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DFT Quantum-Chemical Study of the Hydrolysis Products of Fe(II) and Fe(III) Aqua-Complexes

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Abstract—The quantum-chemical DFT calculations of thermodynamic characteristics of the reactions of formation of binuclear dihydroxobridging $[Fe(H_2O)_4(\mu\text{-}OH)_2Fe(H_2O)_4]^{n+}$ and oxobridging $[Fe(H_2O)_5(\mu\text{-}O)Fe\cdot(H_2O)_5]^{n+}$ (n = 2, 4) cations, the hydrolysis products of cations $[Fe(H_2O)_6]^{m+}$ (m = 2, 3). It is shown that effects of solvation lead to higher energetic stability of the dihydroxobridging binuclear compounds in aqueous solutions.

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Hydrolytic polymerization of the metal aqua-complexes occurs as a result of a combination of processes initiated by deprotonation of aquated ion. The coordinated hydroxyl group resulting from the deprotonation of a metal ion aqua-complex can act as a nucleophile at the formation of polynuclear hydroxo complexes.

$$[M(H_2O)_6]^{n+} \leftrightarrow [M(OH)(H_2O)_5]^{(n-1)+} + H^+. \qquad (1)$$

According to [1], a prerequisite for the polymerization of the metal aqua-hydroxocomplex is the formation of aggregated forms held in sufficient proximity by hydrogen bonds (Fig. 1). The process of polymerization is associated with the substitution of inner-sphere water molecules of one coordination polyhedron $[M(OH)(H_2O)_5]^{n+}$ by the hydroxyl groups coordinated at another polyhedron. Then the binuclear μ-hydroxocomplexes can react with both mono- and binuclear aqua-hydroxocomplexes forming compounds with greater nuclearity. At low concentrations of the metal ion in solution a neutral complex $[Fe(OH)_3(H_2O)_3]$ can exist [2]. The increase in pH or ionic strength leads to the formation of aqua-hydroxo-oligomeric and polymeric forms of both linear and cyclic structure [1].

Biologically active salts of iron(II) and iron(III) ions play an indispensable role in the physiology of living organisms. The prospects of the use of ultrasmall quantities of these salts to create a functioning catalytic systems for medical and biological purposes [3] require a study of the processes of hydrolysis. These processes can affect the subsequent catalytic reactions in the solutions involving these ions. The dominating products of hydrolysis of iron cations are binuclear dihydroxobridging $[Fe^{II}(H_2O)_4(\mu\text{-}OH)_2\cdot Fe^{II}(H_2O)_4]^{2+}$, $[Fe^{III}(H_2O)_4(\mu\text{-}OH)_2Fe^{III}(H_2O)_4]^{4+}$ or oxo-bridging $[Fe^{II}(H_2O)_5(\mu\text{-}O)Fe^{II}(H_2O)_5]^{2+}$, $[Fe^{III}(H_2O)_5\cdot(\mu\text{-}O)Fe^{III}(H_2O)_5]^{4+}$ compounds formed at merging the

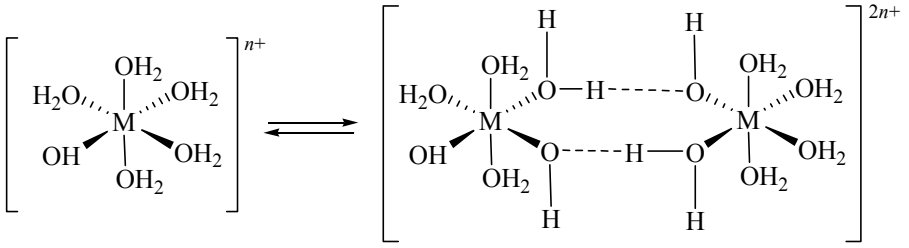

Fig. 1. Diagram of the beginning of the process of aquahydroxocomplex dimerization.

mononuclear particles [Fe (OH)$(H_2O)_5]^{n+}$ [1]. But the question is still controversial, whether the two iron ions are bound in solution by two hydroxobridges or by a μ-oxobridge. In [4, 5] the isolated from aqueous solution crystalline $[Fe(H_2O)_6]^{3+}$ was described and a supramolecular complex containing μ-oxo-bound cation $[Fe^{III}(H_2O)_5(\mu\text{-}O)Fe^{III}(H_2O)_5]^{4+}$ stabilized by the molecules of crown ether [18]crown-6 was studied by X-ray diffraction (XRD). According to [4, 5], the existence of this complex is a strong argument in favor of the presence of two μ-oxo-bound iron(III) ions in the aqueous solutions of their ordinary salts. On the other hand, the obtained and described in [6] μ-dihydroxobridging complex $[Fe^{III}2(\mu\text{-}OH)_2(L)_2](NO_3)_2\cdot 3H_2O$ [where L = *N*-(2-hydroxy-4-nitro)phenylmethyl-*N*-(2-ethylpyridyl)-*N*-(2-pyridilmethyl)amine], as well as the results of study by spectral methods of the aqueous solutions of iron(III) salts [7], can testify in favor of hydroxobridging dimeric hydrolysis products.

The aim of this work is to find the most stable products of hydrolysis of complex cations $[Fe(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$ by the quantum-chemical calculations. Calculations of the electronic structure of compounds were made with the GAMESS 07 program [8] using DFT B3LYP in full-electron basis 6-31G** for all atoms, including the atoms of iron. Analysis of the frequencies of normal vibrations showed that the resulting geometry optimization of the structure of compounds in the gas phase correspond to minima on the potential energy surface. Thermodynamic characteristics of reactions are obtained by calculating the normal vibration frequencies of compounds on the basis of DFT force fields in the harmonic approximation using the following relationships:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \ (T = 298 \text{ K}),$$
$$\Delta H^0 = \Delta E_{total} + \Delta ZPE + \Delta H'.$$

Here E_{total} is the total energy of the system, ZPE is zero energy vibration level, $\Delta H' = E_{oscil.} + E_{rotation} + E_{trans.} + RT$. Solvation energy ($E_{solv}$) of the compounds was calculated with the model of polarizable continuum [9–12]. The results are shown in the table.

According to the experimental data, almost all the Fe(II) and Fe(III) complexes, except for compounds with strong ligand field, are high-spin ones. In the optimized structure of the cation $[Fe(H_2O)_6]^{2+}$ with equal values of the lengths of *trans*-located Fe–O bonds an inequality in the lengths of *cis*-metal–oxygen bonds was observed: 2.115, 2.145, and 2.144 Å. This effect reflects an asymmetry of the electron density distribution of four unpaired 3*d*-electrons in the Fe(II) aqua-ion. A similar result was obtained in DFT calculations of the electronic structure of $[Fe(H_2O)_6]^{2+}$ [13]: 2.118, 2.157, 2.158 Å. At a small difference in the bond lengths obtained in this study and in the quantum chemical studies [13–17], these values fall into the range of the Fe–O interatomic distances determined experimentally by different methods, 2.07–2.19 Å for a number of Fe(II) salts [18–20]. In an aquacomplex $[Fe(H_2O)_6]^{3+}$ five unpaired electrons in the 3d-orbitals give a more symmetrical pattern of distribution of electron density and, consequently, the close values of similar Fe–O bond lengths (2.036, 2.037, 2.039 Å). Reduced metal–oxygen bond length in the Fe(III) aqua-complex compared with Fe(II) compound and an increase in the multiplicity of the values of bond orders calculated by Meyer method[21] from 0.28–0.29 to 0.44 units is in agreement with electrostatic representations of the strengthening of the chemical bond caused by the increasing charge of the metal ion.

The hydrolysis of the aqua-complexes of iron ions with the formation of binuclear products can be

Total energy, E_{total}, thermodynamic quantities ZPE, H', S^0, and solvation energy E_{solv}

Compound	$-E_{total}$, au	ZPE, kJ mol^{-1}	H', kJ mol^{-1}	S^0, J mol^{-1} K^{-1}	$-E_{solv}$, kJ mol^{-1}
H_2O	76.418115	56.1	66.0	194.5	34.7
H_3O^+	76.704791	90.2	100.3	202.7	413.6
$[Fe(H_2O)_6]^{2+}$	1721.736206	393.4	443.5	572.0	893.6
$[Fe(H_2O)_6]^{3+}$	1721.142939	401.2	443.5	499.2	1916.1
$[Fe^{II}(H_2O)_4(\mu\text{-}OH)_2Fe^{II}(H_2O)_4]^{2+}$	3290.030007	609.0	683.8	751.4	820.3
$[Fe^{III}(H_2O)_4(\mu\text{-}OH)_2Fe^{III}(H_2O)_4]^{4+}$	3288.924739	612.5	681.7	697.2	2833.2
$[Fe^{II}(H_2O)_5(\mu\text{-}O)Fe^{II}(H_2O)_5]^{2+}$	3366.442397	682.2	761.8	781.8	814.3
$[Fe^{III}(H_2O)_5(\mu\text{-}O)Fe^{III}(H_2O)_5]^{4+}$	3365.413715	680.5	757.0	745.3	2722.3

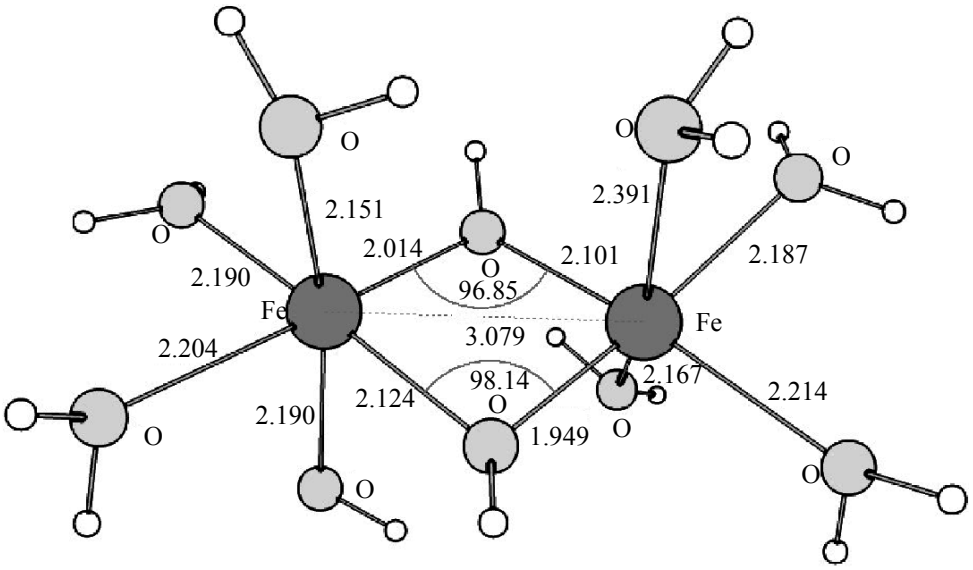

Fig. 2. Optimized structure of $[Fe^{II}(H_2O)_4(\mu\text{-}OH)_2Fe^{II}(H_2O)_4]^{2+}$.

described by the following reactions of proton transfer to a solvent molecule [22]:

$$2[Fe(H_2O)_6]^{n+} + 2H_2O \leftrightarrow 2[Fe(OH)(H_2O)_5]^{(n-1)+} + 2H_3O^+ \leftrightarrow 2H_3O^+ + [Fe(H_2O)_4(\mu\text{-}OH)_2Fe(H_2O)_4]^{(n-1)+} + 2H_2O. \quad (2)$$

Due to the additivity of energy and thermodynamic characteristics in these processes, in the comparative estimations the reaction of formation of mononuclear particles $[Fe(OH)(H_2O)_5]^{(n-1)+}$ can be excluded. In this case the formation of a dihydroxobridging and an oxobridging binuclear products of hydrolysis can be represented by the following equations:

$$2[Fe^{II}(H_2O)_6]^{2+} \leftrightarrow 2H_3O^+ + [Fe^{II}(H_2O)_4(\mu\text{-}OH)_2Fe^{II}(H_2O)_4]^{2+}, \quad (3)$$

$$2[Fe^{II}(H_2O)_6]^{2+} + H_2O \leftrightarrow 2H_3O^+ + [Fe^{II}(H_2O)_5(\mu\text{-}O)Fe^{II}(H_2O)_5]^{2+}, \quad (4)$$

$$2[Fe^{III}(H_2O)_6]^{3+} \leftrightarrow 2H_3O^+ + [Fe^{III}(H_2O)_4(\mu\text{-}OH)_2Fe^{III}(H_2O)_4]^{4+}, \quad (5)$$

$$2[Fe^{III}(H_2O)_6]^{3+} + H_2O \leftrightarrow 2H_3O^+ + [Fe^{III}(H_2O)_5(\mu\text{-}O)Fe^{III}(H_2O)_5]^{4+}. \quad (6)$$

The process of hydrolysis [Eq. (3)] of the iron(II) aqua-complex with the formation of dihydroxy-bridging binuclear cation $[Fe^{II}(H_2O)_4(\mu\text{-}OH)_2Fe^{II}(H_2O)_4]^{2+}$ (Fig. 2) in the gas phase is accompanied by an increase in the value of ΔE_{total} to 86.2 kJ mol^{-1}. Taking into account the changes in the values of ΔZPE, $\Delta H'$, and ΔS^0 of the products and reagents in the reaction (3) the calculated value of ΔG^0(gas) = 82.2 kJ mol^{-1}. The difference in the solvation energy of the reactants and the products of reaction (3) attains 139.7 kJ mol^{-1}. Accounting for this contribution leads to the value of $\Delta G^0(H_2O)$ = 221.9 kJ mol^{-1}. Thus, the positive value of Gibbs energy indicates that both the electronic structure and solvation factors contribute little to the formation of hydrolysis products $[Fe^{II}(H_2O)_4 \cdot (\mu\text{-}OH)_2Fe^{II}(H_2O)_4]^{2+}$.

The formation of oxobridging binuclear cation $[Fe^{II}(H_2O)_5(\mu\text{-}O)Fe^{II}(H_2O)_5]^{2+}$ (Fig. 3) according to the data obtained is even less favorable than the above considered dihydroxobridging cation. Reaction (4) in the gas phase is characterized by the value of ΔG^0(gas) = 175.4 kJ mol^{-1}. Taking into account the solvation of the products and the reagents, the value of $\Delta G^0(H_2O)$ = 355.8 kJ mol^{-1}.

Carrying out similar calculations for the compounds Fe(III) (Figs. 4, 5) in reactions (5) and (6) yielded the following results: for reaction (5) ΔG^0(gas) = –172.5 kJ mol^{-1} $\Delta G^0(H_2O)$ = –0.7 kJ mol^{-1}; for reaction (6) ΔG^0(gas) = –293.6 kJ mol^{-1}, $\Delta G^0(H_2O)$ = 23.8 kJ mol^{-1}.

Analysis of the data for reactions (3)–(6) allows a conclusion on some trends in the reactions of hydrolysis of the Fe(II) and Fe(III) salts. From the calculations in the gas phase it is possible to judge about the ability to deprotonation reaction inherent in the electronic structure of the aqua-complex. From the energy characteristics ΔE_{total} of the proton transfer reactions (3) and (4) follows that for the Fe(II) compound this process is disadvantageous because leads to ΔE_{total} higher by 86.2 kJ mol^{-1} for reaction (3)

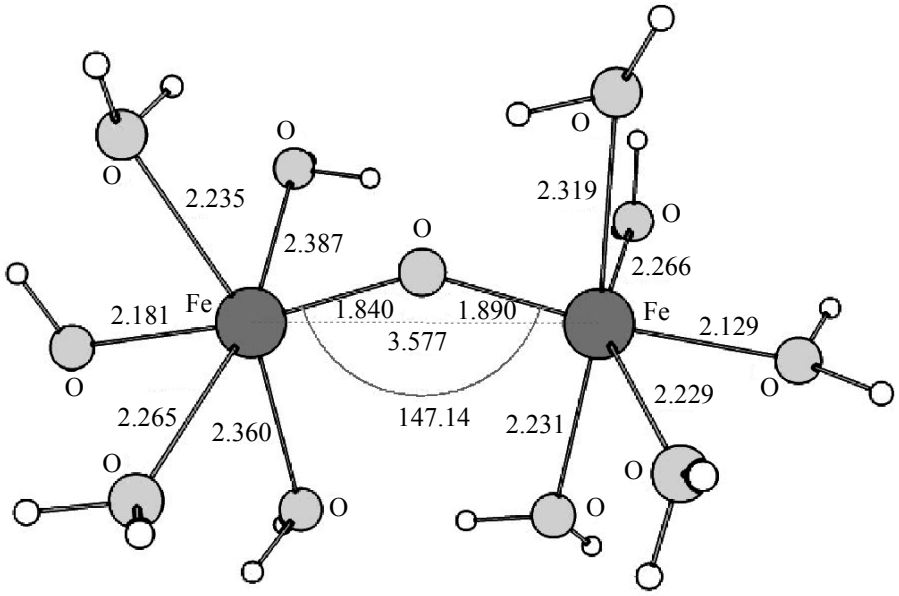

Fig. 3. Optimized structure of $[Fe^{II}(H_2O)_4\ (\mu\text{-}O)Fe^{II}(H_2O)_4]^{2+}$.

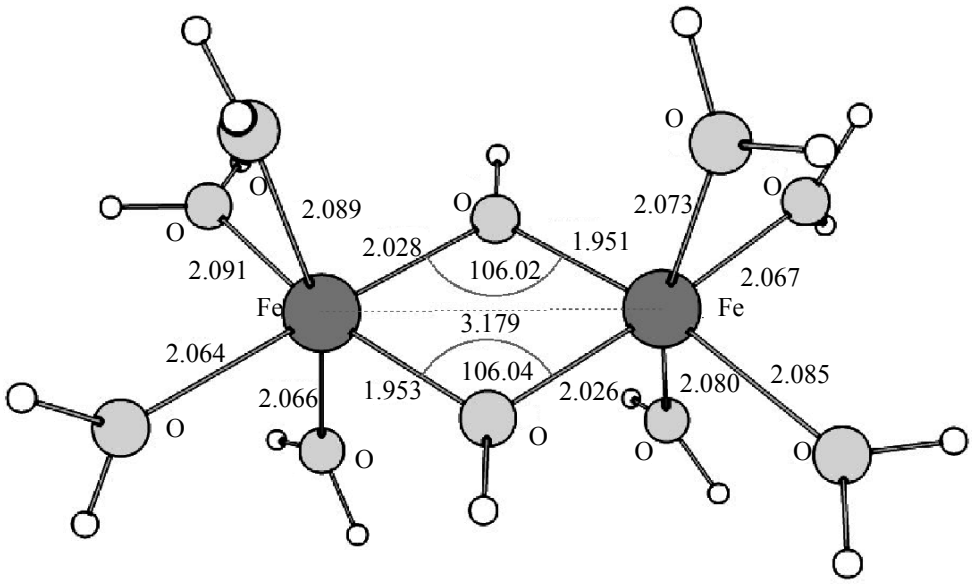

Fig. 4. Optimized structure of $[Fe^{III}(H_2O)_4(\mu\text{-}OH)_2Fe^{III}(H_2O)_4]^{4+}$.

and by 101.2 kJ mol^{-1} for reaction (4). Changes in the zero-energy vibrational level of compounds, ΔZPE, for the products and reagents for reactions (3) and (4), which should be considered in the energy evaluation of the stability of the system, are relatively small, 2.6 and 19.7 kJ mol^{-1}, respectively. In the case of the ion Fe(III) there is a very large decrease in the values of ΔE_{total}: –127.2 kJ mol^{-1} for reaction (5) and –313.2 kJ mol^{-1} for reaction (6) (ΔZPE = –9.5 and 2.4 kJ mol^{-1}). These data indicate that in the gas phase the coordination species $[Fe(H_2O)_6]^{3+}$ are extremely prone to proton transfer and the formation of bridged dimers, particularly μ-oxo compounds $[Fe^{III}(H_2O)_5 \cdot (\mu\text{-}O)Fe^{III}(H_2O)_5]^{4+}$. However, in solutions, the difference in the solvation effects of products and reagents in the reactions (3)–(6) suppresses this ability. Still, it may be noted that for Fe(III) aqua-hydroxocomplexes, in contrast to the Fe(II) aqua-hydroxocomplexes, the calculated values of Gibbs energy in solution are significantly lower. Qualita-

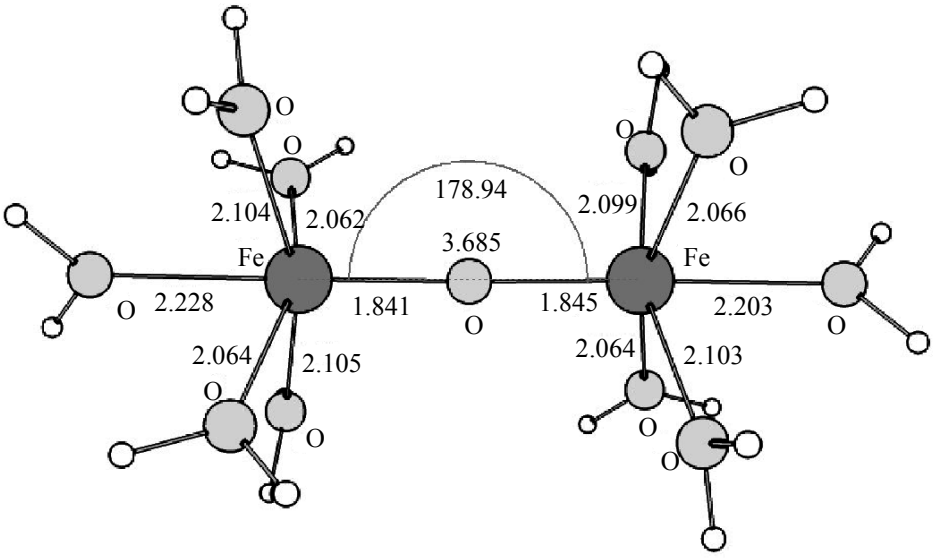

Fig. 5. Optimized structure of $[Fe^{III}(H_2O)_4\ (\mu\text{-}O)Fe^{III}(H_2O)_4]^{4+}$.

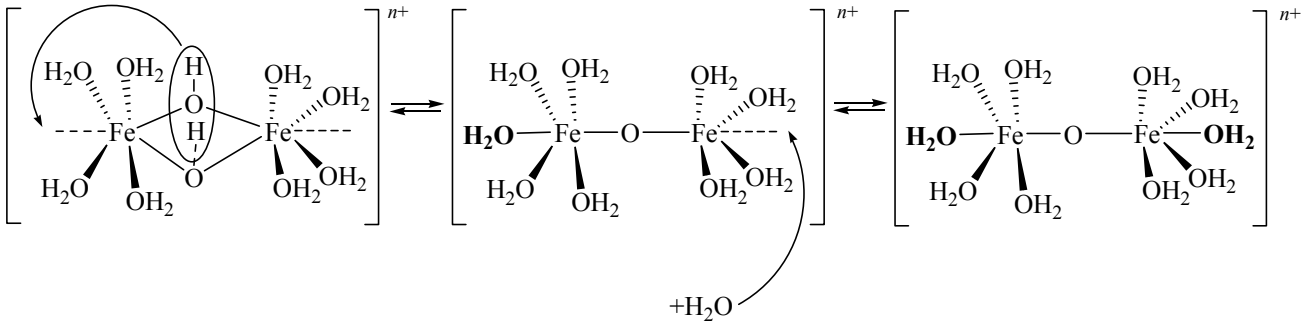

Fig. 6. Schematic representation of Eqs. (6) and (7).

tively this is consistent with the sharp increase in the experimental acid dissociation constants in the complex $[Fe(H_2O)_6]^{3+}$ compared with the constant for $[Fe(H_2O)_6]^{2+}$, 9×10^{-4} and 3×10^{-10} [23], respectively.

The mentioned additivity of thermodynamic quantities makes it possible, at the subtraction of Eq. (4) from Eq. (3) and, similarly, Eq. (6) from Eq. (5), and transferring the term representing dihydroxo-bound dimers to the left side of the equations, to obtain an equation formally relating the binuclear μ-dihydroxy- and μ-oxo-hydrolysis products:

$$[Fe^{II}(H_2O)_4(\mu\text{-}OH)_2Fe^{II}(H_2O)_4]^{2+} + H_2O \leftrightarrow [Fe^{II}(H_2O)_5(\mu\text{-}O)Fe^{II}(H_2O)_5]^{2+}, \quad (7)$$

$$[Fe^{III}(H_2O)_4(\mu\text{-}OH)_2Fe^{III}(H_2O)_4]^{4+} + H_2O \leftrightarrow [Fe^{III}(H_2O)_5(\mu\text{-}O)Fe^{III}(H_2O)_5]^{4+}. \quad (8)$$

The processes described by these equations can be interpreted as a reaction of μ-O-group formation at the dehydration in the central segment of the coordination polyhedron $[(H_2O)_4Fe(\mu\text{-}OH)_2Fe(H_2O)_4]^{n+}$ (Fig. 6). The additional molecule of H_2O in the left side of the equation is necessary for the conservation of the coordination numbers of iron ion.

According to quantum-chemical calculations, for the Fe(II) compounds the process (7) corresponds to the value of ΔG^0(gas) = 93.2 kJ mol^{-1}. Solvation effects lead to further increase in the Gibbs energy: $\Delta G^0(H_2O)$ = 133.9 kJ mol^{-1}. Thus, both in the gas phase and in aqueous solution, the positive values of ΔG^0 indicate a shift of Eq. (7) toward the formation of μ-dihydroxocomplex $[Fe^{II}(H_2O)_4(\mu\text{-}OH)_2Fe^{II}(H_2O)_4]^{2+}$.

In the case of Fe(III) aqua-hydroxocomplexes, the process (8) in the gas phase decreases the Gibbs energy ΔG^0(gas) to –121.1 kJ mol^{-1}, indicating a shift of the considered equilibrium toward the formation of binuclear μ-oxo-complex $[Fe^{III}(H_2O)_5(\mu\text{-}O)Fe^{III}(H_2O)_5]^{4+}$. However, at the accounting for the solvation contribu-

tions in solution the Gibbs energy change in the reaction (8) is positive: $\Delta G^0(H_2O) = 24.5$ kJ mol^{-1}. The latter indicates stabilization of μ-dihydroxocomplex $[Fe^{III}(H_2O)_4(\mu\text{-}OH)_2Fe^{III}(H_2O)_4]^{4+}$ by aqueous solvent.

The obtained indication of the greater stability of μ-dihydroxocomplex $[Fe^{III}(H_2O)_4(\mu\text{-}OH)_2Fe^{III}(H_2O)_4]^{4+}$ in aqueous solution does not contradict the results of [4], which shows the results of XRD of crystalline binuclear μ-oxy-compounds $[Fe^{III}(H_2O)_5(\mu\text{-}O)\cdot Fe^{III}(H_2O)_5]^{4+}$, stabilized by macroheterocyclic polyester [18]crown-6. Formally, the crown ether molecules can be considered as a solvation shell of the complex $[Fe^{III}(H_2O)_5(\mu\text{-}O)Fe^{III}(H_2O)_5]^{4+}$ existing in the crystalline state and replacing the secondary hydration shell which the complex $[Fe^{III}(H_2O)_4(\mu\text{-}OH)_2Fe^{III}(H_2O)_4]^{4+}$ has in aqueous solution. Change of the solvate shell, apparently, causes the oxolation reaction, providing formation of the binuclear μ-oxobridging Fe^{III}–O–Fe^{III} core. Upon the transition from the solution to the solid state a dehydration process could occur in the central fragment of the binuclear μ-dihydroxocomplex with the formation of μ-O-group.

Thus, the results of the quantum-chemical investigations presented in this paper allow us to conclude that that the preferred products of hydrolysis of the aqua-complex cations $[Fe(H_2O)_6]^{2+}$ in the gas phase and in solution are binuclear dihydroxobridging compound $[Fe^{II}(H_2O)_4(\mu\text{-}OH)_2Fe^{II}(H_2O)_4]^{2+}$. In the case of the aqua-complex cations $[Fe(H_2O)_6]^{3+}$ the oxobridging binuclear complexes $[Fe^{III}(H_2O)_5(\mu\text{-}O)\cdot Fe^{III}(H_2O)_5]^{4+}$ are more stable in the gas phase. However, the most stable in solutions are the dihydroxobridging binuclear cations $[Fe^{III}(H_2O)_4(\mu\text{-}OH)_2\cdot Fe^{III}(H_2O)_4]^{4+}$. The reason for stabilization of the μ-dihydroxocomplexes in aqueous solutions is the gain in energy at the secondary hydration of these products of hydrolysis reaction.

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