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Abstract

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STUDIES OF SOME COMPLEXES OF PENTAVALENT CHROMIUM BY THE E.P.R. METHOD

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In the works of Ingram and other authors ([1–6]), observations of e.p.r. spectra in solid compounds of pentavalent chromium ($3d^1, S = 1/2$) were reported.

In the present work, liquid and supercooled solutions of oxyfluorides, oxychlorides, and oxysulfates of pentavalent chromium have been studied by the e.p.r. method. The measurements were carried out on a standard RE-1301 radiospectroscope at temperatures $T = 295, 280, 240$, and 77°K at a frequency of 9320 MHz. The concentration of pentavalent chromium in the solutions was determined by comparison with the e.p.r. line of the free radical DPPH. The line width was determined as the distance, in oersteds, between the maximum and minimum of the first derivative of the absorption curve.

1. A $0.005\,M$ solution of $(NH_4)_2CrOCl_5$ in 20% hydrochloric acid at $T = 280$°K gives a narrow e.p.r. line from the even isotopes of pentavalent chromium, with spectroscopic splitting factor $g = 1.986 \pm 0.02$ and width $\delta H = 3$ oersteds. The small line width from this solution makes it possible to resolve the hyperfine structure of the e.p.r. lines from the odd isotope Cr^{53} (9.52%) (Fig. 1, *a*).

The spectrum observed by us is described by an isotropic spin Hamiltonian of the form

$$\mathcal{H} = g\beta\hat{S}_z + a\left(\hat{I}_x\hat{S}_x + \hat{I}_y\hat{S}_y + \hat{I}_z\hat{S}_z\right) \tag{1}$$

for $S = 1/2$, $I = 0$ for the even isotopes and $I = 3/2$ for the odd isotope Cr^{53}, with $a = 19$ oersteds and $g = 1.986 \pm 0.02$.

We assumed that $(NH_4)_2CrOCl_5$ in hydrochloric acid decomposes into octahedral complex anions $[CrOCl_5]^{2-}$. In these complexes the paramagnetic ion Cr^{5+} is located in an octahedral local field formed by five chlorine atoms and one oxygen atom, with a strong axial component along the Cr–O bond axis. Since in liquid solutions of $(NH_4)_2CrOCl_5$ in hydrochloric acid, despite the narrowness of the e.p.r. line, "superhyperfine" structure from the ligands is not resolved, it

Fig. 1. EPR spectra of liquid and supercooled solutions of pentavalent chromium.

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must be assumed that in this complex there is rapid chlorine exchange between chlorine atoms covalently bound to the complex-forming ion and chloride ions present in the solvent ([7]).

On cooling a solution of $(NH_4)_2CrOCl_5$ in hydrochloric acid to 77°K, an acid glass is formed.

As is seen from Fig. 1, *b*, in this glass a complex spectrum is observed, which is described by the spin Hamiltonian for axial symmetry:

$$\mathcal{H} = g_{\parallel}\beta H_z S_z + g_{\perp}\beta\left(H_x S_x + H_y S_y\right) \tag{2}$$

for $S = 1/2$, $I = 0$ for the even chromium isotopes,

$$g_{\parallel} = 1.995 \pm 0.005; \qquad g_{\perp} = 1.937 \pm 0.005.$$

Owing to the large width of the e.p.r. lines in the glass, the anisotropic h.f.s. from the odd isotope Cr^{53} is not resolved.

It turned out that in liquid and supercooled solutions of CrO_3 in concentrated hydrochloric acid, e.p.r. spectra are observed that are identical to the spectra found in solutions of $(NH_4)_2CrOCl_5$. Apparently, in

during the dissolution of chromium anhydride in hydrochloric acid, along with a high concentration of hexavalent chromyl ions, CrO_2Cl_2, there exists a small (~ 0.001 mole/liter) concentration of complex anions $[CrOCl_5]^{2-}$. Because the resulting oxychloride compound of pentavalent chromium in a solution of CrO_3 in HCl decomposes rapidly at room temperature, the EPR spectra were also recorded at $T = 280$°K.

2. In the course of dissolution of CrO_3 in 20% hydrofluoric acid, oxyfluoride of pentavalent chromium is partially formed. The EPR lines of this solution at 240°K split into five components from four nuclei

Fig. 1. EPR spectra of liquid and supercooled solutions of pentavalent chromium $(NH_4)_2CrOCl_5$ in 20% HCl: *a* −280°K, *b* −77°K; CrO_3 in 20% HF (*v* −240°K, *g* −77°K); CrO_3 in 70% H_2SO_4 (*d* −295°K, *e* −77°K); K_3CrO_8 in H_2O_2 (*zh* −295°K, *z* −77°K).

F^{19} with $g = 1.960 \pm 0.02$ for the central line of the spectrum and with equal spacings between them of 6 oersteds (see Fig. 1, *v*). This splitting is due to the strong covalent bond of the single $3d$ electron with the surrounding F^{19} nuclei.

As is known, in the presence of identical covalent bonds of an unpaired electron with four ligand nuclei having total nuclear spin $2I$, five $2I + 1$ equally spaced lines of isotropic hyperfine structure should be observed, with an intensity distribution of $1 : 4 : 6 : 4 : 1$. However, the experimentally observed distribution of the intensities of the spectral lines proved to be asymmetric and somewhat different from the intensity ratio given above. This asymmetry is explained by the high viscosity of the solution at $T = 240°$K. The EPR spectrum at room temperature, i.e., in solutions of low viscosity, cannot be recorded, since the solution of CrO_3 in HF at $T = 240°$K begins rapidly to destroy the paraffin-coated glass capillaries.

Lowering the temperature of a solution of CrO_3 in HF to 77°K leads to the formation of an acid glass and, as is seen from Fig. 1, *e*, in this case a complex fluorine anisotropic h.f.s. is observed.

In both the liquid and glassy states the h.f.s. from the odd isotope Cr^{53} cannot be resolved, since it is smeared out by the intense fluorine h.f.s. lines from the even isotopes of Cr(V). It follows from the fluorine h.f.s. that the four fluorine atoms in the oxofluoride complex of pentavalent chromium must be practically equivalent, and the term

$$\sum_{i=1}^{4} a_F^i \left(SI_F^i\right).$$

should be included in spin-Hamiltonian (1).

It should be noted that the spectrum we observed in a solution of the oxofluoride CrO_3 in HF at 240°K proved to be similar to the spectrum previously observed by us for a solution of K_2MoOF_5 in hydrofluoric acid, which has the structure of the complex $[MoOF_5]^{2-}$ with a fluorine h.f.s. constant $a_F = 11$ oersted. Hence it follows that, in the process of dissolution of CrO_3 in hydrofluoric acid, a complex having the structure $[CrOF_5]^{2-}$ is formed. In this complex the magnetic ion Cr^{5+} is located inside an octahedron formed by five covalently bonded atoms: four equivalent fluorine atoms and one oxygen atom. The fifth fluorine atom, located trans to oxygen, has a weaker bond and therefore, along the Cr = O bond axis, a strong component of a local field of axial symmetry is formed at the magnetic ion Cr^{5+}.

Finally, from comparison of the values of the fluorine h.f.s. constants for the complexes $[MoOF_5]^{2+}$ and $[CrOF_5]^{2-}$, which differ only in the principal quantum numbers, it may be concluded that the degree of covalency of the metal–fluorine bond for the 4*d* group is twice as high as for the 3*d* group.

In a solution of CrO_3 in 70% sulfuric acid at room temperature, a slightly asymmetric e.p.r. curve from the even isotopes of pentavalent chromium is observed, with $g = 1.966 \pm 0.002$, and a partially resolved h.f.s. from the odd isotope Cr (9.52%).

As is seen from Fig. 1, *d*, the widths of the hyperfine components increase with increasing strength of the constant magnetic field in accordance with the relaxation mechanism proposed by McConnell ([8]). From the resolved hyperfine components it was possible to determine the hyperfine splitting constant $a = 28$ oersted.

Pentavalent oxosulfate, when the concentration of sulfuric acid in CrO_3 solutions is decreased, rapidly decomposes; the e.p.r. line from Cr(V) disappears and a broad e.p.r. line from Cr^{3+} ions appears.

Upon cooling a solution of CrO_3 in sulfuric acid, an acid glass is formed. In this glass a complex spectrum of e.p.r. lines is observed, with mutually superposed lines having $g_{\parallel} = 1.969$ and $g_{\perp} = 1.976$.

The spectra of e.p.r. lines in liquid and supercooled solutions in sulfuric acid proved to be similar to the spectra of $Mo_2O_3(SO_4)_2$ that we had previously ([7]) investigated. Hence one may conclude that, in the process of dissolution of CrO_3 in sulfuric acid, a small concentration of pentavalent chromium oxosulfate, $Cr_2O_3(SO_4)_2$, is probably formed.

The e.p.r. spectrum in a sulfuric-acid glass containing $Cr_2O_3(SO_4)_2$ (see Fig. 1, *e*) proved to be similar to the spectra obtained by us in a frozen solution of K_3CrO_8 in hydrogen peroxide (see Fig. 1, *z*). The values $g_{\parallel} = 1.951$ and $g_{\perp} = 1.985$, determined from this spectrum, proved to be very close to the values $g_{\parallel} = 1.95$ and $g_{\perp} = 1.98$, obtained by McGarvey ([3]) in the study of a K_3CrO_8 single crystal. In this single crystal the paramagnetic ion Cr^{5+} is located within the crystal field created by a dodecahedron formed by eight oxygen atoms. Hence one may conclude that, in solutions of $Cr_2O_3(SO_4)_2$, the Cr^{5+} ion is probably also located inside a dodecahedron formed by oxygen atoms.

"Superhyperfine" structures in solutions of $Cr_2O_3(SO_4)_2$ are absent,

since in this complex the nuclear spins of the ligands—the oxygen atoms—are equal to zero.

It should be noted that at room temperature, in liquid solutions of K_3CrO_8 in H_2O, a narrow EPR line is observed with $\delta H = 3$ oersteds from even isotopes, and hyperfine structure from the odd isotope Cr^{53} (see Fig. 1,). This spectrum is described by the isotropic spin Hamiltonian (1) for $S = 1/2$, $g = 1.973$, and $a = 19$ oersteds.

The observed difference in the EPR spectra of K_3CrO_8 and $Cr_2O_3(SO_4)_2$ is explained by the different viscosities of the liquid state of these solutions.

Finally, it should be noted that at room temperature, in solutions of CrO_3 in hydrobromic and hydroiodic acids, only broad EPR lines from Cr^{3+} ions ($3d^3, S = 3/2$) are observed.

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Note: Figure translations are in progress. See original paper for figures.