

X-Ray Diffraction Study of Isomorphous Crystal Nonahydrates of Aluminum, Gallium, and Scandium Perchlorates

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Received May 23, 2011

Abstract—Crystal structures of isomorphous crystal nonahydrates of aluminum, gallium, and scandium perchlorates were determined by the X-ray crystal analysis at room temperature. The estimate of associates present in concentrated solutions was carried out by the method of X-ray diffraction in aqueous solutions of aluminum perchlorate.

DOI: 10.1134/S1070363212040019

The crystal structure of crystalline nonahydrates of perchlorates of the III group metals of the periodic system can be considered within the limits of the structural conception on concentrated aqueous solutions of electrolytes, which we have developed earlier [1–5]. This conception is based on the comparison of the physicochemical properties and solubility polytherm of a salt [6–8]. According to this model of the structure of aqueous solutions, the concept of sibotactic groups is the key point. The notion of a sibotactic group was used for the first time [9] to develop a model conception of the structure of concentrated solutions [10], where the sibotactic group was defined as a space mode of mutual ordering particles: a structural type of associates formed in solutions of pre-eutectic concentrations and dominant at posteutectic concentrations.

There are published data confirming the presence of sibotactic groups in concentrated solutions of inorganic salts of various character. The associates $\text{Ni}_2\text{Cl}_4 \cdot 12\text{H}_2\text{O}$ were detected and characterized in a concentrated solution of nickel chloride by the neutron scattering method [11]. The presence of M_2Cl_2 species was reported in [12] on the basis of the NMR study of solutions of potassium, rubidium, and cesium chlorides. For example, in cesium chloride solutions, starting from the concentration of 5 mol/1000 g of H_2O (in the pre-eutectic region), the corresponding dimers

appear. The eutectic in the solubility polytherm corresponds to the salt concentration of 8 mol/1000 g of H_2O ($m_e = 8$). The X-ray scattering method applied to study the influence of salt nature on the water structure [13–15] has allowed us to estimate a size of sibotactic groups and the amount of formula units entering in the composition of the groups dominating in solution [13].

It follows from the published data and our data on the size of a sibotactic group [13] that it contains two formula units of a corresponding crystal hydrate or anhydrous salt [14]. To find out a correspondence between the composition of sibotactic groups in the concentrated post-eutectic solution and the composition of the solid phase unit cells, the data on the structure of isomorphous nonahydrates crystallizing from aqueous solutions of their perchlorates at room temperature are necessary. No X-ray structural data on the subjects under study were published.

The X-ray structural study of the crystal structure of the hydrates of aluminum **I**, gallium **II**, and scandium **III** perchlorates under study has shown that they are isomorphous compounds. Metal cations in their structure are bound with six water molecule to form a coordination polyhedron in the form of ideal octahedron (Fig. 1). The adjacent octahedra interact with water molecule by means of hydrogen bonds $\text{O}-\text{H}\cdots\text{O}$ [for compound **I**: $\text{O}^2\cdots\text{O}^1$ 2.639(5), $\text{H}^{2b}\cdots\text{O}^1$

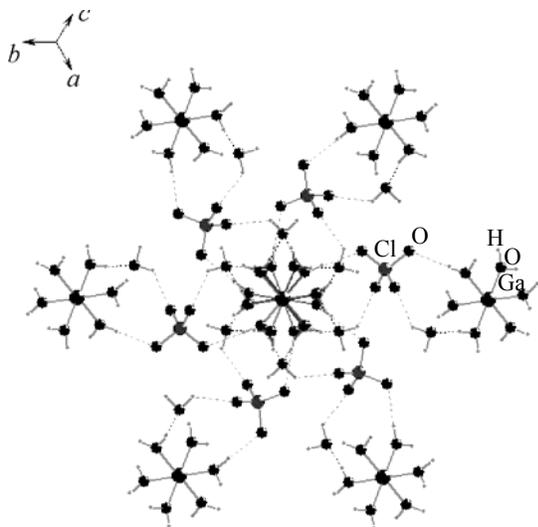


Fig. 1. Structure of crystal nonahydrate of gallium perchlorate.

1.71(5) Å, $O^2H^{2b}O^1$ 172.9°; for compound **II**: $O^1\cdots O^2$ 2.632(5), $H^{1b}\cdots O^2$ 1.75(5) Å, $O^1H^{1b}O^2$ 172.2°; for compound **III**: $O^2\cdots O^1$ 2.636(5), $H^{2a}\cdots O^1$ 1.74(5) Å, $O^2H^{2a}O^1$ 172.8°, to form infinite columns along the third-order axis. Each octahedron is bound with an adjacent octahedron through three water molecules and in total appears to be surrounded by six H_2O molecules (Fig. 2). Such metal-water columns arranged along the third-order axes are separated in the structure by slightly distorted $[ClO_4]^-$ tetrahedra. Weak hydrogen bonds between oxygen atoms of the perchlorate ion and water molecules, both bound and unbound with metal cations, impart the stability to the three-dimensional structure. For compound **I**: $O^1\cdots O^4$ 2.767(5), $H^{1a}\cdots O^4$ 2.15(5) Å, $O^1H^{1a}O^4$ 135.1° and $O^2\cdots O^3$ 2.771(5), $H^{2a}\cdots O^3$ 1.89(5) Å, $O^2H^{2a}O^3$ 173.7(1)°; for compound **II**: $O^2\cdots O^4$ 2.745(5), $H^{2a}\cdots O^4$ 2.06(5) Å, $O^2H^{2a}O^4$ 131.3° and $O^1\cdots O^3$ 2.800(5), $H^{1a}\cdots O^3$ 1.98(5) Å, $O^1H^{1a}O^3$ 174.4(1)°; for compound **III**: $O^1\cdots O^4$ 2.757(5), $H^{1a}\cdots O^4$ 2.22(5) Å, $O^1H^{1a}O^4$ 132.3(1)° and $O^2\cdots O^3$ 2.773(5), $H^{2b}\cdots O^3$ 1.97(5) Å, $O^2H^{2b}O^3$ 167.3° (Fig. 2).

As the quantitative measure of the cation–water interaction we have accepted the symmetrized force constant F_{M-O}^s (A_g) calculated with the use of the totally symmetrical stretching vibration ν_{M-O}^s (A_g) of aqua complexes detected in the Raman spectra of aqueous solutions [16].

$$F_{M-O}^s = k(\nu_{M-O}^s)^2, k = 1.68 \times 10^{-5} \text{ (mdyne cm}^2/\text{Å)} [17].$$

Symmetrized force constants (F_{M-O}^s [mdyne cm²/Å]) and bond lengths (r_{M-O} [Å]) of metal–oxygen bonds

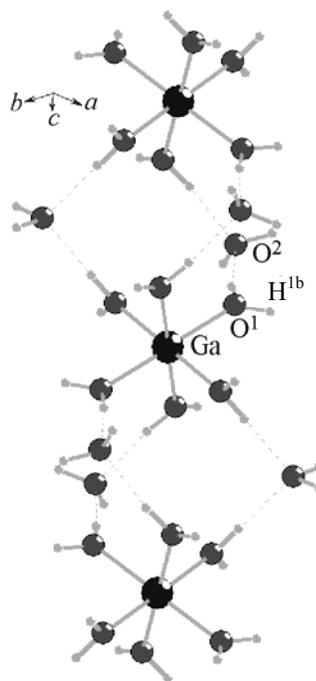


Fig. 2. Fragment of structure of crystal nonahydrate of gallium perchlorate.

(M–O) determined on the basis of X-ray crystal analysis [18–20 and the present work] are compared in Fig. 3. The stronger is the bond of a cation with water of the first hydrated shell, the shorter is the length of the M–O bond in a crystal hydrate of the corresponding perchlorate.

It is seen from Table 1 that the unit cell contains two formula units of a corresponding crystal hydrate ($Z = 2$). The linear dimension of a sibotactic group (diameter) was found from the experiment on X-ray scattering in solution (see below). Diffractograms of aluminum perchlorate solutions in the range of concentrations 0–1.75 mol/1000 of g of water are presented in Fig. 4. Resolved peaks in the region of greater angles belong to a cell material, aluminum. The increase in the aluminum perchlorate concentration results in a decrease in the intensity of water halo, its broadening, and displacement of the maximum to the region of smaller angles. It points to a gradual destruction of the native water structure. The decrease in the halo intensity occurs up to a certain concentration of the salt (eutectic, 1 m. solution), after which the intensity remains practically constant. In the posteutectic 1.5 and 1.75 m. solutions a new halo appears with a maximum which does not coincide with

Table 1. Main crystallographic data and some structure refining parameters

Parameter	Al(ClO ₄) ₃ ·9H ₂ O I	Ga(ClO ₄) ₃ ·9H ₂ O II	Sc(ClO ₄) ₃ ·9H ₂ O III
Formula	H ₁₈ AlCl ₃ O ₂₁	H ₁₈ GaCl ₃ O ₂₁	H ₁₈ ScCl ₃ O ₂₁
<i>M</i> , g mol ⁻¹	487.47	530.21	505.45
Temperature, K	293(2)	293(2)	293(2)
Wavelength, Å	0.71073	0.71073	0.71073
Crystal system	Trigonal	Trigonal	Trigonal
Space group	<i>R</i> -3 <i>c</i>	<i>R</i> -3 <i>c</i>	<i>R</i> -3 <i>c</i>
<i>a</i> , Å	10.120(3)	9.9875(12)	10.109(3)
<i>α</i> , deg	106.72(2)	106.647(9)	106.79(2)
<i>V</i> , Å ³	869.5(4)	837.55(16)	865.1(4)
<i>Z</i>	2	2	2
<i>d_x</i> , g cm ⁻³	1.862	2.102	1.940
<i>μ</i> , mm ⁻¹	0.680	2.227	0.991
Range of <i>θ</i> angles, deg	3.85–36.05	2.54–27.50	2.51–36.00
Amount of collected/independent reflexes	4802/1301	7745/647	8237/1336
Completeness of collecting reflexes (<i>θ</i> / %)	36.05/93.9%	27.50/100.0%	36.00/97.2%
Factor <i>R</i> ₁	0.0766	0.0580	0.0414

that of water. The shift of the maximum into the region of smaller angles, as compared to the water halo, suggests that interplanar distances are changed. It points to the formation of a new structure with different parameters. The cryoscopy data confirm it: the system has a eutectic in a 1.09 M solution, whereas in a 1.5 M solution there is a chemical compound strongly enriched with water, and starting from the concentration 1.75 mol/1000 g of water, the solution vitrifies. The linear dimension (diameter) of a

sibotactic group in a posteutectic solution determined by Debye–Scherer method [21] is 19–21 Å.

Existence in a solution of heterogeneity regions with a size less than two formula units of a corresponding solid compound would not allow the appearance of ordering characteristic of a solid substance, as in this case the main distinctive feature (three-dimensional space reproduction of a structure) would be absent. The appearance of sibotactic groups

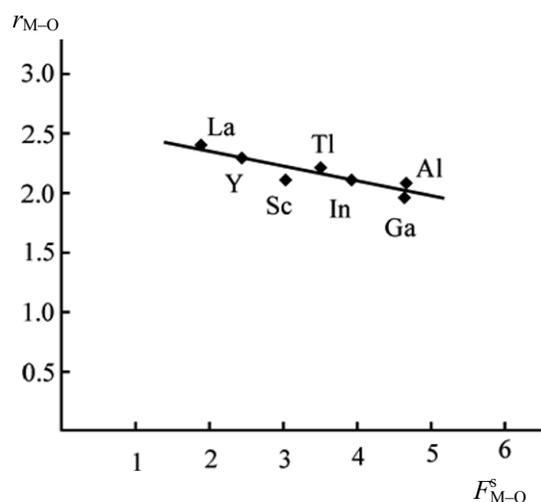


Fig. 3. Correlation of metal-oxygen bond lengths r_{M-O} (Å) and symmetrized force constants F_{M-O}^s (mdyne/Å) of aqua complexes.

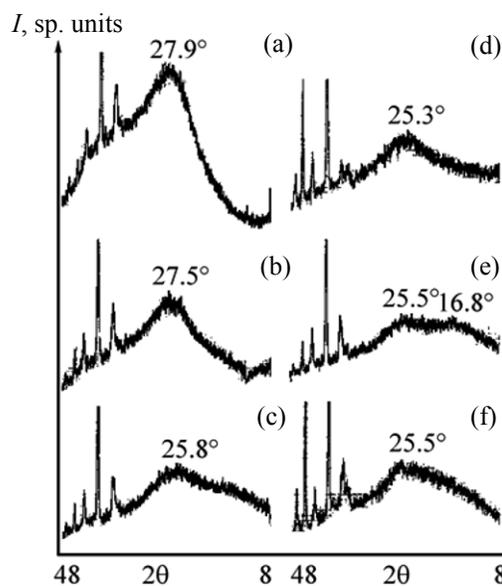


Fig. 4. Diffractograms of aluminum perchlorate solutions. (a) H₂O, (b) 0.5, (c) 1, (d) 1.25, (e) 1.5, (f) 1.75 m. Al(ClO₄)₃ solution in H₂O.

Table 2. Bond lengths (r) and bond angles (φ) in structures of aluminum, gallium, and scandium perchlorates

Bond	r , Å	Angle	φ , deg
Al(ClO ₄) ₃ ·9H ₂ O			
Al ¹ -O ^{2a}	2.0953(19)	O ^{2a} Al ¹ O ^{2b}	92.27(9)
Al ¹ -O ²	2.095(2)	O ^{2b} Al ¹ O ²	87.73(9)
Cl ¹ -O ³	1.431(2)	O ^{3c} Cl ¹ O ³	108.50(19)
Cl ¹ -O ⁴	1.439(4)	O ^{3c} Cl ¹ O ⁴	109.4(2)
O ¹ -H ^{1A}	0.7920	O ^{3c} Cl ¹ O ⁴	108.1(3)
O ² -H ^{2A}	0.8891	O ^{4c} Cl ¹ O ⁴	113.3(4)
O ² -H ^{2B}	0.9284	Al ¹ O ² H ^{2A}	118.0
		Al ¹ O ² H ^{2B}	126.8
		H ^{2A} O ² H ^{2B}	110.9
Ga(ClO ₄) ₃ ·9H ₂ O			
Ga ¹ O ¹	1.951(3)	O ^{1d} Ga ¹ O ^{1e}	90.04(15)
Cl ¹ O ⁴	1.406(6)	O ^{1d} Ga ¹ O ¹	180.0(2)
Cl ¹ O ³	1.425(5)	O ^{1e} Ga ¹ O ¹	89.96(15)
		O ⁴ Cl ¹ O ^{4f}	110.9(6)
		O ⁴ Cl ¹ O ³	109.0(5)
		O ^{4e} Cl ¹ O ³	109.9(4)
		O ³ Cl ¹ O ^{3f}	107.9(5)
Sc(ClO ₄) ₃ ·9H ₂ O			
Sc ¹ O ²	2.0954(13)	O ^{2g} Sc ¹ O ^{2h}	87.67(6)
Cl ¹ O ⁴	1.427(2)	O ^{2g} Sc ¹ O ²ⁱ	92.33(6)
Cl ¹ O ³	1.4306(15)	O ^{2h} Sc ¹ O ²ⁱ	180.0
		O ^{4j} Cl ¹ O ⁴	111.7(2)
		O ⁴ Cl ¹ O ³	109.19(11)
		O ³ Cl ¹ O ^{3j}	108.43(12)

^a Symmetry operators applied to obtain equivalent atoms: $-z, -x, -y$; ^b $-y, -z, -x$; ^c $-z + 1/2, -y - 1/2, -x + 1/2$; ^d $-x + 2, -y, -z$; ^e $-z + 1, -x + 1, -y$; ^f $-y + 1/2, -x + 1/2, -z + 1/2$; ^g y, z, x ; ^h $-z + 1, -x + 1, -y + 1$; ⁱ z, x, y ; ^j $-x + 3/2, -z + 1/2, -y + 1/2$.

larger than two formula units in concentrated aqueous solutions of aluminum perchlorate would mean a possibility of the appearance of regions with a solid structure in a solution, i.e., volume formations, which may be considered already as nuclei of crystals. Such system, probably, would be metastable.

The presence of two formula units in sibotactic groups of solutions of salts crystallizing in anhydrous state is accounted for by an enhanced stability of the fragment M₂Cl₂ formed from two ionic pairs, as compared with separate MCl ionic pairs and M_xCl_x (where $x > 2$) species. As in this case there is no significant effect from hydration, it is obvious that the

main factor, which hinders association, is the entropy factor.

Our research shows that a sibotactic group is an associate containing two formula units. Evidently, owing to a high mobility of particles in a solution, the associate has a short life time insufficient for similar associates to be accumulated in the same place and to form a solid phase. In the case of salts forming crystal hydrates the associates correspond in their composition to the solid unit cell.

EXPERIMENTAL

The crystal hydrate of aluminum perchlorate Al(ClO₄)₃· n H₂O was obtained by dissolution of a freshly precipitated hydrate of aluminum oxide in 57% perchloric acid with subsequent multiple recrystallization from twice distilled water. The crystal hydrate of gallium perchlorate Ga(ClO₄)₃· n H₂O was obtained by the action of 70% perchloric acid (chemically-pure grade) on the corresponding oxide (analytical grade) with a subsequent repeated recrystallization from twice distilled water. The crystal hydrate of scandium perchlorate Sc(ClO₄)₃· n H₂O was obtained by the action of 57% perchloric acid (chemically-pure grade) on the corresponding oxide (analytical grade) with a subsequent double recrystallization from distilled water.

Crystals unstable in air were isolated by isothermal evaporation from aqueous solutions of aluminum, gallium, and scandium perchlorates at room temperature. Among these crystals single crystals suitable for X-ray structural analysis [Bruker SMART CCD-APEX-II, MoK_α, T 210(2) K] were selected. All structures were solved by the direct method and refined in view of anisotropic heat parameters of non-hydrogen atoms using the SHELX-97 program complex [22]. The position of hydrogen atoms was determined by the difference synthesis method. Main crystallographic data and some parameters of structure refining are given in Table 1, and bond lengths and bond angles, in Table 2.

The experiment on the X-ray scattering by aluminum perchlorate solutions was carried out on a DRON 2.0 diffractometer with focusing after Bragg-Brentano with a vertical sample position. Radiation CuK_α (1.54 Å), a Ni filter. The tube operation mode: $U = 18$ kV, $I = 18$ mA. Diffractograms were obtained in the range of (θ) angles from 4° up to 24° at room temperature. The scan rate (θ) was 1 deg min⁻¹. A

duralumin cell of 1 ml capacity supplied by an aluminum foil window for radiation input and output was filled with sample under study. Particle size was estimated by Debye–Scherer formula [21]: $L = \lambda / (B \cdot d \cdot \cos \theta)$, where L is an average size of a scattering particle (Å), λ is the wavelength of CuK_α radiation 1.54 Å, d is the interplanar distance (Å), and θ is a scattering angle (deg). For solutions of posteutectic concentrations 2θ was 25.5°. The sensitivity of the method was 10 nm, and the error of intensity measurement was 3%.

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