Heteronuclear complexation in the system 1-hydroxyethylidenediphosphonic acid—manganese(II)—gadolinium(III) in aqueous solution

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pH-Potentiometric method in combination with mathematical modeling was used to study the system manganese(II)—gadolinium(III)—1-hydroxyethylidenediphosphonic acid (HEDP, H_4L). When both cations simultaneously are present in the solution, the accumulation of heteronuclear forms with the ratio of Gd : Mn : HEDP equal to 1 : 1 : 1, 1 : 1 : 2, and 1 : 1 : 3 was observed already in the strongly acidic pH region, while from homonuclear forms only five complexes were detected in the solution, namely, MnL_2^{6-}, $GdH_4L_2^-$, GdH_2L^+, $KGd_2HL_2\downarrow$, and $K_3Gd_2L_2(OH)\downarrow$. It was concluded that heteronuclear complexes are much stronger and replace homonuclear forms in solution.

Key words: bisphosphonates, 1-hydroxyethane-1,1-diphosphonic acid, complexation, contrast agents, manganese(II), gadolinium(III), magnetic resonance imaging.

In magnetic resonance imaging (MRI), contrast agents (CA) generate images due to the changes in the spin-lattice (longitudinal) T_1 and spin-spin (transverse) T_2 relaxation times of water protons surrounding the contrast agent. Gadolinium(III) and manganese(II) complexes are used as contrast agents the most frequently.[1]

Gadolinium(III)-containing MRI-contrast agents are commonly used to enhance vascular imaging (in MR angiography) or a brain tumor causing destruction of the brain hematoencephalic barrier. For large blood vessels, such as the aorta, the dose of gadolinium can be as low as 0.1 mmol per 1 kg of body weight. Higher concentrations are often used for smaller vascular systems.

Manganese ions (Mn^{2+}) often act as a contrast agent in animal studies. Due to the ability of Mn^{2+} to penetrate cells through calcium (Ca^{2+}) channels, Mn^{2+} can, for example, be used for functional brain imaging.

The manganese(II) compound with diethylenetriaminepentaacetate ions (Pentamang, the relaxation efficiency coefficient (REC_1)[2] equal to 4210 L mol^{-1} s^{-1})[3] has passed preclinical trials and its efficiency was found to be comparable with that of analogous gadolinium(III) complex.

The review of the works on the manganese(II) complexes promising for MRI[4] showed that one of the advantages of complexes based on Mn^{2+} ions in MRI is that the rate of water exchange in them does not limit[5] the relaxivity (REC).

1-Hydroxyethylidenediphosphonic acid (HEDP) binds with d-element cations into stable water-soluble complexes, in contrast to lanthanides, possessing a moderate solubility in acidic media and a poor solubilityь in weakly acidic and weakly basic solutions.[6—8]

In the case of gadolinium(III), complexes with polydentate ligands are usually used, such as diethylenetriaminepentaacetate (DTPA) and 1,4,7,10-tetraazacyclododecan-1,4,7,10-tetraacetate (DOTA), which, as a rule, have one more site for binding a water molecule rapidly exchanging with the bulk solution. These complexes in water are characterized by the REC_1 values of 4020 and 4740 L mol^{-1} s^{-1} (20 MHz, 37 °C), respectively.

The overwhelming majority of highly relaxive CA for MRI, like the already known commercial agents, are developed on the basis of gadolinium(III) complexes. There are arguments in favor of manganese(II) compounds and some other ions, for example, iron(III). Though the choice of gadolinium ions is still in trend, attempts are also undertaken toward the use of advantages of "multimetal" complexation. Thus, the synthesis of a new heteronuclear complex GdMnL is described.[9]

As far as we know, there are no publications on the studies of complexation of gadolinium(III) and manganese(II) with HEDP in a heteronuclear system. In the present work, we carried out a combined pH-metric titration of Gd^{III}, Mn^{II}, and HEDP at different concentrations of reagents with approximately three-fold dilution during titration; the equilibrium and stability constants of the detected forms were obtained; a comparative analysis of the found stability constants with those of complex

forms obtained earlier[10,11] was conducted in order to identify the most suitable for MRI forms.

Experimental

The proton activity was determined on a Ekspert-001potentiometer with an accuracy of 0.005 pH units; the pH-meter was calibrated using standardized aqueous buffer solutions.

The proton magnetic relaxation times were measured on a Minispec MQ20 NMR relaxometer (Bruker) at an operating frequency of 19.75 MHz. The times T_2 were found using the Carr—Parcell sequence (with the Meiboom—Gill modification) with an error of ≤3%. The temperature (25 °C) was maintained using a Haake DC10 cryo-thermostat (Thermo Electron).[12]

The concentration of the HEDP solution (Sigma) was obtained using pH-metric titration with a carbonate-free KOH solution, the concentration of which was determined by titration with a pre-standartized solution (0.1 *M* aqueous HCl) in the presence of the acid-base indicator thymol blue.

To measure the concentration of the solution of manganese(II) nitrate (reagent grade), this solution was titrated with a solution of EDTA at pH ~10 with eriochrome black.[13] The gadolinium(III) nitrate (reagent grade) was titrated with a solution of EDTA with thymol blue and xylenol orange in an acetate buffer at pH ~5.6.[14]

The test titration with the displacement of carbon dioxide with argon showed that this procedure does not lead to significant differences in the titration curves, therefore, the main data array was obtained without purging with argon. A conclusion on the unnecessity of purging with argon at concentrations of ≥10^{-2} mol L^{-1} was made by the authors of the work,[15] who investigated the acid-base equilibrium of alendronic acid solutions.

All the experimental series included at least three parallel series. Since a precipitation was present in the systems containing metal ions over a wide range of pH, a special attention was paid to the time of the attainment of equilibrium state, which was reflected in the installation of a constant pH (3—5 min).

The experimental dependences of physicochemical properties on the composition and acidity of solutions were processed using the CPESSP program (Complex Formation Parameters of Equilibria in Solutions with Solid Phases).[16] The program allows one to process data obtained by different research

Table 1. Concentration conditions for the system Gd—Mn—HEDP*

	C/mmol L^{-1}			Symbol
Mn^{2+}	Gd^{3+}	HEDP	KOH	
9.651	10.08	57.52	225.0	1—1—5
9.651	10.08	34.51	131.3	1—1—3
9.651	10.80	23.01	92.50	1—1—2
9.651	10.20	11.52	44.11	1—1—1

* $V_0 = 50$ mL (for pH-potentiometry), $T = 25$ °C.

methods (NMR, pH-metry, potentiometry, polarimetry, spectrophotometry, *etc.*), a characteristic parameter of which obeys the additivity rule. The essence of the program consists in finding the minimum of the functional F in the course of the iterative procedure.[11]

Results and Discussion

The pH-metric titration of the system Gd^{III}—Mn^{II}—HEDP was carried out at different concentrations indicated in Table 1. The shape of the experimental and theoretically calculated curves (Fig. 1) of the pH-metric titration using available matrices of previously obtained[10,11] forms of manganese (Table 2) and gadolinium (Table 3) homonuclear complexes indicates significant differences in complexation in the heteronuclear system as compared to homonuclear systems, which suggests the formation of heteronuclear complexes.

The introduction of additional heteronuclear forms to the matrix containing gadolinium and manganese complexes, as well as acid-base forms of HEDP,[17] resulted in a significant improvement of the experimental data interpretation. In this case, the mathematical modeling made it possible to correctly describe this system; the Fisher´s F-test was 0.20 (Fig. 2).

The final data on the stoichiometry and formation constants of the corresponding forms are given in Table 4,

Table 2. Stoichiometry matrix, formation constants (K_p), and stability constants (logβ) in the system Mn^{2+}—HEDP (see Ref. 11)

Equilibrium	n	logK_p, δ* ≤ 0.16	logβ, δ* ≤ 0.2
Mn^{2+} + H$_4$L $\rightleftarrows$ MnL^{2-} + 4 H$^+$	4.0	−12.47	11.2
Mn^{2+} + 2 H$_4$L $\rightleftarrows$ MnH$_5$L$_2^-$ + 3 H$^+$	3.0	−0.78	5.5
Mn^{2+} + 2 H$_4$L $\rightleftarrows$ MnH$_4$L$_2^{2-}$ + 4 H$^+$	4.0	−2.50	6.8
Mn^{2+} + 2 H$_4$L $\rightleftarrows$ MnH$_3$L$_2^{3-}$ + 5 H$^+$	5.0	−7.20	9.7
Mn^{2+} + 2 H$_4$L $\rightleftarrows$ MnH$_2$L$_2^{4-}$ + 6 H$^+$	6.0	−13.77	10.6
Mn^{2+} + 2 H$_4$L $\rightleftarrows$ MnHL$_2^{5-}$ + 7 H$^+$	7.0	−21.49	14.4
Mn^{2+} + 2 H$_4$L $\rightleftarrows$ MnL$_2^{6-}$ + 8 H$^+$	8.0	−31.28	16.1
2 Mn^{2+} + 2 H$_4$L $\rightleftarrows$ Mn$_2$H$_3$L$_2^-$ + 5 H$^+$	2.5	−4.21	12.7
2 Mn^{2+} + 2 H$_4$L $\rightleftarrows$ Mn$_2$H$_2$L$_2^{2-}$ + 6 H$^+$	3.0	−8.55	15.9
2 Mn^{2+} + 2 H$_4$L $\rightleftarrows$ Mn$_2$HL$_2^{3-}$ + 7 H$^+$	3.5	−14.75	21.2

* Confidence interval characterizing the measurement error.

Table 3. Stoichiometry matrix, formation constants (K_p), stability constants (logβ), precipitate dissolution constants (K_s), and solubility product (SP) in the system Gd^{3+}—HEDP (see Ref. 10)

H_4L, l	Gd^{3+}, m	K^+, k	$-H^+$, h	n	Form	$\log K_p$* or $\log K_s$**; $\delta \leq 0.19$	$\log\beta$ ($\log$SP); $\delta \leq 0.4$
1	1	0	2	2.0	GdH_2L^+	14.31	19.0
2	1	0	1	0.5	$GdH_7L_2^{2+}$	22.58	24.3
2	1	0	3	1.5	$GdH_5L_2^{0}$	19.87	26.2
2	1	0	4	2.0	$GdH_4L_2^-$	19.03	28.4
2	1	0	5	2.5	$GdH_3L_2^{2-}$	12.87	29.8
2	2	0	8	4.0	$Gd_2L_2^{2-}$	20.17	67.6
2	2	0	9	4.5	$Gd_2L_2(OH)^{3-}$	11.82	73.2
1	2	0	2	2.0	$Gd_2H_2L^{4+}$	17.12	21.8
1	2	0	3	3.0	Gd_2HL^{3+}	16.70	28.9
1	2	0	4	4.0	Gd_2L^{2+}	13.48	37.2
1	2	0	5	5.0	$Gd_2L(OH)^+$	6.38	44.1
1	2	0	6	6.0	$Gd_2L(OH)_2\downarrow$	−1.60**	(−50.1)
2	2	0	6	3.0	$Gd_2H_2L_2\downarrow$	−30.20**	(−54.6)
3	2	0	6	2.0	$Gd_2H_6L_3\downarrow$	−42.61**	(−56.5)
2	2	1	7	3.5	$KGd_2HL_2\downarrow$	−30.49**	(−66.4)
2	2	1	9	4.5	$K_3Gd_2L_2(OH)\downarrow$	−20.45**	(−81.9)

* For equilibrium $k\,K^+ + m\,Gd^{3+} + l\,H_4L \rightleftharpoons [K_kGd_mH_{4l-h}L_l]^{4l-(3m+k+h)} + h\,H^+$.
** For precipitate dissolution: $K_kGd_mH_{4l-h}L_l\downarrow + h\,H^+ \rightleftharpoons k\,K^+ + m\,Gd^{3+} + l\,H_4L$.

the form accumulation proportions depending on the concentration conditions (see Table 1) and the pH values are shown in Fig. 3.

To sum up, the heteronuclear system Gd^{3+}—Mn^{2+}—HEDP was studied by pH-potentiometric method at manganese(II) and gadolinium(III) concentrations of ~10^{-2} mol L^{-1} and at varying ligand concentration. It was found that heteronuclear ($GdMnH_6L_3^-$, $GdMnL_2^{3-}$, $GdMnH_2L_2^-$) complexes are predominantly accumulated in the system Gd^{3+}—Mn^{2+}—HEDP at a large excess of the ligand.

When the ligand is in insignificant excess, a greater variety of predominant heteronuclear forms is detected ($GdMnH_5L_2^{2+}$, $GdMnH_4L_2^+$, $GdMnH_3L_2^0$, $GdMnH_2L_2^-$, $GdMnL_2^{3-}$). In the absence of the ligand excess, the greatest fraction of accumulation was observed for the complexes $Gd_2Mn_2H_2L_2^{4+}$ and $GdMnL^+$, which was not formed in other series. Apart from that, an accumulation of the potassium complex $K_3Gd_2L_2(OH)\downarrow$ was also observed, the fraction of which in other series did not exceed 10—11%. A small amount of the mononuclear bis-complex ($GdH_4L_2^-$) is also present in the system, while
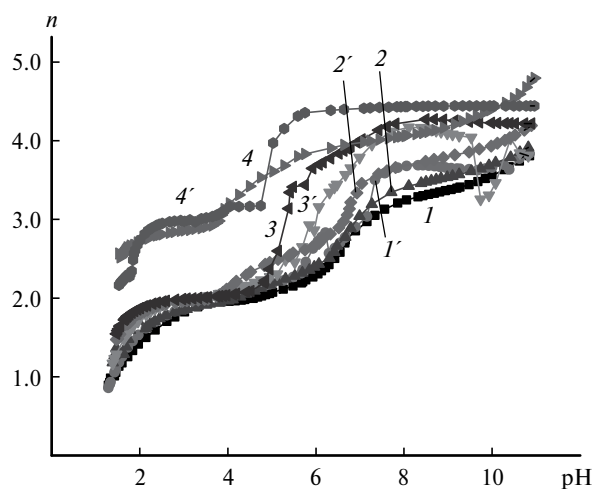
Fig. 1. Dependences of the Bjerrum function on pH, experimentally obtained (*1—4*) and theoretically calculated (*1´—4´*) from the previously published data[10,11] (Tables 2 and 3) without heteronuclear forms with allowance for the concentrations indicated in Table 1: 1—1—5 (*1, 1´*), 1—1—3 (*2, 2´*), 1—1—2 (*3, 3´*), 1—1—1 (*4, 4´*).
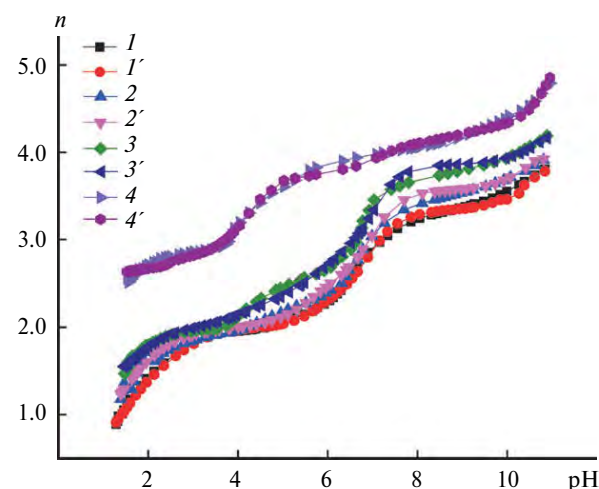

Fig. 2. Experimentally obtained (*1—4*) and theoretically calculated (*1´—4´*) dependences of the Bjerrum function on pH: 1—1—5 (*1, 1´*), 1—1—3 (*2, 2´*), 1—1—2 (*3, 3´*), 1—1—1 (*4, 4´*); $F = 0.20$.

Note. Figure 2 is available in full color on the web page of the journal (http://www.link.springer.com).

Table 4. Stoichiometry matrix, formation constants (K_p), stability constants (logβ) and precipitate dissolution constants (K_s) in the system Gd^{III}—Mn^{II}—HEDP; $F = 0.20$

Equilibrium	n	$\log K_p$ or $\log K_s$*; δ ≤ 0.20	logβ; δ ≤ 0.3
Mn^{2+} + 2 H$_4$L $\rightleftarrows$ MnL$_2^{6-}$ + 8 H$^+$	4.0	−31.28	16.1
Gd^{3+} + 2 H$_4$L $\rightleftarrows$ GdH$_4$L$_2^-$ + 4 H$^+$	2.0	19.03	28.4
Gd^{3+}+Mn^{2+} + 2 H$_4$L $\rightleftarrows$ GdMnH$_5$L$_2^{2+}$ + 3 H$^+$	1.5	31.91	37.5
Gd^{3+}+Mn^{2+} + 2 H$_4$L $\rightleftarrows$ GdMnH$_4$L$_2^+$ + 4 H$^+$	2.0	30.26	39.6
Gd^{3+}+Mn^{2+} + 2 H$_4$L $\rightleftarrows$ GdMnH$_3$L$_2$↓ + 5 H$^+$	2.5	26.28	43.0
Gd^{3+}+Mn^{2+} + 2 H$_4$L $\rightleftarrows$ GdMnH$_2$L$_2^-$ + 6 H$^+$	3.0	20.44	45.0
Gd^{3+}+ Mn^{2+} + 2 H$_4$L $\rightleftarrows$ GdMnHL$_2^{2-}$ +7 H$^+$	3.5	13.01	49.3
Gd^{3+}+ Mn^{2+} + 2 H$_4$L $\rightleftarrows$ GdMnL$_2^{3-}$ + 8 H$^+$	4.0	5.72	53.1
Gd^{3+}+ Mn^{2+} + 2 H$_4$L $\rightleftarrows$ GdMnL$_2$(OH)$^{4-}$ + 9 H$^+$	4.5	−5.73	55.6
Gd^{3+} +Mn^{2+} + 3 H$_4$L $\rightleftarrows$ GdMnH$_7$L$_3$↓ + 5 H$^+$	1.7	30.91	52.4
Gd^{3+} +Mn^{2+} + 3 H$_4$L $\rightleftarrows$ GdMnH$_6$L$_3^-$ + 6 H$^+$	2.0	29.34	43.4
2 Gd^{3+} + 2 H$_4$L $\rightleftarrows$ K$_3$Gd$_2$L$_2$(OH) ↓ + 9 H$^+$	4.5	−20.45*	(−81.9)
Gd^{3+} + H$_4$L $\rightleftarrows$ GdH$_2$L$^+$+ 2 H$^+$	2.0	14.31	19.0
2 Gd^{3+} + 2 H$_4$L + K$^+$ $\rightleftarrows$ KGd$_2$HL$_2$↓+ 7 H$^+$	3.5	−30.49*	(−66.4)
2 Gd^{3+} +2 Mn^{2+} + 2 H$_4$L $\rightleftarrows$ Gd$_2$Mn$_2$H$_2$L$_2^{4+}$+ 6 H$^+$	3.0	37.72	62.2
Gd^{3+}+Mn^{2+} + H$_4$L $\rightleftarrows$ GdMnL$^+$+ 4 H$^+$	4.0	14.02	37.7
Gd^{3+}+Mn^{2+} + H$_4$L $\rightleftarrows$ GdMnL(OH)$_2$↓ + 6 H$^+$	6.0	−6.99*	44.7

* For precipitate dissolution: K$_k$Gd$_m$H$_{4l-k-3m}$L$_l$↓ + h H$^+$ $\rightleftarrows$ k K$^+$ + m Gd^{3+} + l H$_4$L.
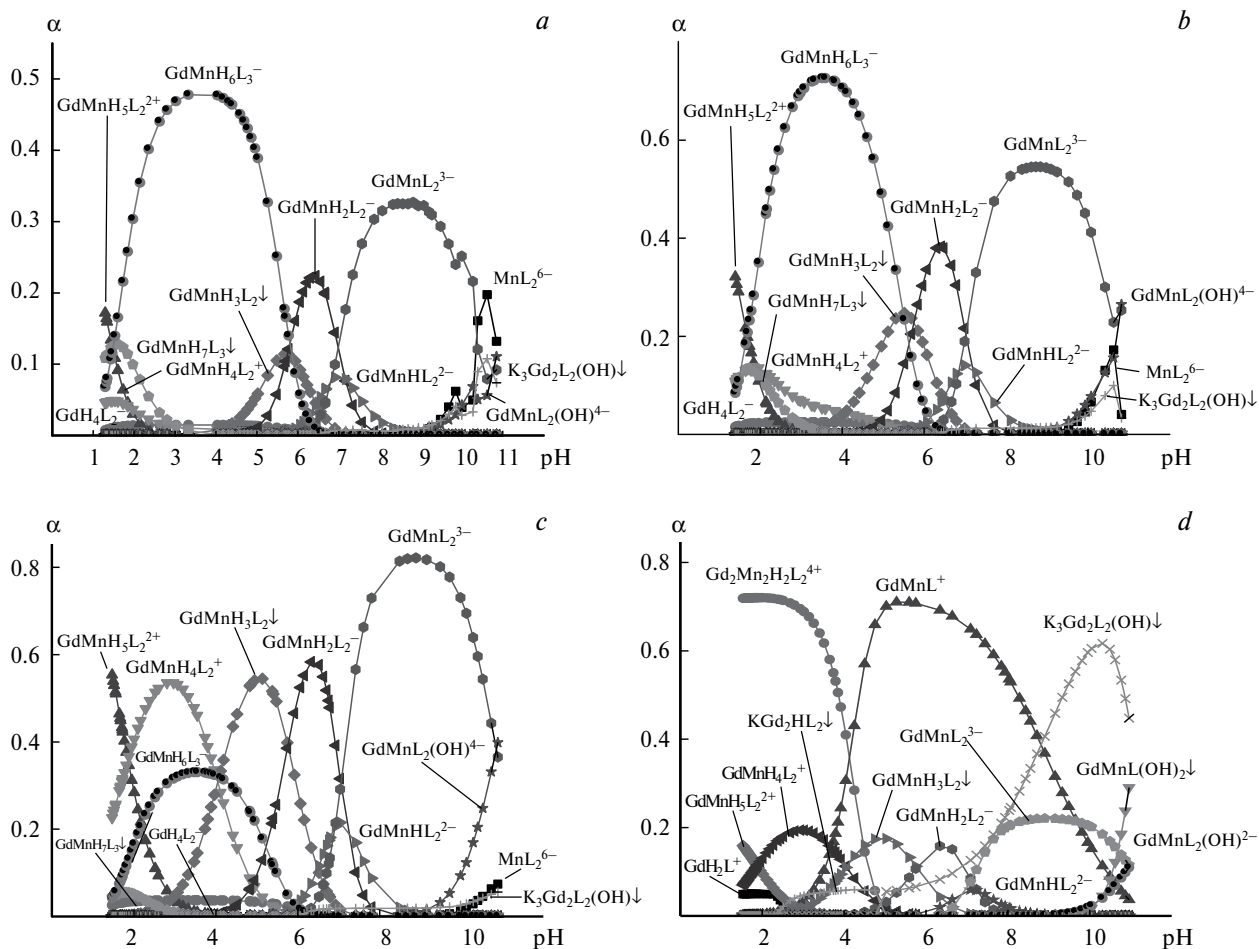
Fig. 3. Dependences of the form accumulation proportions (relative to the ligand) on the medium pH [Mn^{II}] = 9.65 mmol L^{-1}, [Gd^{III}] = 10.08 mmol L^{-1}, and [HEDP] = 57.52 mmol L^{-1} for the system 1—1—5 (*a*), 1—1—3 (*b*), 1—1—2 (*c*), and 1—1—1 (*d*).

the homonuclear manganese complex (MnL_2^{6-}) is accumulated in an alkaline medium with the excess of the ligand.

As it follows from the data obtained earlier, ten forms of complexes (including three binuclear) are formed[11] in the system Mn^{2+}—HEDP, while 16 forms of complexes (including three binuclear) are formed in the system Gd^{3+}—HEDP.[10] Note that manganese(II) complexes are considerably less stable than gadolinium(III) complexes. When the two cations are simultaneously present in the solution, the accumulation of heteronuclear forms is observed already in the strongly acidic pH region, which, as the pH increases, undergo conversion to heteronuclear complexes with the ratio Gd : Mn : HEDP equal to 1 : 1 : 1, 1 : 1 : 2, and 1 : 1 : 3 as a result of the proton abstraction. In this case, only five homonuclear forms of complexes, namely, MnL_2^{6-}, $GdH_4L_2^-$, GdH_2L^+, $KGd_2HL_2\downarrow$, and $K_3Gd_2L_2(OH)\downarrow$, were detected in the solution.

Thus, the heteronuclear complexes are significantly more stable and replace the homonuclear forms, not allowing them to be accumulated in the solution. This can be explained by considerably smaller radius (by 1.5 times) of the manganese(II) ion as compared to the gadolinium(III) ion, which reduces the repulsion between cations in the structure of heteronuclear complexes. The same situation is held in the systems gadolinium(III)—calcium(II)—HEDP (see Ref. 10) and erbium(III)— calcium (II)—HEDP.[18] It cannot be excluded that a combination of a "hard", orbitally controlled covalent binding of the manganese(II) ions and a "labile" electrostatic ionic interaction with the nucleophilic ligand centers in the case of gadolinium(III) leads to the energetically optimal configurations of heteronuclear complexes.

No magneto-relaxation characteristics for different series were obtained at this stage, however, we carried out comparative measurements of the spin-spin relaxation efficiency coefficient in heteronuclear and homonuclear systems under identical concentration conditions and physiological pH (7.4). The REC value for the manganese-containing system[11] is 2500 L mol^{-1} s^{-1}, while for the gadolinium-containing system[10] it is 5500 L mol^{-1} s^{-1}. In the heteronuclear system, the REC is equal to 6700 L mol^{-1} s^{-1} (the sum of concentrations of paramagnetics was used in the calculation). As a result, the heteronuclear system is regarded more preferable as a contrast agent for MRI.

Apart from that, we simulated the administration of a solution (at $[Mn^{II}] = 0.00965$ mol L^{-1}, $[Gd^{III}] = 0.0108$ mol L^{-1}, $[HEDP] = 0.0230$ mol L^{-1}, pH 7.40) with heteronuclear compounds in the human body, providing a 1000-fold dilution. The calculation showed the absence of free cations ($[Mn^{II}] \sim 10^{-11}$ mol L^{-1}, $[Gd^{III}] \sim 10^{-18}$ mol L^{-1}), while only three complexes were found to be present in the solution and they were hetero-

nuclear: $GdMnH_2L_2^-$, $GdMnHL_2^{2-}$, and $GdMnL_2^{3-}$. Their fractions were 30, 29, and 41%, respectively. Thus, the use of the system in choice as an MRI contrast agent can be also substantiated from the point of view of sufficient stability of the accumulating complexes.

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