Physical Chemistry

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1964

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ELECTRON PARAMAGNETIC RESONANCE IN THIOCYANATE COMPLEXES OF Mo(V) AND W(V)

(Presented by Academician A. E. Arbuzov on February 10, 1964)

Thiocyanate complexes of a number of ions find wide application in analytical chemistry. Nevertheless, the structures of many of them cannot be regarded as firmly established. At a frequency of 9320 MHz and at temperatures of 295 and 77°K, we investigated by the method of electron paramagnetic resonance (E.p.r.) liquid and supercooled solutions containing thiocyanate complexes of pentavalent molybdenum ($4d^1$) and tungsten ($5d^1$).

The thiocyanate complexes of both ions were obtained by the action of KSCN on aqueous solutions, acidified with the corresponding acids, of oxyfluoride, oxychloride, and oxysulfate of Mo(V), and of oxyfluoride of W(V). The E.p.r. spectra were studied both directly in aqueous solutions and in solutions in diethyl ether. The latter were obtained by extracting the thiocyanate complexes from aqueous solutions. Both the aqueous and ether solutions had a bright red color for Mo(V) and a green color for W(V).

The concentration of the complexes studied was in all cases sufficiently low that dipole-dipole broadening of the E.p.r. lines was absent.

1. The principal experimental results of our measurements on the thiocyanate complex of Mo(V) proved to be as follows.

The E.p.r. spectrum of this complex does not depend on the composition of the initial oxide complexes of Mo(V). In both aqueous and ether solution this spectrum consists of a narrow intense line (with a width of 11 oersted*)—the spectrum from the even isotopes of molybdenum—and a 6-component hyperfine structure of low intensity from the odd isotopes Mo^{95} (15.7%) and Mo^{97} (9.45%); see Fig. 1a.

The spectrum observed by us is described by the isotropic spin Hamiltonian:

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

Here $S = {}^1/_2$, $I = 0$ (for the even isotopes), $S = {}^5/_2$ (for both odd isotopes); $g = 1.935 \pm 0.002$ and $a = 50 \pm 3$ oersted. In view of the fact that the nuclear

Fig. 1. EPR spectra of thiocyanate complexes of Mo(V) and W(V) in ether at $\nu = 9320$ MHz: K_2[MoO(SCN)$_5$], a–295°K, b–77°K; K_2[WO(SCN)$_5$], v–295°K, g–77°K

Figure 1: Fig. 1. EPR spectra of thiocyanate complexes of Mo(V) and W(V) in ether at $\nu = 9320$ MHz: K_2[MoO(SCN)$_5$], a–295°K, b–77°K; K_2[WO(SCN)$_5$], v–295°K, g–77°K

spins of the isotopes Mo^{95} and Mo^{97} are equal, and their magnetic moments are close to one another, it is not possible to resolve the lines of each of the odd isotopes separately.

In supercooled aqueous and ether solutions of the thiocyanate complex of Mo(V) at 77°K, a complex E.p.r. spectrum is observed, which is described by the spin Hamiltonian for axial symmetry:

$$\mathcal{H} = g_{\parallel}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + A I_z S_z + B(I_x S_x + I_y S_y), \qquad (2)$$

with the following parameters: $S = {}^1/_2$, $I = 0$ for the even isotopes, $I = {}^5/_2$ for the odd isotopes of Mo; $g_{\parallel} = 1.928 \pm 0.005$, $g_{\perp} = 1.944 \pm 0.005$, $A_{\parallel} = 76 \pm 5$ oersted, $A_{\perp} = 38 \pm 5$ oersted.

* Such a small width unambiguously shows that we are dealing specifically with pentavalent molybdenum; for other paramagnetic valence states (i.e., for $S > {}^1/_2$) we would have such broad lines that they would not allow the effect to be observed either in the liquid or in the supercooled state.

We note that the parameters of the anisotropic s.t.s. were found at a signal amplification considerably greater than that shown in Fig. 1b. Comparison of the parameters of the isotropic and anisotropic spectra shows that, for Mo(V) thiocyanate, the following relations hold:

$$g = \frac{g_{\parallel} + 2g_{\perp}}{3}, \qquad (3)$$

$$a = \frac{A_{\parallel} + 2A_{\perp}}{3}. \qquad (4)$$

It follows from this that the signs of the constants $A_{\parallel}$ and $A_{\perp}$ for the odd isotopes of molybdenum are the same. The validity of formula (3) shows that in the frozen solution the local electric field acting on the magnetic ion remains the same as in the liquid solution.

Fig. 1. E.p.r. spectra of thiocyanate complexes of Mo(V) and W(V) in ether at $\nu = 9320$ MHz: K_2[MoO(SCN)$_5$], a–295°K, b–77°K; K_2[WO(SCN)$_5$], v–295°K, g–77°K.

This can be explained by assuming that a local electric field of axial symmetry is created along the double bond Mo = O.

On the other hand, the independence of the spin-Hamiltonian parameters from the nature of the solvent (water, ether, acetone) shows that the first coordination sphere of the complex contains no solvent molecules. Therefore, we may consider that the e.p.r. data lead to the formula of the compound $K_2[\mathrm{MoO(SCN)_5}]$, since the form of the spectrum corresponds to a tetragonally distorted octahedral environment of Mo(V).

This is confirmed by two facts: first, measurements of the infrared spectrum for a solution of our thiocyanate complex in acetone, carried out by I. P. Lipatova, showed the presence of an absorption band characteristic of a metal–oxygen double bond. Second, the compound $\mathrm{(PyH)_2[MoO(SCN)_5]}$ synthesized by us, the composition of which had been established earlier $^{(1)}$, gave an identical e.p.r. spectrum in liquid solutions; in a supercooled solution, however, the spectrum of the pyridine-containing compound differs in some features from the spectrum of $K_2[\mathrm{MoO(SCN)_5}]$, as was to be expected. Finally, it is necessary to address the question of the arrangement of the thiocyanate groups in the complex. Since there is every reason to regard the molybdenum–thiocyanate bond as covalent, and the observed e.p.r. lines are sufficiently narrow, in the case of an Mo–NCS bond we should have observed additional hyperfine structure from N^{14} nuclei ($I = 1$). Since neither resolved structure of this kind nor its influence on the line shape was observed, it should be assumed that the thiocyanate group is directed toward molybdenum by the sulfur atom, and not by nitrogen.

2. The e.p.r. spectrum of the analogous thiocyanate complex of W(V) was studied by us in liquid and supercooled ether solution.

At room temperature, a liquid ether solution of $\mathrm{K_2[WO(SCN)_5]}$ gives a broad line, with $\delta H = 43 \pm 3$ Oe and $g = 1.803 \pm 0.002$ (see Fig. 1b). The hyperfine structure from the odd isotope W^{183} (14%) cannot be resolved in the liquid solution. Hence it may be concluded that the hyperfine-splitting constant a has a value no greater than the line width, i.e., no greater than 43 Oe.

In a supercooled ether solution of $\mathrm{K_2[WO(SCN)_5]}$ the spectrum shown in Fig. 1g was obtained.

For the even isotopes of W(V) it is entirely analogous to the spectrum for the even isotopes of Mo(V) and can be described by the spin Hamiltonian (2) with $S = {}^1/_2$, $I = 0$, $g_\parallel = 1.775 \pm 0.005$, $g_\perp = 1.819 \pm 0.005$.

For the odd isotope W^{183} in the supercooled state it was possible to resolve the anisotropic hyperfine structure with constant $A_\parallel = 156 \pm 5$ Oe. The hyperfine structure for $A_\perp$ is not resolved, as a result of which the value of $A_\perp$ remained undetermined. Analysis of the spectrum shows that $A_\parallel$ and $A_\perp$ apparently have different signs.

Comparison of the isotropic and anisotropic spectra shows that formula (3) is valid also for the case of W(V); hence we may, with a greater degree of probability, assume that the formula of our compound is analogous to that found for molybdenum, i.e., $K_2[WO(SCN)_5]$.

It should be noted that the EPR line width in liquid solutions of $K_2[WO(SCN)_5]$ is greater than in supercooled ones. It follows from this that, at least in liquid solutions, it is determined by spin–phonon interactions.

Comparison of the results obtained for molybdenum(V) and tungsten(V), present in identical complexes, shows that with an increase in the principal quantum number n from 4 to 5 the deviation of the g factors from the value of g for a free electron increases. This indicates an increase, with increasing n, of spin–orbit interactions, as a consequence of which the spin–phonon relaxation time should be shortened. The latter is confirmed experimentally: the spin–phonon width of the absorption line in $K_2[WO(SCN)_5]$ at room temperature is much greater than the width for $K_2[MoO(SCN)_5]$.

In conclusion the authors express their gratitude to I. P. Lipatova for measurements of absorption in the infrared region and to N. A. Glukhova for preparation of the samples.

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Received
7 February 1964

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