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Quantum Chemical Study of the Structures and Stability of Copper(II) Bis(diketonate) Dimers

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Abstract—The quantum-chemical study of the copper diketonate dimers ($[Cu(Acac)_2]_2$ and $[Cu(Acac)Hfac)]_2$) is performed using various functionals (B3LYP, TPSSh, PBE0, and B2PLYP) and basis sets (6-311++G(d,p) and Def2-TZVP) and taking into account dispersion interactions (D3BJ). The calculations using the B3LYP and TPSSh functionals combined with the Def2-TZVP basis set give the best agreement with experiment. The Basis Set Superposition Errors introduce no substantial changes to the stabilization energies of the considered systems. The obtained results show that the quantum-chemical study of similar associates of transition metals should be performed without empirical D3BJ dispersion corrections.

Keywords: copper(II) diketonates, dimers, quantum-chemical calculations, density functional theory, dispersion interactions

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INTRODUCTION

From the moment of the synthesis, the coordination compounds of transition metals with β-diketones attract increased attention of specialists in diverse areas [1]. They are used as catalysts in a series of industrially important organic reactions, for example, alkene isomerization and Mukaiyama epoxidation [2–4], and act as precursors for the fabrication of metal-containing coatings [5, 6]. Increasing interest in the complexes with the β-diketone ligands is due to the possibility of synthesis of mono- and polynuclear systems demonstrating unusual magnetic properties [7–13]. It has recently been shown that compounds of this class are promising as single-molecule magnets (SMM) [11, 12, 14, 15]. The revealed possibility of the mechanical and electrical manipulation of molecular magnetism allows their application in devices of nanomechanics and spintronics [16]. A significant group of magnetically active structures based on bis(diketonates) is represented by the copper complexes with the radical-containing ligands [17–19]. The quantum-chemical methods, the reliability of results of which is determined to a high extent by the type of the approximation used, are applied to explain the magnetic behavior of these heteroligand compounds. The density functional theory (DFT) is used most frequently to study the structures and reaction mechanisms and to explain the physicochemical properties of transition metal complexes containing a high number of atoms (>100). However, unsubstantiated combinations of the functionals and basis sets can result in obtaining incorrect data [20].

We have previously performed the quantum-chemical (DFT B3LYP/6-311++G(d,p)) study of the structures and energy characteristics of oligomers of the Co(II), Ni(II), and Zn(II) diketonates [21]. The nonforming polynuclear structures copper(II) bis(diketonates) that do not form polynuclear structures and the dimers of which were found only in the crystals of the heteroligand complexes, were also considered [22–24]. The calculation schemes that take into account dispersion interactions are shown to substantially overestimate the stability of the studied coordination compounds [21]. Since this result is not consistent with examples of successful application of dispersion corrections in the studies of the complexes containing no transition metals with the open electronic shell [25, 26], an extended theoretical study of the binuclear structures of $[Cu(Acac)_2]_2$ and $[Cu(Acac)(Hfac)]_2$ (Acac is acetylacetonate, and Hfac is hexafluoroacetylacetonate) was performed in this work using four functionals and two basis sets, and also the influence of the D3BJ dispersion corrections [27] applied to the investigation of magnetically active compounds was considered. The dimers of copper bis(diketonates) were chosen as objects of the study, because their formation is not accompanied by a substantial change in the geometry of the monomers, unlike similar cobalt, nickel, and zinc complexes [21], owing to which the reaction route contains no transi-

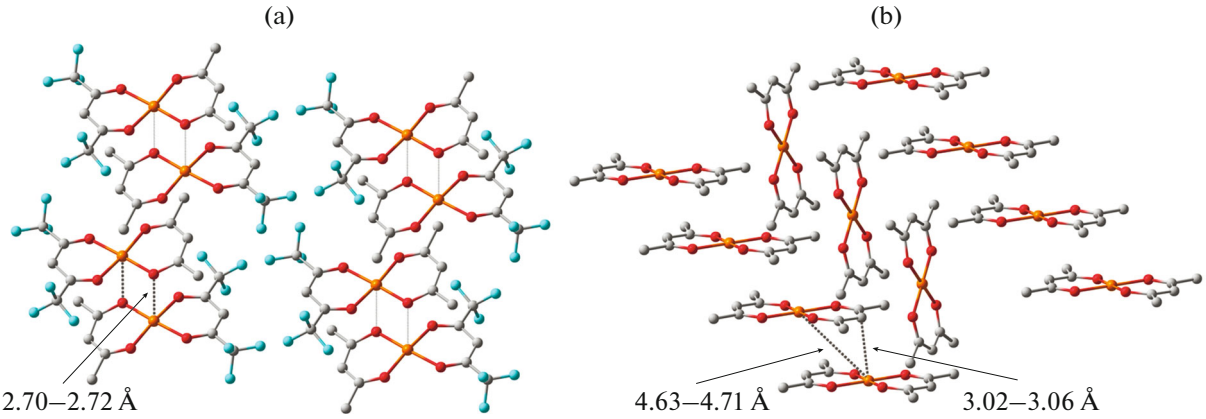


Fig. 1. Packings of molecules (a) Cu(Acac)(Hfac) and (b) $Cu(Acac)_2$ in the crystal according to the XRD data [22, 23, 42–44].

tion states capable of affecting the energy characteristics of the dimerization process under study.

CALCULATION PROCEDURE

Calculations were performed by the DFT method using the Gaussian 16 program [28], the B3LYP [29], TPSSh [30], PBE0 [31], and B2PLYP [32] functionals, and the 6-311++G(d,p) and Def2-TZVP extended basis sets, combinations of which are successfully applied to the study of the transition metal complexes [33–40]. Stationary points were localized on the potential energy surface by the full geometry optimization of molecular structures with the checking of the DFT stability of the wave function and calculation of the force constants. The graphical images of the molecular structures were drawn using the ChemCraft program [41].

RESULTS AND DISCUSSION

According to the crystal-chemical data, the Cu(Acac)(Hfac) complex forms dimers in which the distances between the copper ion and oxygen atom of the adjacent molecules are 2.70–2.72 Å [22, 23] (Fig. 1). These values indicate rather weak intermolecular interactions determined by the dispersion forces and packing effects. In the crystal of $Cu(Acac)_2$, the distance between the molecules of the complexes arranged in stacks reaches 3.02–3.06 Å [42–44], which together with the nearly planar structure of bis(chelates) assumes the formation of these structures only owing to crystal packing.

As shown previously [21], the calculation of $[Cu(Acac)_2]_2$ in the B3LYP/6-311++G(d,p) approximation using the XRD data as the starting geometry results in the structure in which the shortest distance between the atoms of two molecules is 3.481 Å (Fig. 2a) exceeding the values obtained by the XRD data (3.02–3.06 Å) [42–44]. This fact can be explained by non-accounting for the crystal lattice effects in the calculations. The geometry optimization of $[Cu(Acac)_2]_2$ with the applied dispersion correction (B3LYP/6-311++G(d,p) + D3BJ) gives the associate with the distortion of the molecules, which is not characteristic of the copper bis(chelate) dimers. The distance between these molecules is shorter than that found in the crystal (Fig. 2b).

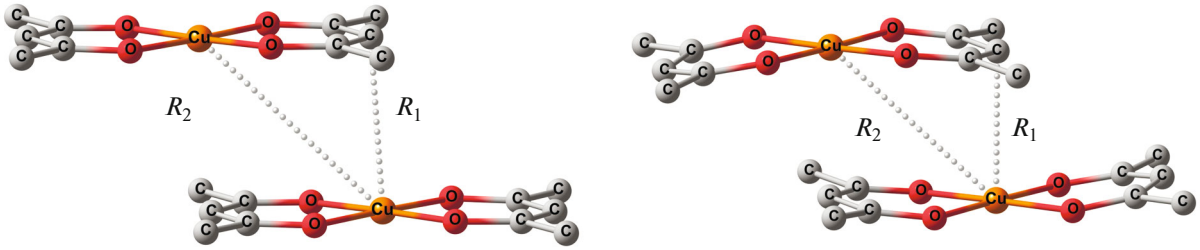
To answer the question whether the predicted distortion is a consequence of the use of the B3LYP/6-311++G(d,p) approximation, we performed the calculations using the TPSSh, PBE0, and B2PLYP functionals and 6-311++G(d,p) and Def2-TZVP basis sets. The results of calculations of the characteristic distances R_1 and R_2 presented in Fig. 2a are consistent with the B3LYP data [21]. The geometry optimization without dispersion interactions leads to the overestimation of the distance between the complexes, whereas the application of the D3BJ dispersion correction to the calculation scheme is accompanied by the shortening of the distances between the molecules and the bent of the chelate cycles (Fig. 2b).

The results of high-level calculations using the B2PLYP double hybrid functional including effects of electron correlation are worthy of special mentioning. As follows from Fig. 2a, the structure with the shortened (compared with those determined by XRD) interatomic Cu–Cu distances was localized using this approximation (Fig. 1). The inclusion of the D3BJ dispersion corrections to the calculation scheme favors a distortion of the bis(chelates) and shortens the intermolecular distances R_1 and R_2 to the values similar to those obtained using the B3LYP, TPSSh, and PBE0 functionals in combination with D3BJ. This result suggests that the application of the aforementioned dispersion corrections leads to an incorrect reproduction of the experimental geometry of the $Cu(Acac)_2$ complex regardless of the chosen functional and basis set.

The coordination compound Cu(Acac)(Hfac) is one of a few copper bis(diketonates) with the dimeric

(a) (b)

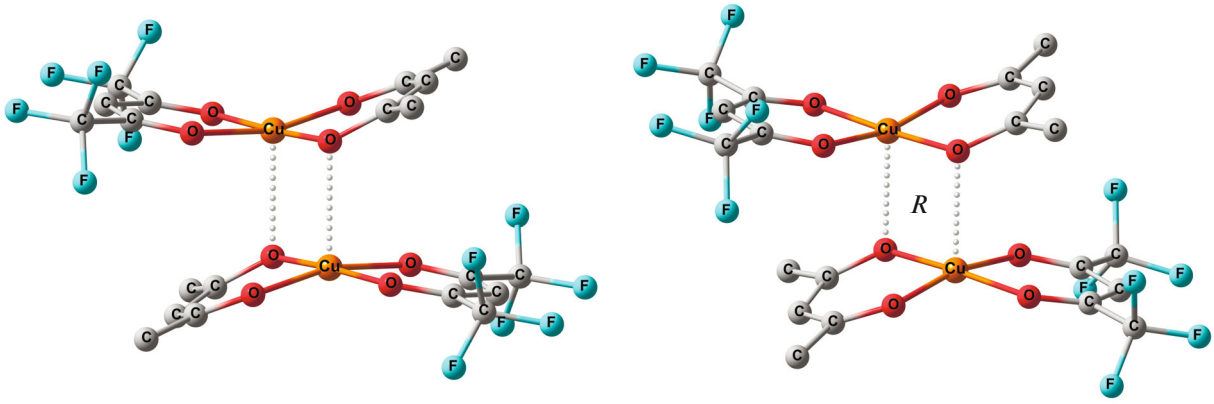
$[Cu(Acac)_2]_2$



	R_1, Å	R_2, Å			R_1, Å	R_2, Å
B3LYP/6-311++G(d,p)	3.481	4.960	B3LYP/6-311++G(d,p)	+D3BJ	2.936	4.450
B3LYP/Def2-TZVP	3.444	4.928	B3LYP/Def2-TZVP	+D3BJ	2.919	4.431
TPSSh/6-311++G(d,p)	3.399	4.859	TPSSh/6-311++G(d,p)	+D3BJ	2.862	4.429
TPSSh/Def2-TZVP	3.342	4.798	TPSSh/Def2-TZVP	+D3BJ	2.871	4.423
PBE0/6-311++G(d,p)	3.115	4.637	PBE0/6-311++G(d,p)	+D3BJ	2.887	4.439
PBE0/Def2-TZVP	3.106	4.624	PBE0/Def2-TZVP	+D3BJ	2.886	4.430
B2LYP/6-311++G(d,p)	3.045	4.543	B2LYP/6-311++G(d,p)	+D3BJ	2.880	4.402
B2LYP/Def2-TZVP	3.062	4.567	B2LYP/Def2-TZVP	+D3BJ	2.894	4.397

(c) (d)

$[Cu(Acac)(Hfac)]_2$



	R, Å			R, Å
B3LYP/6-311++G(d,p)	2.682	B3LYP/6-311++G(d,p)	+D3BJ	2.466
B3LYP/Def2-TZVP	2.838	B3LYP/Def2-TZVP	+D3BJ	2.533
TPSSh/6-311++G(d,p)	2.506	TPSSh/6-311++G(d,p)	+D3BJ	2.412
TPSSh/Def2-TZVP	2.720	TPSSh/Def2-TZVP	+D3BJ	2.584
PBE0/6-311++G(d,p)	2.474	PBE0/6-311++G(d,p)	+D3BJ	2.449
PBE0/Def2-TZVP	2.551	PBE0/Def2-TZVP	+D3BJ	2.552
B2LYP/6-311++G(d,p)	2.447	B2LYP/6-311++G(d,p)	+D3BJ	2.467
B2LYP/Def2-TZVP	2.513	B2LYP/Def2-TZVP	+D3BJ	2.521

Fig. 2. Spatial structures and geometric characteristics of the $[Cu(Acac)_2]_2$ and $[Cu(Acac)(Hfac)]_2$ dimers calculated without (a, c) and with (b, d) allowance for the dispersion corrections.

structure in the crystal [22, 23], and no existence of binuclear structures in the solution was reported. The data presented in Fig. 2c show that the B3LYP functional combined with the 6-311++G(d,p) and Def2-TZVP basis sets well reproduces the geometry of $[Cu(Acac)(Hfac)]_2$. When using the TPSSh functional, correct results were obtained only in the Def2-TZVP basis set, and the application of PBE0 favors a

Table 1. Stabilization energies without (E_{stab}) and with allowance for the zero-point vibration energy $\left(E_{stab}^{ZPE}\right)$ (all values are given in kcal/mol) of the $[Cu(Acac)_2]_2$ and $[Cu(Acac)(Hfac)]_2$ dimers calculated by the DFT method

Basis set	$[Cu(Acac)_2]_2$		$[Cu(Acac)(Hfac)]_2$	
	E_{stab}	E_{stab}^{ZPE}	E_{stab}	E_{stab}^{ZPE}
		B3LYP		
6-311++G(d,p)*	3.1	2.8	2.7	2.6
6-311++G(d,p) + D3BJ	23.3	22.2	22.2	21.1
Def2-TZVP	2.5	2.3	0.6	0.5
Def2-TZVP + D3BJ	23.1	22.0	19.5	18.7
		TPSSh		
6-311++G(d,p)	4.0	3.9	3.8	3.6
6-311++G(d,p) + D3BJ	21.6	20.8	19.4	18.9
Def2-TZVP	3.3	3.1	0.9	0.8
Def2-TZVP + D3BJ	20.9	19.9	17.0	16.3
		PBE0		
6-311++G(d,p)	7.2	7.1	7.0	6.8
6-311++G(d,p) + D3BJ	21.5	20.6	20.3	19.7
Def2-TZVP	6.4	6.1	4.2	4.0
Def2-TZVP + D3BJ	20.6	19.7	17.1	16.4
		B2PLYP		
6-311++G(d,p)	11.3		12.6	
6-311++G(d,p) + D3BJ	23.4		23.8	
Def2-TZVP	9.6		8.3	
Def2-TZVP + D3BJ	21.5		19.3	

* The results of calculations in the B3LYP/6-311++G(d,p) approximation are taken from [21].

substantial decrease in the intermolecular Cu–O contact compared to the XRD data (Fig. 1). The geometry optimization by the double hybrid potential B2PLYP led to dimers in which the distance between the metal ion and oxygen atom of the adjacent molecule turned out to be shorter than that determined in experiment (Fig. 2). This result makes doubtful the applicability of this approximation in the quantum-chemical study of similar systems. Regardless of the functional/basis set combination, the inclusion of the D3BJ dispersion correction into the calculation scheme favors a significant shortening of the distance between the $[Cu(Acac)(Hfac)]_2$ molecules (Fig. 2d) and, as a consequence, overestimation of its stability.

The low stabilization energy (E_{stab}) of the $[Cu(Acac)_2]_2$ dimer predicted by the B3LYP and TPSSh calculations (2–4 kcal/mol, Table 1) is well consistent with the fact that no self-associates are observed in the solution and in the gas phase. The use of the PBE0 and B2PLYP functionals gives E_{stab} ranging from 6 to 11 kcal/mol. These values can be due to packing effects. The inclusion of the dispersion corrections into the calculation scheme is accompanied by the distortion of the molecules and shortening of the distance between the bis(chelates) (Fig. 2b) and also by an increase in the stabilization energy to 20–23 kcal/mol (Table 1). These values are characteristic of the molecular associates stabilized by hydrogen bonds but seem to be overestimated in the complexes in which the distances between the molecules are longer than 3 Å. Similar results were obtained for $[Cu(Acac)(Hfac)]_2$: the expected low values of stabilization energies were predicted by B3LYP and TPSSh, the values found using the PBE0 and B2PLYP functionals, and the D3BJ dispersion corrections overestimate the stability of the dimer (Table 1).

Basis set superposition errors (BSSE) were calculated to evaluate the influence of the inaccuracy of the applied basis sets (6-311++G(d,p) and Def2-TZVP) on the stabilization energies of the dimers [45]. The calculations of BSSE were performed in the B3LYP/6-311++G(d,p)/Def2-TZVP approximations providing a good agreement with the experimental data and a higher variability of taking into account dispersion interactions. The results of calculations of BSSE obtained using various schemes for taking into account dispersion interactions (CAM [46], D3BJ, and their combination CAM+D3BJ) are presented in

Table 2. Energies of complex formation with allowance for the BSSE correction (E_f^{BSSE}) and basis set superposition errors (BSSE) (all values are given in kcal/mol) for the $[Cu(Acac)_2]_2$ and $[Cu(Acac)(Hfac)]_2$ dimers calculated by the DFT method using the B3LYP functional

Basis set	E_f^{BSSE}	BSSE
	$[Cu(Acac)_2]_2$	
*6-311++G(d,p)	1.8	1.8
6-311++G(d,p) CAM-B3LYP	5.5	2.3
6-311++G(d,p) + D3BJ	22.4	2.7
6-311++G(d,p) CAM-B3LYP + D3BJ	20.4	2.7
Def2-TZVP	1.5	1.6
Def2-TZVP CAM-B3LYP	5.4	1.5
Def2-TZVP + D3BJ	22.4	2.5
Def2-TZVP CAM-B3LYP + D3BJ	16.5	2.2
	$[Cu(Acac)(Hfac)]_2$	
6-311++G(d,p)	2.2	2.4
6-311++G(d,p) CAM-B3LYP	8.9	4.3
6-311++G(d,p) + D3BJ	21.3	4.8
6-311++G(d,p) CAM-B3LYP + D3BJ	21.1	4.9
Def2-TZVP	1.9	1.7
Def2-TZVP CAM-B3LYP	7.5	2.4
Def2-TZVP + D3BJ	21.1	2.7
Def2-TZVP CAM-B3LYP + D3BJ	20.2	2.7

* The results of calculations in the 6-311++G(d,p) basis set are taken from [21].

Table 2. The complex formation energy calculated using this approach nearly coincides with that determined ignoring BSSE, and the BSSE are within 3 kcal/mol, except for the calculation of $[Cu(Acac)(Hfac)]_2$ in the B3LYP/6-311++G(d,p) approximation with the inclusion of dispersion corrections in which the inaccuracy reaches 5 kcal/mol. Therefore, the results obtained by the B3LYP calculations contain no systematic errors that affect substantially the formulated results.

Thus, the systematic DFT study of the copper diketonate dimers $[Cu(Acac)_2]_2$ and $[Cu(Acac)(Hfac)]_2$ showed that the use of the dispersion corrections resulted in the overestimation of the stability of these weakly bound associates and was accompanied by a significant distortion of their geometries. The stabilization energies of the copper bis(acetylacetonate) dimers predicted with allowance for the D3BJ empirical corrections (20–23 kcal/mol) allow one to expect the existence of fairly stable binuclear structures that were not detected in either solution, or crystalline state [42–44]. The studies of the dimers using the B3LYP, TPSSh, PBE0, and B2PLYP approximations that takes into account effects of electron correlations show that the B3LYP and TPSSh functionals combined with Def2-TZVP give the best agreement with the experiment, and similar results were obtained by the use of the 6-311++G(d,p) basis set. According to the calculations of BSSE, the errors caused by the superposition of the basis sets range from 3 to 5 kcal/mol and apply no substantial corrections to the stabilization energies of the considered systems.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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