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Abstract

Full Text

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ELECTRON PARAMAGNETIC RESONANCE OF COMPLEX COMPOUNDS OF MOLYBDENUM

In some solutions of molybdenum having oxidation state +5, electron paramagnetic absorption is observed ($^{1-5}$). This phenomenon occurs only in sufficiently acidic media and is associated with the existence of monomeric complexes, for example, $\mathrm{MoOCl_5^{2-}}$. The present work gives some data on solutions of Mo(V) in hydrobromic acid and in a mixture of hydrobromic and hydrochloric acids.

Fig. 1. EPR spectra of Mo(V) in solutions of HCl, HBr, and mixed solutions of HCl + HBr at 20°:
a –8.6 mol/l HBr; *b* –8 mol/l HBr + 0.2 mol/l HCl; *v* –7.5 mol/l HBr + 0.7 mol/l HCl; *g* –6 mol/l HBr + 2.2 mol/l HCl;
d –4 mol/l HBr + 4.2 mol/l HCl; *zh* –8 mol/l HCl

The investigation was carried out on an RE-1301 spectrometer operating at a frequency of ~ 10,000 MHz. The solutions were prepared from potassium molybdate by reduction of Mo(VI) to Mo(V) with hydrazine in a hydrochloric-acid medium, followed by precipitation of Mo(V) hydroxide, washing it with an ammonia solution, and dissolving it in the corresponding acid. Some solutions were prepared by other methods.

In solutions of Mo(V) in the presence of hydrobromic acid at 20°C, a single line of electron paramagnetic absorption from the even isotopes $\mathrm{Mo}^{92,94,96,98,100}$ is observed with $g = 1.994 \pm 0.003$ and $\Delta H = 12$ oersted. Of the six components of the hyperfine structure from the odd isotopes $\mathrm{Mo}^{95,97}$ ($I = 5/2$), four components with $I = \pm 5/2, \pm 3/2$ are resolved (Fig. 1a). The spectrum is described by an isotropic spin Hamiltonian

$$\mathscr{H} = g\beta H_0 \hat{S}_z + A\left(\hat{I}_x\hat{S}_x + \hat{I}_y\hat{S}_y + \hat{I}_z\hat{S}_z\right)$$

with parameters $S = 1/2$, $I = 0$ for the even isotopes and $I = 5/2$ for the odd isotopes of molybdenum, $g = 1.994 \pm 0.003$, $A = 44 \pm 2$ oersted.

The intensity of the EPR signals decreases as [HBr] decreases; the signal disappears at [HBr] < 6 mol/liter, i.e., at a higher acidity of the solution than for the chloride complex, for which this occurs at [HCl] ~ 3 mol/liter.

Unfortunately, at present there are not sufficiently complete and reliable data on the stability constants of the halide and pseudohalide complexes of Mo(V). There is reason to believe that the strength of Mo(V) complexes decreases in the series $F^- > CNS^- > Cl^- > Br^-$. In the same order the magnitude of the g-factor and the hyperfine-splitting constant also change (Table 1). Thus, a definite correlation is observed between the stability of the complexes and the parameters of their EPR spectra.

Table 1

Parameters of the EPR spectra of certain Mo(V) complexes at $t = 20°$

	F^-	CNS^-	Cl^-	Br^-
g	1.906	1.935	1.946	1.994
A, oersted	70	50	52	44
ΔH, oersted	50	11	8	12

Note. The values of g, A, ΔH for the Mo(V) complex with F^-, CNS^-, and Cl^- are taken from Refs. (1–5).

Since the EPR spectra of the bromide and chloride complexes of Mo(V) do not overlap, it is of interest to determine whether they change in mixed chloride-bromide solutions. For this purpose a series of solutions was prepared with a constant total molarity of hydrogen ions (8.2 mol/liter) and a variable ratio $[Cl^-]/[Br^-]$. It turned out that the EPR lines of the bromide complexes of molybdenum are noticeably distorted in the presence of small additions of chloride ions (Fig. 1b). In particular, this occurs even in a solution of Mo(V) in 8.6 mol HBr, obtained by dissolving Mo(V) hydroxide precipitated from a hydrochloric-acid solution. The pure signal of the bromide complex of Mo(V) is observed in solutions prepared from Mo(V) in HBr or by reprecipitating the hydroxide with an HBr solution.

Table 2

Parameters of the EPR spectra and reaction constants for substitution in chloride-bromide complexes

Fig. 2

Figure 2: Fig. 2

	$MoOCl_5^{2-}$	$MoOCl_4Br^{2-}$	$MoOCl_3Br_2^{2-}$	$MoOCl_2Br_3^{2-}$	$MoOBr_5^{2-}$
g ($t = 20^\circ$)	1.949	1.960	1.970	1.983	1.994
A, oersted ($t = -10^\circ$)	50	48	47	45	43
ΔH, oersted ($t = 20^\circ$)	7.0	6.7	9.0	8.0	12
$\overline{K_j}$ ($t = -20^\circ$)	–	$3 \cdot 10^{-1}$	$2 \cdot 10^{-1}$	$2 \cdot 10^{-2}$	$5 \cdot 10^{-5}$

Note. The quantities are determined with the following accuracy: g-factor $-$ ± 0.003, A $-\pm 2$ oersted, ΔH $-\pm 0.5$ oersted, K_j $-\pm 30\%$.

The spectra of Mo(V) solutions in mixtures of HCl+HBr are shown in Fig. 1b, c, d. It is evident that they are not a superposition of signals from the chloride and bromide complexes of Mo(V) with different ratios of the intensities of each signal, as would have been observed if no new compounds were formed. Analysis of the spectra of solutions with different ratios $[Cl^-]/[Br^-]$ showed that, in addition to the lines from the pure bromide and chloride complexes, there are three more groups of lines, each of which is described by the spin Hamiltonian (1), the parameters of which are given in Table 2. Thus, in mixed HCl + HBr solutions molybdenum gives five groups of lines, and the distribution of their intensities is determined by the ratio $[Cl^-]/[Br^-]$. Since in the pure chloride solution the EPR lines belong to the complex $MoOCl_5^{2-}$, and in the bromide solution to $MoOBr_5^{2-}$, it is natural to assume that in HCl + HBr solutions several mixed complexes are formed, each of which gives a group of EPR lines with its own parameters. If all possible

mixed complexes, six groups of lines should have been observed. The absence of a sixth group of lines is probably due to the fact that one of the mixed complexes is not formed. From the dependence of the intensity of each group of lines (taking into account ΔH) on the ratio $[Cl^-]/[Br^-]$, the change in the fraction of each of the five forms as a function of $[Cl^-]/[Br^-]$ was calculated (Fig. 2). Using the calculation methods for determining the composition and stability constants of systems with stepwise complex formation, it can be shown that the system under study is described by the following equilibria:

Fig. 3

Figure 3: Fig. 3

Fig. 2. Dependence of the fraction (in percent) of each of the complexes on the concentration of HBr for the series [HCl] + [HBr] = 8.2 mol/liter

$$\mathrm{MoOCl}_5^{2-} + j\,\mathrm{Br}^- \rightleftarrows \mathrm{MoOCl}_{5-j}\mathrm{Br}_j^{2-} + j\,\mathrm{Cl}^-, \qquad K_j = \frac{[\mathrm{MoOCl}_{5-j}\mathrm{Br}_j^{2-}][\mathrm{Cl}^-]^j}{[\mathrm{MoOCl}_5^{2-}][\mathrm{Br}^-]^j}.$$

As follows from the calculation, the complex $\mathrm{MoOClBr}_4^{2-}$ is not formed in appreciable amounts, i.e., the stepwise character is violated. The values of the equilibrium constants of the substitution reactions are given in Table 2.

It is interesting to note that the concentration ratio of the different complexes depends strongly on temperature. From Fig. 1 *a* and Fig. 3 it is evident that, with decreasing temperature, the equilibrium shifts toward the formation of complexes containing more chlorine ions in their composition. With decreasing temperature, some narrowing of the EPR lines also occurs.

Fig. 3. Dependence of the EPR spectrum of Mo(V) in a solution of 6 mol/liter HBr + 2.2 mol/liter HCl on temperature.
a $-t = -3°$, b $-t = -21°$. The narrow line in the figures is the EPR signal of diphenylpicrylhydrazyl, used as a standard.

Thus, the method of electron paramagnetic resonance proves to be extremely useful in the detection and study of mixed complexes.

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1. N. S. Garif' yanov, V. N. Fedotov, ZhETF, **43**, 376 (1962).
2. N. S. Garif' yanov, V. N. Fedotov, Journal of Structural Chemistry, **3**, 711 (1962).
3. N. S. Garif' yanov, V. N. Fedotov, N. S. Kucheryavenko, Izv. AN SSSR, ser. khim., No. 4, 743 (1964).

4. N. S. Garif' yanov, N. S. Kucheryavenko, V. N. Fedotov, DAN, **150**, 802 (1963).
5. N. S. Garif' yanov, B. M. Kozyrev, V. N. Fedotov, DAN, **156**, 641 (1964).

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