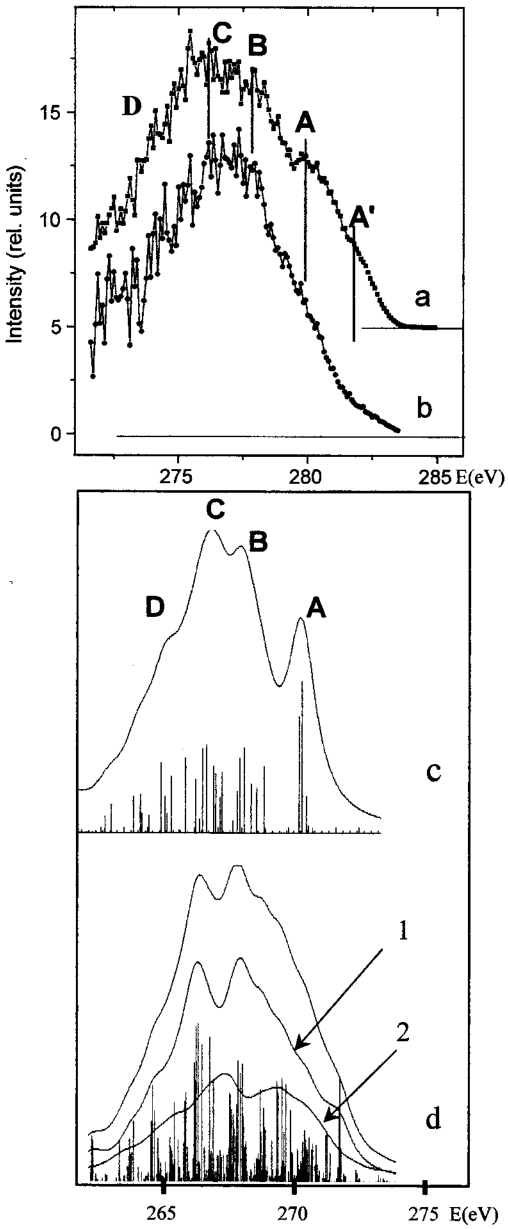

Figure 2. Experimental C Kα spectra of 1,5-COD (a) and (1,5-COD)-Cu(hfac) (b) and theoretical spectra plotted by the result of DFT calculations on 1,5-COD molecule (c) and complex in the experimental geometry (d). The spectrum d is portioned into components corresponding to the electronic states of carbon atoms in the ligands 1,5-COD (line 1) and hfac (line 2).

Since core 1s orbitals are localized, the intensity of X-ray transition from molecular orbital (MO) i was calculated as a sum of squared coefficients at the carbon 2p atomic orbitals (AOs) participating in the considered MO:

$$I_{ij} = \sum_n C_{in}^{\ 2} \tag{2}$$

where the index n runs through the structurally equivalent carbon atoms. The 1,5-COD and complex include, respectively, 2 and 5 kinds of carbon atoms, being different by the binding energy of 1s electrons. Taking into account this nonequivalency, theoretical C Kα spectrum of a molecule was plotted as a sum of partial spectra belonging to the chemically different carbon atoms. The calculated intensities were normalized by the maximal value and broadened by the Lorenzian functions with a half-width at half-maximum of 0.7 eV.

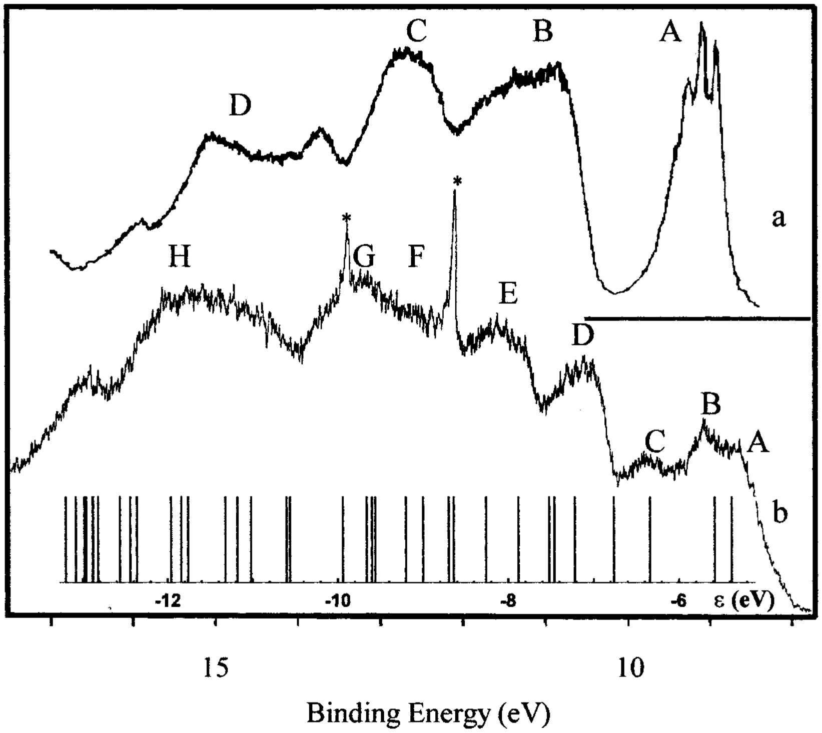

Figure 3. He I spectra of 1,5-COD (a), taken from ref 24, and (1,5-COD)Cu(hfac) (b). The asterisks denote the Xe $^2P_{1/2}$ and Xe $^2P_{3/2}$ lines. The vertical lines correspond to the energetic levels of calculated complex.

To investigate the electron interactions between copper atom and ligands (hfac and 1,5-COD), a linear expansion of the coefficient matrix **C** for complex in respect to the coefficient matrix **C**′ for the ligand was employed:[22]

$$\mathbf{C} = \mathbf{A}\,\mathbf{C}' \qquad (3)$$

The values of matrix **A**, resulted from the eq 3 solution, determine the participation degree of ligand MOs in the formation of concrete MO of complex.

Molecular graphics were prepared with the help of Molden package.[23]

Results and Discussion

The optimized molecular structure of (1,5-COD)Cu(hfac) is presented in Figure 1. The calculated values of selected bond lengths and angles are presented in Tables 1 and 2 and compared with the corresponding crystal data.[16] The experiment indicates the asymmetry of the 1,5-COD ligand coordination to the central copper atom, leading to several values of the same geometrical parameter in the complex of C_{2v} symmetry. However, the averaged experimental values are in agreement with the calculated data and the best coincidence is observed for the chelate ring structure. The asymmetry of (1,5-COD)Cu(hfac) molecule in solid state may be connected with the intermolecular interactions. The assignment of He I bands measured for the gaseous complex was made using the calculated data for optimized molecule. The peculiarities of C Kα spectrum in the solid state were interpreted using the (1,5-COD)Cu(hfac) compound in the experimentally determined geometry.[16] Note that the DFT energy of such structure is higher than that of C_{2v} symmetric structure by 2.8 eV.

Experimental (a, b) and theoretical (c, d) C Kα spectra of 1,5-COD and (1,5-COD)Cu(hfac) are shown in Figure 2. The experimental C Kα spectrum of free 1,5-COD (Figure 2a) exhibits the features A, B, C, and D. Each of them has the evident corresponding feature in the theoretical C Kα spectrum of the molecule (Figure 2c). The short wave shoulder A′ cannot be presumably considered as diagram line and the most likely to be assigned to multiple ionization satellites. The feature A corresponds to the X-ray transitions from two highest occupied MOs (HOMOs) of 1,5-COD, providing π-bonding between carbon atoms of the double bonds. The splitting of intensities, forming maximum A in the theoretical spectrum, reflects the difference in the 1s-electron binding energies for two kinds of carbon atoms in the 1,5-COD molecule. Thus, intensity with the largest energy characterizes the contribution of sp^3-hybridized carbon atoms to the second HOMO. The features B, C, and D correspond to the contributions of carbon 2p AOs participating in σ-type MOs. These features will be analyzed in more details below.

The experimental C Kα spectrum of (1,5-COD)Cu(hfac) (Figure 2b) shows the substantial decrease in the intensity of feature A with respect to that in the spectrum of free ligand (Figure 2a). The same effect is observed from comparison between the theoretical spectra of 1,5-COD and complex (Figure 2c,d). To examine the changes in the valence electronic structure of 1,5-COD on coordination, the theoretical spectrum of complex was parted into two components, computed for 1,5-COD (line 1) and hfac (line 2) ligands. C Kα spectrum of 1,5-COD included in the complex can be seen to undergo substantial transformation in respect to the spectrum of free molecule, being connected with reorganization of electron structure of diene ligand as a result of its coordination with copper atom. Hence, the observed decrease of the intensity of the feature A in the spectrum of (1,5-COD)Cu(hfac) is obviously caused by the interaction of π-type MOs of 1,5-COD with copper atom.

Total density of occupied states is also noticeably changed at the incorporation of 1,5-COD in the (1,5-COD)Cu(hfac) as evident from the comparison between He I spectrum of free 1,5-COD, taken from ref 24, and that of complex (Figure 3). Marked bands in the former spectrum correspond to the described above features of the C Kα spectrum of 1,5-COD.

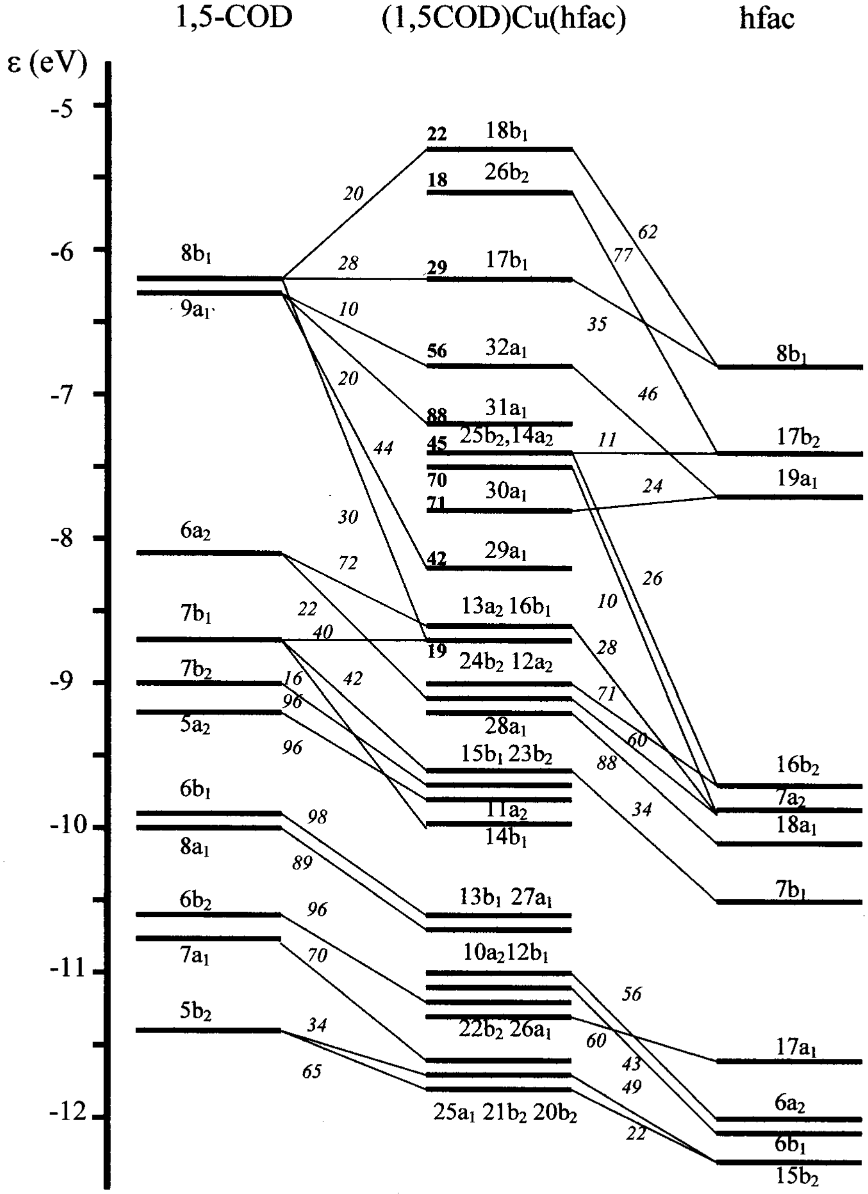

Figure 4. Correlation diagram between the MOs of (1,5-COD)Cu(hfac) and ligands. The numbers near thin lines indicate a percent participation of ligand MO in the construction of complex MO. The bold numbers denote the contribution of copper AOs into corresponding MO of the complex.

He I spectrum of the (1,5-COD)Cu(hfac) is significantly complicated, exhibiting the greater numbers of maxima as compared to the spectrum of ligand. Furthermore, the comparison of spectra indicates the higher value of ionization potential for the complex. The vertical lines depicted under the spectral profile of (1,5-COD)Cu(hfac) correspond to the energetic levels of the calculated molecule. As one can see there is a good agreement in the position of these lines and the bands of He I spectrum. The relative scales of the calculated one-electron energies and the measured binding energies practically coincide. We conclude that the quantum-chemical method may be used to investigate (1,5-COD)Cu(hfac).

The character of the interactions between the copper atom and coordinated ligands can be understood on the basis of the diagram presented in Figure 4. The lines in the center of the diagram correspond to the energy levels of complex. The left and right sides of the diagram depict the energy levels of 1,5-COD and hfac fragments, respectively. The thin lines connect the MOs of ligands with those MOs of complex, where their contribution exceeds 10%. The numbers given near the thin lines indicate the percent of the corresponding contribution, computed from the expansion (3). The percent of contribution of electron states of the copper atom (shown by the bold number) to a certain MO of the complex was calculated as a sum of squared coefficients at 3d, 4s, and 4p AOs. As follows from the presented data, copper AOs noticeably participate in the formation of the 10 highest occupied MOs of (1,5-COD)Cu(hfac). The electron density of lower energy MOs is found to localize, as a rule, within one of ligand fragments. Thus, $28a_1$ and $13b_1$ MOs of the complex are completely analogous to $18a_1$ orbital of hfac fragment and $6b_1$ orbital of the 1,5-COD molecule, respectively. The simultaneous participation of orbitals of both ligands in the formation of some of complex MOs with the absence of the contribution of copper AOs meets the symmetry requirements for this molecule. Examples of MOs are $15b_1$, $21b_2$, and $20b_2$ orbitals of (1,5-COD)Cu(hfac).

The main character of 10 MOs of (1,5-COD)Cu(hfac), by which the copper atom interacts with one or both ligands, is presented in Table 3. These MOs are formed with participation of π-orbitals of 1,5-COD and four fragment orbitals of hfac ligand. The latter orbitals are $8b_1$ and $7a_2$ orbitals of π-type together with $17b_2$ and $19a_1$, being nonbonding toward the

TABLE 3: Character of MOs, Providing Interaction between Copper Atom and Ligands, and Corresponding He I Band Assignments for (1,5-COD)Cu(hfac)

MO	AO Cu (contribution, %)	character of bond with 1,5-COD	character of bond with hfac	band assignment
$18b_1$	d_{xz} (22)	weakly antibonding	π-antibonding	A
$26b_2$	d_{yz} (18)		σ-antibonding	B
$17b_1$	d_{xz} (25), p_x (4)	weakly antibonding	π-bonding	C
$32a_1$	d_{z2} (15), d_{x2-y2} (33), p_z (8)	weakly antibonding	antibonding	D
$31a_1$	d_{z2} (28), d_{x2-y2} (55), s (5)	weakly antibonding	antibonding	D
$25b_2$	d_{yz} (45)		nonbonding	D
$14a_2$	d_{xy} (70)		π-antibonding	D
$30a_1$	d_{z2} (26), d_{x2-y2} (45)	weakly bonding	bonding	E
$29a_1$	d_{z2} (9), d_{x2-y2} (26), s (7)	weakly bonding	bonding	E
$16b_1$	d_{xz} (19)	bonding		E

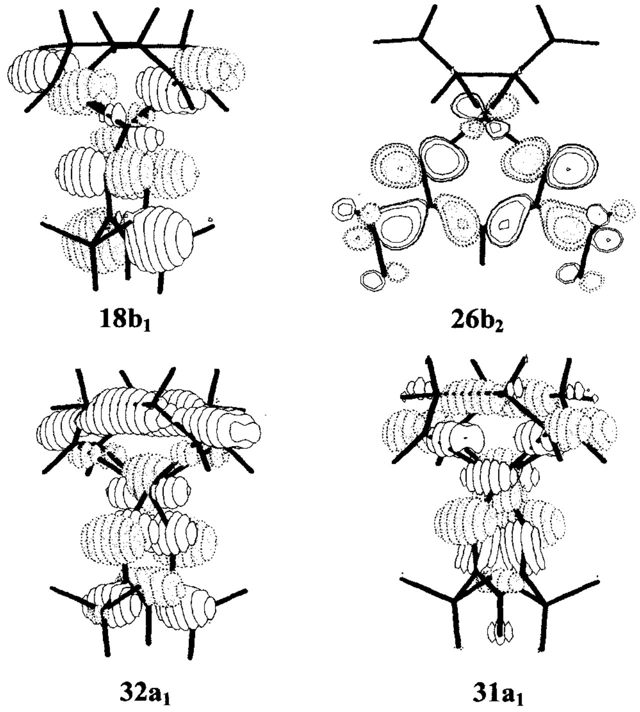

Figure 5. Calculated distribution of electron density from some occupied MO of (1,5-COD)Cu(hfac). Various colors correspond to the different phases of wave function.

overlap of oxygen and carbon AOs in the hfac fragment (see right side of Figure 4). In accordance with symmetry principles, HOMO of 1,5-COD is able to overlap only with copper d_{xz} AO, being perpendicular to the chelate ring (Figure 1). In this case $8b_1$ MO of hfac ligand can be involved into interaction to form $18b_1$ and $17b_1$ orbitals of (1,5-COD)Cu(hfac) corresponding to π-antibonding and π-bonding type of Cu−O bond, respectively. The interaction of the copper atom with 1,5-COD within these MOs has demonstrated a weak antibonding character. The graphical design of HOMO for (1,5-COD)Cu(hfac) is presented in Figure 5. The positive overlap of $8b_1$ MO of 1,5-COD with carbon d_{xz} AO results in the formation of $16b_1$ MO of considered complex, being the most energy-deep of MOs presented in the Table 3. The AOs of hfac atoms do not participate in that MO.

Four MOs for (1,5-COD)Cu(hfac), possessing a_1 symmetry, include the electron densities of both ligands and are formed with participation of $9a_1$ MO of 1,5-COD, $19a_1$ MO of hfac ligand and d_{z2}, d_{x2-y2}, and s AO of the copper atom. The combination of these copper AOs creates a complicated distribution of electron density in the vicinity of atom, providing the antibonding interaction with both ligands by the highest pair of MOs $32a_1$ and $31a_1$ (Figure 5) or the bonding one by the next pair of MOs $30a_1$ and $29a_1$. The degree of antibonding or bonding for 1,5-COD ligand with copper atom can be seen to be less than for hfac ligand. In turn, the geometry of (1,5-COD)Cu(hfac) permits copper d_{yz} and d_{xy} AOs to be effectively overlapped with orbitals of chelate ligand. The overlap of the former copper AO is energetically more favorable with $17b_2$ MO of hfac ligand to form $26b_2$ and $25b_2$ complex MOs giving, respectively, antibonding (Figure 5) or nonbonding combination toward Cu−O interaction. At the same time, $14a_2$ MO for (1,5-COD)Cu(hfac) is mainly determined by copper d_{xy} AO; the contribution of $7a_2$ MO of hfac ligand, being suitable by symmetry, is about 10%. This copper AO being perpendicular to the chelate ring provides the negative overlap with π-type orbitals of oxygen atoms. The donor properties of ligands can be revealed in the formation of $32a_1$ and $17b_1$ MOs of (1,5-COD)Cu(hfac), possessing substantial contributions of vacant 4p AOs of copper.

Energy levels presented in the diagram can be correlated to the features of the experimental spectra. Thus, $8b_1$ and $9a_1$ MOs of 1,5-COD are responsible for the feature A in C Kα and photoelectron spectra of this molecule. The band B in the spectra corresponds to four MOs, being in energy range from −8 up to −9.2 eV. These MOs provide the σ-bonding between one certain pair of atoms. For example, $7b_1$ MO provides the bonding between atoms C1 and C2 and also between the pair of carbon atoms, being symmetrical to them (Figure 1). The feature C in the spectra of 1,5-COD is assigned to MOs, occupying the energy range from −9.8 up to −10.9 eV. The electron density from these MOs is delocalized over the few carbon atoms. The structure of orbitals from the B and C groups has a node coinciding with one of the symmetry planes of 1,5-COD. MOs, belonging the C group, provide C−H bonds just as the lower energy MOs are responsible for formation of the spectral feature D.

Assignment of the higher energy MOs of the complex to the bands of its He I spectrum is made in Table 3. A correlation between the data from the table and Figures 3 and 4 detected that the bands A, C, and D in the He I spectrum of complex are partially originated from the band A of the spectrum of free 1,5-COD. While the band B in the complex spectrum is formed as a result of interaction between copper AO with $17b_2$ orbital of hfac ligand. The bands E and F in He I spectrum of (1,5-COD)Cu(hfac) appear at the splitting of maximum B in the spectrum of 1,5-COD; the intensity of the band E has the substantial contribution of the electron density of chelate ring with some participation of electron states of copper atom. The bands G and H (Figure 3) correspond to the electron interactions within both ligands. The substantial increase of the intensity in the energy range 14−16 eV in the He I spectrum of (1,5-COD)Cu(hfac) in respect to that range in the spectrum of free 1,5-COD (Figure 3) corresponds to the large contribution of fluorine 2p AOs of CF_3 groups into the MOs of the complex. UV (He

I) photoelectron spectra of similar complexes (hfac)Cu·L (L = PMe_3, MeCN) also contain the analogous intensive band in this energy range.[15]

The analysis of electron interactions of the copper atom with 1,5-COD reveals weaker bonding. Highly occupied MOs of (1,5-COD)Cu(hfac) are either weakly antibonding or weakly bonding toward interactions of Cu with 1,5-COD ligand, whereas the third (by energy) MO of the complex provides effective π-bonding between copper atom and oxygen atoms of hfac ligand. The character of intramolecular interactions may explain the observed primary elimination of 1,5-COD molecule from (1,5-COD)Cu(hfac) on the heated substrate under CVD process conditions.[10,25] The decrease of the first ionization potential for (1,5-COD)Cu(hfac) as compared to the free 1,5-COD molecule reveals the antibonding character of HOMO of the complex.

Conclusion

The comparison of spectral data [X-ray emission, UV (He I) photoelectron] and density functional calculations for the (1,5-COD)Cu(hfac) complex and free molecule of the 1,5-COD has revealed the substantial changes of total and partial C_{2p} densities of occupied states of ligands with copper (I) ion. The spatial geometry of the complex together with the relative energies of MOs for free ligands toward 4s and 3d AOs of copper are responsible for the parameters of electronic structure of considered complex.

As follows from the data on the electronic structure of (1,5-COD)Cu(hfac), obtained in the present work, the coordination between copper atom and π-system of 1,5-COD molecule cannot provide the effective bonding with diene ligand. This explains the occurrence of thermolysis of (1,5-COD)Cu(hfac) at relatively low temperatures and can be considered as a basis for its practical application as CVD-precursor. The (1,5-COD)Cu(hfac) complex is characterized by relatively low first ionization potential because of antibonding character of its HOMO and shows high reactivity in the reactions, occurring with participation of frontier orbitals of this compound.

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