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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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STUDY OF SOLUTIONS OF VANADYL CHLORIDE IN ORGANIC SOLVENTS BY THE METHODS OF INFRARED ABSORPTION SPECTRA AND E.P.R. SPECTRA

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It is known that the state of the multiple bond Me=O in complexes of the uranyl, vanadyl, and other types is extremely sensitive to all kinds of intramolecular rearrangements (^{1}). Replacement or addition of ligands in these complexes leads to a change in the frequency corresponding to the stretching vibrations of the Me=O bond.

The present work is devoted to studying the state of the V=O bond in vanadyl complexes. By the method of infrared absorption spectra, solutions of vanadyl chloride $VOCl_2 \cdot 2.5H_2O$ were studied in a whole series of organic solvents (ketones, nitriles, etc.). The choice of liquid solutions was dictated by the fact that in them there are no effects associated with steric strains, and also the interionic interactions are greatly reduced. The concentration of dissolved salt was varied in the range ~0.1-2 mol/l. Measurements were carried out on an IKS-14 spectrometer with an NaCl prism. The solutions were placed between arsenic-glass plates or NaCl windows. The temperature at which the solutions were studied varied from room temperature to 60°.

Fig. 1. Effect of small additions of water on the IR spectrum of a solution of vanadium in acetone (in the region of stretching vibrations of the V=O bond). Concentration of dissolved salt $N = 2$ mol/l, $t \sim 20°$

Fig. 2. Effect of temperature on the stretching-vibration bands of the vanadyl group. (One-molar solution of $VOCl_2 \cdot 2.5H_2O$ in acetonitrile)

In Fig. 1 are presented infrared absorption spectra of acetone solutions of hydrated vanadyl chloride $VOCl_2 \cdot 2.5H_2O$ in the region of stretching vibrations of the V=O bond. The band at 1014 cm^{-1} corresponds to stretching vibrations of

V=O in complexes whose most probable structure is $[VO(H_2O)_2Cl_2]$. The complexes contain tetravalent vanadium with 2 chlorine ions and 2 water molecules in the equatorial plane and a fifth

ligand—the vanadyl oxygen at the apex of the octahedron. The sixth coordination site—in the trans position to the vanadyl oxygen—remains vacant. At this site, upon small additions of water to the solution, an H_2O molecule is introduced. Complexes with sixfold coordination, in which a water molecule is present in the trans position to the vanadyl oxygen, correspond to a broader band with a frequency of 994 cm^{-1}. As the concentration of water in the solutions increases, the intensity of the 994 cm^{-1} band increases, while the intensity of the 1014 cm^{-1} band decreases; thus, beginning approximately with a twofold excess of water, only one band at 994 cm^{-1} is observed (Fig. 1). Further additions of water only slightly shift this band, which apparently corresponds to the "washing out" of chlorine ions from the coordination sphere of vanadium. Therefore the band at 996 cm^{-1} (Fig. 1) should most likely be assigned to stretching vibrations of the V=O bond in the hydrate complex $[VO(H_2O)_5]^{2+}$. This is also indicated by the fact that in purely aqueous solutions of vanadyl chloride the frequency of the stretching vibrations of the V=O bond is also equal to 996 cm^{-1}.

Table 1

Frequencies of V=O stretching vibrations in spectra of vanadyl chloride solutions

No.	Solvent	Frequency $\nu_{V=O}$, cm^{-1}	Frequency $\nu_{V=O}$, cm^{-1}
		$[VO(H_2O)_2Cl_2]$	$[VO(H_2O)_2Cl \cdot H_2O]$
1	Dioxane	1014	–
2	Butyl ethyl ketone	1014	–
3	Methyl hexyl ketone	1014	–
4	Methyl ethyl ketone	1014	996
5	Acetone	1014	994
6	Tetrahydrofuran	1014	992
7	Acetonitrile	1014	990

Table 1 gives the frequencies of the stretching vibrations of the V=O bond when dioxane, butyl ethyl ketone, methyl hexyl ketone, methyl ethyl ketone, acetone, tetrahydrofuran, and acetonitrile are used as solvents.

It is seen that for the complex $[VO(H_2O)_2Cl_2]$ the frequency of the stretching vibrations does not depend on the nature of the solvent. This means that

Fig. 3

Figure 2: Fig. 3

Fig. 4

Figure 3: Fig. 4

molecules of the indicated solvents do not enter the first coordination sphere of the vanadyl complex. In contrast to the 1014 cm^{-1} band, the position of the band corresponding to complexes with sixfold coordination, $[VO(H_2O)_2Cl \cdot H_2O]$, depends somewhat on the solvent chosen. This fact probably indicates a low strength of the vanadium bond with the water molecule located in the trans position to the vanadyl oxygen. The low strength of this bond is also indicated by temperature measurements (Fig. 2): comparatively weak heating of the solution is sufficient for the water molecule located in the trans position to the chlorine atom to leave the coordination sphere of vanadium (in Fig. 2, the departure of the water molecule located in the trans position to the vanadyl oxygen is accompanied by an increase in the intensity of the 1014 cm^{-1} band and a decrease in the intensity of the 994 cm^{-1} band). This process is reversible: in the cooled solution the original pattern is restored (Fig. 2).

In addition to the infrared spectra, EPR spectra were measured (Fig. 3). The work was carried out on a standard RE-1301 spectrometer (frequency of the oscillating magnetic field $\nu_c = 9330$ MHz). The EPR spectra of antimony acetone solutions of vanadyl chloride, as usual [2], consist of 8 components of hyperfine structure corresponding to a nuclear spin $I = 7/2$. The positions of these lines in an applied magnetic field (the effective g-factor and hyperfine intervals) at small

with additions to water solutions changes very little. However, a strong broadening of the spectral components occurs and their asymmetry increases (Figs. 3 and 4). These facts indicate a significant polarization of the V=O bond under the action of a water molecule entering the trans position to the vanadyl oxygen. As a result of this polarization, the effective microviscosity increases; the complexes begin to experience greater electrical friction and to rotate more slowly, which, according to the existing theory ([3]), also leads to the observed increase in the asymmetry of the spectra and to an increase in the width of the hyperfine components.

Fig. 3. EPR spectra of centimolar solutions of vanadyl chloride: *a* –in acetone (complexes $[VO(H_2O)_2Cl_2]$); *b* –in acetone with the addition of a small amount of water (complexes $[VO(H_2O)_2Cl_2 \cdot H_2O]$); *c* –in water (complexes $[VO(H_2O)_5]^{2+}$). Frequency of the oscillating magnetic field $\nu_0 = 9330$ MHz; $t \sim 20^\circ$. The P line in the middle of the spectra is the signal from the free radical α,α-diphenyl-β-picrylhydrazyl (DPPH).

Fig. 4. Dependence of the width of the hyperfine components in centimolar

solutions of vanadyl chloride on the value of the nuclear magnetic quantum number m_I. The curves were constructed from the spectra in Fig. 3; designations as in Fig. 3.

Numerous studies of metal complexes containing the Me=O bond have shown that the frequency of the valence vibrations of this bond depends strongly on the presence and nature of substituents in the equatorial plane. Our measurements on vanadyl show that the Me=O bond in complexes of this kind is also highly sensitive to substitutions along the metal–oxygen axis, being subject to a strong trans influence.

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