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EPR of Pentavalent Molybdenum in Liquid Solutions

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The paramagnetic resonance of Mo^{5+} in liquid solution with two different (chloride and thiocyanate) complexes has been observed. In each case, a hyperfine interaction due to the odd isotopes of molybdenum was observed, in addition to the contribution of the zero-spin isotopes which yield a single line at the center of the spectrum. Upon freezing the solutions, the resonance spectra may be described by spin Hamiltonians possessing axial symmetry. The averages of the g tensor and the hyperfine tensor agree very well with the measured values obtained with the liquid solutions.

THE paramagnetic resonance of Mo^{5+} in liquid solution with two different complexes has been observed. In each case a well resolved hyperfine structure of six lines due to the two isotopes ^{95}Mo and ^{97}Mo (both possessing spin $\frac{5}{2}$ and nuclear moments 0.93 and 0.91 nm, respectively), was observed in addition to the contribution of the zero-spin isotopes which yield a single line at the center of the spectrum. The widths of the lines and the very small difference between the magnetic moments, prevented resolution of the hyperfine structure due to each odd isotope alone. The relative intensity of the central line compared to the sum of the hyperfine line intensities, agrees very well with the known abundance ratio 3:1 of the even to odd isotopes.

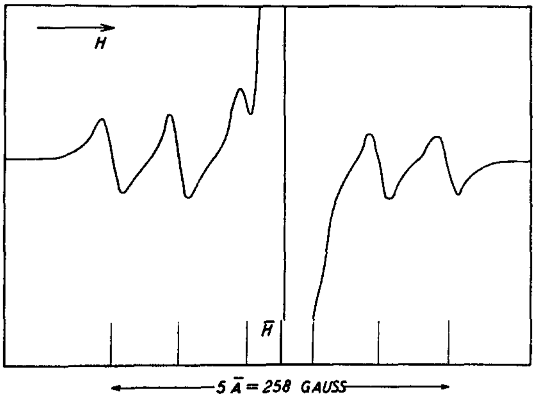

FIG. 1. First derivative of the paramagnetic resonance absorption curve of the complex of Mo^{5+} with Cl^- in concentrated HCl acid. Klystron frequency = 9496 Mc/sec.

MoO_3 dissolved in a strong HCl solution was reduced with Zn or with excess Hg until a light-green color appeared;[1] the green color could not be extracted by ether. These solutions gave a spectrum (see Fig. 1) with $\bar{g}=1.950\pm0.002$ and $\bar{A}=51.7\pm0.8$ G. An identical spectrum (although weaker) was obtained by an incomplete electrolysis of an HCl solution of MoO_3 giving a blue color. The latter color could be extracted with ether with no noticeable changes in the spectrum.

The EPR spectrum of the chloride complex in a frozen solution at liquid-air temperature is given in Fig. 2, and it shows a characteristic powder-pattern shape.[2] Except for a small region of the spectrum between the arrows (of the order of 55 G) drawn in Fig. 2, a good fit is obtained assuming axial symmetry for the complex, with $g_{\parallel}=1.972\pm0.004$, $g_{\perp}=1.942\pm0.005$, $A=81\pm1$, and $B=34\pm4$ G. A "line diagram" for these values is also given in Fig. 2. Our values differ a little from the values $g_{\parallel}\cong1.96$, $g_{\perp}=1.938\pm0.005$; $A=89$ and $B=49$ G obtained previously.[3] The accuracy in the determination of B is much less than that of A.

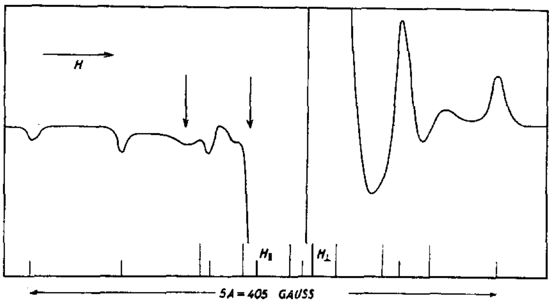

FIG. 2. First derivative of the paramagnetic resonance absorption curve of the complex of Mo^{5+} with Cl^- in frozen solution. Klystron frequency is 9118 Mc/sec. A "line diagram" shows the position of the lines for the complex with the symmetry axis parallel (shorter lines) and perpendicular (longer lines) to the static field.

The intensity of the peak at the left arrow increases at first with dilution, and the region of the spectrum up to 55 G to the right of this peak is sensitive to dilution and also to the addition of NaCl.

In the interpretation of the spectrum it was difficult

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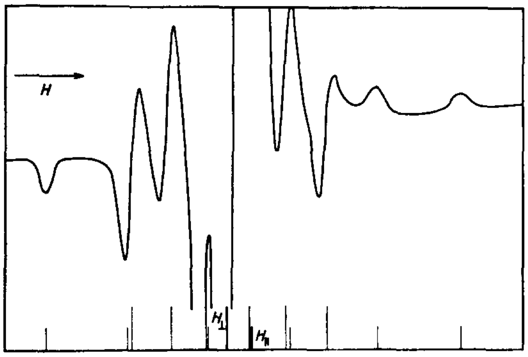

FIG. 3. First derivative of the paramagnetic resonance absorption curve of the complex of Mo^{5+} with $(SCN)^-$ in the frozen solution. A "line diagram" as in Fig. 2 is drawn in this figure. Klystron frequency is 9125 Mc/sec.

to understand the region between the arrows drawn in Fig. 2. We believe that in this zone the observed spectrum shows also the magnetic resonance due to the hydrolysis products of the complex,[4] already present in our solution in concentrated HCl.

To verify this hypothesis, we diluted the original solutions with increasing quantities of water and observed the EPR spectrum; the intensity of the peak marked by the left-hand arrow increased at first with dilution relative to the rest of the spectrum. The saturation of the original solution with NaCl also produced large changes in the same region of the EPR spectrum; this fact confirms the existence of a chemical equilibrium between complexes with different EPR spectra. For all but the highest dilution the rest of the spectrum shown in Fig. 2 is not changed, even when the green solution turns to a brown color. At the highest dilution the intensity of the spectrum was too low for an estimate of the relative peak intensities. Jorgensen's hypothesis[5] that the complex $Cl_6OMo^{=}$ is still present in the brown solution is apparently verified by these results since the EPR spectra is independent of the color of the solutions.

The formation of a paramagnetic dimer[6] could also explain the behavior of the EPR spectrum upon dilution.

The values $\frac{1}{3}(2|g_\perp|+|g_\parallel|)=1.952\pm0.005$ and $\frac{1}{3}(|A|+2|B|)=50\pm3$ G agree within experimental error to the values of $\bar{g}$ and $\bar{A}$ measured at room temperature.[7]

The second complex was formed by adding $NH_4(SCN)$ and a solution of $SnCl_2$ in HCl to a solution of MoO_3 dissolved in HCl, and resulted in a deep red color which was extracted either by ether or by benzyl alcohol.[1] Here $\bar{g}=1.938\pm0.002$; $\bar{A}=48.6\pm0.4$ G in both ether and water. At 0.025 moles Mo/liter H_2O the line shapes were very nearly Gaussian; the linewidths were approximately 14 G and were not appreciably changed by further dilutions.

In Fig. 3 the spectrum of the thiocyanate complex in water at liquid-air temperature is given. Just as for the chloride complex, this spectrum is well described by a spin Hamiltonian with axial symmetry. A good fit was obtained with the values $g_\parallel=1.932\pm0.002$, $g_\perp=1.944\pm0.005$; $A=76.0\pm0.6$, $B=37\pm1$ G. A "line diagram" for these values is also given in Fig. 3.

The values $\frac{1}{3}(2|g_\perp|+|g_\parallel|)=1.940\pm0.004$ and $\frac{1}{3}(|A|+2|B|)=50\pm0.9$ G agree within experimental error with the values of $\bar{g}$ and $\bar{A}$ measured in the liquid solution.

The same spectra were obtained at liquid-air temperature when the thiocyanate complex was extracted with ether or with benzyl alcohol.

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