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The Structure of Dimeric Dysprosium(III) *d*- and *dl*-Tartrates in Aqueous Solution

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The structures of the ligand and hydrate environments of dysprosium(III) have been determined for dysprosium(III) *d*- and *dl*-tartrates in aqueous solution.

The problem of the estimation of stereoselective effects arises in the study of the interaction of metal ions with stereoisomeric ligands (in particular with tartaric acid derivatives). Stereoselectivity is observed if the relative stability $\Delta\lg\beta$ of diastereoisomeric complexes differs from the purely statistical value, *i.e.* the structural factor $\lg Q_{q-n,n}$ [equation (1)] exceeds the error of the determination of $\Delta\lg\beta$,[1,2]

$$\lg\beta = \lg\beta_{q-n,n} - \lg\beta_{q,0} = \lg K_S + \lg Q_{q-n,n} \qquad (1)$$

where the symbol $q-n,n$ refers to the diastereoisomer in which n out of q *d*-ligands have been replaced by *l*-ligands and $K_S = q!/(q-n)!n!$ is the statistical factor.

In the present study, we propose a new approach to the investigation of stereoselectivity, which is applicable to labile complexes of paramagnetically anisotropic metal ions. The principal structural method is that of paramagnetic double refraction.[3–6] The PDR constant mP depends on the spatial dispositions of the bonds relative to the chosen molecular coordinate system and reflects the stereochemistry of the complex [equation (2)].

$$mP = (2\pi N/45kT)(b_{ii}k_{ii} + 6b_{ij}k_{ij}) \qquad (2)$$

Parameters b_{ij} and k_{ij} are the components of the tensors of the optical bond polarisability and magnetic susceptibility (MS) of the metal ions. The structure of the ligand and hydrate environments of the complex is optimised by the method of molecular mechanics (MM). The theoretical constant mP is calculated for each conformation, corresponding to a local minimum. Conformations with the lowest steric energies E and constants mP close to the experimental values are selected as the most reliable. The Dashevskii–Plyamovatyi model (the MIND program), which reliably reproduces the relative steric energies and hence the values of $\lg Q_{q-n,n}$, was used in the molecular mechanics calculations. (The parameters required for the calculations by the MIND program and of the PDR constants were discussed previously).[6] This approach is applicable to the modelling of the structures of dimeric dysprosium(III) *d*- and *dl*-tartrates $Dy_2(d\text{-L})(l\text{-L})^{2-}$ **1** and $Dy_2(d\text{-L})_2^{2-}$ **2** (d-L^{4-} and l-L^{4-} are *d*- and *l*-tartrate anions). The formation of the dimers **1** and **2** is not stereoselective and $\lg Q_{q-1,1} = 0.03$ $\lg\beta$ units. The torsional (φ) and valence (α) angles, which determine the geometry of the dimers **1** and **2**, are presented in Figs. 1(*a*) and 2(*a*). According to the literature[7,8] the tetragonal geometry of the environment of the metal ions is most suitable for the *dl*-dimers [the O(5), O(13), O(7) and O(14)

atoms are in one plane (Fig. 1)]. Both the highly symmetrical forms[9] [σh, i, C_2 (Fig. 1(*a*)] and the forms with only a centre of inversion[10] i [Fig. 1(*b*)] are then produced. The most symmetrical structures of the *d*-dimers have only three C_2 axes. The trigonal-bipyramidal geometry ($\alpha_2 = 180°$, $\alpha_{13\text{-}6\text{-}14} = 120°$, $\varphi_4 = \varphi_7 = \varphi_{11} = 0°$) is then most favourable. The octahedral geometry ($\alpha_2 = 180°$, $\alpha_{13\text{-}6\text{-}14} = 90°$, $\varphi_4 = \varphi_7 = \varphi_{11} = 0°$) is somewhat less favourable. The tetragonal environment {$\varphi_4 = \varphi_7 = \varphi_{11}$, $\varphi_4 > 0$ [Fig. 2(*a*)]} is unfavourable, since the ligand torsional angles φ_2 and φ_9 differ appreciably from the optimum value of 180°. Optimisation of the geometries of the six initial structures of the dimer **1** showed, however, that the low-symmetry conformations, having only a centre of inversion [Fig. 2(*a*)], have the lowest steric energy, while for the dimer **2** the conformations with the trigonal-bipyramidal geometry have the lowest energy. Preliminary calculation of the constants *mP* showed that the experimental constants correspond solely to the tetragonal geometry of the environment of the highly symmetrical conformations of the dimers **1** and **2**. In order to resolve this contradiction, several models of the hydrate environment were considered.

(i) In addition to the donor atoms of the ligand, four water molecules are coordinated to the dysprosium ion [the coordination number (CN) is 8].

(ii) An additional five water molecules are coordinated to each dysprosium ion (CN = 9).

However, the theoretical values of *mP* for the most favourable conformations are also far from the experimental values and the conformations of the skeleton are similar to Fig. 1(*b*) for the dimer **1** and to Fig. 2(*b*) for **2**. In the next stage of the modelling process, the same models **1** and **2** were used but with additional allowance for the possible coordination of the Na^+ ion (the species **1** and **2** predominate in an alkaline medium; a NaOH solution was used in order to alter the basicity of the medium). This can also be promoted (for modelling of the first type) by the presence of a cavity in the dimer **2**, formed by the O(5), O(13), O(7), O(14), O(12), O(17), O(15) and O(26) atoms [Fig. 2(*a*)], in which the Na^+ ion may be stabilised. Such modification of the models **1** and **2** will be henceforth designated as models **3** and **4**, respectively.

Only when the additional hypothesis of the coordination of the Na^+ ion is used do the geometries of the dimers **1** and **2** lead to conformations with acceptable theoretical values of *mP*. For the dimer **1**, the model **3** yields $mP = 829 \times 10^{-15}$ emu (conformation **1a**) while the model **4** gives rise to $mP = 802 \times 10^{-15}$ emu (conformation **1b**). The model **3** yields a somewhat better agreement with the experimental value $mP = 900 \times 10^{-15}$ emu. The parameters determining the geometry of the ligand skeleton in the conformations **1a** and **1b** then differ by not more than 4° and correspond to the highly symmetrical form [Fig. 1(*a*)]. For the dimer **2**, the conformations **2a** and **2b**, corresponding to the model **3** alone, have reasonable values of *mP*: $mP = 766 \times 10^{-15}$ emu for the conformation **2a** and $mP = 1042 \times 10^{-15}$ emu for the conformation **2b**; E**2b** – E**2a** = 0.2 kcal mol^{-1}. In conformity with the difference between the steric energies, the theoretical value of *mP*, calculated on the basis of the Boltzmann distribution, proved to be 874×10^{-15} emu. This is in excellent agreement with the experimental value $mP = 860 \times 10^{-15}$ emu for the dimer **2**.

Thus, the forms in which the dimers **1** and **2** most probably exist in solution are the conformations **1a** [Fig. 3(*a*)] and **2a** [Fig. 3(*b*)], respectively, *i.e.* the model **3** is most reliable. In the conformation **1a**, the environment of the Dy^{3+} ions is represented by a slightly distorted square antiprism; the Na^+ ions have an immediate environment comprising the O(13), O(14), O(15) and O(17) atoms. The environment of Dy^{3+} in the conformations **2a** and **2b** has a distorted tetragonal geometry ($\alpha_2 = 128°$, $\alpha_{13\text{-}6\text{-}14} = 67°$, and $\varphi_4 \simeq \varphi_7 \simeq \varphi_{11}$; $\varphi_4 > 0$). The environment of the Dy^{3+} ions is represented by

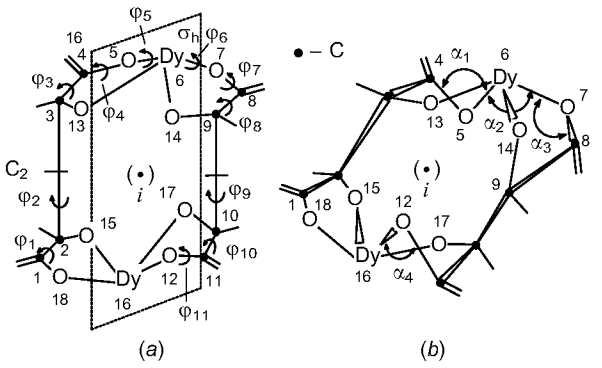

Fig. 1 The idealised tetragonal geometry of dysprosium(III) *dl*-tartrates; parameters specifying the geometry: (*a*) the highly symmetrical form; (*b*) the weakly symmetrical form.

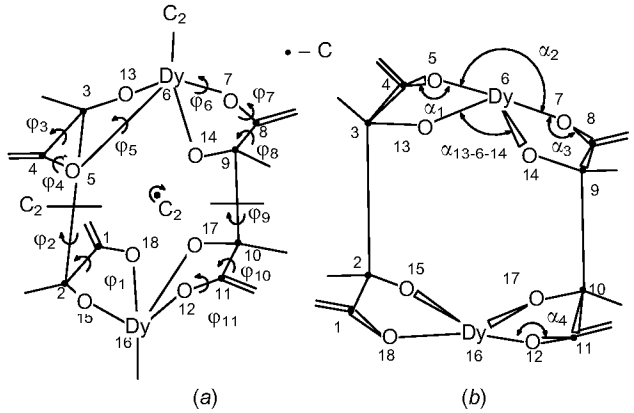

Fig. 2 Parameters determining the geometry of dysprosium(III) *d*-tartrate: (*a*) tetragonal geometry of the environment of Dy^{3+}; (*b*) trigonal-bipyramidal geometry.

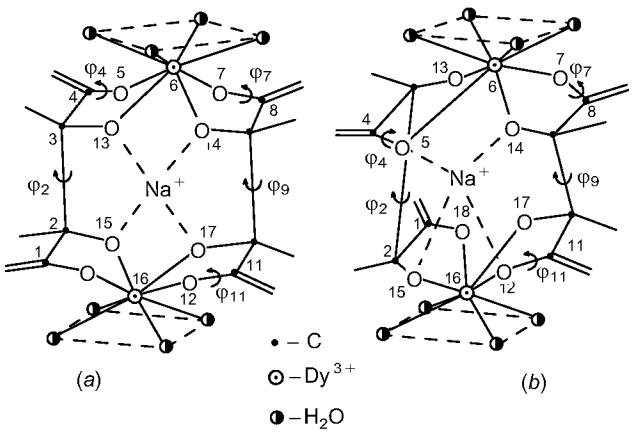

Fig. 3 The most probable forms in which the dimers **1** and **2** exist in aqueous solution: (*a*) conformation **1a** ($\varphi_2 = -177.2°$, $\varphi_9 = 177.1°$, $\varphi_4 = 11.2°$, $\varphi_7 = -8.5°$, $\varphi_{11} = -14.0°$); (*b*) conformation **2a** ($\varphi_2 = -176.6°$, $\varphi_9 = -179.4°$, $\varphi_4 = 27.8°$, $\varphi_7 = 18.2°$, $\varphi_{11} = 27.8°$).

a distorted square antiprism; the Na^+ ions are outside the cavity and are coordinated to the nearest O(5), O(14), O(12) and O(15) oxygen atoms. The molecular mechanics calculations also confirm the absence of stereoselectivity in the formation of the dimer **1**. The difference between the steric energies of the conformations **1a**, on the one hand, and **2a** and **2b**, on the other, does not exceed 0.1 kcal mol^{-1}, which yields $\lg Q_{q-n,n} = 0.073$ lgβ units, *i.e.* a value within the limits of experimental error.

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