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МОЛЕКУЛЯРНАЯ СТРУКТУРА ТРИС-АЦЕТИЛАЦЕТОНАТА ЖЕЛЕЗА ПО ДАННЫМ МЕТОДА ГАЗОВОЙ ЭЛЕКТРОНОГРАФИИ И КВАНТОВО-ХИМИЧЕСКИХ РАСЧЕТОВ

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Структура молекулы трис-ацетилацетоната железа, $Fe(acac)_3$, была определена в рамках синхронного электронографического/масс-спектрометрического эксперимента, а также с помощью квантово-химических расчетов методом DFT/UB3LYP/cc-pVTZ. Наилучшее согласие между рассчитанными и экспериментальными функциями интенсивности рассеяния электронов было достигнуто для модели молекулы симметрии D_3 с высокоспиновым электронным состоянием. DFT расчеты также указывают на высокоспиновое электронное состояние $^6A_1$ как основное при равновесной геометрической конфигурации молекулы D_3 симметрии.

Ключевые слова: трис(ацетилацетонат) железа, спиновое состояние, молекулярная структура, дифракция электронов

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MOLECULAR STRUCTURE OF TRIS(ACETYLACETONATE)IRON STUDIED BY GAS-PHASE ELECTRON DIFFRACTION AND DFT CALCULATIONS

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The molecular structure of tris(acetylacetonate)iron, $Fe(O_2C_5H_7)_3$, has been determined by synchronous gas-phase electron diffraction and mass spectrometric experiment along with quantum chemical calculations at the DFT/UB3LYP/cc-pVTZ theory level. The best agreement between theoretical and experimental intensity curves of scattered electrons was obtained for the high spin model with the symmetry D_3 of molecule. The DFT calculations also resulted in high spin electronic state $^6A_1$ of the molecule $Fe(O_2C_5H_7)_3$ as the ground one at the geometrical configuration of D_3 symmetry.

Key words: tris(acetylacetonate)iron, spin state, molecular structure, electron diffraction

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Experimental studies of the structure of the iron (III) acetylacetonate complex in the gas phase have not been carried out so far. The purpose of this work is to determine the geometric structure of individual molecule $Fe(acac)_3$ by gas-phase electron diffraction supported by DFT calculations. The electron diffraction patterns and the mass spectra of the iron complex were recorded simultaneously using the EMR-100/APDM-1 equipment complex [1] at T=388 (5) K. The mass spectral monitoring of the vapor at this temperature indicates that all the registered ions are formed from a single molecular form of $Fe(acac)_3$.

Table 1

Structural parameters of $Fe(acac)_3$ complex according to electron diffraction (GED) data and DFT calculations

***Таблица 1.* Структурные параметры комплекса $Fe(acac)_3$ согласно электронографическим (GED) данным и DFT расчетам**

Parameters, Å, deg	DFT	GED
	r_e	r_{h1}
Fe-O	2.022	2.018(4)
O-C	1.269	1.268(3)
C-C_r	1.400	1.399(3)
C-C_m	1.508	1.507(3)
C_m-H_{aver}	1.088	1.070(5)
∠OFeO	85.9	87.4(4)
∠CC_rC	123.6	123.2(4)
∠FeOC	130.5	129.0(4)
∠OCC_m	115.5	115.9(5)
τ(HC_mCO)	0.6	11(28)
φ*	32.0	34.5(11)
R_f , %		5.5

Note: * ligand rotation about Fe-C axes from D_{3h} symmetry
Примечание: * вращение лиганда вокруг осей Fe-C D_{3h} симметрии

The $Fe(acac)_3$ complex within the framework of the crystal field theory can be represented as consisting of a triple-charged Fe^{3+} ion ($3d^5$ electron configuration) surrounded by six oxygen atoms of three ligands forming the octahedral symmetry field.

In the case of a weak field, each of the five d-electrons occupies one of the d-AOs of the Fe^{3+} ion leading to a multiplicity of 6. The calculations DFT/UB3LYP/cc-pVTZ resulted in configuration of D_3 symmetry corresponding to the minimum on the PES and electronic state $^6A_1$ (Fig. 1).

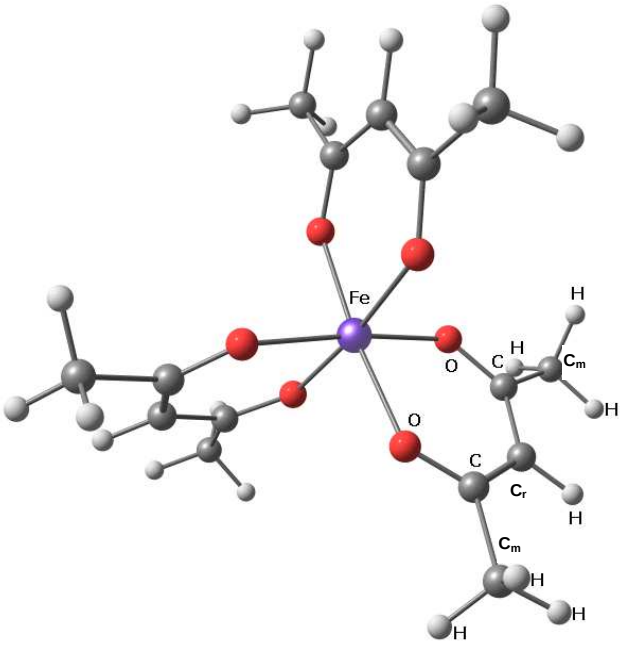

Fig. 1. Molecular structure of $Fe(acac)_3$ with D_3 symmetry
Рис. 1. Молекулярная структура $Fe(acac)_3$ симметрии D_3

Interpretation of the electron diffraction data was carried out for the model of molecule with D_3 symmetry, which included 11 independent parameters (Table 1): internuclear distances r(Fe–O), r(O–C), r(C–C_r), r(C_r–H), r(C_m–H), the bond angles ∠OFeO, ∠ FeOC, ∠OCC_m, ∠CC_mH and dihedral angles φ (the rotation angle of the ligands around the C_2 axis passing through the Fe and C_r atoms, and γ (the angle of rotation of the CH_3-groups relative to the axis passing through the C and C_m atoms).

The structural parameters of the complex $Fe(acac)_3$, corresponding to the best agreement between the experimental and theoretical curves of the molecular scattering intensity, are given in Table 1 along with the parameters calculated by the DFT/UB3LYP/cc-pvtz method.

Analysis of Table 1 clearly shows that the geometric model of symmetry D_3 is consistent with the results of the electron diffraction experiment. The obtained electron diffraction data do not contradict to the high-spin electronic state of $^6A_1$ as the ground state of the iron tris-acetylacetonate complex in the gas phase under the conditions of the GED experiment.

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