Dimeric D- and DL-dysprosium(III) tartrates: paramagnetic birefringence, molecular mechanics, stereoselectivity

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The molar constants of paramagnetic birefringence (PBR) for the dimeric dysprosium(III) D- and DL-tartrates, $Dy_2(D\text{-}Tart)(L\text{-}Tart)^{2-}$ (**1**) and $Dy_2(D\text{-}Tart)_2{}^{2-}$ (**2**) have been determined by means of pH-metric and PBR measurements. The simulation of the structure of the ligand and solvate environment has been carried out using the method of molecular mechanics (Dashevsky—Plyamovaty model, the MIND program). In addition to the four oxygen atoms from the ligand, each Dy^{III} ion coordinates four molecules of water and a Na^+ ion.

Key words: paramagnetic birefringence; molecular mechanics; dysprosium, complexes.

The analysis of stereoselectivity effects is one of the aspects of the thermodynamic study of the formation of tartrate complexes in aqueous solutions. Stereoselectivity occurs if the relative stability of the diastereomeric tartrates differs from its purely statistical value, *i.e.*, if the structure factor $\log Q_{q-n,n}$ exceeds the standard error in the determination of the stability constants $(\Delta\log\beta)$[1,2].

In our purely thermodynamic studies we systematized the $\log Q_{q-n,n}$ data and made several assumptions concerning the structure of the complexes. The development of the method of paramagnetic birefringence[3,4] made the analysis of the relationship between the structures of diastereomers and stereoselectivity effects more reliable. The PBR constant of a complex ($_mP$) serves as a basis for simulating its most likely structure:

$$_mP = (2\pi N/45kT)(\Sigma b_{ij}k_{ij} + 6\Sigma b_{ij}k_{ij}) \qquad (1)$$

Here b_{ij} and k_{ij} are components of the optical polarizability tensor of the ligand bonds and of the magnetic susceptibility (MS) tensor of paramagnetic ions, respectively. The structure of the ligand and solvate environment of the complex was optimized by the method of molecular mechanics (MM). The theoretical constant $_mP$ is, in general, computed for the set of conformations having the smallest values of the steric energy E and $_mP$, which are close to experimental. In the geometry optimization we used the MIND program[5] based on the Dashevsky—Plyamovaty model. The benefit of the program for such studies consists in a good reproducibility of the values of the relative conformational energies E. Hence, by using it, one can compute $\log Q_{q-n,n}$ for diastereomeric complexes with fairly high accuracy.

This approach was used to simulate the structure of the dimeric D- and DL-dysprosium(III) tartrates $Dy_2(D\text{-}Tart)(L\text{-}Tart)^{2-}$ (**1**) and $Dy_2(D\text{-}Tart)_2{}^{2-}$ (**2**) in aqueous solutions ($D\text{-}Tart^{4-}$, $L\text{-}Tart^{4-}$ are anions of D- and L-tartaric acid). Prior to that procedure, the stability constants and $_mP$ for **1** and **2** were determined by pH-metric titration and PBR methods: $\log\beta$ (**1**) = −13.79; $\log\beta$ (**2**) = −13.83; $_mP_{exp}$(**1**) = $900 \cdot 10^{-15}$ emu, $_mP_{exp}$(**2**) = $862 \cdot 10^{-15}$ emu. The relative stability $(\Delta\log\beta)$ of **1** and **2** was determined by the statistical factor alone; $\log Q_{q-1,1} = 0.09$.

Let us consider first the simulation of structure **1** (specifications for the parameters for the MIND calculations has been presented previously[6]). Six conformations were chosen as the first approxmation. The parameters specifying the geometry of **1** are shown in Fig. 1, *a*, and their numerical values are listed in Table 1. The most symmetric forms (**1a**, **1b**, **1f**) contain all of the symmetry elements of binuclear DL-tartrates[7], that is, the symmetry plane σ_h, the inversion center C_i, and the C_2-axis; they differ only in the values of the ligand torsional angles. In this case the following relationships are valid: $\varphi_1 = -\varphi_8 = -\varphi_{10}$; $\varphi_2 = -\varphi_9$, $\varphi_3 = -\varphi_8 = -\varphi_{10}$, $\varphi_4 = -\varphi_7 = -\varphi_{11}$. The optimization of the geometry resulted again in six conformations (Table 2). Comparing the data of Tables 1 and 2 one can note that there is no "classical" tetragonal geometry in **1**, *i.e.*, the angle between the planes

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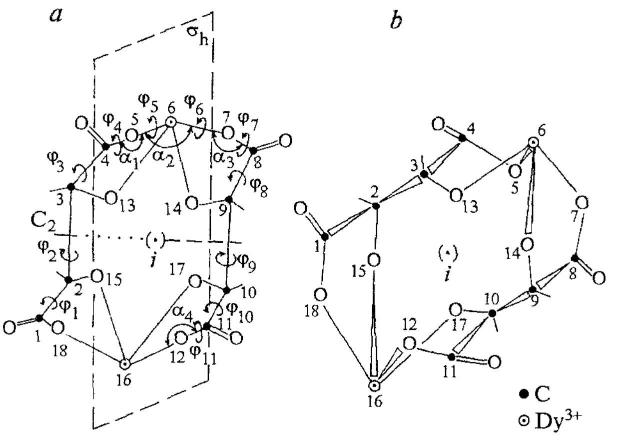

Fig. 1. Idealized tetragonal geometry for the DL-tartrate of dysprosium(III); parameters defining the geometry; high symmetry form (*a*); low symmetry form (*b*).

Table 1. Parameters of initial conformations of **1**

Angle*	Conformation (E/kcal mole^{-1})					
	1a (692.0)	**1b** (978.5)	**1c** (344.8)	**1d** (396.4)	**1e** (690.2)	**1f** (145.0)
φ_1	120.0	90.0	90.0	90.0	90.0	120.0
φ_2	−175.0	−175.0	−175.0	−175.0	−175.0	−175.0
φ_3	120.0	90.0	120.0	90.0	120.0	120.0
φ_4	−5.0	48.0	35.0	1.0	−10.0	15.0
φ_5	−138.0	−140.0	−130.0	−165.0	−152.0	−135.0
φ_6	130.0	155.0	165.0	175.0	178.0	142.0
φ_7	5.0	−48.0	−60.0	−20.0	−20.0	−15.0
φ_8	−120.0	−90.0	−90.0	−90.0	−90.0	−120.0
φ_9	175.0	175.0	175.0	175.0	175.0	175.0
φ_{10}	−120.0	90.0	−120.0	−90.0	−120.0	−120.0
φ_{11}	5.0	−48.0	−35.0	−1.0	10.0	−15.0
α_1	115.0	115.0	115.0	115.0	115.0	120.0
α_2	98.0	75.0	60.0	110.0	110.0	65.0
α_3	115.0	115.0	115.0	115.0	115.0	120.0
α_4	115.0	115.0	115.0	115.0	115.0	115.0

* Here and hereafter angular parameters are given in degrees.

O(5)—Dy(6)—O(13) and O(7)—Dy(6)—O(14) is fairly large (Fig. 1, *a*). The Dy^{3+} ion has a pseudo-tetragonal—pyramidal environment. The conformations with no symmetry except the inversion center (namely, **1g** and **1i**) Fig. 1, *b*, possess the smallest steric energy. For them the following relationships hold true : $\varphi_1 = -\varphi_8$, $\varphi_2 = -\varphi_9$, $\varphi_3 = -\varphi_{10}$, $\varphi_4 = =-\varphi_{11}$, $\alpha_1 = \alpha_4$.

The theoretical values of $_mP$ constants were calculated for **1g**—**1i** assuming a structureless hydrate environment. The optical polarizability values were taken from literature[8]. The axial approximation of the Dy^{3+} MS tensor was applied; the paramagnetic anisotropy value used was $\Delta k = k_{\parallel} - k_{\perp} = -2860 \cdot 10^{-29}$ cm^3, previously obtained[4] for Dy^{3+} tartrates with a structure similar to that of **1** and **2**, in which Δk is oriented along the highest order axis of the local environment[9]. In the calculations of $_mP$ (the CONKER program) the Δk-orientation was defined by the "torsional" and "valence" angles Ψ_1, β_1 and Ψ_2, β_2; P_{26} and P_{27} are pseudoatoms (Fig. 2). Preliminary calculations of $_mP$ showed that their experimental values corresponded to the high symmetry conformations (**1h**). At the same time, the **1h** contribution at higher E values does not exceed 10 %. To resolve that contradiction two models of the hydrate environment corresponding to the most probable coordination numbers (CN) of Dy^{3+} in aqueous solution were considered: 1) each Dy^{3+} ion coordinates four water molecules in addition to the donor atoms of the ligand (CN = 8); 2) each Dy^{3+} ion is additionally coordinated by five water molecules (CN = 9).

Table 2. Parameters of optimized conformations of **1**

Angle	Conformation (E/kcal mole^{-1})					
	1g (98.2)	**1h** (101.2)	**1i** (88.1)	**1j** (103.0)	**1k** (98.5)	**1l** (98.4)
φ_1	135.7	92.0	132.4	91.5	157.2	111.9
φ_2	−172.6	−182.5	−172.1	−181.5	−174.6	−174.7
φ_3	113.1	90.6.	113.5	82.3	135.7	126.6
φ_4	49.0	43.2	49.3	4.8	11.5	−29.7
φ_5	−169.3	−152.8	−172.1	−116.9	−123.8	−93.6
φ_6	83.6	156.2	78.1	177.5	123.9	132.7
φ_7	31.6	−45.7	36.7	−10.8	−3.5	−11.1
φ_8	−128.4	−96.1	−132.1	−91.1	−107.4	−136.6
φ_9	172.1	182.4	172.0	180.9	173.8	174.8
φ_{10}	−119.3	89.4	−114.2	−85.9	−135.0	−146.6
φ_{11}	−43.5	−44.3	−48.6	5.2	−24.9	50.0
α_1	104.4	115.1	103.6	117.8	120.9	119.4
α_2	75.8	72.9	75.6	104.2	85.2	93.4
α_3	118.8	113.0	116.7	123.3	124.6	120.7
α_4	106.9	114.9	104.1	115.2	114.4	110.0

The theoretical values of $_mP$ for most favorable conformations are far from the experimental values, as well as from the skeleton conformation similar to that presented in. Fig. 1, *b*. Thus, it is impossible to design the

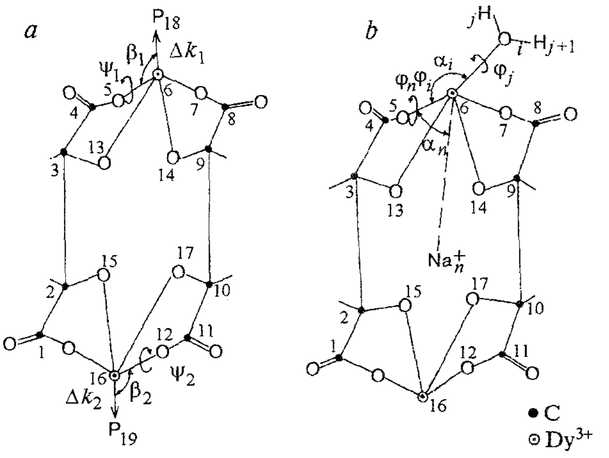

Fig. 2. Definition of the Δk direction in **1** (*a*) and the location of the Na^+ ion (*b*).

Table 3. Parameters of optimized structures of hydrated DL-tartrate of dysprosium(III) with allowance for the coordination of Na^+

Angle	Structure (E/kcal mole^{-1})	
	model 3	model 4
	1m (122.3)	**1n** (127.1)
φ_1	122.2	120.6
φ_2	−177.2	−176.0
φ_3	123.8	124.3
φ_4	11.2	13.3
φ_5	−131.1	−130.8
φ_6	128.1	128.5
φ_7	−8.5	−10.9
φ_8	−124.5	−123.2
φ_9	177.1	176.1
φ_{10}	−119.1	−123.7
φ_{11}	−14.0	−12.5
α_1	124.0	123.4
α_2	77.4	74.3
α_3	124.4	124.1
α_4	124.0	123.7

Table 4. Geometric parameters of structure **1m**

Angle	Value	Angle	Value	Angle	Value
φ_1	122.2	α_1	124.0	φ_{38}	−63.9
φ_2	−177.2	α_2	77.4	α_{38}	78.2
φ_3	123.8	α_3	124.4	φ_{41}	−146.3
φ_4	11.2	α_4	124.0	α_{44}	82.3
φ_5	−131.1	φ_{26}	149.5	φ_{47}	166.9
φ_6	128.1	α_{26}	78.6	α_{47}	148.8
φ_7	−8.5	φ_{29}	13.7	φ_{47}	−11.1
φ_8	−124.5	α_{29}	136.1	α_{47}	137.0
φ_9	177.1	φ_{32}	−162.6	φ_{50}	−78.7
φ_{10}	−119.1	α_{32}	147.9	α_{50}	52.3
φ_{11}	−14.0	φ_{35}	63.8	d_{50}	
		α_{35}	75.8		

Note. φ_{50}, α_{50}, and d_{50} determine the position of the Na^+ ion.

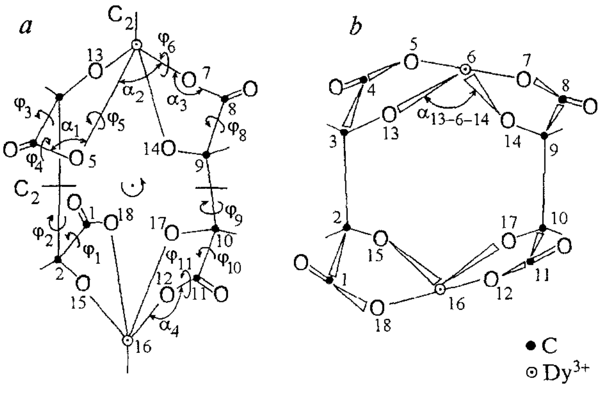

Fig. 3. Parameters defining the geometry of the D-tartrate of dysprosium(III): tetragonal geometry of the environment (*a*); trigonal-bipyramidal geometry (*b*).

structure of the complex in question by merely simulating its hydrate environment. The coordination of the Na^+ ion can be assumed to affect the formation of highly symmetric structures; in fact, **1** and **2** were dominant at pH 11.0 when NaOH was used as a base.

The position of the potassium ion with respect to the skeleton of **1** was defined by the angles φ_n(C(4)—O(5)—Dy(6)—$Na^+{}_n$), and α_n (O(5)—Dy(6)—Na^+n) and the bond length D_n (Dy(6)—Na^+n). The position of the water molecules H(j)—O(i)—H(j+1) were defined by the angles φ_i(C(4)—O(5)—Dy(6)—O(i)), α_i (O(5)—Dy(6)—O(i)), and φ_j (O(5)—Dy(6)—O(i)—H(j)) (see. Fig. 2).

As in the preceding cases, two variants of the solvate environment were considered: Dy_2(D-Tart)(L-Tart)$(H_2O)_8{}^{2-} \cdot Na^+$ (model 3) and Dy_2(D-Tart)(L-Tart)$(H_2O)_{10}{}^{2-} \cdot Na^+$ (model 4). The skeleton variables for the optimized conformations **1m** and **1n** and the geometric parameters of **1m** are listed in Tables 3 and 4. Despite the differences in CN, the parameters of the **1m** and **1n** skeletons are very close, with differences never exceeding 4°. The theoretical constants ${}_mP$ for **1m** and **1n** are $829 \cdot 10^{-15}$ emu and $802 \cdot 10^{-15}$ emu, respectively, which is in satisfactory agreement with ${}_mP_{\text{exp}}(\mathbf{1}) = 900 \cdot 10^{-15}$ emu.

For D-dimer **2** the most symmetric forms have three C_2-*axes* (Fig. 3). In this case the trigonal-bipyramidal geometry of the environment of metal ions[10] (α_2 = 180°, α_{13-6-4} = 120°, $\varphi_4 = \varphi_7 = \varphi_{11}$ = 0°) is most favorable. A little less favorable is the octahedral geometry (α_2 = 180°, $\alpha_{13-6-14}$ = 90°, $\varphi_4 = \varphi_7 = \varphi_{11}$ = 0°). The tetragonal environment ($\varphi_4 = \varphi_7 = \varphi_{11}$, $\varphi_4 > 0$; Fig. 3, *a*) is not favorable, since the torsional angles φ_2,

Table 5. Optimized parameters of the structures of hydrated dysprosium(III) D-tartrate with allowance for the coordination of Na^{++}

Angle	Structure (E/kcal mole^{-1})			
	model 3		model 4	
	2a (122.2)	**2b** (122.4)	**2c** (131.1)	**2d** (130.0)
φ_1	120.6	83.0	104.7	97.8
φ_2	−176.6	−180.2	−177.4	−183.7
φ_3	126.8	128.7	118.0	118.2
φ_4	27.8	28.5	44.3	−33.2
φ_5	−75.7	−77.5	−77.8	−69.6
φ_6	−55.5	−66.5	−55.1	−52.5
φ_7	18.2	36.6	11.4	10.4
φ_8	106.2	94.8	122.6	131.9
φ_9	−179.4	−176.3	−171.3	−172.0
φ_{10}	129.2	126.0	112.8	117.0
φ_{11}	28.7	22.3	35.9	21.7
α_1	116.4	115.1	107.3	116.6
α_2	126.8	126.9	120.9	125.1
α_3	123.6	117.9	124.1	122.5
α_4	115.4	119.7	116.2	122.1

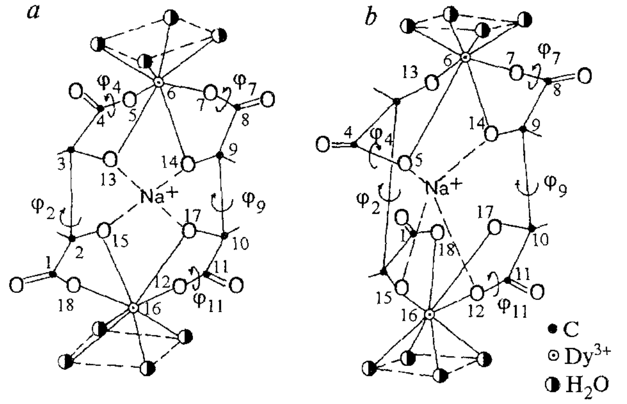

Fig. 4. Most probable forms of **1** and **2** in aqueous solution; *a*-conformation **1a**: $\varphi_2 = -177.2°$, $\varphi_9 = 177.1°$, $\varphi_4 = 11.2°$, $\varphi_7 = -8.5°$, $\varphi_{11} = -14.0°$; *b*-conformation **2a**: $\varphi_2 = -176.6°$, $\varphi_9 = -176.4°$, $\varphi_4 = 27.8°$, $\varphi_7 = 18.2°$, $\varphi_{11} = 27.8°$.

φ_9 of the ligand differ markedly from the optimum value 180 °C. Optimization of the geometry (without regard to the hydrate environment) showed that the smallest E values corresponded to the conformation with trigonal-bipyramidal geometry; while the theoretical PBR constants correspond to the tetragonal geometry. As in the case of **1**, agreement with the experiment is achieved only if the hydrate environment of the Dy^{3+} ion and coordination of the Na^+ ion to **2** are considered. As compared with **1**, the cavity in **2**, formed by the O(5), O(13), O(7), O(14), O(12), O(17), O(15), O(18) atoms must favor coordination. Analogously to the case of **1**, the same procedure was used for model 3 — $Dy_2(D\text{-Tart})(H_2O)_8{}^{2-} \cdot Na^+$ and model 4 $Dy_2(D\text{-Tart})(H_2O)_{10}{}^{2-} \cdot Na^+$. The optimized skeletal variables for conformations **2a**, **2b** (model 3) and **2c**, **2d** (model 4) are listed in Table 5. Rather close agreement with ${}_mP_{\text{exp}}(\mathbf{2})$ is observed only for **2a**, **2b**, that is, only model 3 fits the experiment. In **2a**, **2b** the Dy^{3+} ion is outside the cavity and coordinated by the nearest oxygen atoms O(5), O(14), O(12), O(15) (Fig. 4, *b*). In accordance with the E values for **2a**, **2b** the theoretical value of ${}_mP$, determined by the Boltzmann factor, is $874 \cdot 10^{-15}$ emu, this coincides with the experiment within the limits of 5 %. A detailed description of the geometry of the solvate environment for **2** (exemplified by **2a**) is given in Table 6.

Thus, the most probable form of **1** in aqueous solutions is conformation **1a** (Fig. 4, *a*); for **2** it is **2a** (Fig. 4, *b*), *i.e.*, model 3 is the most reliable. For **1a** the Dy^{3+} environment is a slightly distorted quadratic antiprism ; the Na^+ ion has the O(13), O(14), O(15), O(17) atoms in its nearest environment. Dy^{3+} in **2a**, **2b** is in a distorted tetragonal environment ($\alpha_2 = 128°$, $\alpha_{13-6-14} = 67°$, $\varphi_4 \geq \varphi_7 \geq \varphi_{11}$; $\varphi_4 > 0$). The environment of the Dy^{3+} ions is a distorted quadratic antiprism; the Na^+ ion is outside the cavity and is coordinated by the nearest oxygen atoms, O(5), O(14), O(12), O(15). Molecular mechanics calculations also confirm the absence of the stereoselective formation of **1**. The steric energy differences for **1a** and **2a**, **2b** do not exceed 0.1 kcal mole^{-1}, amounting to log $Q_{q-1,1}$ = 0.073 u logβ, which is within the limits of experimental error.

Table 6. Geometry parameters of structure **2a**

Angle	Value	Angle	Value	Angle	Value
φ_1	120.6	α_1	116.4	φ_{38}	153.0
φ_2	−176.6	α_2	126.8	α_{38}	70.8
φ_3	126.8	α_3	123.6	φ_{41}	71.9
φ_4	27.8	α_4	115.4	α_{41}	72.7
φ_5	−75.7	φ_{26}	13.9	φ_{44}	13.3
φ_6	−55.5	α_{26}	117.3	α_{44}	118.1
φ_7	18.2	φ_{29}	−183.8	φ_{47}	−200.8
φ_8	106.2	α_{29}	143.0	α_{47}	143.7
φ_9	−179.4	φ_{32}	72.2	φ_{50}	−93.1
φ_{10}	129.2	α_{32}	71.5	α_{50}	38.7
φ_{11}	27.8	φ_{35}	155.4	d_{50}	3.55 E
		α_{35}	71.7		

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