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Paramagnetic Birefringence of Heteronuclear Erbium(III), Thulium(III), and Iron(III) *d*- and *dl*-Tartrates

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Abstract—Formation of heteronuclear erbium(III), thulium(III), and iron(III) *d*- and *dl*-tartrates was studied by proton magnetic relaxation, pH-metry, and paramagnetic birefringence in combination with mathematical simulation. The paramagnetic birefringence constants *mP* of the complexes were calculated.

Magnetooptical studies of heteronuclear hydroxy acid complexes of 3*d* and 4*f* elements are urgent in lanthanide coordination chemistry [1, 2]. Data on paramagnetic birefringence of late rare-earth elements in aqueous solutions are particularly scarce. In this work we studied the composition and stability of heteronuclear erbium(III), thulium(III), and iron(III) tartrates and optimized their paramagnetic birefringence constants *mP* bearing stereochemical information [3].

The following designations will be used: H_4L, tartaric acid; dH_4L, *d*-tartaric acid; dlH_4L, racemic tartaric acid; B_m, total concentration of metal ion M^{Z+}; and C_{H_nL}, total concentration of ligand H_nL^{k-}.

The primary data on the stoichiometry of the heteronuclear complexes were obtained similarly to [4] by proton magnetic relaxation, namely, by analytical processing of the dependences of the relaxation efficiency on the concentration parameters. Figure 1 shows the dependences of the relaxation efficiency K_{e1} on pH of the medium at various concentrations of the ligand and of Fe^{3+} and Tm^{3+} ions. As seen, the curves corresponding to similar concentrations of the reactants strongly differ for the systems with racemic and optically active tartaric acid. This may be due to both stereoselective and stereospecific effects [4–6].

Mathematical simulation showed that stereospecific formation of heteronuclear *d*- and *dl*-tartrates of various compositions occurs at the molar ratio iron(III) : lanthanide(III) : ligand of 1 : 1 : 2, and the stereoselective formation, at the ratio of 1 : 1 : 3. The complexation pattern was confirmed by the method of paramagnetic birefringence. In simulation of equilibria in the systems Fe^{3+}–Ln^{3+}–*d*-(*dl*-)H_4L we took as initial species the complexes whose formation is the most probable for *d*-tartrates ($FeLnHL_2^-$, $Fe_2Ln_2HL_4^{3-}$, $Fe_3Ln_3HL_6^{5-}$, $Fe_3Ln_3L_6^{6-}$, $Fe_3Ln_3L_6(OH)_2^{3-}$, and $FeLnH_2L_3^{4-}$) and for *dl*-tartrates ($FeLnHL_2^-$, $Fe_2Ln_2L_4^{4-}$, $Fe_4Ln_4L_8(OH)_2^{10-}$, $FeLn(HL)_3^{3-}$, $FeLnH_2L_3^{4-}$, and $Fe_2Ln_2H_2L_6^{10-}$) (Ln = Er^{3+}, Tm^{3+}) [7]. The simulation results are listed in Tables 1 and 2. As seen, models no. 4 are the most adequate. The optimized stability constants of the corresponding Er(III), Tm(III), and Fe(III) tartrates are listed in Table 3.

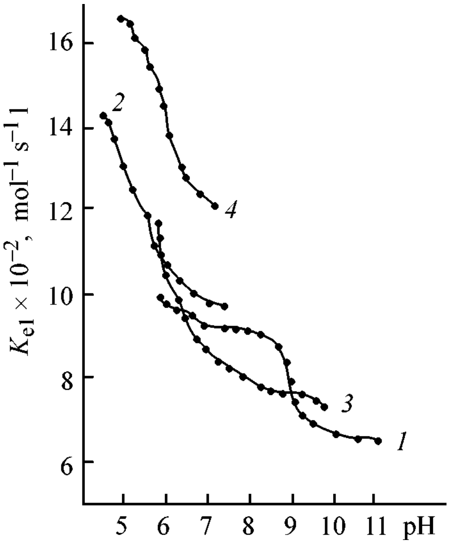

Fig. 1. Relaxation efficiency K_{e1} as a function of pH for the systems Tm^{3+}–Fe^{3+}–dH_4L and Tm^{3+}–Fe^{3+}–dlH_4L; concentrations in M. (*1*) B_{Tm} = 0.0200, B_{Fe} = 0.0199, and C_{dlH_4L} = 0.0418; (*2*) B_{Tm} = 0.0200, B_{Fe} = 0.0199, and C_{dlH_4L} = 0.0608; (*3*) B_{Tm} = 0.0201, B_{Fe} = 0.0201, and C_{dH_4L} = 0.0419; and (*4*) B_{Tm} = 0.0201, B_{Fe} = 0.0291, and C_{dlH_4L} = 0.0609.

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Table 1. Simulation of the systems Fe^{3+}–Ln^{3+}–dH_4L (Ln = Er^{3+}, Tm^{3+}) based on nuclear magnetic relaxation data: (a) B_{Fe} = 0.0201, B_{Ln} = 0.0201, and C_{dH_4L} = 0.0419 M; (b) B_{Fe} = 0.0201, B_{Ln} = 0.0201, and C_{dH_4L} = 0.0608 M

Model no.	Model	F_{min}	
		(a)	(b)
1	$FeLnHL_2^-$, $Fe_2Ln_2HL_4^{3-}$, $Fe_3Ln_3HL_6^{5-}$, $FeLnH_2L_3^{4-}$, $Fe_3Ln_3L_6^{6-}$, $Fe_3Ln_3L_6(OH)_2^{8-}$, $FeLn(HL)_3^{3-}$	20.75, 22.68	4.10, 3.92
2	$FeLnHL_2^-$, $Fe_2Ln_2L_4^{4-}$, $Fe_4Ln_4L_8(OH)_2^{10-}$, $FeLn(HL)_3^{3-}$, $FeLnH_2L_3^{4-}$	10.02, 12.30	5.27, 5.40
3	$FeLnHL_2^-$, $Fe_2Ln_2L_4^{4-}$, $Fe_2Ln_2L_4(OH)_2^{6-}$, $FeLn(HL)_3^{3-}$, $FeLnH_2L_3^{4-}$	12.42, 14.13	80.70, 86.52
4	$FeLnHL_2^-$, $Fe_2Ln_2HL_4^{3-}$, $Fe_3Ln_3L_6^{6-}$, $Fe_3Ln_3L_6(OH)_2^{8-}$, $FeLn(HL)_3^{3-}$, $FeLnH_2L_3^{4-}$	3.38, 2.36	0.30, 1.82

Table 2. Simulation of the systems Fe^{3+}–Ln^{3+}–dlH_4L (Ln = Er^{3+}, Tm^{3+}) based on nuclear magnetic relaxation data: (a) B_{Fe} = 0.020, B_{Ln} = 0.020, and C_{dlH_4L} = 0.0418 M; (b) B_{Fe} = 0.020, B_{Ln} = 0.020, and C_{dlH_4L} = 0.0608 M

Model no.	Model	F_{min}	
		(a)	(b)
1	$FeLnHL_2^-$, $Fe_2Ln_2L_4^{4-}$, $Fe_4Ln_4L_8(OH)_2^{10-}$, $FeLn(HL)_3^{3-}$, $FeLnH_2L_3^{4-}$, $Fe_2Ln_2H_2L_6^{10-}$	7.20, 8.46	1.92, 2.12
2	$FeLnHL_2^-$, $Fe_2Ln_2HL_4^{3-}$, $Fe_3Ln_3L_6^{6-}$, $Fe_3Ln_3L_6(OH)_2^{8-}$, $FeLn(HL)_3^{3-}$, $FeLnH_2L_3^{4-}$, $Fe_2Ln_2H_2L_6^{10-}$	11.40, 13.68	3.40, 3.12
3	$FeLnHL_2^-$, $Fe_2Ln_2L_4^{4-}$, $Fe_2Ln_2L_4(OH)_2^{6-}$, $FeLn(HL)_3^{3-}$, $FeLnH_2L_3^{4-}$	8.34, 8.50	2.75, 3.08
4	$FeLnHL_2^-$, $Fe_2Ln_2L_4^{4-}$, $Fe_4Ln_4L_8(OH)_2^{10-}$, $FeLn(HL)_3^{3-}$, $FeLnH_2L_3^{4-}$	4.50, 2.42	0.62, 0.88

Table 3. Composition and stability of erbium(III), thulium(III), and iron(III) *d*- and *dl*-tartrates

Stoichiometric coefficients in Eq. (1)				log β[a]			
				Er^{3+}		Tm^{3+}	
Fe^{3+}	Ln^{3+}	H_2L^{2-}	H^+	*d*	*dl*	*d*	*dl*
1	1	2	3	4.75	4.88	4.90	5.04
1	1	3	3	9.13	10.40	10.10	11.06
1	1	3	4	2.54	4.20	4.08	5.08
2	2	4	7	6.04	–	6.06	–
2	2	4	8	–	0.27	–	0.50
2	2	6	10	–	–	–	–
2	2	6	12	–	–	–	–
3	3	6	12	1.11	–	1.42	–
3	3	6	14	–16.21	–	–15.58	–
4	4	8	18	–	–15.40	–	–14.84

[a] The error in determination of log β does not exceed 0.2.

Table 4. Optimized values of *mP* for heteronuclear erbium(III) and thulium(III) *d*- and *dl*-tartrates

Stoichiometric coefficients in Eq. (1)				$mP \times 10^{15}$, emu			
				Er^{3+}		Tm^{3+}	
Fe^{3+}	Ln^{3+}	H_2L^{2-}	H^+	*d*	*dl*	*d*	*dl*
1	1	2	3	–5	–5	–10	–40
1	1	3	3	–20	–20	–35	–35
1	1	3	4	–20	–20	–35	–35
2	2	4	7	–14	–	–26	–
2	2	4	8	–	–184	–	–312
3	3	6	12	–51	–	–60	–
3	3	6	14	–205	–	–309	–
4	4	8	18	–	–772	–	–992

The magnetooptical curves for the systems thulium(III)–iron(III)–*d*(*dl*)-tartaric acid are shown in Fig. 2. Comparative consideration of the magnetooptical curves confirms the proton magnetic relaxation data concerning stereoeffects in complex formation.

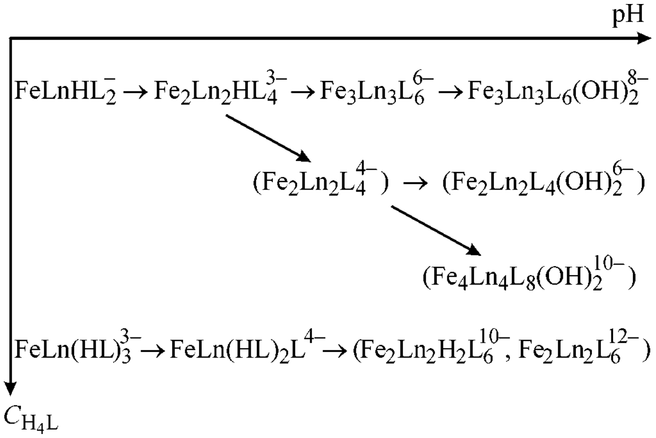
Combined analysis of the magnetooptical and relaxation data allowed us to reliably determine the stability constants and paramagnetic birefringence constants of heteronuclear Er(III), Tm(III), and Fe(III) tartrates (Tables 3, 4).

In Table 3 are given the optimized stability constants corresponding to formalized equations

$$m\mathrm{Fe}^{3+} + p\mathrm{Ln}^{3+} + q\mathrm{H_2L}^{2-} = \mathrm{Fe}_m\mathrm{Ln}_p\mathrm{L}_q\mathrm{H}_{2q-r}^{3(m+p)-2q-r} + r\mathrm{H}^+. \qquad (1)$$

Hence, if the stoichiometry with respect to Fe^{3+}, Ln^{3+}, $\mathrm{H_2L}^{2-}$, and H^+ is, respectively, m, p, q, and r (Table 3), the stability of the heteronuclear complex $\mathrm{Fe}_m\mathrm{Ln}_p\mathrm{L}_q\mathrm{H}_{2q-r}^{3(m+p)-2q-r}$ will be characterized by the constant β_{mpqr}: $\beta = [\mathrm{Fe}_m\mathrm{Ln}_p\mathrm{L}_q\mathrm{H}_{2q-r}][\mathrm{H}]^r[\mathrm{Fe}]^{-m}[\mathrm{Ln}]^{-p}[\mathrm{H_2L}]^{-q}$; charges are omitted.

The optimized molar birefringence constants of the heteronuclear complexes are listed in Table 4. In view of data of [7] and of this work, the overall scheme of formation of heteronuclear tartrate complexes can be represented as follows (the species forming only with *dl*-tartaric acid are given in parentheses):



Based on data in Table 3, we calculated the characteristics of stereoselective formation of the species $\mathrm{FeLn(HL)_3^{3-}}$ and $\mathrm{FeLn(HL)_2^{4-}}$: structural contributions $\log Q_{q-n,n}$ [Table 5, Eq. (2)].

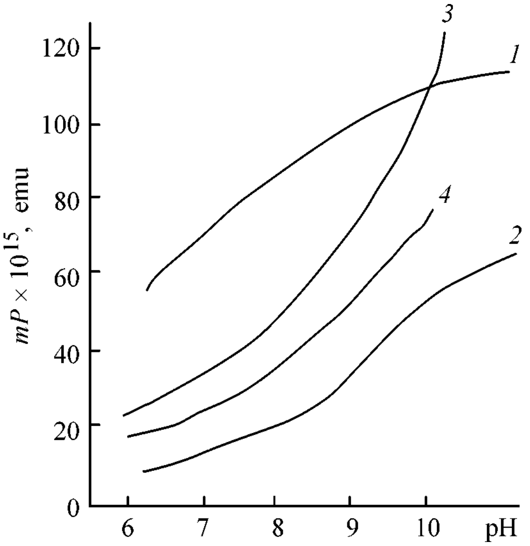


Fig. 2. Magnetooptical titration curves for the systems $\mathrm{Tm^{3+}}$–$\mathrm{Fe^{3+}}$–$d\mathrm{H_4L}$ and $\mathrm{Tm^{3+}}$–$\mathrm{Fe^{3+}}$–$dl\mathrm{H_4L}$; concentrations in M. (*1*) $B_{\mathrm{Tm}} = 0.0098$, $B_{\mathrm{Fe}} = 0.0099$, and $C_{dl\mathrm{H_4L}} = 0.0202$; (*2*) $B_{\mathrm{Tm}} = 0.0098$, $B_{\mathrm{Fe}} = 0.0099$, and $C_{d\mathrm{H_4L}} = 0.0202$; (*3*) $B_{\mathrm{Tm}} = 0.0098$, $B_{\mathrm{Fe}} = 0.0099$, and $C_{dl\mathrm{H_4L}} = 0.0309$; and (*4*) $B_{\mathrm{Tm}} = 0.0098$, $B_{\mathrm{Fe}} = 0.0099$, and $C_{d\mathrm{H_4L}} = 0.0308$.

$$\log \beta_{q-n,\,n} = \log K_s + \log \beta_{q,\,0} + \log Q_{q-n,\,n} \qquad (2)$$

Here $\beta_{q,0}$, $\beta_{q-n,n}$ are the stability constants of the diastereomeric complexes one of which contains q *d*-ligands and the other, $(q - n)$ *d*-ligands and n *l*-ligands, respectively; $K_s = q!/(q-n)!n!$ is the statistical factor, and $\log Q_{q-n,n}$ is the structural factor. Since in this case the structural factor exceeds the error in determination of $\log \beta$ for the *dl*-diastereomers of $\mathrm{LnFe(HL)_3^{3-}}$ and $\mathrm{LnFe(HL)_2L^{4-}}$, we can speak about their stereoselective formation (Table 5).

Table 5. Structural contributions $\log Q_{q-n,\,n}$ to $\Delta\log \beta$ of heteronuclear diastereomeric tartrates of $\mathrm{Fe^{3+}}$ and $\mathrm{Er^{3+}}$, $\mathrm{Tm^{3+}}$

Complex	Parameter				
	$\log \beta_{q,\,0}$	$\log \beta_{q-n,\,n}$	$\Delta\log \beta$	K_s	$\log Q_{q-n,\,n}$
$\mathrm{ErFeHL_2^-}$	4.75	5.28	0.53	0.3	0.23
$\mathrm{TmFeHL_2^-}$	4.90	5.45	0.55	0.3	0.25
$\mathrm{ErFe(HL)_3^{3-}}$	9.13	11.00	1.87	0.48	1.39
$\mathrm{TmFe(HL)_3^{3-}}$	10.10	11.65	1.55	0.48	1.07
$\mathrm{ErFe(HL)_2L^{4-}}$	2.53	4.80	2.27	0.48	1.79
$\mathrm{TmFe(HL)_2L^{4-}}$	4.08	5.67	1.59	0.48	1.11

EXPERIMENTAL

Erbium(III) and thulium(III) nitrates and chlorides were of chemically pure grade; iron(III) nitrate and chloride and *d*-tartaric acid were of analytically pure grade. Racemic tartaric acid (pure grade) was recrystallized three times from water. The experimental procedure was the same as in [8]. The composition, properties, and relaxation characteristics of the complexes were calculated similarly to [9, 10] using CPES [8] and CPESSP [9] programs. In calculations by these programs, the adequacy criterion was the target function F defined as follows:

$$F = \Sigma\ (X_{k\,\mathrm{exp}} - X_{k\,\mathrm{theor}})^2/W_k, \quad (3)$$

where $X_{k\,\mathrm{exp}}$ is an experimentally measured property of solution in kth experiment, $X_{k\,\mathrm{theor}}$ is its theoretical analog, and W is the weight of the kth point, introduced to compensate for the loss of the accuracy of particular method in certain measurement ranges.

The Bjerrum function $\tilde{n}$ was calculated as

$$\tilde{n} = \left(10^{-\mathrm{pH}}V + C_{\mathrm{OH}}V_{\mathrm{OH}} - 10^{(\mathrm{pH}-14)}V\right)/C_{\mathrm{H_4L}}V, \quad (4)$$

where C_{OH} is the concentration of alkali titrant, $C_{\mathrm{H_4L}}$ is the concentration of the acid being titrated, V_{OH} is the volume of the alkali added, and V is the total volume of the system taking into account the alkali added.

The paramagnetic birefringence constants mP were determined with an installation assembled in the Arbuzov Institute of Organic and Physical Chemistry by V.F. Nikolaev and S.G. Vul'fson. The installation consists of a temperature-controlled cell with a test solution, placed in the interpolar space of an electromagnet, and a monochromatic source of plane-polarized light (He–Ne laser); the electric vector of the laser beam makes an angle of 45° with the direction of the lines of force of the magnet and analyzer with which the ellipticity of the beam that passed the cell is determined. The analyzer transforms the birefringence into the proportional quantity, optical rotation angle. The molar constant mP (in 10^{-16} emu units) is calculated by

$$mP = 6\Delta\varphi\lambda n/[(n^2 + 2)^2 B], \quad (5)$$

where $\Delta\varphi$ is the optical rotation angle (deg), n is the refractive index of the solution, B is the concentration of the paramagnetic ion (M), λ is the wavelength of the light emitted by the laser (λ 632.8 nm); 1 emu = 1 $\mathrm{cm^3\,G^{-2}\,mol^{-1}} = 1.579 \times 10^{-10}\ \mathrm{m^5\,A^{-2}\,mol^{-1}}$. The installation and measuring cells were calibrated at 25°C with benzene whose birefringence constant under these conditions is 50.09×10^{-12} emu [11]. Solutions were added to the cell through a finely porous glass frit. The procedure of the magnetooptical experiment is described in sufficient detail in [12].

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