Изв. вузов. Химия и хим. технология. 2017. Т. 60. Вып. 4

DOI: 10.6060/tcct.2017604.5555

УДК: 544.18,539.27

МОЛЕКУЛЯРНАЯ СТРУКТУРА *ТРИС*-АЦЕТИЛАЦЕТОНАТА МАРГАНЦА В РАЗНЫХ СПИНОВЫХ СОСТОЯНИЯХ

Р.Й.Ф. Бергер, Г.В. Гиричев, Н.И. Гиричева, А.А. Петрова, В.В. Слизнев, Н.В. Твердова

Рафаэль Йохан Фридрих Бергер

Факультет материаловедения и физики, Зальцбургский университет им. Париса Лодрона, Австрия,
ул. Якоба-Харингера, 2А, Зальцбург, 5020, Австрия.
E-mail: raphael.berger@sbg.ac.at

Георгий Васильевич Гиричев *, Анжелика Алексеевна Петрова, Валерий Викторович Слизнев, Наталия Вячеславовна Твердова

Кафедра физики, Ивановский государственный химико-технологический университет, Шереметевский просп., 7, Иваново, Российская Федерация, 153000
E-mail: girichev@isuct.ru *, paa-1@mail.ru, sliznev@isuct.ru, tverdova@isuct.ru

Нина Ивановна Гиричева

Кафедра органической и физической химии, Ивановский государственный университет, ул. Ермака, 39, Иваново, Российская Федерация, 153025
E-mail: n.i.giricheva@mail.ru

Электронное и геометрическое строение, силовое поле и колебательный спектр молекулы трис-ацетилацетоната марганца в электронных состояниях с мультиплетностью M = 1, 3 и 5 были изучены с помощью квантово-химических расчетов, выполненных методом DFT/UB3LYP при использовании корреляционно-согласованного набора базисных функций cc-pVTZ. Структура молекулы в высокоспиновом состоянии S=2 (тип симметрии электронного состояния ^5B) и с типом симметрии равновесной конфигурации C_2 характеризуется наименьшей энергией. При этом, координационный полиэдр MnO_6 имеет форму вытянутого октаэдра. Высокоспиновое состояние ^5A соответствует седловой точке на ППЭ, при этом координационный полиэдр приобретает форму сжатого октаэдра. Искажение октаэдрической структуры координационного полиэдра значительно, и этот факт свидетельствует о проявлении сильного эффекта Яна-Теллера (вибронного эффекта) в электронном состоянии ^5E. Расчеты для низкоспинового состояния с S=0 завершились получением неожиданного результата. Оптимизация структуры симметрии C_2 для электронного состояния ^1B привела к структурным параметрам молекулы, близким к параметрам, полученным для электронного состояния $^3A_2$. При этом межъядерные расстояния Mn-O в пределах 0,001 Å оказались совпадающими с расстояниями, полученными для структуры D_3-симметриии со спином S=1. Этот результат соответствует ситуации, когда два электрона заселяют разные орбитали 1e, обладая противоположными спинами. Электронные состояния $^3A_2$ и ^1B лежат выше, чем высокоспиновое состояние на 5,2 и 17,3 ккал/моль, соответственно. Заселенность молекулярных орбиталей находится в хорошем согласии с предсказаниями теории кристаллического поля, свидетельствуя о том, что d-орбитали иона Mn^{3+} подвергаются заметному воздействию поля лигандов.

Ключевые слова: эффект Яна-Теллера, вибронный эффект, *трис*-ацетилацетонат марганца, спиновое состояние

UDC: 544.18,539.27

MOLECULAR STRUCTURE OF MANGANESE *TRIS*-ACETYLACETONATE IN DIFFERENT SPIN STATES

R.J.F. Berger, G.V. Girichev, N.I. Giricheva, A.A. Petrova, V.V. Sliznev, N.V. Tverdova

Raphael Johann Friedrich Berger

Department of Materials Research and Physics; Chemistry of Materials, Paris Lodron University of Salzburg,
Jakob-Haringerstr. 2A, Salzburg, 5020, Austria
E-mail: raphael.berger@sbg.ac.at

Georgiy V. Girichev *, Angelika A. Petrova, Valery V. Sliznev, Nataliya V. Tverdova

Department of Physics, Ivanovo State University of Chemistry and Technology, Sheremetievskiy ave., 7,
Ivanovo, 153000, Russia
E-mail: girichev@isuct.ru *, paa-1@mail.ru, sliznev@isuct.ru, tverdova@isuct.ru

Nina I. Giricheva

Department of Organic and Physical Chemistry, Ivanovo State University,
Ermak st., 39, Ivanovo, 153025, Russia
E-mail: n.i.giricheva@mail.ru

Quantum chemical calculations of the geometric structure, force fields and harmonic vibration frequencies of the molecule $Mn(acac)_3$ for electronic states with multiplicities M = 1, 3 and 5 were performed using the GAUSSIAN 09 program in the framework of density functional theory (DFT/UB3LYP) with correlation-consistent valence three-exponential basis functions cc-pVTZ. The structure with high-spin state S=2 (symmetry of electronic state ^5B) possesses the lowest energy and it is characterized by C_2 symmetry. The coordination polyhedron MnO_6 possesses the shape of "elongated octahedron". The high-spin state ^5A is characterized by structure of compressed octahedron. The distortion of octahedral structure of coordination polyhedron in the states ^5A and ^5B is significant, and this fact testifies to the strong Jahn-Teller effect, or vibronic effect, in ^5E electronic state. The calculations for low-spin state S=0 are notable for some specifics. The optimization resulted in C_2 symmetry of molecule having the symmetry of electronic state ^1B. The bond distances Mn-O within 0.001 Å were equal to values obtained for structure with D_3 symmetry with S=1. This result corresponds to the situation if two electrons occupy different 1e orbitals possessing opposite spins. The spin states $^3A_2$ and ^1B lie higher than the high-spin state by 5.2 and 17.3 kcal/mol, respectively. The structural features are explained well in a framework of simple crystal field theory indicating that d-orbitals of Mn^{3+} ion undergo the significant influence of ligand field.

Key words: Jahn-Teller effect, vibronic effect, manganese tris-acetylacetonate, spin state

Для цитирования:
Бергер Р.Й.Ф., Гиричев Г.В., Гиричева Н.И., Петрова А.А., Слизнев В.В., Твердова Н.В. Молекулярная структура *трис*-ацетилацетоната марганца в разных спиновых состояниях. *Изв. вузов. Химия и хим. технология*. 2017. Т. 60. Вып. 4. С. 47–53.
For citation:
Berger R.J.F., Girichev G.V., Giricheva N.I., Petrova A.A., Sliznev V.V., Tverdova N.V. Molecular structure of manganese *tris*-acetylacetonate in different spin states. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* 2017. V. 60. N 4. P. 47–53.

INTRODUCTION

The Jahn−Teller, or vibronic coupling effect (JTE), manifests as a distortion of molecular structure if some electronic state is associated with degeneracy. The structure of manganese *tris*-beta-diketonato complexes is a typical example of the manifestation of a Jahn-Teller effect, although the authors of early work [1] suppose that the distortion of the octahedral configuration of oxygen ligands about the manganese atom appears to be the result of altered oxygen-metal-oxygen bond angles rather than of a Jahn-Teller mechanism. According to later works [2-4], octahedral manganese *tris*-beta-diketonato complexes are high-spin complexes that can undergo Jahn–Teller distortion due to the partial filling of the two-fold degenerate *e* orbitals. The character of distortion can be different. For example, in references [5-8] it is reported, that coordination polyhedron MO_6 in the crystalline phase of some compounds is elongation, whereas the works [3,9] testify the opposite type of deformation for other compounds. The authors of [4] draw attention to the results of the work [3], according to which the manganese *tris*-acetylacetonato demonstrates an irreversible solid–solid phase transition with temperature lowering. At the temperature about 100 K the solid phase shows the Jahn–Teller orthorhombic distortion while at the room temperature the large errors in the bond lengths do not allow to assign the type of Jahn–Teller distortion with any certainty.

It should be noted that the intermolecular interaction in crystal can affect the distortion of coordination polyhedron, which, in turn, predetermines the realized electronic state.

Authors of [2] give an overall description of the vibronic problem in case of $Mn(acac)_3$. The coordination polyhedron MO_6 in a molecule possessing D_3 symmetry decreases this symmetry to C_2 in accordance with the Jahn-Teller theorem getting the elongated or compressed shape which corresponds, in turn, to the minimum or a saddle point on the PES. The calculations at B3LYP/6-31G*(H, O, C),VTZ(Mn) resulted in the structure with elongated polyhedron MnO_6.

Authors of [4] carrying out the calculations at OLYP/TZP approximation have got also the structures with elongated and compressed coordination polyhedron for ^5A and ^5B electronic states of $Mn(acac)_3$ correspondingly. However, they did not study the character of the stationary point on PES for electronic state ^5A and considering this structure as equilibrium one and using the Boltzmann equation found that the population of $Mn(acac)_3$ will occur with the elongation-distortion is 79%, relative to the 21% population found to have compression-distortion.

The theoretical works [2,4] studied only high-spin state of *tris*-beta-diketonato complexes of Mn paying the attention to Jahn-Teller effect. In this connection it seems to be interesting to study the structures in all possible spin states arising from electronic states of free cation Mn^{3+} corresponding to different occupations of *d*-orbitals by four electrons. The manganese *tris*-acetylacetonato complex, in further referred as $Mn(acac)_3$, was studied aiming this purpose.

COMPUTATIONAL METHODS

Quantum chemical calculations of the geometric structure, force fields and harmonic vibration frequencies of the $Mn(acac)_3$ for states with multiplicities M = 1, 3 and 5 were performed using the GAUSSIAN 09 program [10] in the framework of density functional theory (DFT/UB3LYP) [11-13] with correlation-consistent valence three-exponential basis functions cc-pVTZ [14, 15]. The composition of canonic MOs were obtained on the base of calculations at the theory level ROHF/cc-pvtz and fixed geometries which were optimized by UB3LYP/cc-pVTZ. The program ChemCraft [16] was used for visualization of MOs.

RESULTS AND DISCUSSION

According to the crystal field theory, the ground and low-lying exited electronic states of $Mn(acac)_3$ molecule arise from the states of isolated cation Mn^{3+} with open valence $3d^4$-shell. In the high symmetrical D_3 structure of $Mn(acac)_3$, fivefold degenerated 3*d*-orbitals of Mn^{3+} cation are split and form the a_1 molecular orbital and two couples of *1e* and 2*e* orbitals.

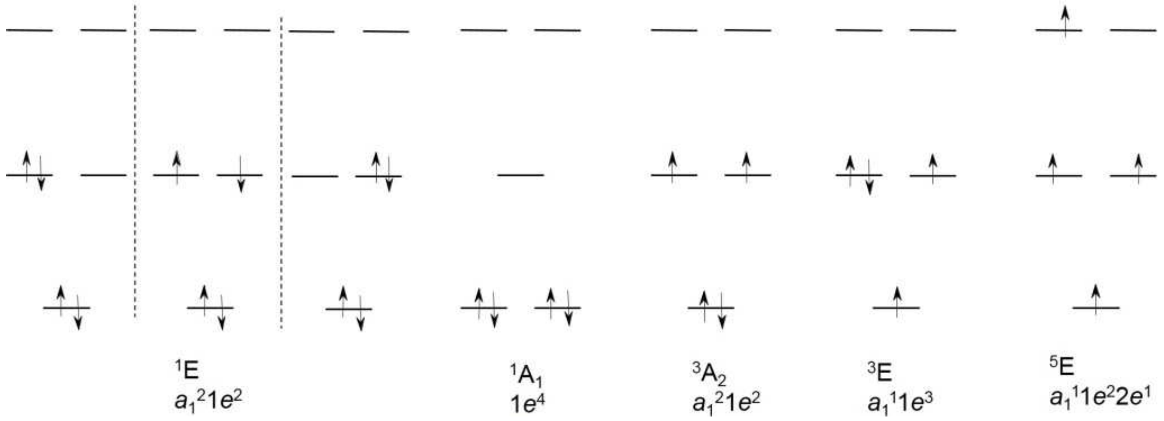

Fig. 1. Electronic configurations and d-orbital diagram for most energetically favorable electronic states of $Mn(acac)_3$ with D_3 structure
Рис. 1. Электронные конфигурации и диаграмма d-орбиталей для молекулы $Mn(acac)_3$ симметрии D_3 в низших электронных состояниях

Table

Bond length of Mn-O, folding angle of chelate rings along O···O axes and relative electronic energy in structures, which are realized in different spin states of $Mn(acac)_3$ molecule (according to DFT/UB3LYP/cc-pVTZ calculations)

***Таблица.* Длина связи Mn-O, угол складывания хелатных колец по оси O··O и относительная электронная энергия для структур молекулы $Mn(acac)_3$, реализующихся в разных спиновых состояниях (по данным DFT/UB3LYP/cc-pVTZ расчетов)**

Parameter Å deg kcal/mol	Spin Electronic state Symmetry				
	S=0, ^1B, C_2	S=1, $^3A_2$, D_3	S=2, ^5B, C_2		
			this work	[2] [a]	[4] [b]
Mn – O	1.938	1.937	2.168	2.147	2.245
Mn – O′	1.937		1.935	1.934	1.974
Mn – O″	1.938		1.949	1.951	1.993
Mn-O-O′-C(H)	179.3	180.0	177.2		
Mn-O″-O″-C(H)	180.0		180.0		
E_{rel}	17.3	5.2	0		

Notes: [a] OLYP/TZP, [b] B3LYP/6-31G* (H,C,O), Ahlrichs' VTZ (Mn)
Примечания: [a] OLYP/TZP; [b] B3LYP/6-31G* (H,C,O), Ahlrichs' VTZ (Mn)

The a_1 molecular orbital contains d_{z^2}-AO while the combinations of $d_{x^2-y^2}$, d_{xy}, d_{xz} and d_{yz} atomic orbitals are involved in degenerate 1*e* and 2*e* orbitals. Spatial orientations of *d*-orbitals into coordination polyhedron MnO_6 of D_3 symmetry allow us to range the MO energies as $\varepsilon(a_1) < \varepsilon(1e) < \varepsilon(2e)$. Four electrons are distributed among five molecular orbitals (a_1, *1e* and *2e*) resulting in the electronic states with multiplicities (M) 1, 3 and 5. Most energetically favorable electronic states $^1E(a_1^2 1e^2)$, $^1A_1(1e^4)$, $^3A_2(a_1^2 1e^2)$, $^3E(a_1^1 1e^3)$ and $^5E(a_1^1 1e^2 2e^1)$ can be constructed by consecutive occupation of the orbitals a_1, *1e* and *2e* (Fig. 1).

Electronic states ^1E, ^3E and ^5E are the orbital degenerated, and their geometry configuration symmetry D_3 must go down to C_2 in accordance with Jahn-Teller theorem. The optimization of initial molecular geometry C_2 for the multiplicities M=1 and M=3 resulted in the structures with six equal (within 0.001 Å) Mn-O bonds giving the structure D_3 practically and corresponding the orbital occupations $a_1^2 1e^2$ (^1E and $^3A_2$). The optimization at D_3 symmetry was successful for M=3 giving the state $a_1^2 1e^2$ ($^3A_2$) but resulted in C_2 structure with practically equal bond lengths Mn-O for M=1.

For the multiplicity M=5 the optimization under symmetry D_3 was unsuccessful. In turn, the structure optimization at C_2 symmetry resulted in the structure with compressed or elongated coordination polyhedron MO_6 and corresponding to the electronic states ^5A or ^5B, respectively. The analysis of the Hessian matrix showed, that the compressed structure of $Mn(acac)_3$ in the electronic state ^5A is characterized by first order saddle point on PES being the transition state between two equivalent minima corresponded to ^5B states.

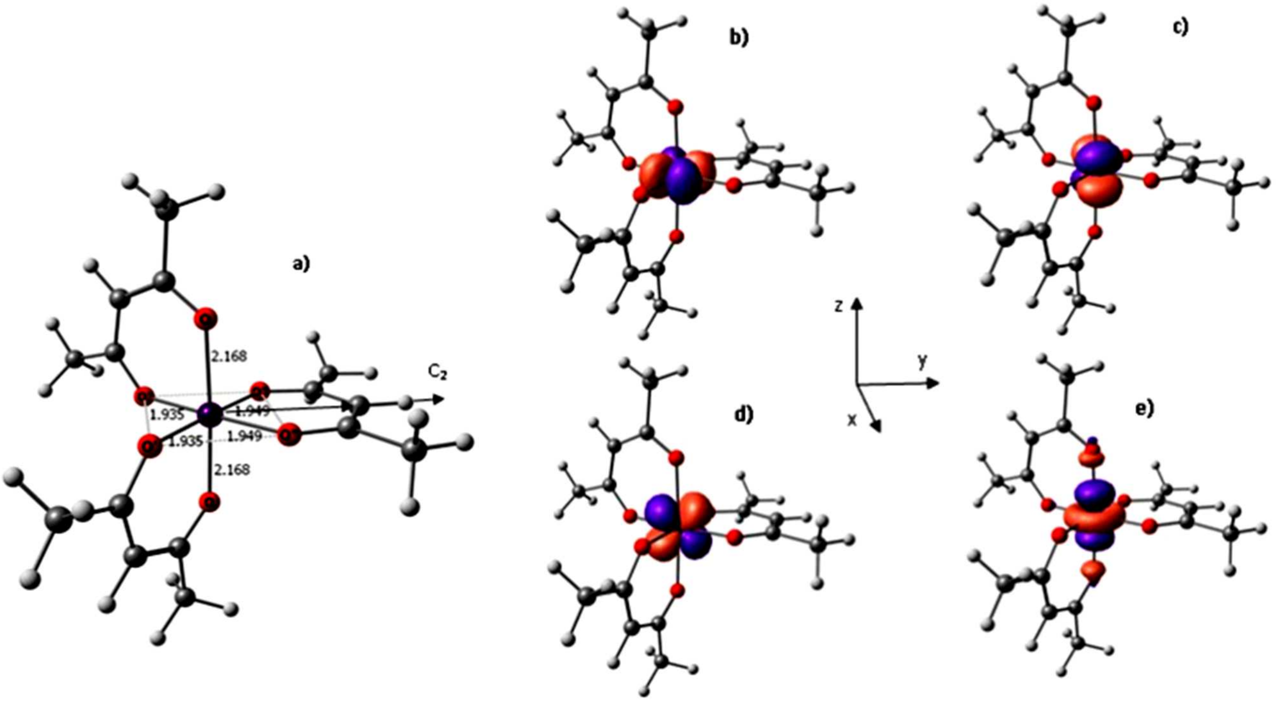

Fig. 2. Mn(acac)3 structure in high-spin state (M=5, ^{5}B): a) parameters of coordination polyhedron; occupied d-orbitals in local Cartesian coordinates: b) d_{x2-y2}, c) d_{xz}, d) d_{yz}, e) d_{z2}. Orbital d_{z2} is responsible for elongation of Mn-O bonds; axes y coincides with symmetry axes C_2
Рис. 2. Структура молекулы $Mn(acac)_3$ в высокоспиновом состоянии (M=5, ^{5}B): a) параметры координационного полиэдра; заселенные d-орбитали в локальной системе координат: b) d_{x2-y2}, c) d_{xz}, d) d_{yz}, e) d_{z2}. Орбиталь d_{z2} ответ-ственна за удлинение связи Mn-O; ось y совпадает с осью симметрии C_2

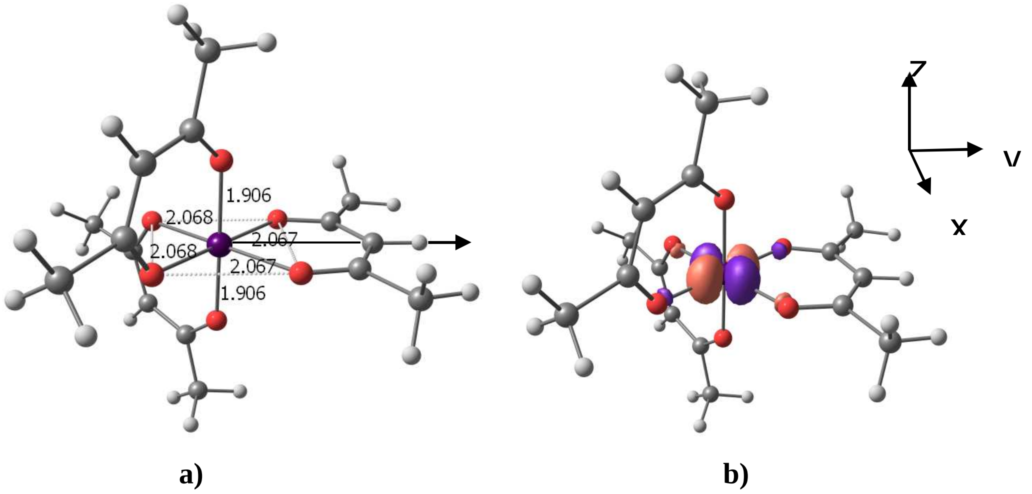

Fig. 3. The structure of Mn(acac)$_3$ in high-spin state ^{5}A (corresponding to first order saddle point on PES). a) parameters of coordination polyhedron; b) occupied d_{x2-y2}-orbital in local Cartesian coordinates

Рис. 3. Структура молекулы Mn(acac)$_3$ в высокоспиновом состоянии ^{5}A (соответствует седловой точке первого порядка на ППЭ). a) параметры координационного полиэдра; b) заселенная d_{x2-y2}-орбиталь в локальной декартовой системе координат

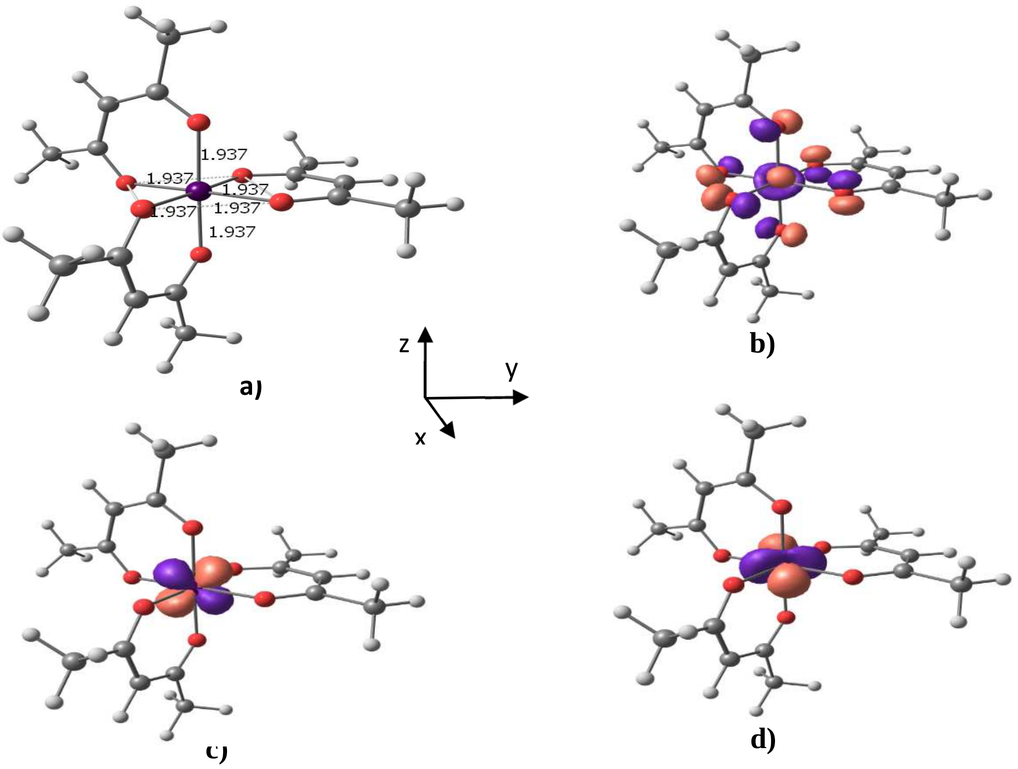

Fig. 4. The structure of Mn(acac)$_3$ in electronic state $^3A_2$ (middle-spin state M=3) and occupied d-orbitals: a) parameters of coordination polyhedron; occupied d-orbitals in local Cartesian coordinates: b) mixed, c) d_{yz}, d) d_{x2-y2}

Рис. 4. Структура молекулы Mn(acac)$_3$ в электронном состоянии $^3A_2$ (среднеспиновое состояние M=3) и заселенные d-орбитали: a) параметры координационного полиэдра; b) смешанная, c) d_{yz}, d) d_{x2-y2}

The bond distances r(Mn-O) and relative energy for discussed electronic states of Mn(acac)$_3$ are listed in the Table. Calculated bond distances Mn-O confirm the conclusion [2, 4] about the character of Jahn-Teller distortion of the molecule Mn(acac)$_3$. Atom designation is given in Fig. 2.

Fig. 2-4 show the shape of occupied canonic MOs of Mn(acac)$_3$ with dominating contribution of *d*-orbitals of Mn^{3+} ion for the equilibrium structures at different spin states.

Fig. 2 shows, if the symmetry of molecule goes down from D_3 to C_2, an occupation by one electron $3d_z^2$

AO leads to the elongation of two axial Mn-O bonds for high-spin state ^5B as it was obtained in Ref. 4. In opposite, in the state ^5A the elongation of four equatorial bonds Mn-O takes place due to an occupation of $3d_{x^2-y^2}$ AO instead of $3d_{z^2}$ AO (Fig. 3).

For exited electronic states ^1B (C_2 symmetry) and $^3A_2$ (D_3 symmetry), the distances r(Mn-O) are equal and shorter than for high-spin state ^5B. Table reports that in spite of the fact that the average bond Mn-O in the high-spin complex is longer, the energy of this complex is lower than the energy of the low-spin complexes due to the high energy electron coupling in the last two.

The calculations for low-spin state M=1 met some uncertainty. The optimization at the theory level UB3LYP/cc-pVTZ resulted formally in C_2 symmetry of molecule having the symmetry of electronic state ^1B. The bond distances Mn-O within 0.001 Å were equal to values obtained for structure M=3 with D_3 symmetry. This result does not contradict the situation if two electrons occupy different 1*e* orbitals possessing opposite spins.

According to Table, the structural parameters of the MnO_6 polyhedron in complexes with M=1 and M=3 are practically equal because in both spin states the lobes of occupied 3*d*-AOs are directed between bonds Mn-O and do not affect significantly the chemical bonding.

The energy difference for electronic states $^3A_2$ and ^5B is equal to 5.2 kcal/mol only, and complex $Mn(acac)_3$ in some crystals possesses the structures with six close bond lengths Mn-O because the state $^3A_2$ is realized possibly due to packing forces. In this connection it is interesting to study by gas-phase electron diffraction the structure, which is realized in the gas phase.

CONCLUSIONS

The high-spin electronic state ^5B was found to be preferable for $Mn(acac)_3$ molecule as calculated at the theory level UB3LYP/cc-pVTZ. In this state the molecule has C_2 symmetry with two long and four short Mn-O bonds. The state ^5A lies higher than state ^5B by 1 kcal/mol and corresponds to the first order saddle point. Obviously, these states appear due to Jan-Teller distortion of D_3 structure possessed ^5E electronic state. The distortion of octahedral structure of MnO_6 polyhedron in the states ^5A and ^5B is significant, and this fact testifies to strong Jahn-Teller effect in ^5E electronic state. The spin states $^3A_2$ and ^1B lie higher than the high-spin state by 5.2 and 17.3 kcal/mol, correspondingly. The coordination polyhedron is characterized by D_3 symmetry for state $^3A_2$ and very close to this symmetry for ^1B state. The structural features are explained well in framework of simple crystal field theory indicating that *d*-orbitals of Mn^{3+} ion undergoes the influence of crystal field.

Acknowledgements. *This work was supported by the Russian Foundation for Basic Research (Grant No. 16-03-00855a); computational resources were provided by grant of Ministry of Education and Science N 4.3232.2017PP.*

ЛИТЕРАТУРА

1. **Morosin B., Brathovde R.** The crystal structure and molecular configuration of trisacetylacetonatomanganese(III). *J. Acta Cryst.* 1964. V. 17. P. 705-711. DOI: 10.1107/S0365110X64001761.
2. **Diaz-Acosta I., Baker J., Hinton J.F., Pulay P.** Calculated and experimental geometries and infrared spectra of metal tris-acetylacetonates: vibrational spectroscopy as a probe of molecular structure for ionic complexes. Part II. *Spectrochim. Acta Part A.* 2003. V. 59. P. 363–377. DOI: 10.1016/S1386-1425(02)00166-X.
3. **Geremia S., Demitri N.** Crystallographic Study of Manganese(III) Acetylacetonate: An Advanced Undergraduate Project with Unexpected Challenges. *J. Chem. Educ.* 2005. V. 82. P. 460–465. DOI: 10.1021/ed082p460.
4. **Freitag R., Conradie J.** Understanding the Jahn–Teller Effect in Octahedral Transition-Metal Complexes: A Molecular Orbital View of the Mn(β-diketonato)3 Complex. *J. Chem. Educ.* 2013. V. 90. N 12. P. 1692–1696. DOI: 10.1021/ed400370p.
5. **Freitag R., Muller T.J., Conradie J.** X-Ray Diffraction and DFT Calculation Elucidation of the Jahn–Teller Effect Observed in Mn(dibenzoylmethanato)3. *J. Chem. Crystallogr.* 2014. V. 44. P. 352–359. DOI: 10.1007/s10870-014-0522-6.
6. **Stults R.B., Marianelli R.S., Day V.W.** Distortions of the coordination polyhedron in high-spin manganese(III) complexes. 3. Crystal and molecular structure of .gamma.-

REFERENCES

1. **Morosin B., Brathovde R.** The crystal structure and molecular configuration of trisacetylacetonatomanganese(III). *J. Acta Cryst.* 1964. V. 17. P. 705-711. DOI: 10.1107/S0365110X64001761.
2. **Diaz-Acosta I., Baker J., Hinton J.F., Pulay P.** Calculated and experimental geometries and infrared spectra of metal tris-acetylacetonates: vibrational spectroscopy as a probe of molecular structure for ionic complexes. Part II. *Spectrochim. Acta Part A.* 2003. V. 59. P. 363–377. DOI: 10.1016/S1386-1425(02)00166-X.
3. **Geremia S., Demitri N.** Crystallographic Study of Manganese(III) Acetylacetonate: An Advanced Undergraduate Project with Unexpected Challenges. *J. Chem. Educ.* 2005. V. 82. P. 460–465. DOI: 10.1021/ed082p460.
4. **Freitag R., Conradie J.** Understanding the Jahn–Teller Effect in Octahedral Transition-Metal Complexes: A Molecular Orbital View of the Mn(β-diketonato)3 Complex. *J. Chem. Educ.* 2013. V. 90. N 12. P. 1692–1696. DOI: 10.1021/ed400370p.
5. **Freitag R., Muller T.J., Conradie J.** X-Ray Diffraction and DFT Calculation Elucidation of the Jahn–Teller Effect Observed in Mn(dibenzoylmethanato)3. *J. Chem. Crystallogr.* 2014. V. 44. P. 352–359. DOI: 10.1007/s10870-014-0522-6.
6. **Stults R.B., Marianelli R.S., Day V.W.** Distortions of the coordination polyhedron in high-spin manganese(III) complexes. 3. Crystal and molecular structure of gamma.-

tris(acetylacetonato)manganese(III): a tetragonally elongated octahedral form. *Inorg. Chem.* 1979. V. 18. P. 1853–1858. DOI: 10.1021/ic50197a028.

7. **Зайцева Е.Г., Байдина И.А., Стабников П.А. Борисов С.В. Игуменов И.К.** Кристаллическая и молекулярная структура трис(дибензоилметаната) марганца(III). *Ж. Структ. Химии.* 1990. Т. 31. С. 184-189.
8. **Barra A.L., Gatteschi D., Sessoli R., Abbati G.L., Cornia A., Fabretti A.C., Uytterhoeven M.G.** Electronic Structure of Manganese(III) Compounds from High-Frequency EPR Spectra. *Angew. Chem. Int. Ed.* 1997. V. 36. P. 2329-2331. DOI: 10.1002/anie.199723291.
9. **Fackler J.P., Avdeef A.** Crystal and molecular structure of tris(tropolonato)manganese(III), Mn(O2C7H5)3, a high-spin complex having structural features consistent with Jahn-Teller behavior for two distinct MnO6 centers. *Inorg. Chem.* 1974. V. 13. P. 1864–1875. DOI: 10.1021/ic50138a016.
10. **Frisch M.J., Trucks G.W., Schlegel H.B., Scuseria G.E., Robb M.A., Cheeseman J.R., Scalmani G., Barone V., Mennucci B., Petersson G.A., Nakatsuji H., Caricato M., Li X., Hratchian H.P., Izmaylov A.F., Bloino J., Zheng G., Sonnenberg J.L., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Vreven T., Montgomery J.A., Jr., Peralta J.E., Ogliaro F., Bearpark M., Heyd J.J., Brothers E., Kudin K.N., Staroverov V.N., Kobayashi R., Normand J., Raghavachari K., Rendell A., Burant J.C., Iyengar S.S., Tomasi J., Cossi M., Rega N., Millam J.M., Klene M., Knox J.E., Cross J.B., Bakken V., Adamo C., Jaramillo J., Gomperts R., Stratmann R.E., Yazyev O., Austin A.J., Cammi R., Pomelli C., Och-terski J.W., Martin R.L., Morokuma K., Zakrzewski V.G., Voth G.A., Salvador P., Dannenberg J.J., Dapprich S., Daniels A.D., Farkas Ö., Foresman J.B., Ortiz J.V., Cioslowski J., Fox D.J.** Gaussian 09. Wallingford CT: Gaussian, Inc. 2009.
11. **Becke A.D.** Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* 1993. V. 98. N 7. P. 5648-5652. DOI: 10.1063/1.464913.
12. **Becke A.D.** Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys. Rev. A.* 1988. V. 38. N 6. P. 3098-3010. DOI: 10.1103/PhysRevA.38.3098.
13. **Lee C., Yang W., Parr R.G.** Development of the Colic-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B.* 1988. V. 37. N 2. P. 785-789. DOI: 10.1103/PhysRevB.37.785.
14. **Dunning T.H.** Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. *J. Chem. Phys.* 1971. V. 55. P. 716-723. DOI: 10.1063/1.1676139.
15. **Balabanov N.B., Peterson K.A.** Systematically convergent basis sets for transition metals. I. All-electron correlation consistent basis sets for the 3d elements Sc–Zn. *J. Chem. Phys.* 2005. V. 123. P. 064107-1 – 064197-15.
16. Chemcraft program, Version 1.8 http://www.chemcraftprog.com.

tris(acetylacetonato)manganese(III): a tetragonally elongated octahedral form. *Inorg. Chem.* 1979. V. 18. P. 1853–1858. DOI: 10.1021/ic50197a028.

7. **Zaitseva E.G., Baidina I.A., Stabnikov P.A., Borisov S.V., Igumenov I.K.** Crystal and molecular structure of tris (dibenzoylmethanate) manganese (III). *Russ. J. Struct. Chem.* 1990. V. 31. P. 184-189.
8. **Barra A.L., Gatteschi D., Sessoli R., Abbati G.L., Cornia A., Fabretti A.C., Uytterhoeven M.G.** Electronic Structure of Manganese(III) Compounds from High-Frequency EPR Spectra. *Angew. Chem. Int. Ed.* 1997. V. 36. P. 2329-2331. DOI: 10.1002/anie.199723291.
9. **Fackler J.P., Avdeef A.** Crystal and molecular structure of tris(tropolonato)manganese(III), Mn(O2C7H5)3, a high-spin complex having structural features consistent with Jahn-Teller behavior for two distinct MnO6 centers. *Inorg. Chem.* 1974. V. 13. P. 1864–1875. DOI: 10.1021/ic50138a016.
10. **Frisch M.J., Trucks G.W., Schlegel H.B., Scuseria G.E., Robb M.A., Cheeseman J.R., Scalmani G., Barone V., Mennucci B., Petersson G.A., Nakatsuji H., Caricato M., Li X., Hratchian H.P., Izmaylov A.F., Bloino J., Zheng G., Sonnenberg J.L., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Vreven T., Montgomery J.A., Jr., Peralta J.E., Ogliaro F., Bearpark M., Heyd J.J., Brothers E., Kudin K.N., Staroverov V.N., Kobayashi R., Normand J., Raghavachari K., Rendell A., Burant J.C., Iyengar S.S., Tomasi J., Cossi M., Rega N., Millam J.M., Klene M., Knox J.E., Cross J.B., Bakken V., Adamo C., Jaramillo J., Gomperts R., Stratmann R.E., Yazyev O., Austin A.J., Cammi R., Pomelli C., Och-terski J.W., Martin R.L., Morokuma K., Zakrzewski V.G., Voth G.A., Salvador P., Dannenberg J.J., Dapprich S., Daniels A.D., Farkas Ö., Foresman J.B., Ortiz J.V., Cioslowski J., Fox D.J.** Gaussian 09. Wallingford CT: Gaussian, Inc. 2009.
11. **Becke A.D.** Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* 1993. V. 98. N 7. P. 5648-5652. DOI: 10.1063/1.464913.
12. **Becke A.D.** Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys. Rev. A.* 1988. V. 38. N 6. P. 3098-3010. DOI: 10.1103/PhysRevA.38.3098.
13. **Lee C., Yang W., Parr R.G.** Development of the Colic-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B.* 1988. V. 37. N 2. P. 785-789. DOI: 10.1103/PhysRevB.37.785.
14. **Dunning T.H.** Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. *J. Chem. Phys.* 1971. V. 55. P. 716-723. DOI: 10.1063/1.1676139.
15. **Balabanov N.B., Peterson K.A.** Systematically convergent basis sets for transition metals. I. All-electron correlation consistent basis sets for the 3d elements Sc–Zn. *J. Chem. Phys.* 2005. V. 123. P. 064107-1 – 064197-15.
16. Chemcraft program, Version 1.8 http://www.chemcraftprog.com.

Поступила в редакцию 26.12.2016
Принята к опубликованию 13.03.2017

Received 26.12.2016
Accepted 13.03.2017