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Abstract

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THE NEAREST HYDRATE ENVIRONMENT OF Cu^{2+} IONS IN DILUTE AQUEOUS SOLUTIONS OF $Cu(II)$ SALTS

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The literature data on the hydration numbers of Cu^{2+} ions are contradictory ($^{1-4}$); there is also no agreement in resolving the question of the composition and structure of the nearest environment of these ions in aqueous solutions. In dilute aqueous solutions the Cu^{2+} ion is assigned both coordination number 4 (^{5,6}) and coordination number 6 ($^{7-11}$). In the latter case it is assumed that the H_2O molecules forming the nearest environment of the copper ion in solutions are oriented either at the vertices of a tetragonal bipyramid (^{7,8}), or form a regular octahedron ($^{9-11}$).

In the present work the composition and structure of the nearest environment of the Cu^{2+} ion in dilute aqueous solutions are determined by comparing the electronic absorption spectra of solutions of $Cu(ClO_4)_2$, $CuSO_4$, $CuCl_2$ with the spectra of those crystalline aquocomplexes of Cu(II) in which the nearest environment of the Cu^{2+} ions consists only of water molecules. As such comparison objects we took single crystals:

$$Cu(ClO_4)_2 \cdot 6H_2O,\ CuSiF_6 \cdot 6H_2O,\ (NH_4)_2Cu(SO_4)_2 \cdot 6H_2O,$$

$$K_2Cu(SO_4)_2 \cdot 6H_2O,\ Cs_2Cu(SO_4)_2 \cdot 6H_2O.$$

In the first of these the ion $Cu(H_2O)_6^{2+}$ has the form of a regular octahedron (^{12,13}); in $CuSiF_6 \cdot 6H_2O$ the octahedral ion $Cu(H_2O)_6^{2+}$ is distorted to a small degree trigonally ($^{14-17}$). In crystals of Tutton salts the octahedron $Cu(H_2O)_6^{2+}$ is distorted either tetragonally (^{15}) or rhombically (^{18}).

The spectral absorption curves of plates cut from single-crystalline aquocomplexes, measured by us in natural radiation on an SF-4 spectrophotometer, are shown in Fig. 1.

The absorption spectra of the same preparations were also studied in polarized radiation.

In the latter case, a Frank-Ritter prism was mounted in the SF-4 spectrophotometer; by rotating it, the plane of oscillation of the polarized ray was brought into coincidence with one of the crystallographic axes of the crystal.

As experience showed, the pleochroism of the listed crystals is very considerable: a change in the orientation of the crystal relative to the plane of oscillation of the polarized ray is accompanied by a change in the absorption index of the crystal by up to 50%. At the same time, the positions of the maxima on the spectral absorption curves remain unchanged when the orientation of the crystals is changed (Fig. 1).

It follows from Fig. 1 that the absorption spectrum of $Cu(H_2O)_6^{2+}$ ions in the region 600-900 mμ is very sensitive to the symmetry of the field created by the ligands. The absorption curve of octahedral $Cu(H_2O)_6^{2+}$ ions in the crystal $[Cu(H_2O)_6](ClO_4)_2$ has only one maximum at 798-800 mμ. A slight trigonal distortion of the same ion in the crystalline complex $[Cu(H_2O)_6][SiF_6]$ does not cause splitting of the absorption band, but leads to a shift of the absorption maximum to 830 mμ. On the spectral absorption curve of the $Cu(H_2O)_6^{2+}$ ion in crystals $M_2[Cu(H_2O)_6](SO_4)_2$ there is observed

several inflection points, which gives grounds for regarding this curve as the result of superposition of three absorption curves; such a character of the absorption band of Tutton salts is in good agreement with the assumption of low symmetry of the ions $Cu(H_2O)_6^{2+}$ in their crystal lattices.

The spectral absorption curves of aqueous solutions of $CuCl_2$, $CuSO_4$, and $Cu(ClO_4)_2$ in the region 220-1000 mμ were measured by us point by point on an SF-4 spectrophotometer. The concentration of Cu^{2+} ions was varied from 0.5 g-ion/l to 0.005 g-ion/l. To prevent hydrolysis of the salts, the solutions were acidified with $HClO_4$; the concentration of the latter in the solutions was 1-3 g-mol/l.

In the absorption spectra of aqueous solutions of $CuCl_2$, $CuSO_4$, and $Cu(ClO_4)_2$ two absorption bands are observed; the maximum of the first of them is apparently located in the ultraviolet region, and the maximum of the second in the red region. The absorption of solutions in the region $\lambda < 240$ mμ can hardly be attributed only to the hydrated Cu^{2+} ion, since this radiation is also absorbed by the anions Cl^-, SO_4^{2-}, and ClO_4^-. In the red region of the spectrum the listed anions do not absorb; the absorption band of dilute aqueous solutions of Cu(II) salts, located in the interval 600-900 mμ, does not change its position with a change in the nature of the anion. The optical density of these solutions at an ion concentration $C_{Cu^{2+}} < 0.05$ g-ion/l, measured at $\lambda = 600$-900 mμ, obeys the Bouguer-Beer law.

All these facts give grounds for considering that the long-wavelength absorption band of dilute aqueous solutions of Cu(II) belongs to the hydrated Cu^{2+} ion.

Fig. 1. Spectral absorption curves (χ_λ): **I** —crystals of $Cu(ClO_4)_2 \cdot 6H_2O$ in natural radiation; *a*, *b*, *v* —the same crystal in polarized radiation. *a* —

Fig. 1

Figure 1: Fig. 1

vector **E** of the beam parallel to the 001 axis, b –vector **E** along the 010 axis, v –vector **E** along the 100 axis of the crystal. **II** –aqueous solutions of $CuCl_2$, $CuSO_4$, $Cu(ClO_4)_2 \cdot 6H_2O$. Concentration of Cu^{2+} ions 0.05 g-ion/l. **III** –$CuSiF_6 \cdot 6H_2O$. **IV** –$(NH_4)_2Cu(SO_4)_2 \cdot 6H_2O$, $K_2Cu(SO_4)_2 \cdot 6H_2O$, $Cs_2Cu(SO_4)_2 \cdot 6H_2O$, measured in natural radiation.

Literature data on the position of the absorption band of $Cu(H_2O)_6^{2+}$ ions vary from 790 mμ (7) to 820 mμ (19, 20). In this connection the absorption curves of solutions of Cu(II) salts were measured by us repeatedly; the calibration of the spectrophotometer was checked against the lines of a mercury lamp.

The absorption curve of hydrated Cu^{2+} ions found in our experiments is given in Fig. 1. In its contour and in the position of the maximum, this curve coincides with the absorption curve of $Cu(H_2O)_6^{2+}$ ions in the crystalline aquo complex $[Cu(H_2O)_6](ClO_4)_2$. Taking into account this coincidence of the spectra and the high sensitivity of the latter to changes in the symmetry of the $Cu(H_2O)_6^{2+}$ ions, it may be asserted that the nearest hydrate environment of Cu^{2+} ions in dilute aqueous solutions has the same composition and spatial structure as in the crystal $[Cu(H_2O)_6](ClO_4)_2$: the nearest environment of the Cu^{2+} ion in such solutions consists of six H_2O molecules, forming a regular octahedron, with a Cu–O distance equal to 2.18 Å.

A large difference is noteworthy in the numerical values of the absorption index of $Cu(H_2O)_6^{2+}$ ions in aqueous solution and in the crystal-

···phase. A similar phenomenon was observed by us earlier for the ions $Co(H_2O)_6^{2+}$ (21) and is probably associated with the influence, on the oscillator strength of the $Cu(H_2O)_6^{2+}$ ions, of the field created by the outer coordination sphere (22).

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