Supplementary materials

Interactions of dinitrosyl iron complexes with water: theoretical study of the Fe^+ and $[Fe(NO)_2]^+$ ion hydration

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Calculation results

Table S1 Binding energy contributions [a] and electronic properties of $[M(H_2O)]^+$ from the CCSD(T) calculations

M^+		R_{min} [b]	$E_{el}(M^+...W^c)$	$-E_b'$	BSSE	$-E_b^{corr}$	$<S_z>$	$<S^2>$ [d]	ρ_{MPA} [e]	q_{MPA} [e]
Cu^+	M=1	(1.872)	–1715.968973	168.6	13.2	156.2	-	-	-	0.866
		1.922	–1715.969412	169.8	11.6	158.9				
Li^+	M=1	1.834	–83.713905	145.3	2.6	142.8	-	-	-	0.813
Ag^+	M=1	2.210	–223.003914	127.6	4.0	123.9	-	-	-	0.907
Na^+	M=1	2.203	–238.310960	104.9	5.9	99.0	-	-	-	0.923
K^+	M=1	2.607	–675.693877	76.2	3.6	72.6	-	-	-	0.962
Rb^+	M=1	2.811	–100.242645	65.6	1.9	63.7	-	-	-	0.966
Cs^+	M=1	(2.872)	–96.251521	77.1	21.2	55.9	-	-	-	0.955
		3.022	–96.250686	74.9	17.7	57.2				
Fe^+	M=2[c]	1.963	– 1339.175793	164.9	12.1	153.3	0.500	1.755 (0.789)	1.001	0.884
Fe^+	M=4	(1.973)	–1339.213766	164.1	11.9	152.5	1.500	3.767 (3.750)	2.999	0.886
		2.023	–1339.213344	163.2	10.4	153.1				
Fe^+	M=6	2.060	–1339.212700	148.8	9.1	140.2	2.500	8.754(8.750)	4.985	0.857

[a] The electronic energies of monohydrate complexes, $E_{el}(M^+...W^c)$, are in Hartree while E_b', BSSE, and E_b^{corr} terms are in $kJ \cdot mol^{-1}$ (see description below); [b] R_{min} – the $M^+...O$ distance in the minimum of reaction coordinate from the CCSD(T) calculations, the optimized distance in the minimum from the MP4 calculations are given in parenthesis in the cases when it differs from the minimum distance from the CCSD(T) calculations, distances are in Å; [c] the CCSD(T) scan was not performed; [d] the expectation values of the $<S_z>$ and $<S^2>$ spin operators from the unrestricted HF calculations of $[Fe(H_2O)]^+$, the values of $<S^2>$ after annihilation of the first spin contaminant are given in parenthesis; [e] the Mulliken spin densities ρ_{MPA} on Fe^+ и partial electronic charges q_{MPA} on M^+ from the HF electron density.

Binding energy contributions in the $[M(H_2O)]^+$ *complexes in* **Tables 1** *and* **S1**.

W – water molecule with the geometry optimized in gas phase, W^c – water molecule with the geometry taken from the optimized geometry of monohydrate complex.

Difference of the electronic energies of water configurations:

$\Delta E_{el}^{relax}(W) = E_{el}(W^c) - E_{el}(W)$

Electronic binding energies in the monomer basis set without the BSSE correction, i.e. the raw complexation energy in Gaussian-09:

$E_b^{raw} = E_{el}(M^+...W^c) - E_{el,mbs}(M^+) - E_{el,\,mbs}(W^c)$

Electronic binding energies in the dimer basis set with the BSSE correction (Table **S1**), i.e. corrected complexation energy in Gaussian-09:

$E_b^{corr} = E_{el}(M^+...W^c) - E_{el,dbs}(M^+) - E_{el,dbs}(W^c)$

$BSSE = E_b^{corr} - E_b^{raw}$

Electronic binding energies without the BSSE correction (Table **S1**) for separated reactants:

$E_b'(M^+...W^c) = E_{el}(M^+...W^c) - E_{el}(M^+) - E_{el}(W)$

Electronic binding energies with the BSSE correction (Table **1**) for separated reactants:

$E_b(M^+...W^c) = E_b'(M^+...W^c) + BSSE = E_b^{corr} + \Delta E_{el}^{relax}(W)$

Таблица S2 Electronic energies and spin values of Fe^+ in three spin states from the UHF, MP4 and CCSD(T) calculations with the def2-QZVPP basis set [a]

Ion	E_{el}(HF)	E_{el}(MP4)	E_{el}(CCSD(T))	$\langle S_z \rangle$	$\langle S^2 \rangle$ [b]
Fe^+ M=6 $3d^6 4s^1$	–1262.220687 (0.0)	–1262.758755 (0.0)	–1262.768054 (0.0)	2.500	8.753 (8.750)
Fe^+ M=4 $3d^7$	–1262.162057 (153.9)	–1262.758123 (1.7)	–1262.763288 (12.5)	1.500	3.758 (3.750)
Fe^+ M=2 $3d^7$	–1262.101347 (313.3)	–1262.706228 (137.9)	–1262.724992 (113.1)	0.500	1.754 (0.916)

[a] electronic energies in Hartree; The relative energies of the states in $kJ \cdot mol^{-1}$ (in parenthesis); [b] the expectation values of the $\langle S_z \rangle$ and $\langle S^2 \rangle$ spin operators from the unrestricted HF calculations, the values of $\langle S^2 \rangle$ after annihilation of the first spin contaminant are given in parenthesis.

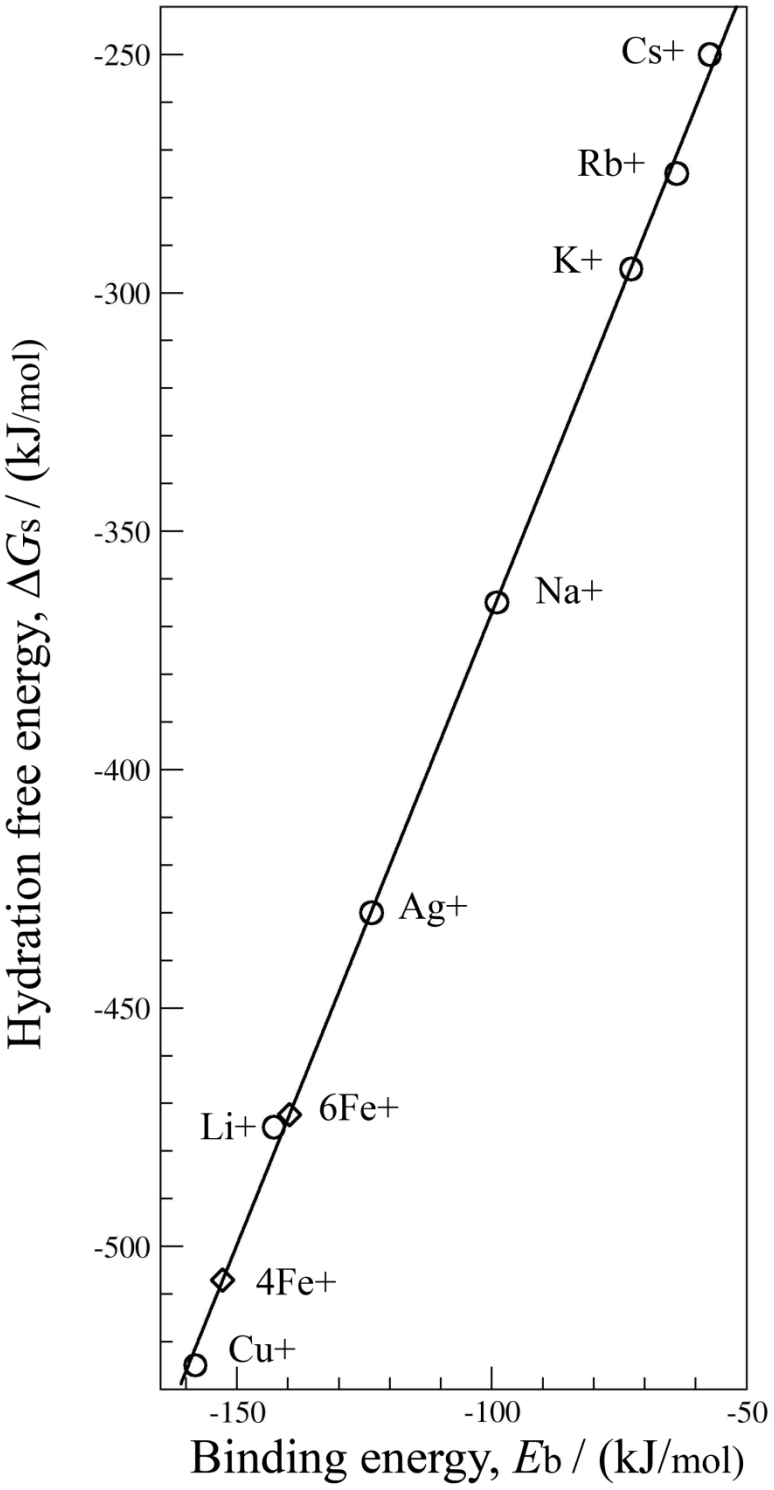

Figure S1 Binding energies of monohydrates and hydration free energies of M^+: ○ – training set of cations, ◊ – calculation for the test set of Fe^+ ions with *M*=4 and *M*=6. The straight line corresponds to linear regression (1).

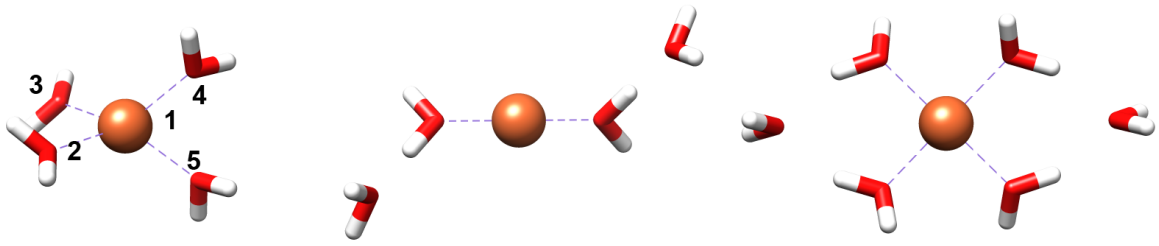

Рисунок S2 Molecular images of the optimized structures of Fe^{+} in the complex with 4 and 6 H_2O molecules.

Optimized coordinates and electronic properties of the dinitrosyl iron complex $[Fe(NO)_2(H_2O)_2]^{+}$

ump4(SDQ,FC1) Def2TZVP, HF=-1673.0064739, MP4SDQ=-1674.8938264,

S2=4.241781\S2A=12.078199

1	26	0.121040	-0.155943	0.730247
2	7	-1.316176	0.700213	1.288743
3	7	1.116466	-0.949581	1.950811
4	8	-2.169722	1.174150	1.897042
5	8	1.578959	-1.368169	2.917283
6	8	-0.441265	-1.561324	-0.705715
7	1	-1.283638	-1.573119	-1.173967
8	1	-0.029653	-2.423557	-0.832686
9	8	1.312189	1.160600	-0.365732
10	1	2.275810	1.155262	-0.385673
11	1	1.021826	2.005700	-0.726961

Optimized coordinates and electronic properties of the dinitrosyl iron complex $[Fe(NO)_2(H_2O)_3]^{+}$

ump4(SDQ,FC1) Def2TZVP, HF=-1749.0969468, MP4SDQ=-1751.2589198,

S2=4.310521\S2A=12.299127

1	26	0.132512	-0.063908	0.111119
2	7	-0.800097	1.091929	1.074010
3	7	1.036304	-1.299707	0.999284
4	8	-1.307042	1.699640	1.920047
5	8	1.517451	-1.978838	1.805115
6	8	-1.587509	-1.365536	-0.499663
7	8	1.868706	1.283063	-0.332176
8	1	-1.548665	-2.312752	-0.321117
9	1	-2.486622	-1.091176	-0.283033
10	1	2.761081	0.989929	-0.112299
11	1	1.823099	2.211492	-0.074208
12	8	0.165276	0.027724	-2.015897
13	1	-0.448466	-0.425308	-2.602302
14	1	0.796247	0.528558	-2.542042

Optimized coordinates and electronic properties of the dinitrosyl iron complex $[Fe(NO)_2(H_2O)_4]^+$

ump4(SDQ,FC1) Def2TZVP, HF=-1825.1716713, MP4SDQ=-1827.615754,

S2=4.3484\S2A=12.422099

1	26	0.131497	-0.133338	0.176594
2	7	-0.802491	0.901506	1.294675
3	7	1.061837	-1.260461	1.203151
4	8	-1.202271	1.320533	2.304768
5	8	1.467044	-1.774489	2.163825
6	8	-1.426139	-1.557381	-0.469120
7	8	1.797562	1.217226	-0.344253
8	1	-1.739688	-2.222308	0.155048
9	1	-2.212030	-1.163474	-0.865513
10	1	2.473136	1.403625	0.318228
11	1	1.542253	2.067800	-0.720093
12	8	-0.812903	1.046228	-1.652340
13	1	-0.566088	0.799888	-2.550558
14	1	-1.438686	1.775804	-1.707953
15	8	0.948710	-0.990948	-1.864925
16	1	0.730416	-1.912988	-2.042222
17	1	1.899857	-0.906458	-1.996926

Optimized coordinates and electronic properties of the tetrahedral $[Fe(H_2O)_4]^+$ complex

ump4(SDQ,FC1) Def2TZVP, HF=-1566.5064103, MP4SDQ=-1568.0818799,

S2=3.839859\S2A=3.750937

1	26	-0.000448	-0.000182	-0.000307
2	8	0.538840	0.149937	2.080135
3	8	2.140979	-0.149901	-0.186282
4	8	-1.426686	-1.387887	-0.826070
5	8	-1.253224	1.387782	-1.070894
6	1	-0.036377	0.465947	2.784115
7	1	1.137440	-0.486988	2.486551
8	1	-1.557401	-2.294780	-0.531488
9	1	-1.649337	-1.374283	-1.763836
10	1	2.612813	-0.465772	-0.963418
11	1	2.723693	0.487117	0.242488
12	1	-1.018605	2.294527	-1.292479
13	1	-2.211687	1.374482	-0.969151

Optimized coordinates and electronic properties of the linear $[Fe(H_2O)_4]^+$ complex

ump4(SDQ,FC1) Def2TZVP, HF=-1566.5361425, MP4SDQ=-1568.0684199,

S2=4.46546\S2A=3.760097

1	26	0.004611	0.079995	-0.686405
2	8	3.512698	-1.653263	0.434902
3	8	-3.521303	1.504439	0.765096
4	8	-1.250724	1.540254	-0.522530
5	8	1.260020	-1.379597	-0.855580
6	1	3.653063	-2.169600	1.234529
7	1	4.380421	-1.363022	0.137317
8	1	-1.144516	2.395390	-0.950181
9	1	-2.113539	1.528139	-0.033324
10	1	-4.384371	1.294239	0.395410
11	1	-3.673485	1.817087	1.662204
12	1	1.161067	-2.109104	-1.474813
13	1	2.116061	-1.484962	-0.365673

Optimized coordinates and electronic properties of the $[Fe(H_2O)_6]^+$ complex

ump4(SDQ,FC1) Def2TZVP, HF=-1718.679875, MP4SDQ=-1720.7827923,

S2=4.50155\S2A=3.757201

1	26	-0.041533	0.043902	-0.001510
2	8	-0.507859	2.075343	-0.513170
3	1	-1.187099	2.278060	-1.162439
4	1	-0.607641	2.706204	0.214916
5	8	0.286853	-3.299637	-2.030937
6	1	1.098257	-3.766410	-2.261933
7	1	-0.426670	-3.829447	-2.404835
8	8	-0.369864	3.387515	2.027950
9	1	0.293134	4.080911	2.124124
10	1	-1.130712	3.690704	2.536674
11	8	0.216866	-2.019478	0.529219
12	1	0.182173	-2.670993	-0.186585
13	1	-0.244841	-2.397573	1.282798
14	8	0.173026	0.576485	2.066420
15	1	0.870047	0.192853	2.605863
16	1	0.118508	1.516805	2.291978
17	8	-0.048097	-0.456651	-2.088466
18	1	0.395861	0.102340	-2.732236
19	1	0.140894	-1.376307	-2.326305