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Conduction Microcalorimetry and ^{13}C NMR Spectroscopic Studies on the Complexing Ability of D-*erythro*-L-*manno*-D-*gluco*-dodecitol with Selected Lanthanide Salts in Water Solutions

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Complexing ability of D-*erythro*-L-*manno*-D-*gluco*-dodecitol (**1**) with lanthanides salts: $La(NO_3)_3 \cdot 6H_2O$ and $PrCl_3 \cdot 6H_2O$ in water by conduction microcalorimetry and ^{13}C NMR spectroscopy was studied. It was compared to the complexing ability of known D-galactitol (**2**), D-mannitol (**3**), and D-glucitol (**4**) under the same conditions.

Key words: D-*erythro*-L-*manno*-D-*gluco*-dodecitol, complexing ability between lanthanides and alditols, conduction microcalorimetry, ^{13}C NMR spectroscopy

Alditols are polyols resulting from reduction of a carbonyl function in carbohydrate molecule. Lower alditols, containing up to six carbon atoms, are readily available from naturally occurring C_3 - C_6 sugars. However, there are examples of isolation of higher alditols (having more than six carbon atoms in the molecule) from natural products [1], but usually they are available by a tedious stereocontrolled synthesis. The most known method of their preparation is undoubtedly a multi-step Brimacombe's C_2 iteration methodology [2]. Recently we presented another approach, leading to higher carbon sugars by coupling of two suitably activated monosaccharide precursors. By reaction of a C_7-sugar phosphonate with a C_5-sugar aldehyde followed by functionalization of the newly created (*E*)-enone system we were able to prepare alditol containing twelve carbon atoms in the molecule: D-*erythro*-L-*manno*-D-*gluco*-dodecitol (D-EMG, **1**) in a rather large scale (0.5 g) [3].

There are only two other examples of such complex C_{12} alditols: a side product isolated during electrochemical reduction of D-glucose [4] and dodeca-*O*-acetyl-L-*threo*-L-*galacto*-L-*galacto*-dodecitol obtained during total synthesis of *hikizimycin* [5].

Alditols are known to be good complexing agents for various metal cations [6–11]. Interactions between both partners are usually weak (stability constant < 10) but selective: univalent cations remain uncomplexed and trivalent cations form strongest complexes. Stability of the complex depends on the structure of alditol (alditols having the *threo-threo* arrangement form stronger complexes) [10] and the cation (the

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best complexed are lanthanides; especially Sm^{3+}) [9,11]. Usually a 1:1 stoichiometry of complexes between metal cations and C_5 - C_6 alditols is observed. Among pentitols and hexitols only one exception is known for the D-galactitol (**2**), which forms a 1:2 complex with Pr^{3+} [9]. Formation of a complex between compound **2** and two praseodymium cations enables a free rotation of terminal CH_2OH groups and, therefore, formation of a double semi-*threo-threo* (Fig. 1) arrangement of hydroxyl groups in the molecule of galactitol (**2**).

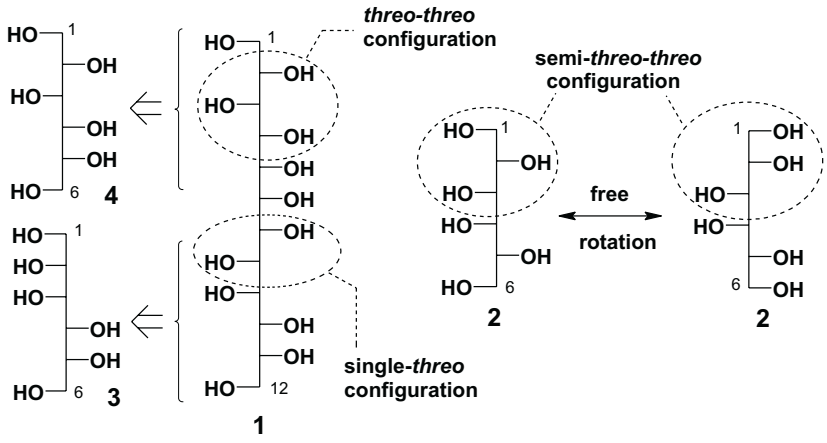

Figure 1

Complexing abilities of alditols may be applied for chromatographic purposes in separation of alditols from sugars, which form weaker complexes than alditols [10,12] and for thermal stabilizing of enzymes, *e.g. pullulanase* [13].

Because of the low accessibility of higher alditols, most of the literature data deal with interactions of lower alditols and various metal cations. Having available an unique dodecitol D-EMG **1** in reasonable amounts, we decided to study its complexing properties in comparison with known hexitols and to find out if the length of the carbon chain has any influence on the formation of a complex between alditol **1** and lanthanides.

RESULTS AND DISCUSSION

Different methods are used for determination complexing properties of alditols. Most frequently applied are chromatography [9,11], calorimetry [14], and NMR spectroscopy [8,15]. First of them requires a series of similar-by-weight compounds, which differ only in configuration at stereogenic secondary carbinol centers in the aliphatic chain. The low R_f values, observed on the TLC plates coated with cation-exchange resin, point at the formation of the strongest complex, but in our case this methodology cannot be, however, applied.

It is known that titration microcalorimetry enables simultaneous estimation of the enthalpy (ΔH) of the reaction, stability constant (K) and the stoichiometry (n) of the complex formed [16]. Possibility of determination of these values (ΔH, K, n) depends on the range of the constant of the reaction, available concentration of tested material in a proper solvent and sensitivity of the calorimeter. Hydrophilic character of D-EMG **1** and its potential application to study interactions with biological systems bring us to the conclusion that the most suitable solvent for performing experiments is water. Because of remarkably low solubility of **1** in water (*ca* 0.012 mol/L at room temperature), La^{3+} and especially Pr^{3+} cations, which are known as one of the most suitable for complexation of alditols, were chosen as complexing partners. Formation of a stronger complex should result in a greater heat of the reaction and – on the other hand – should compensate low concentration of D-EMG **1** in examined solutions.

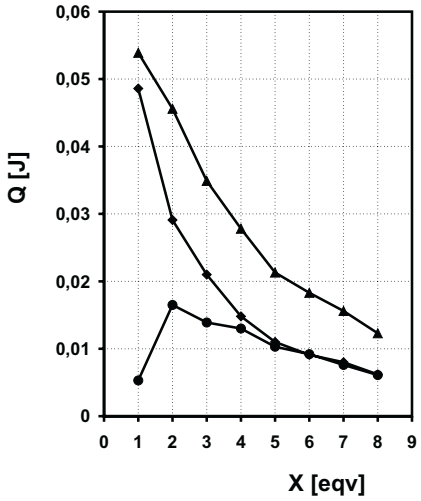

Chart 1. An example of calorimetric measurement of the heat of reaction between D-EMG **1** (C_{Ald} = 0.0134 mol/L) and $La(NO_3)_3$ (C_{La} = 0.2975 mol/L) in water (triangles – overall heat effect; aquares – heat of dilution; circles – heat of reaction).

The results of preliminary calorimetric determinations are presented in Chart 1. The heat effect of the reaction of the lanthanum cation with D-EMG **1** is relatively small in comparison with the heat of dilution of the lanthanum salt in water, hence, produces significant error. However, the positive values of the heat effect accompanying the addition of successive portions of a salt solution indicate formation of a complex or association. Slow decreasing of these heats *versus* number of equivalents of salt added suggests very small value of equilibrium constant of the complex. It is significant that the first value of heat of reaction is lower than the second one. It can be supposed that similarly as for lower alditols [14], particularly in the first period of reaction, unfavourable entropy of desolvation of lanthanide cation compensates partially the favourable enthalpy of its complexation.

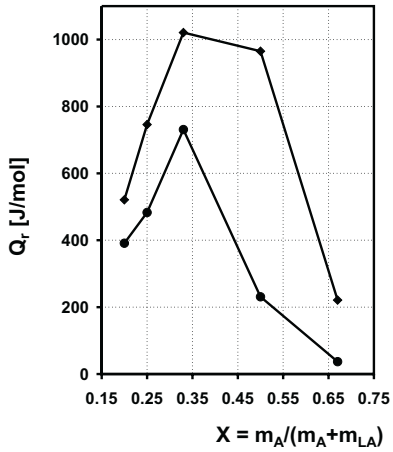

Chart 2. Heat of reaction between D-EMG **1** (C_{Ald} = 0.0134 mol/L) and $La(NO_3)_3$ (circles; C_{La} = 0.1481 mol/L) or $PrCl_3$ (squares; C_{Pr} = 0.1421 mol/L) in water.

In the analogous calorimetric determinations for praseodymium cation (Chart 2) larger heat effects were observed, but the conclusions on the complexation process were similar to those, obtained with La^{3+}. In both cases (La^{3+}, Pr^{3+}) the conditions necessary for application of classical titration microcalorimetry were not fulfilled, because of a small heat of reaction in comparison with heat of dilution of the salt added, the low solubility of D-EMG **1** and, presumably, very small equilibrium constant [16]. Therefore, we decided to estimate the complexing ability of D-EMG **1** with lanthanides by comparison with known lower alditols under the same conditions. Molecule of D-EMG **1**, counting from C-1 and C-12 ends, has the same configuration as configuration at first five carbon atoms of D-mannitol and D-glucitol (**3**, and **4** respectively, see Fig. 1). Because the nature of complex formation between D-EMG **1** and lanthanide cations is not known, galactitol (**2**), which forms complexes in a slightly different manner, should also be considered. Thus all alditols **1–4** were dissolved in water at the same concentration and the heats of reaction with two equivalents of lanthanum nitrate or praseodymium chloride were measured. The results, after subtraction of the heat of dilution of lanthanide salts in water, are collected in Table 1.

Table 1. Collected heats of complexation of alditols **1–4** with 2 equivalents of $La(NO)_3$ or $PrCl_3$.

Alditol	Heat of complexation* with 2 equivalents of $La(NO_3)_3$ [J/mol]	Heat of complexation* with 2 equivalents of $Pr(Cl)_3$ [J/mol]
D-EMG **1**	1000	2100
D-galactitol **2**	310	540
D-mannitol **3**	180	370
D-glucitol **4**	750	1700

C_{Al} = 0.01198 mol/L; C_{La} = 0.232 mol/L; C_{Pr} = 0.246 mol/L

*estimated error ±10%.

These data show that in both cases the heat effect accompanying complexation of lanthanide cations to D-EMG **1** is greater than for simple alditols. Among tested alditols only D-EMG **1** and D-glucitol **4** have the *threo-threo* arrangement. It is worth to note that, because of the configuration of the D-EMG **1** molecule (see Figure 1), there is no possibility for simultaneous complexation involving D-glucitol-like mechanism [15] (one lanthanide cation binding to the C-2–C-4 hydroxyl groups as in **4**) and D-galactitol-like mechanism [9] (one lanthanide cation binding to the C-1–C-3 hydroxy groups as in **2**). Especially for praseodymium is clearly seen that the heat related to complexation with D-EMG **1** equals to the sum of heats obtained for D-glucitol (**4**) and D-mannitol (**3**), what may suggest that D-EMG **1** forms a complex with two lanthanide cations. One of them could bind to the *threo-threo* site of D-EMG **1**, while the second one to a not specified site with the strength similar to D-mannitol (**3**). Indeed, a 1:2 stoichiometry of a D-EMG **1** – lanthanum cation complex was deduced on the basis of measurements of the transfer molar volume (see Chart 3).

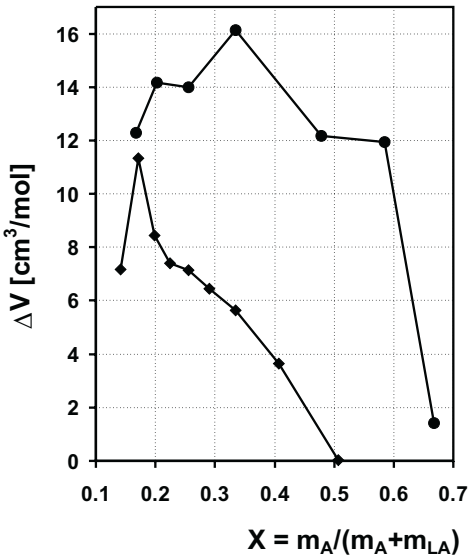

Chart 3. Transfer molar volume of D-EMG **1** and $La(NO_3)_3$ (circles) or $PrCl_3$ (squares) in water.

The maximum observed at X = 0.33 for lanthanum nitrate solution proved a 1:2 stoichiometry. The same experiment repeated for $PrCl_3$ solution gave no unequivocal answer. This might result from a greater strength of the complex formation between D-EMG **1** and praseodymium chloride, what could cause significant conformational changes in D-EMG **1** molecule during the complexation process.

All these observations were supported by the ^{13}C NMR spectroscopic measurements. This technique is especially suitable for estimation of the equilibrium constants of the complexation of alditols by lanthanide cations. On the basis of changes

of δ_C of C-2 in D-glucitol (**4**) complexation stability constant was easily determined [15]. Despite the fact, that formation of a complex (in which D-EMG **1** provides a potential multi-dentate ligand part) is a much more complex phenomenon, we decided to measure changes of the δ_C parameters of D-EMG **1** *versus* lanthanide cation/D-EMG **1** concentration ratio. Then the results were compared with those obtained (under the same conditions) for known C_6 alditols **2**, **3** and **4** (see Tables 2, 3, 4, and 5).

Table 2. ^{13}C NMR data (δ) in ppm of complexed alditol **1** with La^{+3} and Pr^{+3}.

lines	**A****	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**	**J**	**K**	**L**
a)	74.16	73.38	73.02	72.34	72.23	71.36	70.49	70.45	69.92	69.38	64.54	63.66
c_{La}/c_{ald}*												
0.3	74.25	73.35	73.05	72.57	72.24	71.35	70.49	70.49	69.93	69.41	64.52	63.67
0.8	74.38	73.32	73.05	72.84	72.27	71.35	70.49	70.58	69.95	69.46	64.48	63.67
1.0	74.44	73.31	73.08	72.94	72.27	71.34	70.49	70.62	69.96	69.46	64.48	63.68
1.2	74.52	73.29	73.09	73.09	72.29	71.34	70.49	70.65	69.96	69.49	64.47	63.69
1.5	74.57	73.27	73.11	73.22	72.3	71.34	70.49	70.69	69.97	69.49	64.46	63.69
2.05	74.65	73.25	73.11	73.37	72.31	71.33	70.5	70.73	69.98	69.52	64.44	63.69
2.3	74.67	73.25	73.11	73.43	72.33	71.34	70.51	70.75	69.99	69.53	64.45	63.7
2.7	74.74	73.23	73.13	73.57	72.34	71.32	70.5	70.79	70	69.54	64.42	63.7
3.8	74.86	73.21	73.13	73.83	72.39	71.33	70.53	70.84	70.02	69.6	64.39	63.71
5.8	75.03	73.19	73.14	74.17	72.47	71.32	70.56	70.92	70.06	69.66	64.36	63.74
7.5	75.12	73.17	73.17	74.38	72.54	71.32	70.61	70.97	70.09	69.74	64.32	63.77
10.5	75.24	73.17	73.17	74.63	72.66	71.32	70.68	71	70.14	69.84	64.27	63.8
c_{Pr}/c_{ald}												
0.4	74.16	73.27	73.14	72.15	72.23	70.78	70.41	70.41	69.76	69.32	64.53	63.78
0.8	74.21	73.22	73.22	72.07	72.25	71.4	71.4	71.4	69.67	69.29	64.53	63.87
1.3	74.26	73.16	73.33	71.98	72.28	70	70.31	70.39	69.55	69.25	64.52	63.98
1.7	74.26	73.16	73.33	71.98	72.28	70	70.31	70.39	69.55	69.25	64.52	63.98
2.1	74.28	73.15	73.36	71.92	72.3	69.73	70.26	70.35	69.48	69.2	64.53	64.05
2.7	74.32	73.12	73.42	71.89	72.3	69.55	70.21	70.34	69.41	69.17	64.54	64.09
3.1	74.34	73.1	73.47	71.84	72.32	69.36	70.19	70.32	69.36	69.12	64.54	64.15
3.6	74.38	73.09	73.49	71.89	72.35	69.22	70.16	70.29	69.31	69.09	64.54	64.19
4.3	74.41	73.09	73.51	71.86	72.38	69.98	70.08	70.24	70.02	69.22	64.55	63.26

a) The chemical shift of alditol without any salt added.
* The molar ratio of lanthanum cation to dodecitol **1**.
The resonances in the spectra were described as lines **A–L.

Table 3. δ values of complexed galactitol **2** with La^{+3} and Pr^{+3}.

c_{La}/c_{ald}	C-2,5	C3,4	C1,6	c^{Pr}/c^{ald}	C-2,5	C3,4	C1,6
0.0	71.38	70.57	64.47	*0.0*	71.38	70.57	64.47
1.1	71.39	70.77	64.53	*0.8*	71.05	70.36	64.52
2.4	71.4	70.94	64.58	*2.1*	70.58	70.06	64.58
3.9	71.39	71.13	64.65	*4.1*	70.58	70.06	64.58
10.7	71.4	71.75	64.89				

Table 4. δ values of complexed mannitol **3** with La^{+3} and Pr^{+3}.

c_{La}/c_{ald}	C-2,5	C3,4	C1,6	c^{Pr}/c^{ald}	C-2,5	C3,4	C1,6
0.0	72.03	70.47	64.44	*0.0*	72.03	70.47	64.44
0.9	72.09	70.52	64.4	*0.7*	71.99	70.31	64.38
2.6	72.17	70.62	64.34	*1.5*	71.95	70.15	64.33
4.0	72.23	70.69	64.23	*4.2*	71.85	69.72	64.18
10.5	72.46	70.96	64.13				

Table 5. δ values of complexed glucitol **4** with La^{+3} and Pr^{+3}.

c_{La}/c_{ald}	C2	C4	C5	C3	C6	C1	c^{Pr}/c^{ald}	C2	C4	C5	C3	C6	C1
0.0	74.15	73.32	72.19	70.87	64.03	63.34	*0.0*	74.15	73.32	72.19	70.87	64.03	63.34
1.0	74.42	72.78	72.21	70.89	63.96	63.68	*0.8*	74.33	72.3	72.08	70.27	63.92	63.82
2.3	74.63	73.13	72.22	70.89	63.9	63.71	*2.2*	74.61	72.33	71.94	69.58	63.79	64.07
4.0	74.86	73.52	72.24	70.91	63.84	63.74	*4.3*	74.86	72.38	71.84	69.09	63.68	64.29
10.5	75.32	74.29	72.29	70.96	63.71	63.84							

Assignments of the δ_C resonances of lower alditols **2–4** were made on the basis of literature data [17]. The changes in ^{13}C NMR resonances of alditols **1–4** for different concentrations of lanthanide salt point at the pseudocontact interaction of lanthanide cation with particular carbon atoms [18]. The lanthanide salt/alditol ratio was assorted in such a manner that in a whole range of concentrations it is known which particular signal accords with the corresponding signal, recorded for free alditol without addition of lanthanide salt.

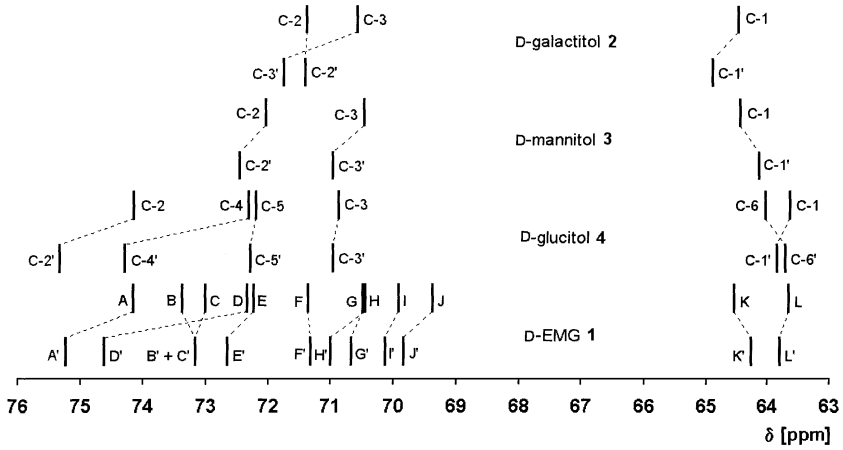

Chart 4. The changes of the δ_C values of alditols **1–4** *versus* $La(NO_3)_3$/alditol concentration ratio. Only initial and final (assigned as′) δ_C values are shown.

In the Chart 4 and Chart 5 only the initial and final (assigned with ′) δ_C values are shown, what makes the obtained results easier to compare. From the ^{13}C NMR experiments with La^{3+} (Tables 2–5) the following conclusions could be deduced. Excellent agreement of the δ_C values of C-1 and C-2 signals of D-glucitol (**4**) with **L** and **A** signals of D-EMG **1** and C-1 signal of D-mannitol (**3**) and **K** signal of D-EMG **1** in a whole range of concentrations of lanthanum salt suggest that there are two sites of

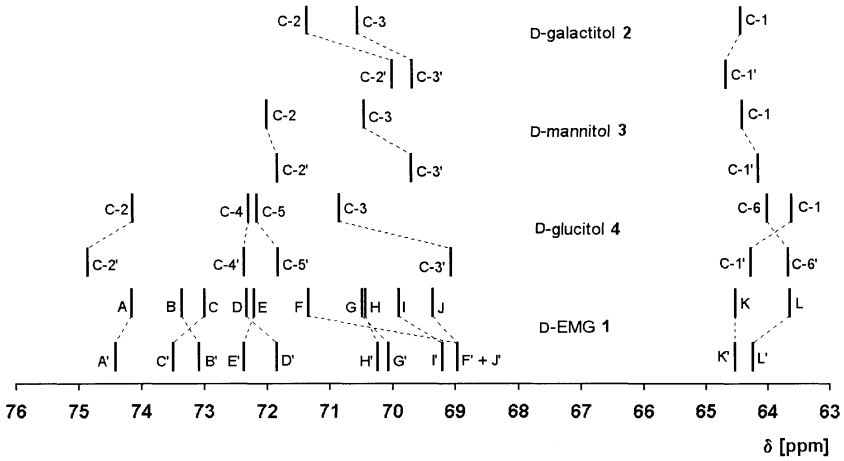

Chart 5. The changes of the δ_C values of alditols **1–4** *versus* $PrCl_3$/alditol concentration ratio. Only initial and final (assigned as′) δ_C values are shown.

binding of La^{3+} to the D-EMG **1** molecule. One of them is a *threo-threo* arrangement at the *gluco* part (C-2–C-4) of D-EMG **1**. Because of other similarities: C-4 resonance of D-glucitol (**4**) and **D** signal of D-EMG **1**, C-2, C-3 signals of D-mannitol (**3**) and **E**, **H** signals, respectively, of D-EMG **1** it could be postulated that the second site of complexation is localised within the *manno* part (that is C-8–C-12) of D-EMG **1**. It seems that both these sites bind lanthanum cations independently, like two separated molecules of the D-glucitol (**4**) and D-mannitol (**3**), what support observations made on the basis of the calorimetric experiments (see Table 1). Since there is no space for simultaneous complexation of two lanthanum cations in D-glucitol- and galactitol-like fashion in one molecule of D-EMG **1** and, because of little similarity of the changes of the δ_C values during complexation of galactitol (**2**) and D-EMG **1**, assumption that the lanthanum cation could bind to D-EMG **1** molecule in a D-galactitol-like fashion should be rather excluded. Results obtained from the ^{13}C NMR experiments with Pr^{3+} (see Tables 2–5) are not so clear. Only one C-1 signal of D-glucitol (**4**; complexed with La^{3+}) is in good agreement with the **L** signal of D-EMG **1** in a whole range of concentrations. It is interesting, that signal **K** of D-EMG **1** during complexation behaves rather like C-1 signal of galactitol (**2**) and not like C-1 signal of D-mannitol (**3**). Complexes between alditols and praseodymium cation are known to be one of the strongest [9,11]. Since the ^{13}C NMR δ_C value is a resultant of a paramagnetic interaction of a lanthanide cation and geometrical changes of the alditol molecule, it seems that in this case the changes of the δ_C values of D-EMG **1** *versus* praseodymium chloride concentrations cannot be compared with the corresponding changes of the δ_C for lower alditols (praseodymium cation can interact even with free rotated $-CH_2OH$ grouping of D-galactitol (**2**) [9] and could cause significant conformational changes of D-EMG **1** molecule, what disturbs the observed δ values). Although, the calorimetric data of complexation of D-EMG **1** with Pr^{3+} (see Table 1)

suggest a 1:2 stiochiometry, this was neither supported by transfer molar volume measurements nor by ^{13}C NMR spectroscopy experiments. The nature of interaction between D-EMG **1** and praseodymium cation remains not clear yet.

EXPERIMENTAL

$La(NO_3)_3 \cdot 6H_2O$ and $PrCl_3 \cdot 6H_2O$ were purchased from Aldrich. All solutions were prepared with degassed and deionized distilled water.

Calorimetric experiments were performed in an isothermal heat conduction microcalorimeter [19] with a sensitivity of 0.103 mV/mW, using a 3 mL sample cell equipped with a mechanical stirrer rotating with a constant speed of 60 rpm. An aqueous solution of alditol was placed in the sample cell. By means of the automated dosimetric device, the sets of injections of water solution of lanthanide salt [$La(NO_3)_3$, $PrCl_3$] at required doses (containing *e.g.* 1, 2 equivalents of alditol in the sample cell) were realized. The concentration of salt solution in the syringe was habitually 10÷20 times greater than alditol concentration. In separate experiments the respective measurements of heat of dilution were carried out. The calorimetric response to heat evolved during each injection was controlled by a Keithey 181 Nanovoltmeter and stored in the computer memory. The heat effects were calculated using equation:

$$Q = \alpha \int_0^t \Delta(t)dt$$

where Q is the total heat evolved in the time interval (0, t), $\Delta(t)$ – changes of a calorimetric signal at the time from the beginning of each injection until the time t, when a new thermal equilibrium is attained, α – heat loss coefficient, determined in separate calibration experiment. Heat effects related to complexation were evaluated as the difference of overall heat effect and heat of dilution.

Error of values obtained by microcalorimetry experiments: Series of separate measurements of the heat of dilution with 2 equivalents of lanthanide nitrate in water (C_{La} = 0.232 mol/L, according to the results shown in Table 1) gave the following values: 0.074, 0.071, 0.076, 0.071, 0.070 J. Thus, the mean error of the heat determination in this experiment should not exceed 0.0036 J (±5%). The final value, *i.e.* heat of complexation, is a difference of the overall heat effect and the heat of dilution, the error of the complexation heat value in these experiments should not exceed 0.0072 J (±10%). The values obtained from other experiments, in which smaller heats were measured, could have relatively larger error.

Transfer molar volume: Molar volume as a derivative of Gibbs energy, is a thermodynamic property particularly sensitive to molecular interactions between solution components. For this reason, determination of changes of apparent molar volume of aqueous alditol solutions caused by the presence of lanthanide salt, ΔV_3 (transfer of molar volume), was applied for studying possible complexation of alditol **1** with lanthanide cations [20]. $\Delta V_3 = V_{\varphi 3}$ (alditol + water + cation) – $V_{\varphi 3}$ (alditol + water). Determination of apparent molar volumes, $V_{\varphi i}$, was realized by density measurements, using an Anthon Paar DMA 60/602 digital densimeter, at 298.15 K. The apparent molar volumes $V_{\varphi i}$ of solute were calculated from densities using equation:

$$V_{\varphi i} = \frac{M_i}{d} - \frac{1000(d - d_0)}{n_i d d_0}$$

where M_i is a molar mass of solute, d_0, and d are the densities of water and the solution, respectively, n_i is the molality of the solution. Water was the reference solvent for binary solutions and aqueous lanthanide solution at various concentrations for ternary solutions.

^{13}C NMR: Spectra were recorded with a Varian Gemini 200 Spectrometer. All samples were prepared in the following manner: alditol (20 mg) was dissolved in D_2O (0.8 mL) in 5 mm NMR tube and dioxane (δ_C = 67.8 ppm) was added as internal standard. After addition of lanthanide salt, closed NMR tube was heated for 5 minutes up to 90°C and then cooled to room temperature.

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