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STUDIES OF CERTAIN SOLUTIONS OF PENTAVALENT MOLYBDENUM BY THE E.P.R. METHOD

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Previously, in papers ([1], [2]), solutions of the salts $MoOCl_3$ and $(NH_4)_2[MoOCl_5]$ in various solvents were investigated by the method of electron paramagnetic resonance (e.p.r.). In the present work, using the e.p.r. method at frequencies of 9320 and 300 MHz and at temperatures of 77, 295, and 380°K, liquid and supercooled acidic solutions of $MoOCl_3$ and $Mo_2O_3(SO_4)_2$, as well as liquid solutions of $MoOCl_3$ in nonpolar solvents (C_6H_6, CCl_4, $CHCl_3$ and $C_6H_5CH_3$), were studied. Pentamolybdenyl sulfate $Mo_2O_3(SO_4)_2$ was obtained by electrolysis of a solution of $MoO_2(SO_4)_2$ in concentrated sulfuric acid, and also by reduction of this solution with a stream of hydrogen sulfide. Solutions of the oxychloride $MoOCl_3$ were prepared in three ways: by electrolytic reduction of a solution of MoO_3 in hydrochloric acid, by dissolving $MoOCl_3$ in nonpolar solvents, and by dissolving $MoCl_5$ in hydrochloric acid.

Measurements at a frequency of 9320 MHz were carried out on a standard RE-1301 radiospectroscope, and the linewidth δH was determined as the distance between the maximum and minimum of the first derivative of the absorption curve. At a frequency of 300 MHz, integral curves were studied, and the linewidth ΔH was determined as the distance between the points of the curve at half intensity from the absorption maximum. $1/\nu = 9320$ MHz.

A 0.001 mol/l solution of $MoOCl_3$ in 20% hydrochloric acid at 295°K gives an e.p.r. line from the even isotopes of pentavalent molybdenum with $g = 1.946 \pm 0.02$ and $\delta H = 6$ oersted. Owing to the small linewidth, a six-component hyperfine structure (h.f.s.) from the odd isotopes Mo^{95} (15.7%) and Mo^{97} (9.45%) can be detected (Fig. 1a). It should be noted that, since the nuclear magnetic moments of Mo^{95} and Mo^{97} are close and the values of the nuclear spins coincide, the hyperfine components with identical projections of the nuclear spin m_I are not resolved. The spectrum observed by us is described by an isotropic spin Hamiltonian of the form

$$\mathcal{H} = g\beta H_0 \hat{S}_z + a(\hat{I}_x \hat{S}_x + \hat{I}_y \hat{S}_y + \hat{I}_z \hat{S}_z) \tag{1}$$

for $S = 1/2$ and $I = 0$ for the even isotopes, and $I = 5/2$ for Mo^{95} and Mo^{97}; $g = 1.949 \pm 0.002$ and $a_{av} = 52 \pm 1$ oersted.

In all the $MoOCl_3$ solutions in nonpolar solvents investigated by us at $T = 295°K$, unlike the solution of $MoOCl_3$ in hydrochloric acid, it is possible to resolve only the hyperfine components with projections of the nuclear spins $m_I = \pm 5/2$ and $\pm 3/2$, while the components with $m_I = \pm 1/2$ are smeared out by the intense broad line from the even isotopes of Mo(V).

In these solutions the spectral parameters, within experimental error, coincide, are described by the spin Hamiltonian (1), and have the following values: $\delta H = 14 \pm 1$ oersted, $g = 1.947 \pm 0.002$, $a_{av} = 53 \pm 1$ oersted.

A 0.01 mol/l solution of $Mo_2O_3(SO_4)_2$ in sulfuric acid* gives, because of the high viscosity of the solution and the large mass of the SO_4 ions, a broad asymmetric e.p.r. line from the even isotopes, caused by anisotropy of the g-factor, pentavalent molybdenum with $g = 1.925 \pm 0.02$ and $\delta H = 20 \pm 2$ oersted, and a partially resolved h.f.s. from the odd isotopes Mo^{95} and Mo^{97} (Fig. 1b). When the temperature is raised to 380° K, owing to the decrease in the viscosity of the solution, the contribution to the linewidth from the anisotropy of the g-factor is averaged out, and the e.p.r. line from the even isotopes becomes symmetric and narrows to $\delta H = 12 \pm 1$ oersted (Fig. 1c). As is seen from Fig. 1d, the width of the hyperfine components increases with increasing magnetic-field strength in accordance with the relaxation mechanism proposed by McConnell (^{3}). From the resolved hyperfine components it is possible to determine the constant $a_{cp} = 62 \pm 2$ oersted. Reducing the viscosity of a 70% sulfuric-acid solution of $Mo_2O_3(SO_4)_2$ by dilution with water does not lead to the desired results, since a further decrease in the acidity of the solution leads to the formation of molybdenum blue. As is known, elements of the palladium transition group readily form strong covalent bonds between the ligands and the complex-forming agent. In this case, an additional h.f.s. from the magnetic moments of the ligand nuclei appears in the e.p.r. spectrum (^{4,5}). The addition of small amounts of aqueous solutions of NaCl, KCl, or HCl to a 0.01 mole/liter solution of $Mo_2O_3(SO_4)_2$ in sulfuric acid causes the e.p.r. line from the even isotopes, and each hyperfine component from Mo^{95} and Mo^{97}, to split into four hyperfine components from the nuclei Cl^{35} and Cl^{37} ($I = 3/2$), with $a_{Cl} = 10$ oersted, $g = 1.935 \pm 0.002$ (Fig. 1d). The h.f.s. constant from the odd isotopes is $a_{cp} = 54$ oersted.

Fig. 1. E.p.r. lines at $\nu = 9320$ MHz in liquid solutions: a–$MoOCl_3$ in 20% HCl; b, c–$Mo_2O_3(SO_4)_2$ in 70% H_2SO_4; d–$MoOClSO_4$ in H_2SO_4.

It should be noted that a chlorine h.f.s. is also observed from a solution of $MoOCl_3$ in sulfuric acid.

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* In the dimeric complex $Mo_2O_3(SO_4)_2$, the large h.f.s. indicates the absence of exchange between the magnetic Mo(V) ions.

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Because of the high viscosity of the solution under study, the widths and intensities of the h.f.s. lines are different. On the basis of the chlorine h.f.s. we propose that, in the presence of chlorine ions in a sulfuric-acid solution of $Mo_2O_3(SO_4)_2$, the complex compound $MoOClSO_4$ is formed. In this complex the chlorine atom is covalently bonded to the complex-forming agent, as is evidenced by the presence of a chlorine h.f.s.* Upon further dilution of a solution of $MoClSO_4$ with hydrochloric acid, the h.f.s. caused by the moments of the nuclei Cl^{35} and Cl^{37} begins to disappear, and at the ratio $HCl : H_2SO_4 \approx (1 : 1)$ a single narrow line from the even isotopes of Mo(V) is observed, with $g = 1.948 \pm 0.02$ and $\delta H = 6$ oersted, i.e., the spectral parameters coincide, within experimental error, with the parameters of the spectrum observed from a solution of $MoOCl_3$ in hydrochloric acid.

The disappearance of the chlorine h.f.s. apparently may be explained by the presence of exchange between chlorine ions covalently bonded to the complex-forming agent and chlorine ions located in the solvent. In this case, from of the chlorine h.f.s. constant, one can estimate the lower limit of the chlorine-exchange frequency as $\omega_{\text{exch}} > 10^8$ s^{-1}. In view of the fact that in acidic solutions containing chlorine complexes, at $T = 77$°K chlorine exchange should be absent, we carried out further investigations in acid glasses (supercooled solutions). At a temperature of 77°K, in acid glasses containing $MoOCl_3$ and $MoOClSO_4$, a complex spectrum is observed, consisting of anisotropic h.f.s. from the isotopes Mo^{95} and Mo^{97} and a broad line, due to g-factor anisotropy, from the even isotopes. Therefore in these glasses at $\nu = 9320$ MHz the chlorine h.f.s. is not resolved. As shown in papers (1, 6, 7), in glasses, as the frequency of the oscillating magnetic field is decreased, the contribution to the linewidth from g-factor anisotropy will decrease, and at $\nu = 300$ MHz the linewidth will be determined only by spin-lattice interactions (7); provided the strong-field condition is fulfilled–by unresolved h.f.s. from the moments of the nuclei of the complex-forming atom or of the ligand nuclei. $2/\nu = 300$ MHz, $T = 77$°K.

A supercooled solution of $Mo_2O_3(SO_4)_2$ in sulfuric acid gives a symmetric narrow line from the even isotopes of Mo(V) with $g = 1.93 \pm 0.01$ and $\Delta H = 6$ Oe.* Hyperfine structure from the odd isotopes is not observed, since at this frequency the strong-field conditions for the hyperfine splittings of Mo^{95} and Mo^{97} are not fulfilled.

* It is not possible to determine the degree of covalency of the bond between the complex-forming agent and the acid residue, since the magnetic moments of the nuclei S^{32} and O^{16} are equal to zero.

In the acid glass $MoOClSO_4$, obtained by adding NaCl, KCl, or HCl to a solution of $Mo_2O_3(SO_4)_2$ in sulfuric acid, a four-component chlorine h.f.s. is observed, with $a_{Cl} = 10$ Oe and $g = 1.94 \pm 0.01$. With a further increase in the concentration of Cl ions in the $MoOClSO_4$ glass, a broad EPR line with $g = 1.94 \pm 0.01$ and $\Delta H = 20$ Oe is observed, due to unresolved chlorine h.f.s. An analogous EPR line with $\Delta H = 20$ Oe and $g = 1.94 \pm 0.01$ is also observed in a supercooled solution of $MoOCl_3$ in hydrochloric acid. It may therefore be concluded that in a supercooled solution of $MoOCl_3$ in hydrochloric acid, owing to the absence of chlorine exchange, the linewidth is also due to unresolved chlorine h.f.s. Evidently, the broad EPR lines in liquid solutions of $MoOCl_3$ in nonpolar solvents, observed by us at a frequency of 9320 MHz at a temperature of 295°K, are likewise due to unresolved chlorine h.f.s. as a consequence of the absence of chlorine exchange in these solutions.

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* The study of EPR lines in glasses at $\nu = 300$ MHz was carried out in the absence of saturation.

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

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