The effect of covalent contact between solvent molecules and the $VO(DMSO)_5^{2+}$ ion on the electronic structure of the ion

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The dissolution of the vanadyl complex $VO(DMSO)_5(CLO_4)_2$ in alcohols ROH (R = Me, Et, or Pr^n) results in the appearance of a new absorption band at 372 nm in the electronic absorption spectra of the vanadyl ion. The calculation of the OVO_5^{2+} ion by the Xα-scattering wave method is carried out to interpret the spectra. It is shown that the new band in the spectrum of the $VO(DMSO)_4OHR^{2+}$ complex corresponds to the $b_2 \rightarrow a_1$ transition in the OVO_5^{2+} ion. However, this transition is not a pure d—d transition due to strong covalent bonding and a significant contribution from the AO 2p of oxygen to the a_1 MO. The appearance of the new absorption band in the electronic spectra of the vanadyl complexes is caused by the participation of ligand orbitals in bond formation.

Key words: vanadyl complexes, electronic structure; electronic spectra.

In the electronic spectra of the vanadyl ion, the number of bands and their intensities can vary depending on the solvent. Either three (~900—600, ~600—400, and ~400—200 nm) or two bands appear in the visible spectral region in the spectra of different complexes.[1]

The experimental results obtained by UV, IR, and ^{1}H NMR spectrosopies are usually interpreted in terms of the classic Ballhausen—Gray scheme of molecular orbitals (B—G).[2] The VOL_5^{2+} complex has the symmetry of a tetragonally distorted octahedron, C_{4v}, with five equal V—L bonds at four equatorial V—L$_e$ and one axial V—L$_a$ positions. According to C_{4v} symmetry, there is one antibonding d_{xy} orbital in the energy level scheme, *i.e.*, the "pure" atomic orbital (AO) of vanadium, which does not interact with ligand AO's (b_2 symmetry) on which an unpaired electron is located in the absence of π-bonding in the equatorial plane. Two π-bonds are formed due to the d_{xy},d_{xz} and p_x,p_y AO of vanadium and ligands L (e symmetry). Six σ-bonds are formed between the vanadium and oxygen atoms due to the 4s,3d_{z^2} AO and the ligand p_z,s AO, respectively. Finally, the *trans*-atom is bonded to the central atom by the σ-bond due to the 3d_{z^2},4p_z and p_z AO. The scheme of the energy levels, which is important for the interpretation of the spectra, is presented in Fig. 1. It includes the highest bonding molecular orbital (MO) of the vanadyl ion, the antibonding b_2 MO, and the first vacant MO. Usually, either "pure" d—d transitions or "pure" charge-transfer transitions (CTT) are observed in such a scheme.[1] Actually, in the case of σ-bonding, the b_2-MO is the antibonding orbital of the vanadium and the admixture of the ligand AO in the antibonding a_1-MO is not taken into account in the interpretation of the spectra, which does not reflect in full measure the fine effects of the chemical bond and does not allow one to explain the appearance of new bands in the electronic spectra.[2]

In addition, the study of such complexes by X-ray structural analysis shows[3] that the V—L$_e$ distances differ from the V—L$_a$ distances by 0.1 to 0.6 Å, *i.e.*, these complexes are strongly distorted and the O=V—L$_e$ angles are 102° or greater. Thus, the symmetry of the complexes is closer to C_{2v} or even lower. The additions to this scheme could make it possible to account for these circumstances.

In this work, the electronic absorption spectra of the ionic vanadyl complex $VO(DMSO)_5(ClO_4)_2$ have been studied for the complex dissolved in alcohols ROH (R = Me, Et, and Pr^n) and in the cource of its reaction with *trans*-1-methoxy-2-cyclohexanol (TMCH), which is the product of the addition of ROH to 1,2-epoxycyclohexane in the presence of $VO(DMSO)_5(ClO_4)_2$ (see Ref. 4). The formation of complexes with solvents and with TMCH is shown to affect the electronic structure of the vanadyl ion. This in turn results in changes in the electronic absorption spectra and makes it possible to judge the changes in the reactivity of the complex.

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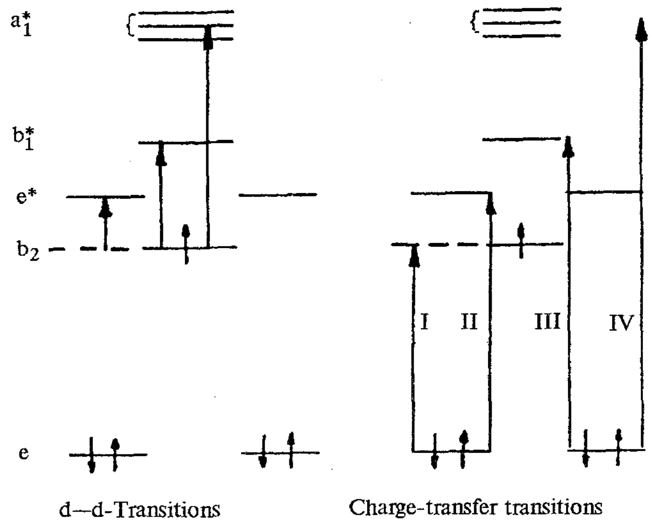

Fig. 1. Scheme of the energy levels of VOL_5^{2+} with the C_{4v} symmetry.

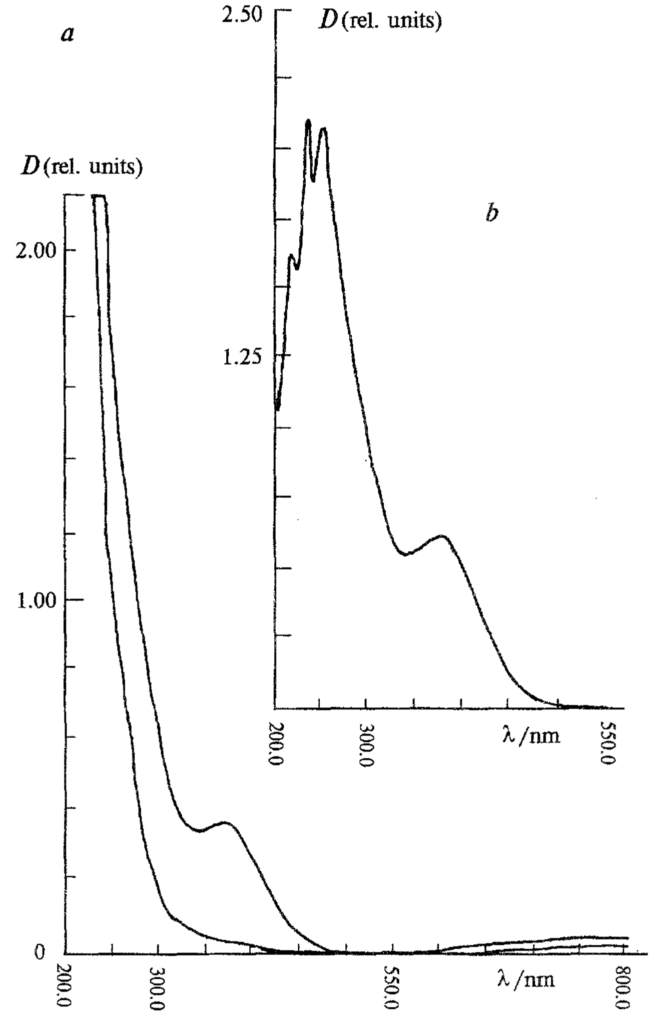

Fig. 2. Electronic absorption spectra of the ionic vanadyl complex: *a*, initial (*1*) and after the formation of a complex with an alcohol (*2*); *b*, with the addition of excess (compared to the concentration of vanadyl) alcohol.

Similar solvent effects have been studied[5,6] by analyzing the chemical shift of the ^{51}V nuclei in the reactions involving $VOCl_3$ and have been called[6] the "effect of covalent contact with the solvent".

Experimental

Electronic absorption spectra were recorded on a Beckman DU-8 spectrophotometer at room temperature, using quartz cells 1 cm in length. The ionic complex $VO(DMSO)_5(ClO_4)_2$ was synthesized by the procedure described previously.[7] Solvents were purified by standard methods.

Results and Discussion

The electronic absorption spectra of the ionic vanadyl complex $VO(DMSO)_5(ClO_4)_2$ in alcohols is characterized by two broad bands in the visible region at λ_{max} = 780 and 650 nm (~12800 and ~15400 cm^{-1}) and one intense band at λ = 228 nm (~43850 cm^{-1}) in the UV region. The appearance of a new band with a maximum at λ = 372 nm is related to the formation of the $VO(DMSO)_5ORH^{2+}$ complex, which has been studied[8] by ESR spectroscopy. The addition of excess (compared to the concentration of VO^{2+}) TMCH to an alcoholic solution of $VO(DMSO)_5(ClO_4)_2$ results in the disappearance of the intense band in the UV region with a maximum at λ = 228 nm and the appearance of a group of less intense bands with maxima at λ = 215, 232, and 246 nm (energies ~40650, 43100, and 46500 cm^{-1}) (Fig. 2).

According to the B—G scheme, the groups of bands in the electronic absorption spectra are usually attributed to the $b_2 \to e^*$, $b_2 \to b_1^*$, and $b_2 \to a_1^*$ energy transitions. These transitions without the admixed $4p_z$ AO in the a_1^* MO and $4p_x$,$4p_y$ AO in the e^* MO are forbidden by symmetry; therefore, they are weak. Electronic-vibrational, magnetic-dipole, and electric quadrupole interactions are considered to remove the symmetry restriction; however, there is another possible mechanism for removing the restrictions, which is associated with the ligand effect.

Apparently, the greater the admixture of the $4p_z$ AO of vanadium in the antibonding MO, the more intense the so-called d—d transitions. The admixture of the 2p AO also results in partial removal of the restriction. Thus, the transition can be more or less intense depending on the extent of mixing with the ligand AO. Mixing of this type leads to less intense charge-transfer bands. Therefore, the theoretical calculation of the contribution of the ligand orbitals to the antibonding MO is very important.

The composition of the MO responsible for the absorption bands in the electronic spectra is obtained from a calculation performed in terms of the Xα-scattering wave method for the model $(VO^2O^1{}_4O^3)^{2+}$ = $(VO_6)^{2+}$ cation (where the vanadyl oxygen is denoted as O^2, O^1 are the oxygen atoms in the equatorial plane, and O^3 is the oxygen atom at the *trans*-position relative to the V=O double bond), using the following parameters:[9] $R_{V-O^2} = 1.591$, $R_{V-O^1} = 2.034$, $R_{V-O^3} = 2.18$ Å, $\alpha_O = 0.74447$, and $\alpha_V = 0.715$. The composition of the highest bonding and antibonding orbitals are presented below.

$$f(a_1{}^*) = 0.0772\ 2s(O^1) - 0.0360\ 2p_z(O^1) - \\ - 0.2002\ 2p_z(O^1) - 0.1056\ 2s(O^2) - 0.3323\ 2p_z(O^2) - \\ - 0.0376\ 2s(O^3) + 0.1190\ 2p_z(O^3) - 0.1046\ 4s(V) + \\ + 0.1479\ 4p_z(V) - 0.8338\ 3d_{z^2}(V) + Q,$$

$$f(b_1{}^*) = 0.1015\ 2s(O^1) - 0.3363\ 2p_{x,y}(O^1) + \\ + 0.9079\ 3d_{x^2-y^2}(V) + Q,$$

$$f(e^*) = -0.0011\ 2s(O^1) + 0.1841\ 2p_z(O^1) + \\ + 0.003\ 2p_x(O^1) + 0.0317\ 2p_x(O^2) - 0.0202\ 2p_x(O^3) - \\ - 0.0011\ 4p_x(V) + 0.9346\ 3d_{xz}(V) + Q,$$

$$f(b_2{}^*) = 0.3662\ 2p_{x,y}(O^1) + 0.9309\ 3d_{xy}(V) + Q,$$

where Q is the portion of the electron density related to the area between the atomic spheres and beyond the external sphere.

The energies of these MO are presented in Table 1.

As follows from the calculation, the AO of σ-type ligands mostly contribute only to the MO corresponding to the a_1 representation. Approximately 69.5 % of the antibonding $a_1{}^*$ MO is from the $3d_{z^2}$ AO of vanadium, and the contribution of the 2p AO of the ligands and the 4p AO of vanadium is ~20 %. Thus, the nature of this MO is not pure d_{z^2}. The contribution of atomic orbitals to the MO varies in the sequence: $3d_{z^2} > 4p_z > 2p_x, 2p_y$, *etc.*

It can be seen that the maximum contribution is made by the σ-orbital of the vanadyl oxygen. Therefore, the addition of a non-equatorial oxygen atom or any other change in the *trans*-bond results in a change in the contribution of the 2p AO of the vanadyl oxygen.

At the same time, the $b_2{}^*$ AO is not antibonding due to the admixture of the $2p_\pi$ AO of the equatorial ligands (~7 %). In the case of σ-ligands, this orbital also remains antibonding.

It is evident from the results obtained that the existence of the covalent σ-bond in representation a_1 and the admixture of the π-bond in representation b_2 increases the intensity of the d—d transition. The calculated value of the $b_2 \rightarrow a_1{}^*$ transition is 27018 cm^{-1} or 370 nm, which agrees well with the experimental data. Thus, changes in the bond with the *trans*-ligand and the enhancement of the π-bond between the central atom and the equatorial ligands cause the appearance of the band at 372 nm (~26880 cm^{-1}).

Table 1. Energies and composition of MO responsible for the absorption bands in the electronic spectra

MO	*E*/eV	Composition of MO
$a_1{}^*$	−1.657	3d(V), 2p(O^1, O^2, O^3)
$b_1{}^*$	−4.134	3d(V), 2p(O^1)
b_2	−5.007	3d(V), 2p(O^1)
e^*	−5.397	3d(V), 2p(O^1, O^2, O^3), 4p(V)
a_2	−9.749	2p(O^1)
e	−9.843	2p(O^1)
a_1	−9.946	2p(O^1, O^3)
b_1	−9.968	2p(O^1)

It follows from the analysis of the literature data[1,2] that the d—d transitions lie in the ~900 to 320 nm range (~11000 to 31000 cm^{-1}), while CTT lie in the ~430 to 230 nm range (~23000 to 43000 cm^{-1}). Therefore, the possibility of attributing the ~27000 cm^{-1} transition to CTT should be considered.

In our MO scheme, the $e \rightarrow b_2$, $e \rightarrow e^*$, $e \rightarrow b_1{}^*$, and $e \rightarrow a_1{}^*$ transitions correspond to CTT. In Fig. 1 they are denoted as I, II, III, and IV, respectively. It follows from the calculation that the highest occupied levels belong to the a_2, e, and b_1 representations and have similar energies of ~9.96 to 9.75 eV. The transitions from these levels to the antibonding levels result in the appearance of charge-transfer bands with λ lower than 221 nm, which approximately corresponds to the experimental data.

The distortion of the complex to decrease the symmetry results in splitting of the bonding e-level. Thus, two bands instead of one appear in the UV range of the electronic absorption spectrum of the complex. It is precisely these changes that are observed in the interaction of VO^{2+} with TMCH, which can be explained by the formation of bidentate bonding in the equatorial plane.

Let us consider the effect of the redistribution of the electron density over the centers on the reactivity of the complex. When the bond between the central atom and the ligand becomes more covalent, a portion of the electron density is redistributed from the ligand to the bond and to the central atom. This results in enhancement of the acceptor properties of the ligands and donator properties of the central atom. When a DMSO molecule is replaced by a more electronegative ligand at the *trans*-position, the electron density on the vanadyl oxygen changes most of all. When the ligand is less electronegative than DMSO, the V=O bond shortens due to excess positive charge on the vanadyl oxygen. This is confirmed by the positions of the OH^- and DMSO groups as σ-ligands in the electrochemical series.[2] Enhancement of the π-bond in the equatorial plane results in a change in the energy of the b_2 MO, namely it becomes greater than that of the antibonding MO, which corresponds to a decrease in the electron affinity.

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When $VO(DMSO)_5(ClO_4)_2$ is dissolved in alcohols ROH (R = Me, Et, or Pr^n), a band with a maximum at 372 nm appears in the electronic absorption spectra of the complex. The model cation $(OVO_5)^{2+}$ was calculated by the SCF-Xα-SW method. Based on the analysis of the electronic structure of $(OVO_5)^{2+}$, it is assumed that the appearance of the new band in the electronic absorption spectra of the vanadyl complex is caused by a change in the nature of the antibonding MO. The change in the reactivity of the complex due to the change in its electronic structure is discussed.

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