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Study Of The Electronic Structure Of The Vanadyl (Ii) Monochloroacetate Monomer Molecule

Muzafarov Farux Ixtiyorovich
Bukhara State Medical Institute, Uzbekistan

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Abstract: In this work, density functional theory (DFT)–based quantum-chemical calculations were employed to investigate the molecular and electronic structure of vanadyl(II) acetate and vanadyl(II) monochloroacetate monohydrates. While the soluble tetrameric form of vanadyl(II) acetate hemihydrate has been experimentally synthesized, the monomeric monochloroacetate derivative has not yet been synthesized under laboratory conditions. To elucidate the reason for this synthetic inaccessibility, optimized geometries, bond parameters, and Mulliken charge distributions were determined, and the frontier molecular orbitals (HOMO and LUMO) were analyzed. The calculated HOMO–LUMO energy gap (ΔE), global reactivity descriptors, and potential energy distributions provided insight into charge-transfer processes and stability trends. Comparative analysis revealed that the monomeric monochloroacetate exhibits a larger HOMO–LUMO gap, suggesting enhanced electronic stability; however, cyclic bidentate coordination of the carboxylate group induces structural distortions within the vanadium coordination sphere. This electronic and geometric strain is identified as the most probable reason for the failure to synthesize vanadyl(II) monochloroacetate experimentally. The present findings highlight the importance of integrating quantum-chemical methods with experimental approaches for studying vanadyl carboxylates and related transition-metal complexes.

Keywords: Vanadyl carboxylates; vanadyl acetate; vanadyl monochloroacetate; density functional theory (DFT); quantum-chemical calculations; HOMO–LUMO gap; electronic structure; molecular stability; coordination chemistry; frontier molecular orbitals.

INTRODUCTION:

In recent years, quantum-chemical calculation (QCC) methods have undoubtedly become the most universal and reliable means of studying a wide variety of molecular and electronic structures, as well as for determining the reactivity of substances that cannot be synthesized despite repeated experimental attempts under real laboratory conditions. Among the special types of such compounds that require simultaneous theoretical and experimental investigation, along with comparison of their results to establish the composition, structure, and coordination features of the ligand and the central atom, are the carboxylates of the vanadyl ion.

It should be noted that the soluble form of vanadyl(II) acetate hemihydrate has been synthesized, and its tetrameric structure, corresponding to the general formula $[VO(CH_3COO)_2 \cdot 0.5H_2O]$⍰ (where n = 4), was established by comparing the unusual experimental EPR spectrum (consisting of 29 equidistant lines instead of 8) with theoretical calculations [2]. However, neither the reason for the formation of specifically the tetrameric form—rather than monomeric or dimeric analogues—nor its diverse physicochemical, spectral, and magnetic properties that distinguish this compound from its polymeric precursors have yet been investigated or clarified.

The aim of the present study is to investigate the possible molecular and electronic structure, the most probable function of the carboxylate group, and the reason for the possibility or impossibility of forming vanadyl(II) monochloroacetate (n = 1) using quantum-chemical calculations (QCC).

Based on the calculations performed, the theoretical values of bond lengths and bond angles were established, and the atomic charge distribution was determined using Mulliken population analysis. In addition, the potential energy distribution (PED) was obtained within the framework of density functional theory (DFT). The energy differences between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), as well as the magnitude of this gap, were used to interpret the nature of charge transfer in the studied molecule.

The theoretical quantum-chemical calculations have revealed the nature of the frontier molecular orbitals of the vanadyl(II) carboxylate complex in both the ground and excited states. The analysis of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) provides important insights into the electronic configuration and potential charge-transfer processes within the complex. In particular, the spatial distribution of these orbitals indicates that the carboxylate ligand plays a dominant role in electronic transitions, as well as its contribution to the stabilization of the coordination sphere around the vanadyl(II) center.

The table presents the quantum-chemical parameters of vanadyl(II) monomeric monochloroacetate: electronic chemical potential (Pi), absolute electronegativity (χ), absolute hardness (η), absolute softness (σ), global softness (S), global electrophilicity (ω), and the additional electronic charge (ΔNmax), calculated using the equations reported in [2]. Based on the magnitude of the molecular orbital energy gap (ΔE), it can be concluded that the monomeric form of monochloroacetate is more stable than the vanadyl(II) acetate monomer.

Calculated quantum-chemical parameters of the monomeric vanadyl(II) monochloroacetate monohydrate molecule*

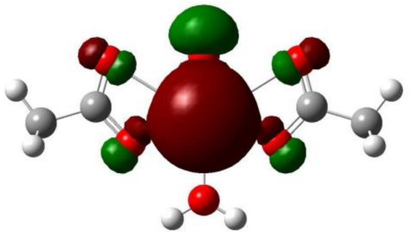
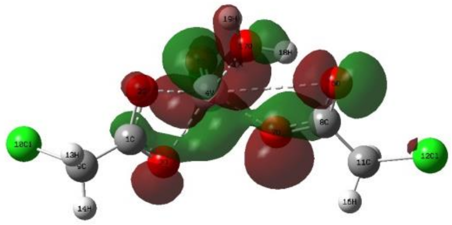
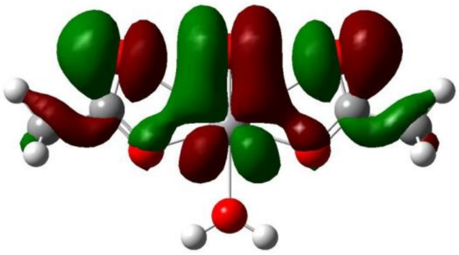
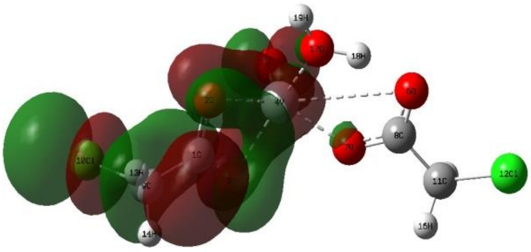
Table 1

Compound	$E_{(HOMO)}$ eV	$E_{(LUMO)}$ eV	ΔE	χ	η	σ	-Pi	S	ω	ΔNmax
Vanadyl acetate monohydrate	-0.1586	-0.0722	0,0864	0,1154	0,0432	23,148	-0,1154	11,57	0,154	2,67
Vanadyl monochloroacetate monohydrate	-0.2752	-0.1018	0.1733	-0.0866	0.0866	11,53	0,0866	5,76	0,043	-1

Table 1 summarizes, for comparison, the results of quantum-chemical calculations for the vanadyl(II) acetate monohydrate monomer.

Parameter	**Symbol**	**Definition**
Electronic chemical potential	**Pi**	Measure of the escaping tendency of electrons from equilibrium; defined as the negative of electronegativity.
Absolute electronegativity	**χ**	Tendency of a molecule to attract electrons, defined as $\chi = -(EHOMO + ELUMO)/2$.
Absolute hardness	**η**	Resistance to charge transfer, defined as $\eta = (ELUMO - EHOMO)/2$.
Absolute softness	**σ**	Inverse of hardness, $\sigma = 1/\eta$.
Global softness	**S**	Alternative measure of molecular polarizability, $S = 1/(2\eta)$.
Global electrophilicity	**ω**	Electrophilic character of the molecule, $\omega = \mu^2/2\eta$.

Additional electronic charge	**ΔNmax**	Maximum number of electrons that a system may accept, ΔNmax = –μ/η.

 $E_{(HOMO)}$= -0.1586 eV *Electronic structure of the vanadyl monochloroacetate molecule: LUMO.*	 $E_{(HOMO)}$= -0.2752 eV *Electronic structure of the vanadyl monochloroacetate molecule: HOMO.*
 $E_{(LUMO)}$= -0.0722 eV *Electronic structure of the vanadyl acetate molecule: LUMO.*	 $E_{(LUMO)}$= -0.1018eV *Electronic structure of the vanadyl monochloroacetate molecule: LUMO*

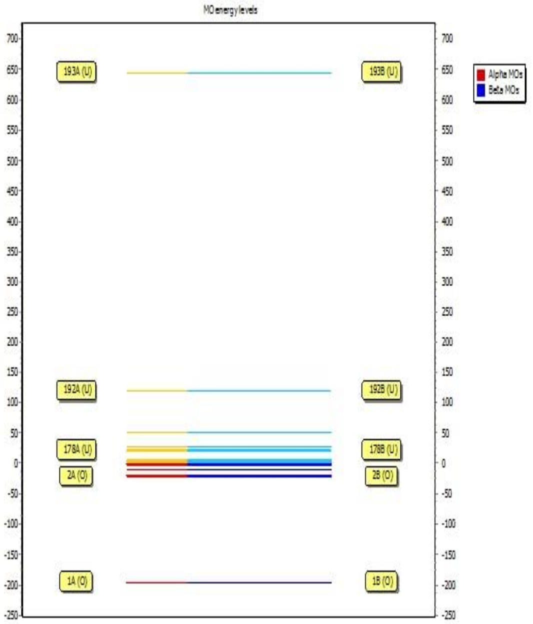


Figure X presents the energy level diagram of vanadyl acetate, showing the distribution of the frontier molecular orbitals (HOMO and LUMO).

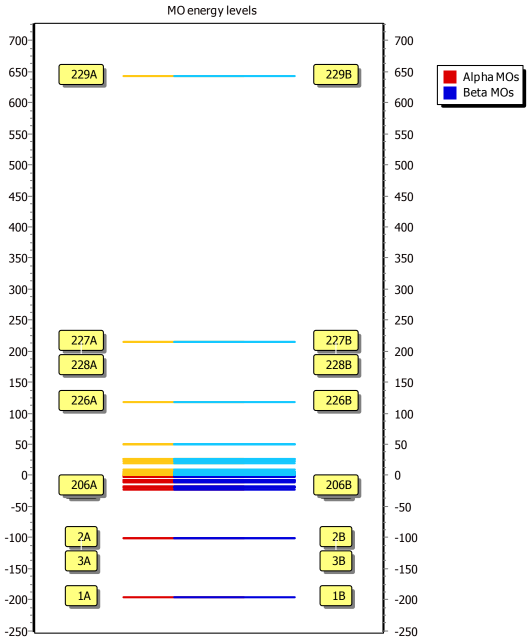


Figure X illustrates the energy level diagram of vanadyl monochloroacetate, highlighting the frontier molecular orbitals (HOMO and LUMO). The calculated HOMO–LUMO energy gap (ΔE) provides insight into the electronic stability and charge-transfer characteristics of the molecule.

CONCLUSION

According to the results of quantum-chemical calculations, the most probable structure of the vanadyl monomeric monochloroacetate was determined, which could not be synthesized experimentally. The compound exhibits cyclic bidentate coordination of the carboxylate group, experiencing electronic and structural instability in the equatorial plane of the vanadium coordination environment due to the displacement of the central vanadium atom from the coordination plane toward the strongly bound oxygen atom. This appears to be the most likely reason for the inability to form the monomeric vanadyl monochloroacetate and for the experimental failure to synthesize this compound.

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