Steric structure and thermodynamic aspects of the complexes of dysprosium(III) with aminobenzoic acids in aqueous solutions

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Steric structures of dysprosium(III) aminobenzoate complexes with the 1:1 and 1:2 molar ratio in aqueous solutions were determined on the basis of pH-metric and paramagnetic birefringence data. An increase in conjugation observed for the series of the acids, *viz.*, benzoic, *meta*-, *ortho*-, and *para*-aminobenzoic acids, results in the increased stability of the complexes with the 1:1 and 1:2 composition. In the case of *para*-aminobenzoic acid, the polyhedra $[DyL(H_2O)_6]^{2+}$ and $[DyL_2(H_2O)_4]^+$ are cubes with the ligands coordinated to one and two edges, respectively. In the case of *meta*-aminobenzoic acid, the polyhedra $[DyL(H_2O)_6]^{2+}$ and $[DyL_2(H_2O)_4]^+$ are a dodecahedron with the ligand coordinated to one edge and a square anti-prism with the ligands coordinated to two edges, respectively. In the case of *ortho*-aminobenzoic acid, both the 1:1 and 1:2 complexes have structures that are intermediate between the structures of *meta*- and *para*-aminobenzoic acids.

Key words: dysprosium(III), aminobenzoic acids, complex, structure, stability, paramagnetic birefringence.

The purpose of the present work is to investigate the stability constants and the structures of the complexes of dysprosium(III) ion with aminobenzoic acids in aqueous solutions. Aminobenzoates are of interest due to the conjugation effect between the NH_2 group and the phenyl ring. This conjugation affects not only the stability of the complexes with rare-earth elements[1] (REE), but also their steric structure.

The main method for investigating the structure of the complexes of rare-earth ions (REI) in the solutions is the paramagnetic birefringence method (PMB) using the characteristic parameter ${}_mP$, which depends on the anisotropy of the optical polarizability of the ligand environment (Δb) and the anisotropy of the paramagnetic susceptibility (γ_k) of the central ion (Eq. (1)).

$$ {}_mP = 4\pi N_A \Delta b \gamma_k, \qquad (1) $$

where N_A is Avogadro's number.

Results and Discussion

The dysprosium(III) ion, which exhibits considerable magnetic anisotropy,[2] was chosen as the central ion. The stability constants and the molar constants of paramagnetic birefringence of the aminobenzoate complexes are given in Table 1. The stability constants of the *meta*-aminobenzoate complexes are close to those of the benzoate complexes.[3] In the case of the *ortho*- and *para*-isomers, the increased stability of the complexes are caused by the opposite effects of two factors. The negative charge on the carboxyl group of the *ortho*- and *para*-aminobenzoates is increased due to the conjugation with the amino group, which favors the increasing stability of the complexes. On the other hand, an increase in the negative charge on the carboxyl group results in more effective hydration of the anion and the decreased stability of the corresponding complexes in aqueous solutions.[4] The values of ${}_mP$ given in Table 1 may be used for structural analysis of the complexes by

Table 1. Constants of dissociation and complex formation of *ortho*-, *meta*-, and *para*-aminobenzoic acids

Dy^{3+}	Acid	H^+	log β_{stab}	${}_mP \cdot 10$/emu
		pK = 4.84±0.05 (*meta*)		
1	1	0[a]	1.4±0.02	100±40
1	1	1[b]	2.1±0.1	220±30
1	2	2[c]	4.0±0.05	230±10
		pK = 5.0±0.05 (*ortho*)		
1	1	1	2.18±0.05	341±22
1	2	2	4.46±0.09	510±34
		pK = 4.95±0.05 (*para*)		
1	1	1	2.25±0.05	430±34
1	2	2	4.63±0.07	860±34

[a] 1:1:0 — Dy^{3+} + HL = $[DyHL]^{3+}$. [b] 1:1:1 — Dy^{3+} + HL = $[DyL]^{2+}$ + H^+. [c] 1:2:2 — Dy^{3+} + 2 HL = $[DyL_2]^+$ + 2 H^+.

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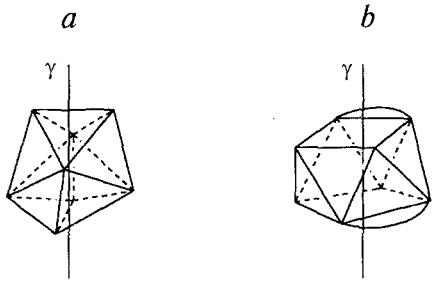

Fig. 1. Dodecahedron and square anti-prism as the structures of the coordination polyhedra of the Dy^{III} benzoate and aminobenzoate complexes with the 1:1 (*a*) and 1:2 (*b*) compositions.

making a comparison between them and the ${}_mP$ values calculated for a particular structure.

The value of Δb, which is determined by the tensor additive scheme, depends on the ligand orientation with respect to the main magnetic axis of the central ion.[2] According to the stereochemical Kipert model (see Ref. 6), the octa-vertex polyhedron characteristic of the Dy^{3+} aqua-ion and its complexes may exist as a square anti-prism, dodecahedron, and cube. Earlier, we showed[2] that the complex $[Dy(BzO)(H_2O)_6]^{2+}$ (BzO is the benzoate-anion) is a distorted dodecahedron, in which BzO^- is coordinated to one of its edges (see Fig. 1, *a*). The coordination of the second ligand results in a structure similar to a square anti-prism (Fig. 1, *b*), in which the dihedral angle between the ligands is 110° (see Ref. 5). As we have noted before, involving the unshared electron pair (UEP) of the NH_2 group in conjugation results in an increase in the electron-donating ability of the carboxyl group,[1] which should stabilize the protonated form and the *ortho*- and *para*-aminobenzoate complexes, but destabilize the anion form. Therefore, the components of the polarizability tensor of the molecular, but not the anionic form of the ligand, were used for calculating the Δb of the coordinated ligand (Table 2). The components of the polarizability tensor of aminobenzoic acids and their ions given in Table 2 have been calculated by the additive scheme using the corresponding

Table 2. Main components of the tensor of polarizability of the molecular and anionic forms of aminobenzoic acids

Acid	Form of acid	b_1	b_2	b_3
para	HL	22.93	15.99	10.74
	L^-	19.68	16.09	10.69
ortho	HL	20.61	18.31	10.74
	L^-	17.36	18.41	10.69
meta	HL	20.61	18.31	10.74
	L^-	17.36	18.41	10.69

Note. HL and L^- are the molecular and anionic form of the acid.

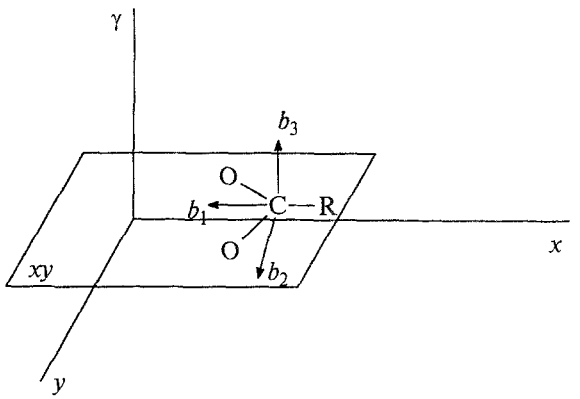

Fig. 2. Orientation of aminobenzoate anions to the main magnetic axis of dysprosium(III) in the investigated complexes ($R = C_6H_4NH_2$).

values for benzoic acid, anions of benzoic acid, and the C(arom)—NH_2 bond (see Ref. 7, 8). In fact, the maximum ${}_mP_{theor}$ value, calculated using the components of the polarizability tensor of the *para*-aminobenzoic acid anion, is $353 \cdot 10^{15}$ emu, while the experimental value is $430 \cdot 10^{15}$ emu. It coincides with the value of ${}_mP$ calculated using the b_1, b_2, and b_3 values of the molecular form of the *para*-isomer, which is situated in the *xy*-plane perpendicular to the main magnetic axis of Dy^{3+} (Fig. 2). When the structure of *ortho*-aminobenzoate is analyzed, the conjugation effect should be also taken into account. However, unlike the *para*-isomer, the experimental value (${}_mP = 341 \cdot 10^{15}$ emu) is lower than the value calculated under conditions of the coordination in the *xy*-plane (${}_mP = 430 \cdot 10^{15}$ emu) (Fig. 2). This may be caused by both the bend of the NH_2 group by the $\varphi = 21°$ angle relative to the plane of the ring (Fig. 3), which results in the following expressions for b_1, b_2, and b_3:

$$b_1 = b_1\cos^2 60° + b_2\sin^2 60°$$

$$b_2 = b_1\sin^2 60°\cos^2\varphi + b_2\cos^2 60°\cos^2\varphi + b_3\sin^2\varphi$$

$$b_3 = b_1\sin^2 60°\sin^2\varphi + b_2\cos^2 60°\sin^2\varphi + b_3\cos^2\varphi,$$

and by the bend of the plane of the carboxyl group relative to the *xy*-plane due to the realization of the *a* structure (see Fig. 1).

The experimental value of ${}_mP$ of the *meta*-aminobenzoate is $220 \cdot 10^{15}$ emu, which is in agreement with the value calculated for $[Dy(BzO)(H_2O)_6]^{2+}$ (see Fig. 1, *a*). According to the experimental value of ${}_mP$, the coordination of the second *meta*-aminobenzoate results in formation of a structure analogous to the structure of $[Dy(BzO)_2(H_2O)_4]^+$ (see Fig. 1, *b*).

However, the ${}_mP_{exp}$ values of the 1:2 complexes of the *ortho*- and *para*-isomers are not in agreement with those calculated for a square anti-prism. Thus, the ${}_mP_{exp}$ of the *para*-isomer corresponds to the coordination of the ligands to the *xy*-plane. The orientation of *ortho*-

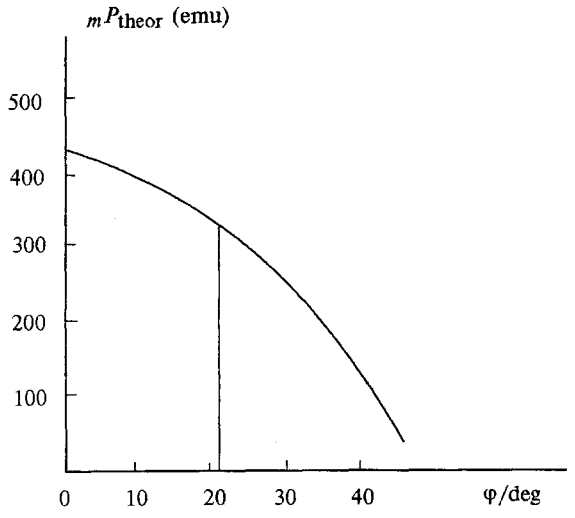

Fig. 3. Dependence of $_mP_{theor}$ of the *ortho*-aminobenzoate complex with the 1:1 composition on the bend angle of the NH_2 group relative to the ring plane (φ).

aminobenzoates to each other (the dihedral angle between the planes is 129°) indicates a structure intermediate between the structures of the *meta*- and *para*-isomers.

It was suggested by Kipert[5] that the ML_2Y_4 complexes, where M is the central ion, L is a bidentant ligand, and Y is a monodentant ligand, could be described by seven structures corresponding to the minimum of the total energy of repulsion of all of the chemical bonds in the complex. The structures $[Dy(BzO)_2(H_2O)_4]^+$ and $[Dy(AcO)_2(H_2O)_4]^+$ (AcO is the acetate ion) are identical to one of the above-mentioned structures. However, in the Kipert configurations, the bidentant ligands can not be situated in one plane perpendicular to the local symmetry axis of the highest order, which coincides with the main magnetic axis of Dy^{3+}. The analysis of the X-ray structural data performed by Kipert[5] attests to the fact that the coordination of the ligands with a prolonged π–system does not agree with their stereochemical disposition relative to the central ion, which is found on the basis of the minimization of the total energy of the chemical bond repulsion. Thus, in the $[Ba(Phen)_2(H_2O)_4]^+$ and $[Sr(Phen)_2(H_2O)_4]^+$ complexes (see Ref. 5), the 1,10-phenanthroline molecules are situated in one plane (see Fig. 4) perpendicular to the local symmetry axis of the highest order. Taking into account the above mentioned considerations, it is natural to conclude that the coordination of two *para*-aminobenzoates results in a structure analogous to that depicted in Fig. 4.

Thus, the structure of the 1:1 and 1:2 complexes of the *meta*-isomer does not differ from the structure of the benzoate complexes of the analogous composition. The complexes of the *para*-isomer exhibit a distorted cubic structure, while the structure of the *ortho*-isomer is intermediate between the structures of the complexes of

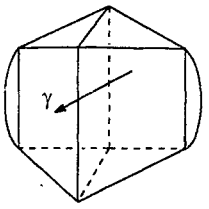

Fig. 4. Distorted cube as the structure of the coordination polyhedron of the Dy^{III} *para*-aminobenzoate complex with the 1:1 and 1:2 compositions.

the *meta*- and *para*-isomers. Therefore, an increase in the conjugation effect in *ortho*- and *para*-aminobenzoates compared to that in *meta*-aminobenzoates results not only in the increased stability of the complexes of the former with Dy^{3+}, but also in changes in their structures.

Experimental

The paramagnetic birefringence was measured on a device described earlier.[9] The molar constant $_mP$ was calculated with the formula

$$_mP = \frac{CMSn}{(n^2+2)^2wd},$$

where C is a constant of the instrument, M — molecular weigh, w — a weigh proportion of the dissolved substance, S — value of birefringence, n — index of refraction, and d — density of the solution. pH-Metric titration was performed on a 673 M pH-meter using varying volume. All of the measurements were carried out in thermostatically controlled cells at 25±0.05 °C for the different ratios between Dy^{3+} and the ligand in the 2.0—7 pH interval. The $_mP$ values of the complexes that formed were obtained by mathematically processing the paramagnetic birefringence data (using the CPEESSP program[10]) on the basis of the complexation constants calculated from the pH-metric data. Concentrations of the solutions of dysprosium(III) nitrate of pure analytical grade were determined by titration with Trilon B.[11] The aminobenzoic acids of pure grade were purified to remove impurities by re-crystallization from water—ethanol solutions.

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