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Abstract

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ELECTRON PARAMAGNETIC RESONANCE IN SOME AQUEOUS COMPLEXES OF Ti^{3+} SALTS

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In our laboratory (^{1}), studies of e.p.r. were carried out in aqueous, alcoholic, and glycerol solutions of the violet modification of the salts $TiCl_3 \cdot 6H_2O$ and $Ti_2(SO_4)_3 \cdot 4H_2O$. E.p.r. lines in alcoholic and glycerol solutions were detected both in the liquid and in the supercooled states; moreover, the intensity of the lines in the liquid state was very small. Resonance absorption in aqueous solutions of these salts could not be detected.

In this note we report the results of studies of e.p.r. lines in aqueous complexes of the salts TiF_3, TiJ_3, and $TiBr_3$. Green hydrated complexes* $[TiF_n(H_2O)_{6-n}]^{3-n}$ and $[TiJ_n(H_2O)_{6-n}]^{3-n}$ were obtained by dissolving the salts TiF_3 and TiJ_3, respectively, in hydrofluoric and hydroiodic acids. The solutions obtained were diluted with water. On dissolving the salt $TiBr_3$ in water, a violet aqueous complex $[Ti(H_2O)_6]^{3+}$ was obtained.

For measurement, two concentrations of solutions were prepared, 0.01 and 0.001 *M*. The measurements were carried out in thin glass capillaries at a frequency of 9430 MHz at 295° K on a standard EPR-2 radiospectroscope. The line width δH was determined as the distance between the maximum and minimum of the first derivative of the absorption curve. Intense e.p.r. lines were found in green aqueous complexes with spectroscopic splitting factor $g = 1.946 \pm 0.001$ and width $\delta H = 20$ oersted for $[TiF_n(H_2O)_{6-n}]^{3-n}$, and $g = 1.948 \pm 0.001$ and $\delta H = 16$ oersted for $[TiJ_n(H_2O)_{6-n}]^{3-n}$. It proved that in these complexes δH and the value of the g-factor are practically preserved when the concentration of the solutions is changed from 0.01 to 0.001 *M*. Evidently, the invariance of δH with the concentration of the solution indicates the absence of an influence of magnetic dipole-dipole interaction on the width. In addition to the relaxation width, which will be discussed below, the magnetic moments of protons and of the corresponding nuclei F^{19} or J^{127} also make a fairly large contribution to δH. As is seen from Fig. 1, the e.p.r. curves are somewhat asymmetric. This asymmetry of the lines is explained by losses of radio-frequency power to conductivity (^{2}), since the complexes studied are stable only in an acid medium and the solutions possess high conductivity. The following fact supports the argument given:

Fig. 1. E.p.r. curves in aqueous complexes of Ti^{3+} salts, 0.1 M/l, $\nu = 9430$ MHz at 295° K; a—for $[\mathrm{TiF}\ (H_2O)_6\ ]^{3-n}$ and b—for $[\mathrm{TiJ}\ (H_2O)_6\ ]^{3-n}$

Figure 1: Fig. 1. E.p.r. curves in aqueous complexes of Ti^{3+} salts, 0.1 M/l, $\nu = 9430$ MHz at 295° K; a—for $[\mathrm{TiF}\ (H_2O)_6\ ]^{3-n}$ and b—for $[\mathrm{TiJ}\ (H_2O)_6\ ]^{3-n}$

Fig. 1. E.p.r. curves in aqueous complexes of Ti^{3+} salts, 0.1 M/l, $\nu = 9430$ MHz at 295° K; *a*—for $[\mathrm{TiF}_n(H_2O)_{6-n}]^{3-n}$ and *b*—$[\mathrm{TiJ}_n(H_2O)_{6-n}]^{3-n}$.

that when the diameter of the glass capillaries is increased, the asymmetry of the curve increases.

Resonance absorption in violet solutions of $TiBr_3$ could not be detected. The absence of EPR in these solutions is explained by the fact that in the octahedral complexes $[Ti(H_2O)_6]^{3+}$, by analogy with the model adopted in work (3) for the violet aqueous complexes $[Cr(H_2O)_6]^{3+}$, the electric field at the magnetic ion has, in the main, cubic symmetry with a small admixture of fields of lower symmetry, caused by particles of the second coordination sphere. Since the component of the electric field of low symmetry is small, the resulting splitting Δ of the lower orbital triplet will also be small. In view of this, the spin-lattice relaxation time ρ_1 at room temperature proves to be too short.

In asymmetric complexes $[\mathrm{TiF}_n(H_2O)_{6-n}]^{3-n}$ and $[\mathrm{TiJ}_n(H_2O)_{6-n}]^{3-n}$, if $n \neq 0$ and $n \neq 6$, there is a fairly large component of the axial field, and the magnitude of the splitting Δ proves to be so considerable that the relaxation time at room temperature will be long, since $\rho_1 \sim \Delta^6$.

Another explanation of the long spin-lattice relaxation time in aqueous complexes consists in the possible tetrahedral environment of the magnetic ion. In this case the levels for Ti^{3+} will be analogous to the levels of Cu^{2+}, i.e., an orbital singlet will be the lowest.

In conclusion, the authors express their gratitude to B. M. Kozyrev for discussion of the results.

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