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Synthesis, Structure and Properties of Heteroligand Complex Compounds of VO(II) Ion with Aminobenzoic Acids and Biuret

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Abstract:

This study presents the synthesis and characterization of novel heteroligand vanadyl(IV) complexes incorporating aminobenzoic acids (o-aminobenzoic acid and p-aminobenzoic acid) and biuret as ligands. Three new complexes were synthesized: [VO(L2)2]•SO4 (KB1), [VO(o-ABK)2•L2] (KB2), and [VO(p-ABK)2•L2] (KB3), where L2 represents biuret, o-ABK is o-aminobenzoic acid, and p-ABK is p-aminobenzoic acid. The compounds were characterized using infrared (IR) spectroscopy and electron paramagnetic resonance (EPR) spectroscopy. IR analysis confirmed the coordination of carbonyl oxygen atoms from biuret to the vanadyl center, while EPR spectroscopy provided insights into the electronic structure and coordination environment of the V4+ ion. The results indicate the formation of octahedral coordination complexes with potential polymeric structures in the case of the sulfate-containing complex. These findings contribute to the understanding of vanadyl chemistry and may have implications for catalytic and biological applications.

Keywords: Vanadyl complexes, heteroligand compounds, aminobenzoic acids, biuret, IR spectroscopy, EPR spectroscopy

Introduction

Vanadium compounds have attracted considerable attention due to their diverse biological activities and catalytic properties [1-3]. Among vanadium oxidation states, vanadyl(IV) complexes (VO^{2+}) are particularly interesting due to their stability and unique magnetic properties arising from the d^1 electronic configuration. The vanadyl ion exhibits a characteristic square pyramidal geometry with a short V=O bond, making it an excellent probe for studying coordination environments and electronic structures [4-6].

Heteroligand complexes, containing two or more different types of ligands, offer enhanced flexibility in tuning the properties of metal complexes compared to their homoligand counterparts. The combination of aminobenzoic acids with biuret as co-ligands presents an interesting case study, as both ligands possess multiple potential coordination sites and can form stable chelate complexes [5, 7-9].

Biuret ($NH_2CONHCONH_2$) is known to coordinate to metal ions through its carbonyl oxygen atoms or deprotonated NH_2 groups, forming different types of chelate rings. The coordination behavior depends on the pH of the solution and the nature of the metal ion [10-14]. Aminobenzoic acids, on the other hand, are versatile ligands that can coordinate through their carboxylate and amino groups, potentially acting as bidentate ligands [15, 16].

The study of vanadyl complexes with mixed organic ligands is of particular importance due to their potential applications in catalysis, medicine, and materials science. Vanadyl complexes have shown promise as insulin-mimetic agents and as models for vanadium-containing enzymes. Furthermore, understanding the structural and electronic properties of these complexes contributes to the broader field of coordination chemistry.

This work presents the synthesis and comprehensive characterization of three novel heteroligand vanadyl(IV) complexes using spectroscopic techniques. The objective is to elucidate the coordination modes, electronic structures, and bonding characteristics of these compounds. The aim of this research is to synthesize and characterize new heteroligand VO(IV) complexes involving biuret and o-/p-aminobenzoic acids, and to elucidate their structural features using IR and EPR spectroscopy.

Materials and Methods

All chemicals were of analytical grade and used without further purification. Vanadyl sulfate trihydrate ($VOSO_4 \cdot 3H_2O$), biuret ($C_2H_5N_3O_2$), o-aminobenzoic acid (o-ABK), p-aminobenzoic acid (p-ABK), and potassium hydroxide (KOH) were obtained from commercial sources. Solvents (water, ethanol) were distilled before use.

Synthesis of Complexes

$[VO(L^2)_2] \cdot SO_4$ (KB1)

0.217 g of vanadyl sulfate trihydrate ($VOSO_4 \cdot 3H_2O$) was dissolved in 10 mL of water, yielding a solution with pH = 1.99. 0.206 g of biuret ($C_2H_5N_3O_2$) was dissolved in 10 mL of water, forming a solution with pH = 5.75. The $VOSO_4$ and biuret solutions were mixed (pH = 2.53). To reduce acidity, 1 mL of KOH was added dropwise (pH = 3.94). The resulting complex precipitated from solution.

$[VO(o\text{-}ABK)_2 \cdot L^2]$ (KB2)

0.217 g of vanadyl sulfate trihydrate ($VOSO_4 \cdot 3H_2O$) was dissolved in 10 mL of ethanol, yielding a solution with pH = 2.04. 0.137 g of o-ABK was dissolved in 10 mL of ethanol, forming a light brown solution with pH = 3.54. When the $VOSO_4$ and o-ABK solutions were mixed, the pH became 2.62.

0.206 g of biuret ($C_2H_5N_3O_2$) was dissolved in 10 mL of water, forming a solution with pH = 5.50. The biuret solution was added to the $VOSO_4$ and o-ABK mixture (pH=2.74), resulting in a turbid green solution. 2 mL of KOH was added dropwise (pH=4.65). A precipitate formed at the bottom of the beaker.

$[VO(p\text{-}ABK)_2\cdot L^2]$ (KB3)

The synthesis procedure was identical to that of KB2, except p-aminobenzoic acid was used instead of o-aminobenzoic acid. The same pH values and color changes were observed during the synthesis.

Characterization Methods

Infrared Spectroscopy

The infrared spectra of the synthesized complexes were recorded using a Fourier-transform infrared (FTIR) spectrometer IRTracer-100 (SHIMADZU CORP., Japan, 2017), equipped with a MIRacle-10 attenuated total reflectance (ATR) accessory using a diamond/ZnSe prism. The measurements were carried out in the mid-infrared (MIR) region, within the range of 4000–400 cm^{-1}. The spectral resolution was 4 cm^{-1}, and the signal-to-noise ratio exceeded 60,000:1. The scanning speed was 20 spectra per second.

Electron Paramagnetic Resonance (EPR) Spectroscopy

To investigate the structure of the paramagnetic vanadyl(IV) complexes, EPR spectra were recorded for both polycrystalline samples and diluted solutions in acetone. The measurements were performed using a SPINSCAN X EPR spectrometer (ADANI RUS, Belarus) operating at X-band frequency (9.44 GHz). A stable free radical, 2,2-diphenyl-1-picrylhydrazyl (DPPH), was used as an external standard ($g = 2.0037 \pm 0.0002$) for g-factor calibration. EPR spectra were recorded at room temperature to investigate the electronic structure and coordination environment of the vanadyl ion (V^{4+}). The spectra provide information about g-factors and hyperfine coupling constants.

Results and Discussion

Complex Formation and Stoichiometry

The synthesis of the three vanadyl complexes proceeded smoothly under the described conditions. The formation of complexes was evidenced by color changes and precipitation. The stoichiometry of the complexes was determined based on the synthetic procedures and analytical data.

In the case of $[VO(L^2)_2]\cdot SO_4$ (KB1), the biuret ligands coordinate through carbonyl oxygen atoms, as evidenced by IR spectroscopy. The sulfate anion acts as a counter-ion and potentially as a bridging ligand, leading to polymeric structure formation. For complexes KB2 and KB3, the aminobenzoic acids coordinate through their carboxylate groups, while biuret coordinates through carbonyl oxygen atoms, forming mixed-ligand complexes with octahedral geometry around the vanadyl center.

Infrared Spectroscopy Analysis

The IR spectra of the synthesized complexes in the range of 2000-250 cm^{-1} provide valuable information about ligand coordination modes and structural features. Table 1 summarizes the main vibrational frequencies observed for all complexes.

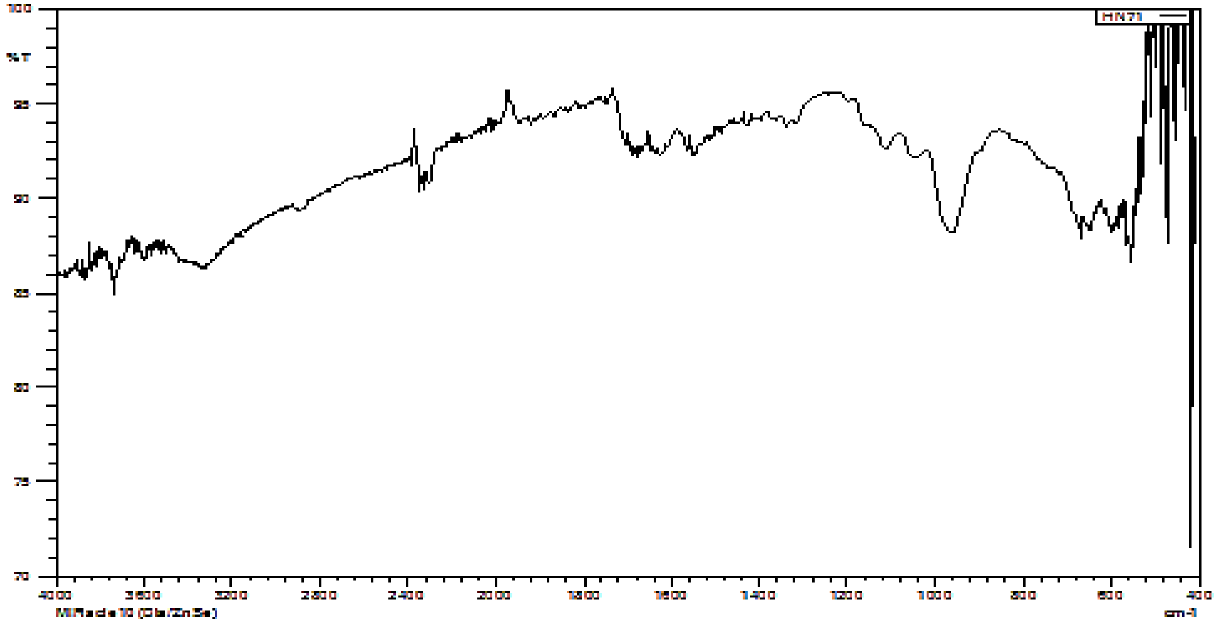

Fig. 1. IR spectra of KB1

The characteristic V=O stretching vibration appears in the range of 965-972 cm^{-1} for all complexes, confirming the presence of the vanadyl moiety. This frequency is typical for vanadyl complexes and indicates that the V=O bond remains intact upon complexation (Fig. 1, Table 1).

Table 1. Main vibrational frequencies (cm^{-1}) in IR spectra of VO(II) heteroligand complexes

$VO(L^2)_2Cl_2\cdot 3H_2O$	KB1	KB2	KB3	Assignment
1700	1712	1724	1722	$\nu(C=O) + \delta(NH_2)$
1640, 1605	1665, 1630 sh	1622.1, 1647.0 L2	1618.6, 1639.8 L2	$\delta(H_2O) + \delta(NH_2)$
1559.5	1540.8	1515.5	1524.2	$\nu_{as}(COO^-)$
1404.55	1395.9	1395.4	1339.9	$\nu_s(COO^-)$

801.98	803.4	827.8	803.4	δ(COO^-)
1098.41	1116.2	1109.72	1107.57	ν(SO_4)
972	965	972.7	968.4	ν(V=O)
591.09	592.5	592.5	596.8	ν(V-N)
434.71	451.9	473.4	441.8	ν(V-O)

The coordination of biuret through carbonyl oxygen atoms is evidenced by the appearance of ν(C=O) vibrations in the range of 1712-1724 cm⁻¹. The shift compared to free biuret confirms coordination to the metal center (Table 1).

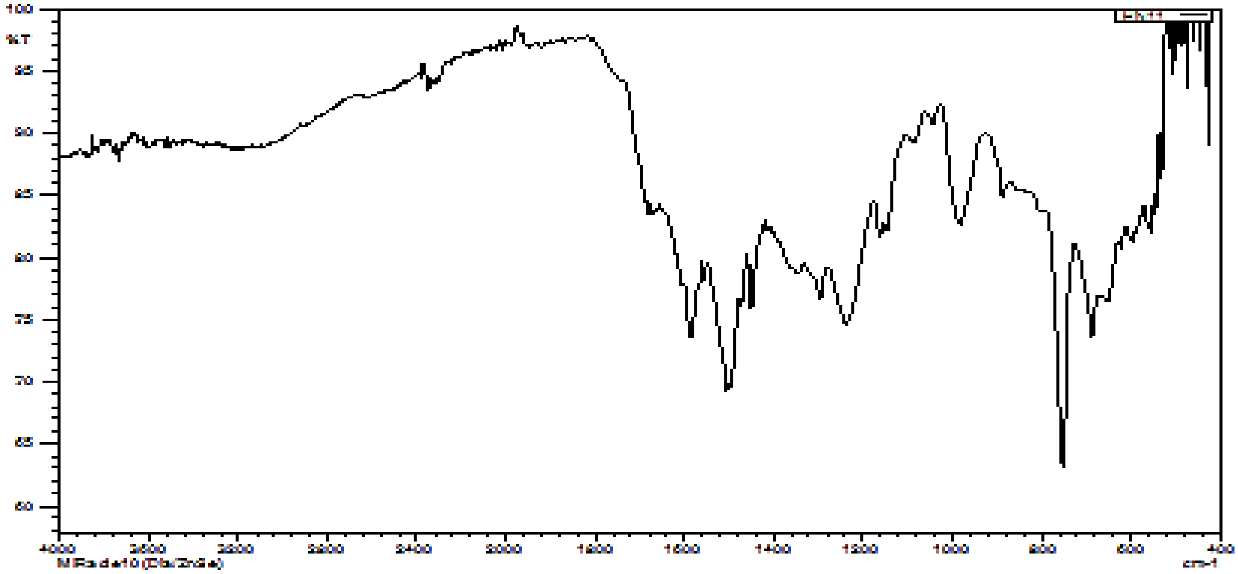

Fig. 2. IR spectra of KB2

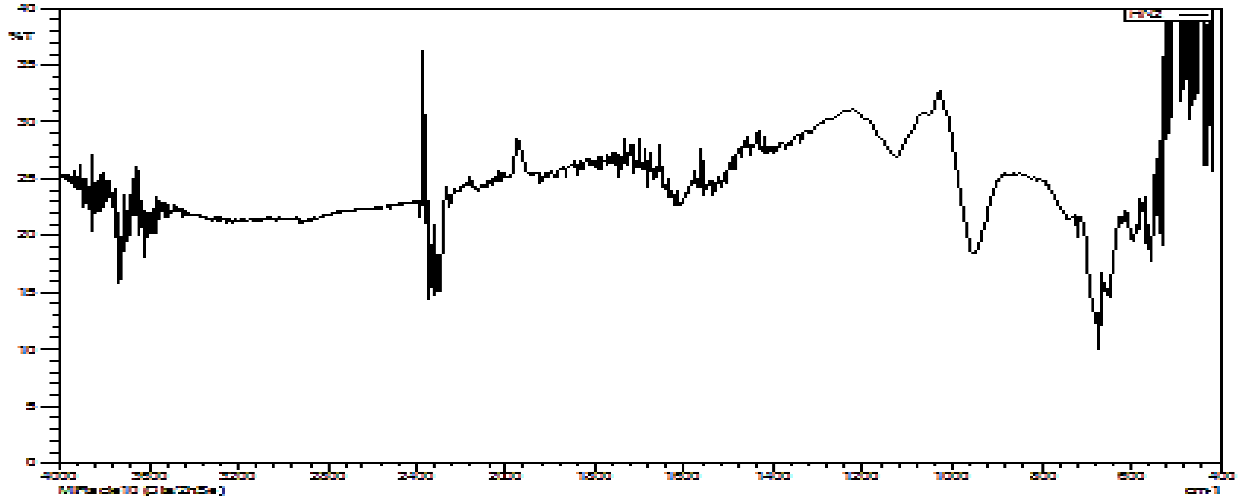

Fig. 3. IR spectra of KB3

For complexes containing aminobenzoic acids (KB2 and KB3), the presence of asymmetric and symmetric carboxylate stretching vibrations at ~1515-1524 cm^{-1} and ~1339-1395 cm^{-1}, respectively, indicates coordination through the carboxylate groups (Fig. 2,3). The complex KB1 shows additional bands related to coordinated sulfate groups, suggesting a polymeric structure where sulfate acts as a bridging ligand. The spectral characteristics of SO_4^{2-} vibrations indicate the presence of bidentate bridging sulfato groups [14, 16].

Electron Paramagnetic Resonance (EPR) Spectroscopy

The EPR spectrum of complex KB2 ($[VO(o\text{-}ABK)_2 \cdot L^x]$) provides detailed information about the electronic structure and coordination environment of the vanadyl ion (V^{4+}) (Fig. 4).

Spectral Features

The EPR spectrum exhibits several key features:

1. **Multiline signal structure**: The spectrum shows multiple distinct peaks resulting from hyperfine interaction between the electron spin of V^{4+} and the nuclear magnetic moment. The ^{51}V nucleus ($I = 7/2$) typically produces eight lines in isotropic conditions, and approximately this number is observed in the spectrum.
2. **Central intense signal**: The most intense signal is observed around 325 mT, corresponding to the main resonance line of the vanadyl ion.
3. **Anisotropic characteristics**: The line shapes and widths indicate anisotropy, suggesting that the vanadyl ion is in an anisotropic environment within the crystal lattice or complex structure.
4. **Line width variations**: The lines show moderate broadening, which may indicate spin-spin interactions or sample heterogeneity.

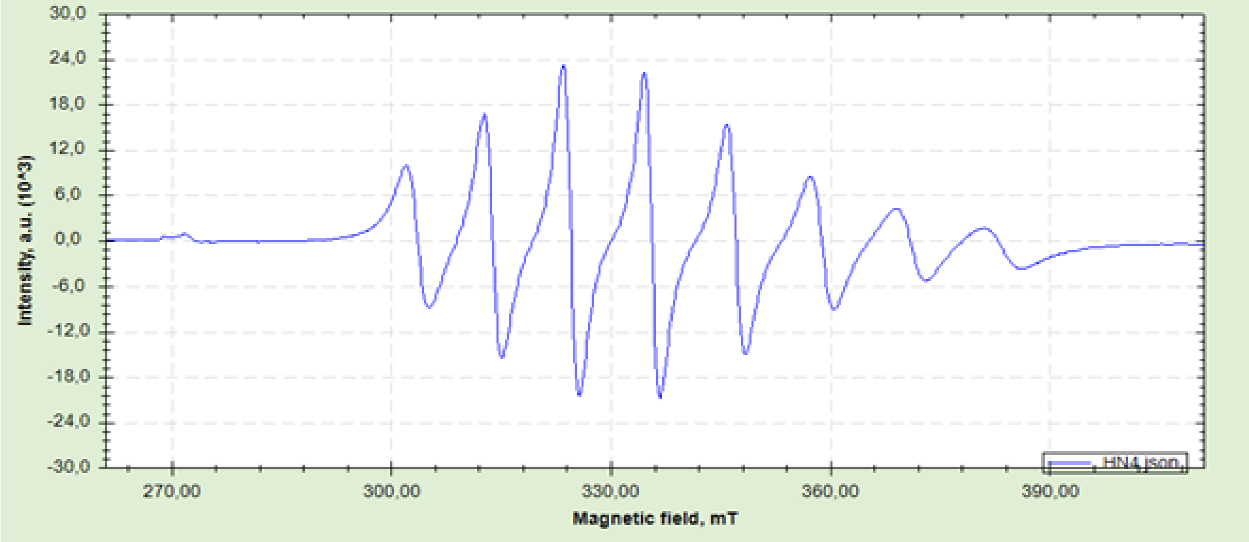

Fig. 4. EPR spectra of KB2

EPR Parameters and Interpretation

The EPR spectrum allows determination of important parameters:

- **g-factor**: The position of the central signal enables calculation of the g-factor value, which provides information about the electronic environment of the vanadyl ion.
- **Hyperfine coupling constant (A)**: The spacing between lines reflects the hyperfine coupling constant between the ^{51}V nucleus and the unpaired electron, providing insights into the metal-ligand bonding.
- **Anisotropic parameters**: Analysis of line shapes and positions allows determination of $g_\parallel$, $g_\perp$, $A_\parallel$, and $A_\perp$ values, which reveal information about the electronic structure and ligand field symmetry around the vanadyl ion.

The coordination of o-aminobenzoic acid and biuret ligands creates a specific electronic environment that influences these EPR parameters. The spectrum indicates successful complex formation with the vanadyl ion maintaining its characteristic d^1 electronic configuration.

Structural Considerations

Based on spectroscopic evidence, the following structural features can be proposed:

1. **KB1 Complex**: The biuret ligands coordinate through carbonyl oxygen atoms, forming a polymeric structure with sulfate bridges. The coordination environment around vanadyl is likely octahedral, with the V=O bond occupying one coordination site.
2. **KB2 and KB3 Complexes**: These complexes exhibit mixed coordination with aminobenzoic acids coordinating through carboxylate groups and biuret through carbonyl oxygen atoms. The coordination geometry is probably octahedral with the vanadyl oxygen in the axial position.
3. **Ligand Coordination Modes**: Biuret demonstrates its versatility by coordinating through carbonyl oxygen atoms rather than through deprotonated NH_2 groups, likely due to the pH conditions during synthesis.

Comparison with Related Complexes

The synthesized complexes show similarities to previously reported vanadyl-biuret complexes, particularly in terms of the characteristic V=O stretching frequency and coordination through carbonyl groups. However, the incorporation of aminobenzoic acids as co-ligands introduces unique structural and electronic features.

The IR spectroscopic data are consistent with those reported for bis(biuret) copper(II) dichloride and nickel(II) analogues, supporting the proposed coordination modes. The EPR parameters provide valuable information for understanding the electronic structure differences arising from the mixed-ligand environment.

Conclusion

Three novel heteroligand vanadyl(IV) complexes have been successfully synthesized and characterized. The complexes $[VO(L^2)_2]\cdot SO_4$ (KB1), $[VO(o\text{-}ABK)_2\cdot L^2]$ (KB2), and $[VO(p\text{-}ABK)_2\cdot L^2]$ (KB3) represent interesting examples of mixed-ligand coordination chemistry.

Key findings include:

1. Successful synthesis of stable heteroligand vanadyl complexes under mild conditions.
2. Confirmation of biuret coordination through carbonyl oxygen atoms, as evidenced by IR spectroscopy.
3. Evidence for octahedral coordination geometry around the vanadyl center with retention of the characteristic V=O bond.
4. Demonstration of the ability of aminobenzoic acids to act as co-ligands in vanadyl complexes.
5. EPR spectroscopy providing detailed insights into the electronic structure and coordination environment.

The polymeric nature of the KB1 complex, evidenced by the rapid precipitation and sulfate coordination, suggests potential applications in materials science. The mixed-ligand nature of these complexes may offer advantages in terms of solubility, stability, and biological activity compared to homoligand analogues.

Future work should focus on single-crystal X-ray diffraction studies to confirm the proposed structures, as well as investigation of the biological and catalytic activities of these compounds. The successful synthesis of these heteroligand complexes opens new avenues for the development of vanadyl-based materials with tailored properties.

Acknowledgment

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Conflict of interest

The authors declare no conflicts of interest.

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