Chemistry

1962

SovietRxiv

Fig. 1. HFS spectrum in aqueous solutions, 0.005 mol/l Cr5+; $\nu = 9320$ MHz and T = 295°K

Figure 1: Fig. 1. HFS spectrum in aqueous solutions, 0.005 mol/l Cr5+; $\nu = 9320$ MHz and T = 295°K

Abstract

Full Text

Chemistry

N. S. GARIF' YANOV and N. F. USACHEVA

ELECTRON PARAMAGNETIC RESONANCE IN SOLUTIONS OF Cr5+

(Presented by Academician A. E. Arbuzov, March 20, 1962)

Previously, liquid solutions of Cr3+ (1,2) and Cr1+ (3) had been investigated by the EPR method. We have detected EPR in liquid solutions of pentavalent chromium, whose compounds have been studied chemically very little. The ion Cr5+ ($3d^1$, $S = {}^1/_2$) is in the ground ${}^2D$ state and, consequently, narrow EPR lines can be observed only in those cases in which a local field of low symmetry is created around the magnetic ion Cr5+, as is characteristic for the well-known isoelectronic ion Ti3+ (4,5).

Solutions containing Cr5+ were prepared as follows: crystals of $K_2Cr_2O_7$ were boiled in glycerol until a greenish-brown coloration appeared. (During boiling, glycerol is oxidized, and chromium is partially reduced to the pentavalent state.) The concentration of Cr5+ in this solution was determined relative to the standard free radical DPPH and depended both on the relative amounts of $K_2Cr_2O_7$ and glycerol and on the heating time. The initial Cr5+ solutions were diluted with water or glycerol to a concentration of Cr5+ $\simeq$ 0.005 mol/liter. Boiling crystals of K_2CrO_4 or $(NH_3)_2Cr_2O_7$ in glycerol also leads to the formation of a solution containing Cr5+. Measurements were carried out at frequencies $\nu_1 = 9320$ MHz and $\nu_2 = 450$ MHz in the temperature interval 295-360° K.

Fig. 1. HFS spectrum in aqueous solutions, 0.005 mol/l Cr5+; $\nu = 9320$ MHz and $T = 295$°K

At the frequency $\nu_1 = 9320$ MHz, at room temperature, a very narrow and symmetric EPR line from the even isotope Cr52 is observed in aqueous solutions of Cr5+. The linewidth, measured between the points of maximum slope of the first derivative of the absorption curve, δH, is equal to 2 oersted; the g factor is 1.975 ± 0.002. The line shape is Lorentzian. At higher gain it is possible to detect a fully resolved HFS of the EPR line from the isotope Cr53 (see Fig. 1).

The EPR spectrum of the isotope Cr53 consists of four almost equidistant HFS peaks. The width of each component is equal to the width of the EPR line from the isotope Cr52. The intensities of the hyperfine components are equal to one another. The intensity of an individual component is 2% of the intensity of the Cr52 line. The observed spectrum is well described by the spin Hamiltonian

$$H = g\beta H_0 \hat{S}_z + a\hat{I}\hat{S}, \tag{1}$$

where $S = {}^1/_2$, $I = 0$ for Cr52 and $I = {}^3/_2$ for Cr53, $a = 20 \pm 1$ oersted, $g = 1.975 \pm 0.002$. The shape, linewidth, and g factor do not change when the temperature is raised from 295 to 360° K and when H_2O is replaced by D_2O. At the frequency $\nu_2 = 450$ MHz, the appearance of the spectrum also remains unchanged, since at this frequency the strong-field conditions are preserved for the HFS.

In a glycerol solution of Cr5+, at the frequency $\nu_1 = 9320$ MHz, a symmetric EPR line from the isotope Cr52 is observed. The width of this line δH decreases —

decreases from 7 to 4 Oe when the temperature of the solution is raised from 295 to 360° K. The spectrum of Cr^53 in glycerol solution consists of partially resolved outer hyperfine components with nuclear-spin projections $m = \pm 3/2$. The hyperfine components with $m = \pm 1/2$ proved to be completely smeared out by the intense line from the isotope Cr^52. Raising the temperature to 360° K leads to complete resolution of the peaks with $m = \pm 3/2$ and to partial resolution of the peaks with $m = \pm 1/2$. Lowering the frequency from $\nu_1 = 9320$ MHz to $\nu_2 = 450$ MHz leads to a narrowing of the line in glycerol solution at 295° K from 7 to 4 Oe.

The spectrum observed in glycerol solution is described by the spin Hamiltonian (1), with $a = 19 \pm 1$ Oe, $g = 1.978 \pm 0.002$. By the method of saturation of the EPR lines at the frequency $\nu_2 = 450$ MHz at 295° K, it was possible to show that the spin-lattice relaxation time T_1 for aqueous and glycerol solutions of Cr^5+ is of the order of 10^{-7} sec.

At the frequency $\nu_1 = 9320$ MHz, owing to the high viscosity of the glycerol solution of Cr^5+ at room temperature, the anisotropy of the g-factor contributes to the linewidth determined by the Al' tshuler–Valiev mechanism (6). Raising the temperature to 360° K reduces the viscosity of the Cr^5+ solution and leads to a narrowing of the line by motion with the averaged

$$g = \frac{g_\parallel + 2g_\perp}{3}.$$

As for the relaxation mechanism proposed by McConnell (7), it is clearly not applicable to interpretation of the hfs spectrum from the odd chromium isotope, since there is no dependence of the hyperfine components on the nuclear-spin projections of Cr^53. The narrow EPR lines in Cr^5+ solutions at room temperature and the comparatively long T_1 for the liquid state, as well as the value of the g-factor, fairly close to 2, and its small anisotropy, allow us to conclude that the orbital splittings of the levels of the Cr^5+ ion are very large. From this we conclude that the Cr^5+ ion is in a local field of very low symmetry. The degree of covalency of the chromium bonds in this complex must be insignificant, since the hyperfine-splitting constant for the isotope Cr^53 has a large value. In the process of reduction by glycerol of compounds of hexavalent chromium, organometallic compounds are not formed. This follows from the fact that we do not observe hfs from protons. We do not yet give the structure of the complex, since this requires additional studies of our solutions by infrared spectroscopy and X-ray structural analysis. Finally, the following is evidence that in the solutions investigated the EPR lines are due only to pentavalent chromium ($S = 1/2$). In the works of B. M. Kozyrev and one of the authors (1,4,5) it was shown that narrow EPR lines for aqueous, alcoholic, and glycerol solutions (polar organic solutions) can be detected only for paramagnetic ions with $S = 1/2$ (Ti^3+, Vo^2+, Cu^2+). For paramagnetic ions having $S > 1/2$ (Cr^3+, V^2+, Mn^2+, Fe^3+, and Gd^3+) (1,8), broad lines are observed in aqueous solutions, while in alcoholic and glycerol solutions EPR lines cannot be detected.

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

Physical-Technical Institute
Kazan Branch of the Academy of Sciences of the USSR

Received
14 III 1962

REFERENCES

1. B. M. Kozyrev, Doctoral dissertation, Moscow, 1957.
2. V. I. Avvakumov, N. S. Garif’ yanov et al., ZhETF, 37, 1564 (1959).
3. J. Bernal, S. E. Harrison, J. Chem. Phys., 34, 102 (1961).
4. V. I. Avvakumov, N. S. Garif’yanov, E. I. Semenova, ZhETF, 39, 11 (1960).
5. N. S. Garif’ yanov, E. I. Semenova, DAN, 140, No. 1, 157 (1961).
6. S. A. Al’ tshuler, K. A. Valiev, ZhETF, 35, 947 (1958).
7. H. M. McConnell, J. Chem. Phys., 25, 709 (1956).
8. N. S. Garif’ yanov, DAN, 138, No. 3, 612 (1961).