A Mössbauer study on iron(II) complex of 2-acetyl-1,3-indandione – spin-crossover or structural changes

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ABSTRACT

An air stable Fe(II) complex of a cyclic β-triketone, 2-acetyl-1,3-indandione (2AID) was obtained in two different ways and studied by Mössbauer spectroscopy. The Mössbauer data at room temperature point to six-coordinated, high spin Fe(II) complex. The temperature-dependent measurements indicate a phase transition in going from 293 to 77 K. Further lowering the temperature, however, do not cause the expected changes for spin-crossover transition. This data provoked application of quantum chemical methods to determine the origin of the observed appearance of spectral component attributable to low spin Fe(II) complex at 77 K. Based on the results from the theoretical calculations of the Mössbauer parameters of several different geometries and spin states of the Fe complexes of 2AID it was possible to conclude that the obtained Fe(II) complex has a pseudo-octahedral geometry. The experimentally observed temperature-dependence of the Mössbauer spectra is attributed to changes of the axial Fe-O bonds, rather than to spin transition. Discussion is given on the role of the type of the axial ligands for conditioning a spin-crossover process, as suggestion for experimental modelling of novel target materials with desired magnetic properties.

1. Introduction

2-Acetyl-1,3-indandione (2AID) is a cyclic β-triketone known for the fast excited state intramolecular proton transfer (ESIPT) process it can undergo upon irradiation with UV light [1]. This phenomenon was supposed to explain also the high photostability of the compound - another interesting feature that has been observed [2]. High photostability was obtained for Cu(II) and Zn(II) metal complexes of 2AID even in hydrogen-bond breaking solvents in which the free ligand loses its photostability. On the other hand, 2AID was suggested as an extracting and spectrophotometric agent for isolation and detection of Fe^{3+} ions [3,4] and the formed complex has been characterized by optical methods. Challenged by the optical and complexation properties of 2AID we have studied a series of its metal complexes [2,5,6] by means of spectroscopic and theoretical methods as well as of its derivatives [7-9]. X-ray structures of metal complexes of 2AID were reported for the Co(II) [6] and the Fe(III) [5] complexes along with detailed magnetochemical, Mössbauer and EPR data. The application of exhaustive Mössbauer measurements in wide temperature range (4.2-293.0 K) and in presence of strong external magnetic field on the Fe(III) complex of 2AID has demonstrated the ability of the Mössbauer spectroscopy, in combination with theoretical simulations, to predict fine structural information about the close surrounding of the ferric nuclei [5].

The fact that the Mössbauer spectral parameters: isomer shift (δ) and quadrupole splitting (ΔE$_Q$) are very sensitive to geometry, oxidation and spin states of Fe nucleus [10,11] allowed for useful application of quantum-chemical calculations in predicting and verifying the geometric and electronic structures of Fe sites by comparing the computed properties with experimental results [12,13]. The isomer shift is proportional to the difference in electron density [ρ(0)] at the studied Fe nuclei and a reference system, which is usually α-Fe at 300 K in the experimental data. Similar treatment can be used for the calculated electron density using simple correlation formula, such as:

$$\delta = A[\rho(0) - B] + C \qquad (1)$$

where B is a constant chosen close to the electron density at Fe nucleus in the reference state. Han and Noodleman have proposed several correlation formula by doing linear regression fit of the calculated ρ(0) and δ$_{exp}$ isomer shift, IS, as well as for the quadrupole splitting, QS, on large sets of experimentally availble data and using different theoretical models [14-16].

Table 1. Mössbauer parameters from the best-fit results of the temperature dependent experimental spectra for Fe(II) complexes **a** and **b**.

Parameter	293 K		77 K		
	Fe(III) component	Fe(II) component	Fe(III) component	Fe(II) component	New Fe(II) component
For complex a					
IS [mm/s]	0.42(5)	1.16(1)	0.55(5)	1.27(1)	0.57(5)
ΔE_Q [mm/s]	0.87(5)	2.70(1)	0.63(5)	2.79(1)	1.55(5)
Γ_{exp} [mm/s]	0.64(5)	0.26(1)	0.56(5)	0.27(1)	0.35(5)
I $_{rel}$ [%]	41.2(5)	58.8(1)	30.6(5)	56.1(1)	13.3(5)
For complex b					
IS [mm/s]	0.80(1)	1.15(1)	0.80(5)	1.26(1)	0.70(5)
ΔE_Q [mm/s]	0.25(9)	2.66(1)	0.22(5)	2.78(1)	1.13(5)
Γ_{exp} [mm/s]	1.01(1)	0.26(1)	0.34(5)	0.34(1)	0.60(5)
I $_{rel}$ [%]	14.0(1)	86.0(1)	6.2(5)	70.0(1)	23.8(5)

By using some of the proposed correlations, we attempted to find explanation of the experimentally observed Mössbauer spectral features and propose the most probable structure of the Fe(II) complex of 2AID.

2. Experimental

All reagents and solvents used were of AR grade.

2.1. Instrumentation

The IR spectra were recorded on a Perkin-Elmer FTIR-1600 spectrophotometer (in KBr tablets) and EPR spectra were recorded on a X-band EPR spectrometer Bruker B-ER 420. The Mössbauer spectra were recorded with a conventional constant acceleration spectrometer combined with a multichannel analyzer. A source ^{57}Co/Rh with activity of about 25 mCi was used. The source was kept at room temperature, while the absorber (enclosed in a Plexiglas pellet, 1.2 cm^2 area) was mounted in a continuous flow cryostat (CF, Oxford Instruments). The cryostat was equipped with Mylar foil windows. The isomer shifts are referred to the standard α-Fe foil of 25 μm in thickness at room temperature. The Mössbauer spectra were computer processed and decomposed to Lorentzian curves by least-square fitting program.

2.2. Synthesis

The ferrous complexes were obtained in aerobic conditions from two different starting salts of Fe(II), namely Fe(NH$_4$)$_2$(SO$_4$)$_2$.6H$_2$O and Fe(CH$_3$COO)$_2$.6H$_2$O, following a similar procedure. The metal salt was dissolved in aq. 1 M HCl solution and mixed with ethanolic solution of 2AID with metal-to-ligand ratio equal to 1:2. A dark red precipitate was obtained almost immediately, which was filtered off and washed with small portions of ethanol. FT-IR (KBr, cm^{-1}): 3420-3200 ν(OH) (br, water), 1705 ν(C=O) (non-coordinated), 1679 ν(C=O) (coordinated). Anal. calcd. for FeC$_{22}$H$_{14}$O$_6$: C, 61.42; H, 3.28. Found: C, 61.28; H, 3.07%. This synthesis was repeated under Ar but the reaction product still shows presence of Fe(III) impurities as was seen from the room-temperature EPR spectra.

2.3. Quantum chemical calculations

All calculations were performed with the ADF2008.01 package of programs [17], employing the GGA functionals OPBE and PW91. The geometry optimizations were performed with triple-ζ plus polarization functions (TZP) basis set for the Fe atom, and double-ζ plus polarization functions (DZP) basis set for all other elements. Octahedral and tetrahedral structures for the Fe(II) complex of 2AID were modeled and optimized for different spin states, S = 0, S = 1 and S = 2, and accounting for the solvent effect by the conductor-like screening model (COSMO) [18] with ε = 32.7 for methanol. For the optimized structures all-electron single-point calculations, with TZP basis set for all elements, were performed in order to obtain the

electronic density at the iron nucleus, which was done with the hypers2003 program [19], kindly provided by Han and Noodleman. For calculations of the Mössbauer isomer shifts the following correlation formulas, as suggested by Han and Noodleman [16], were used:

$$\delta_{cal}(Fe^{2+, 2.5+}) = -0.405[\rho(0) - 11884.0] + 0.735 \text{ [mm/s]}$$
for PW91 (2)

$$\delta_{cal}(Fe^{2.5+, 3+}) = -0.393[\rho(0) - 11884.0] + 0.435 \text{ [mm/s]}$$
for PW91 (3)

$$\delta_{cal}(Fe^{2+, 2.5+}) = -0.318[\rho(0) - 11877.0] + 0.633 \text{ [mm/s]}$$
for OPBE (4)

The quadrupole splitting is the other important Mössbauer parameter because it is very sensitive on, and thus, informative about the electronic structure of the Fe ions and their ligand environment. The QS arises from the interaction of the quadrupole moment of the first nuclear excited state of ^{57}Fe (I = 3/2) with the electric field gradient (EFG) surrounding the Fe nucleus. As a result the ^{57}Fe (I = 3/2) nucleus levels split into two doubly degenerate states (m$_I$ ±1/2 and m$_I$ ±3/2) with energy difference equal to

$$\Delta E_Q = \tfrac{1}{2}eQV_{zz}(1+\eta^2/3)^{1/2}$$ (5)

where e is the positive electric charge, Q is the nuclear quadrupole moment (in barns, taken as 0.16 barns [10]), V$_{zz}$ is the electric field gradient, and η is an asymmetry parameter defined as (V$_{xx}$ - V$_{yy}$)/V$_{zz}$ with |V$_{zz}$| ≥ |V$_{yy}$| ≥ |V$_{xx}$. The calculated ΔE_Q is calibrated using the following correlation formulae [16]

$$\Delta E_Q(exp) = 1{,}055 \times \Delta E_Q(calc) + 0{,}227 \text{ [mm/s] for PW91}$$ (6)

3. Results and discussion

3.1. Experimental data

The Fe(II) complexes of 2AID were isolated in solid state as deep red powder. The IR spectra show strong shift of the stretching band for one of the carbonyl groups to lower frequencies (from 1740 to 1679 cm^{-1}), indicating coordination of the carbonyl group. The presence of Fe(III) impurities was detected with EPR measurements at room temperature. Our synthesis under inert (Ar) atmosphere, in attempt to avoid oxidation of the ferrous ion by the air oxygen, still led to a product with presence of Fe(III). Therefore, in the current study, we present the results from the synthesis in aerobic conditions as obtained from two different salts: **a** - from Mohr's salt (ammonium iron(II)sulfate) and **b** - from iron(II)acetate. The only difference between both products is seen in their Mössbauer spectra. The Mössbauer parameters of both synthetic products show large amount of Fe(III) component for complex **a** and about 14 % for complex **b** (see Table 1). Therefore, our discussion will be limited to complex **b**, and the data for complex **a** are shown for illustration of the role of the

starting metal salt for stabilization of Fe(II) complex with O-donor ligand under air. As far as the complexation properties of 2AID are concerned, it is well documented that it acts as a bidentate ligand coordinating after deprotonation of the exocyclic enolic group and including the metal ion in a 6-membered chelate ring. Such coordination mode is proved by the IR spectra of the currently studied complexes, too. More interesting is the overall geometry of the Fe(II) complex and its spin state. Therefore the Mössbauer spectra of the Fe(II) complex **b** were recorded in a wide temperature range. The spectra obtained at 293 and 77 K are presented in Figure 1. The spectrum at liquid helium temperature (not shown) is virtually the same as that at 77 K. In all cases the spectra are characterized with composite structure and were simulated as superposition of two or three components. The best-fit results of the experimental spectra of both Fe(II) complexes **a** and **b** are listed in Table 1.
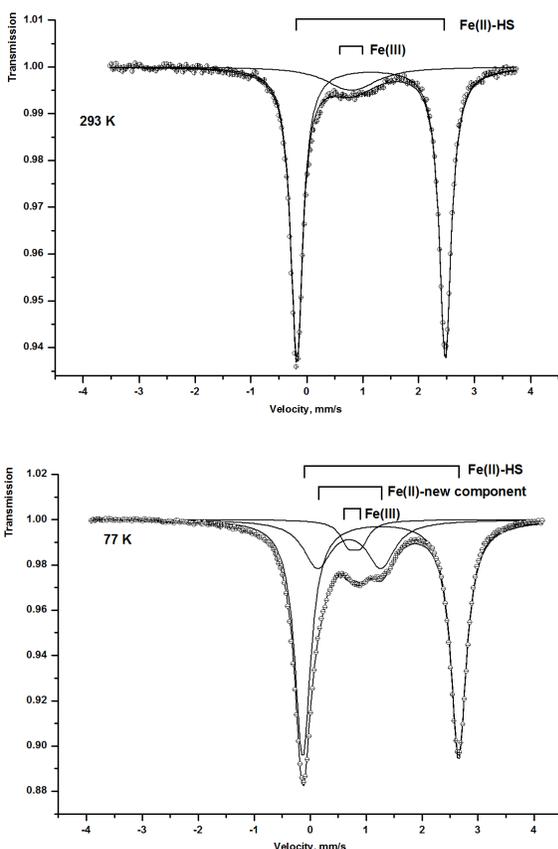
Figure 1. Mössbauer spectra of Fe(II) complex **b** of 2AID recorded at 293 and 77 K. Bar diagrams indicate the quadrupole doublets originating from the Fe(III) and Fe(II) species. The solid curves represent simulations with the parameters given in Table 1.

The room temperature measurement of complex **b** shows the presence of mainly Fe(II) signal, although small amount of Fe(III) species is detected. The quadrupole doublet with relative intensity of 86.0(1) % has Mössbauer parameters typical for high-spin Fe(II) ions. The second quadrupole doublet with relative intensity of 14.0(1) % is typical for high-spin Fe(III). The measured IS and the experimental line widths for the Fe(III) component at RT are unusually large (Table 1, complex **b**), similarly to the already reported Fe(III) complex of 2AID [5]. This was explained by temperature dependent Mössbauer measurements with spin-spin relaxation effects.

Lowering the temperature to 77 K does not lead to large changes of the Mössbauer parameters of both Fe(II)- and

Fe(III)- components, but 23.8(5) % of the total experimental area is due to a new component with values of IS and ΔE_Q that are characteristic for iron (II) in low-spin state (S = 0). These results suggest that the so-called spin-crossover process probably takes place. However, the Mössbauer spectrum recorded at 4.2 K do not show further changes remaining identical to the one at 77 K. The main component is still the one attributed to the high-spin Fe(II) containing compound (with relative intensity of 70.0(1) %). This fact rises the question whether the observed spectral changes are caused by spin-crossover process with very low rate due to the presence of ferric(III) ions in high-spin state, which stabilize the high-spin state for ferrous(II) ions, or has another origin.

The value of isomer shift of the subspestrum attributed to Fe(II) complex is 1.26 mm/s at 77 K, which is typical for ferrous ion in octahedral environment. As is already known [20], for four coordination with oxygen ligands a value for IS of 1 mm/s is expected at temperatures below 77 K, whereas six-coordination leads to IS > 1.2 mm/s. This is explained with shorter bond lengths in four-coordination mode with respect to six-coordination one, which would increase the s-density at Fe nucleus and hence reduce the isomer shift. That is why it has been concluded that the high-spin ferrous (II) ion in the studied complex is six-coordinated. Based on these results we suggest an octahedral structure for Fe(II) complex of 2AID where two ligand molecules lie in the equatorial plane and the axial positions are occupied with O-atom of the non-coordinated carbonyl group from neigbouring complex molecules.

Another feature of the temperature dependent Mössbauer measurements of the Fe(II) complex of 2AID is the increase of the spectral intensity. The Mössbauer effect measured at room temperature is about 6 %, whereas the one observed at 77 K is about 12 %. Such two times increase in the intensity with the temperature decrease would suggest that the central iron ions are weakly bound to the ligands, which allows large variations of the nuclei positions with large mean square displacement. This also explains the increase of the experimental line widths with lowering the temperature, from 0.26 to 0.34 mm/s.

3.2. Quantum chemical calculations

In order to find explanation of the obtained Mössbauer parameters we performed quantum chemical calculations on model structures of Fe(II) complexes of 2AID. As suggested from the experimental data the complex has composition of Fe(2AID)$_2$ pointing to tetrahedral structure. On the other hand the measured isomer shift of 1.26 mm/s is more typical for an Fe(II) bound to six O-atoms, as discussed above. Therefore, it might be supposed that the axial position of the octahedron are occupied with the non-coordinated carbonyl oxygens from neighbouring molecules. In order to model such intermolecular interaction with a reasonable computational cost, octahedral structures for the Fe(II) complex were constructed by coordinating water molecules on the axial positions. The model structures were optimized with two different functionals (PW91 and OPBE). Optimizations were performed for the three different spin states originating from the d^6 electron configuration of Fe(II) with total spin S = 0, 1 or 2. Following the procedure for quantum chemical calculations of isomer shift (IS) and the quadrupole splitting (QS), suggested by Han and Noodleman, we used their correlation formula as listed in the experimental part (Equations 2-5). Although spin-orbit coupling is non-negligible for the Fe-compounds, several reports have demonstrated that the correlation fit parameters are almost insensitive to the type of the employed method, non-relativistic or the scalar relativistic ZORA DFT [12,21,22]. That was the reason for our choice of correlation formulas based on the computational methods with TZVP basis set and different functionals.

Table 2. Calculated Mössbauer parameters: isomer shift (IS) and quadrupole splitting (QS) for optimized and non-optimized, denoted with (*), model structures of Fe(II) complexes of 2AID using PW91-TZP-COSMO (methanol) quantum-chemical method.

Model structure	Total spin S	Structure details	Calculated electron density, [ρ(0)]	Calculated IS	Calculated QS
Fe2_Oh_HS	2	Oh	11882.75295	1.240	2.314
Fe2_Oh_LS	0	Oh	11883.34668	0.999	2.043
Fe2_Td_HS	2	Td	11882.84386	0.889	1.549
Fe2_H2O_204	2	*Oh (Fe-OH$_2$: 2.04 Å)	11882.9414	1.164	2.614
Fe2_H2O_214	2	*Oh(Fe-OH$_2$: 2.14 Å)	11882.8212	1.212	2.395
Fe2_H2O_224	2	Oh(Fe-OH$_2$: 2.24 Å)	11882.75295	1.240	2.314
Fe2_H2O_234	2	*Oh(Fe-OH$_2$: 2.34 Å)	11882.71053	1.257	2.310
Fe2_H2O_244	2	*Oh(Fe-OH$_2$: 2.44 Å)	11882.69023	1.265	2.348
Fe2_NH3_Oh_HS	2	Oh	11882.81392	1.215	2.361
Fe2_NH3_Oh_LS	0	Oh	11883.49270	0.940	1.119

Octahedral model
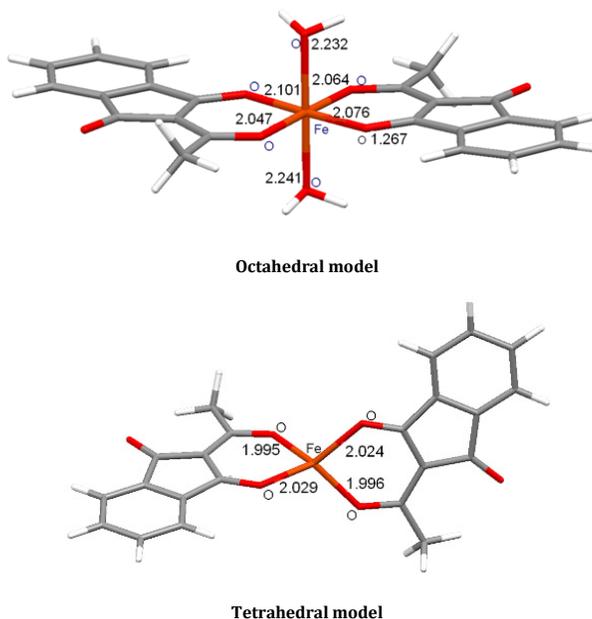
Tetrahedral model

Figure 2. Optimized structures (PW91-DZP) for high-spin (S = 2) Fe(II) complex of 2AID, suggesting octahedral and tetrahedral environment. Selected bond lengths (Fe-O) are given as well.

General observation in our case is that the OPBE optimization leads to unacceptably long Fe-O bond lengths. Therefore, we focus our discussion on the geometries and Mössbauer parameters as obtained from PW91 calculations in solvent media - methanol. All possible models for six- and four-coordinated Fe(II) were optimized. Reasonable geometries were obtained for octahedral and tetrahedral structures, and are depicted in Figure 2. Furthermore, the Fe-O bond lengths with the axial water molecules were manually changed, without optimization, in order to monitor the effect of this structural parameter on the calculated IS and QS. The results from the calculations are listed in Table 2.

Basically, it was seen that the IS and QS are sensitive to the spin state and the Fe-O bond lengths of the octahedral ferrous center, but not to the extent that is seen in the experimental data. The Mössbauer parameters calculated for the octahedral models, optimized for high spin (S = 2) and low spin (S = 0) states of the Fe, reveal that the changes in the calculated IS and QS are too small (ca. 0.24 mm/s) as compared to the experimentally observed ones (0.5 and 1.65 mm/s for the IS and QS, respectively). These data suggested that most probably the observed decrease in the Mössbauer parameters with the temperature lowering is not caused by change in the spin state of the studied Fe(II) complex. Therefore, we focused on selected structural parameters as potential origin of the detected new component in the spectrum, all the more that in

the used model of octahedral coordination the water molecules are added only to approximate an eventual coordination with a free carbonyl group from a proximal complex molecule. The Fe-O(w) bond lengths with the coordinated water molecules in the optimized, high-spin state (S = 2), octahedral Fe are equal to 2.232 and 2.241 Å (see Figure 2). The calculated IS and QS for this geometry deviate from the experimentally observed ones (see Tables 1 and 2). By changing these Fe-O(w) bond lengths, from 2.04 to 2.44 Å, we tried to modulate the expected intermolecular interactions with the neighbouring molecules. The resulting IS and QS altered in such way that unambiguous definition about the exact type of the structural changes, responsible for the observed changes in the experimental Mössbauer parameters, was hard to be given. Generally, elongation of the Fe-O(w) bonds leads to increase in the calculated IS and decrease for the QS. At Fe-O(w) of 2.44 Å the calculated IS shift (1.265 mm/s) is almost equal to the one observed for the main component in the Mössbauer spectrum, 1.26(1) mm/s. However, anomalous value for the QS was obtained in this case. On the other hand, shortening the Fe-O(w) bonds to 2.02 Å results in a calculated value of QS of 2.614 mm/s agreeing very well with the experimental one (2.78(1) m/s). Although giving useful information about the general trends, it seems that the employed simple change in the Fe-O(w) bond lengths is not sufficient to account for the other possible structural changes affecting the IS and QS.

Full optimization (with PW91 and DZP basis set) of four-coordinated, high-spin Fe(II) resulted in the tetrahedral structure depicted in Figure 2. As could be seen, the Fe-O bonds are shorter than that in the octahedral model. Interestingly, the calculated IS and QS are much closer to the values obtained for the new component, appearing in the low-temperature Mössbauer spectrum, if compared to the previously discussed structural or spin-state effects. Although not in perfect agreement, this quantum-chemical data give us the right to assume that weak intermolecular interactions between the complex molecules of Fe(2AID)$_2$ are present in the solid state and are prone to changes by decreasing the temperature. It can be supposed that the non-coordinated carbonyl groups from each complex molecule interact with the Fe centers in their close proximity leading to pseudo-octahedral geometry. These are additionally facilitated by the intermolecular aromatic π-stacking as were observed in the Fe(III) complex of 2AID [5]. Presumably, at lower temperatures the Fe-O intermolecular interactions are almost absent but the structure deviates from the perfect tetrahedral symmetry due to the interactions between the aromatic parts of the ligand. Thus flattened tetrahedral geometry is partially formed giving rise to the observed new component in the Mössbauer spectrum at 77 K.

The proposed explanation for the observed temperature dependence of the Mössbauer spectra agree with their, already discussed, two other features: the temperature effect is limited, so it is not resulting from purely energy driven state-transitions but has steric origin; and the very large increase in the Mössbauer effect that could be attributed to the very large structural (Fe-O) deviations. Additionally, we wanted to prove that a real spin-crossover transition would result in a strong decrease in the calculated QS as indication for formation of a low-spin state. Therefore, the axial water ligands were substituted with N-coordinating ammonia. The calculated IS and QS for optimized octahedral structures in high-spin (S = 2) and low-spin (S = 0), see Table 2, clearly show the experimentally expected strong decrease in the calculated QS by more than 1.1 mm/s. This result illustrates the role of the coordinating ligands in ruling the electronic structure of the complexes and the possible spin-transitions.

4. Conclusion

The main problem we aimed to solve by the theoretical calculations was to find out the origin of the new component that appears in the Mössbauer spectrum at 77 K of the Fe(II) complex of 2AID. The fact that its relative intensity remains unchanged by further lowering the temperature indicates that a spin-crossover process is either not operative or is suppressed by the presence of high-spin Fe(III) species. Our calculations, supported by the experimental data, suggested that the Fe centers are tightly bound to two ligand molecules, bringing in total four oxygen donor atoms. However, at higher (room) temperature the non-coordinated carbonyl groups from the proximate complex molecules do interact with Fe centers most probably leading to pseudo-octahedral environment. Our quantum-chemical calculations suggested that the geometry changes to flattened tetrahedron when the temperature is lowered, giving rise to the observed new component in the low-temperature Mössbauer spectrum. It was demonstrated that spin-crossover process is not active in the case of oxygen-coordinated Fe(II), in contrast to coordination with N-donor atoms, which facilitates the spin-transition due to stronger covalent interactions. Although incomplete spin-crossover is also possible, it is less probable in our case because, to the best of our knowledge, spin-crossover phenomenon for metallo-organic complexes of Fe(II) coordinated only with oxygens is not reported in the literature.

To put it in a nutshell, we attempted to demonstrate that the integrated approach of theoretical and experimental studies is the preferred way in the search of explanation of complicated phenomena, instead of making inconsiderate conclusions.

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