



SYNTHESIS AND SPECTRAL STUDIES OF OXOVANADIUM(IV) SCHIFF BASE COMPLEXES DERIVED FROM 1,1'-OXALYLDIIMIDAZOLE AND AROMATIC AMINES

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New Schiff base (L), derived from condensation of 1,1'-oxalyldiimidazole with *o*-phenylenediamine has been prepared. Five new oxovanadium(IV) complexes (one is [VO(L)]SO₄ and four [VO(mac)]SO₄) have been carried out by using *in situ* method of preparation where vanadyl ion act as kinetic template for the Schiff bases. The synthesized complexes were characterized by elemental analyses, conductometric measurements, magnetic moments, IR, ESR and electronic spectroscopy. These complexes contain VO²⁺ group and have square pyramidal geometry wherein Schiff bases act as tetradentate chelating ligands.

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Introduction

In fact, Schiff base ligands are able to stabilize many different metals in various oxidation states. They controlling the performance of metals in a large variety of applications in clinical, analytical and biological in addition to catalysis.^{1,2} A large number of Schiff base complexes have biological interest.^{3,4} It is known that the existence of metal ions bonded to biologically active compounds may enhance their activities.^{5,6} In metal coordination chemistry, Schiff bases occupy an important position as ligand due to the incorporation of transition metals into Schiff bases. This result in an increment in biological activity of the ligand and decrease in the cytotoxic effects of both ligand and metal ion on the host.⁷ The progress in the field of bioinorganic chemistry has increased the interest in Schiff base complexes. The coordination behavior of vanadium complexes is of great interest due to its presence in biological system as trace element. It has been observed that oxovanadium(IV) complexes are more stable than five or six coordinated vanadium.⁸ The *o*-phenylenediamine can form chelate ring using *in-situ* method of synthesis in presence of metal cation due to kinetic template effect.⁹⁻¹¹

With these assumptions a new series of oxovanadium(IV) complexes were synthesized using *in situ* method of synthesis by condensation of β -diketones viz. acetylacetone, benzoylacetone, thenoyltrifluoroacetone and dibenzoylmethane with *o*-phenylenediamine in molar ratio 1:2 in the presence of VO²⁺ cation as kinetic template using 1,1'-oxalyldiimidazole. These complexes were isolated in solid state and their tentative structures have been assigned on the basis of elemental analyses, molar conductance, magnetic susceptibility measurements and spectral (IR, ESR and electronic) data.

Experimental

Materials

Oxovanadium(IV) sulfate, oxalyldiimidazole and *o*-phenylenediamine were procured from Aldrich. The β -diketones viz. acetylacetone, benzoylacetone, thenoyltrifluoroacetone and dibenzoylmethane were purchased from Sisco Research Laboratories Pvt. Ltd., Mumbai, India.

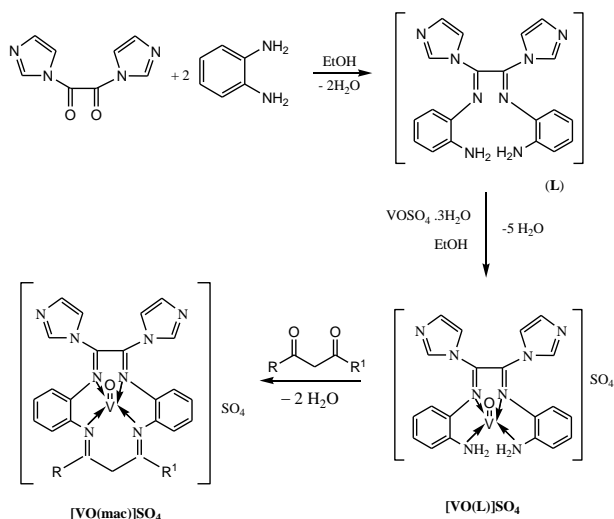
Analytical and physical measurements

Vanadium was estimated gravimetrically as its vanadate, after decomposing the oxovanadium complex with concentrated nitric acid.¹² Sulfur was estimated as barium sulfate.¹³ The melting point (uncorrected) determination was done by using sulfuric acid bath. Toshniwal conductivity bridge, model no. CLO102A was used for measurement of conductance at room temperature. The magnetic susceptibilities of the complexes in powder form were carried out at room temperature using Gouy's balance. Mercury tetrathiocyanatocobaltate(II), Hg[Co(CNS)₄], ($\chi_g = 16.44 \times 10^{-6}$ c.g.s. unit at 20 °C), was used as calibrant in conductance measurement. The electronic spectra of these complexes were recorded on Beckmann DU-2 spectrophotometer in the range 2000-185 nm. The room temperature and LNT ESR spectra were recorded at RSIC, IIT, Chennai, India. The IR spectra of the complexes in the range 4000-200 cm⁻¹ were recorded in KBr on Perkin-Elmer 621.

Synthesis of oxovanadium(IV) complexes

In order to prepare [VO(mac)]SO₄, an ethanolic solution of vanadyl sulfate (2 mmol, 1.630 g) was added gradually to a refluxing solution of 1,1'-oxalyldiimidazole (2 mmol, 0.380 g) and *o*-phenylenediamine (4 mmol, 0.432 g) in ethanol (50 mL) in RB flask (Scheme 1). The color of the reaction mixture turned into dirty green after mixture was refluxed for 2 h. Precipitate was filtered off and washed with cold ethanol. Solid product was dried under in vacuum

desiccator over silica gel. Purity of the complex was checked by TLC (yield: 55 %, type I). Ethanolic mixture of type I complex further reacted for 2 h with β -diketones (such as acetylacetone, benzoylacetone, thenoyltrifluoroacetone or dibenzoylmethane) in ratio 1:1 to get macrocyclic complex (type II). The purity of the macrocyclic product was checked by TLC.



Scheme 1. Synthesis of oxovanadium(IV) complexes.

[VO(L)]SO₄

Yield 45 %. F. W. 533.42. Decomposition temp. 218 °C. IR (KBr): 1624 (C=N), 304 (V-N), 982 (V=O), 1140 (SO₄⁻), 958 (SO₄⁻), 608 (SO₄⁻), 3350 (N-H_{asym}), 3179 (N-H_{sym}) cm⁻¹. Anal. Calcd. for C₂₀H₁₈N₈VSO₅: C 45.0, H 3.4, N 21.0, V 9.6, S 6.0 Found: C 44.9, H. 3.3, N 20.9, V 9.6, S 5.9. μ_{eff} . BM (300 °C): 17.6.

[VO(mac¹)]SO₄

Yield 50 %. F. W. 517.47. Decomposition temp. 221 °C. IR (KBr): 1620 (C=N), 303 (V-N), 980 (V=O), 1133 (SO₄⁻), 955 (SO₄⁻), 604 (SO₄⁻) cm⁻¹. Anal. Calcd. for C₂₃H₂₀N₈VSO₅: C 48.3, H 3.5, N 19.6, V 8.9, S 5.6 Found: C 48.3, H. 3.8, N 19.5, V 8.8, S 5.5. μ_{eff} . BM (300 °C): 17.2.

[VO(mac²)]SO₄

Yield 48 %. F. W. 633.54. Decomposition temp. 217 °C. IR (KBr): 1618 (C=N), 300 (V-N), 980 (V=O), 1133 (SO₄⁻), 956 (SO₄⁻), 602 (SO₄⁻) cm⁻¹. Anal. Calcd. for C₂₈H₂₂N₈VSO₅: C 53.1, H 3.5, N 17.7, V 8.0, S 5.1 Found: C 52.7, H. 3.4, N 18.0, V 7.9, S 5.0. μ_{eff} . BM (300 °C): 17.1.

[VO(mac³)]SO₄

Yield 55 %. F. W. 693.54. Decomposition temp. 220 °C. IR (KBr): 1622 (C=N), 302 (V-N), 982 (V=O), 1134 (SO₄⁻), 955 (SO₄⁻), 604 (SO₄⁻) cm⁻¹. Anal. Calcd. for

C₂₆H₁₇N₈VS₂O₅F₃: C 45.0, H 2.5, N 16.2, V 7.4, S 9.3 Found: C 44.9, H. 2.4, N 16.1, V 7.3, S 9.2. μ_{eff} . BM (300 °C): 17.2.

[VO(mac⁴)]SO₄

Yield 55 %. F. W. 695.61. Decomposition temp. 229 °C. IR (KBr): 1622 (C=N), 302 (V-N), 984 (V=O), 1133 (SO₄⁻), 956 (SO₄⁻), 602 (SO₄⁻) cm⁻¹. Anal. Calcd. for C₃₃H₂₄N₈VSO₅: C 57.0, H 3.5, N 16.1, V 7.3, S 4.6 Found: C 56.5, H. 3.4, N 16.0, V 7.3, S 4.5. μ_{eff} . BM (300 °C): 17.5.

where, L = Ligand derived by condensation of 1,1'-oxalyldiimidazole with o-phenylenediamine (1:2), mac¹ = macrocyclic ligand derived by condensation of L with acetylacetone, mac² = macrocyclic ligand derived by condensation of L with benzoylacetone, mac³ = macrocyclic ligand derived by condensation of L with thenoyltrifluoroacetone, mac⁴ = macrocyclic ligand derived by condensation of L with dibenzoylmethane.

Results and Discussion

The oxovanadium(IV) complexes were synthesized by initially refluxing the reaction mixture of 1,1'-oxalyldiimidazole with o-phenylenediamine and vanadyl sulfate in 1:2:1 molar ratio in aqueous ethanol and then reacting the products with β -diketones. The reactions appear to proceed according to the Scheme 1. Elemental analyses of the complexes, given above, proved 1:1 molar ratio of metal to ligand stoichiometry.

Infrared Spectra

The important bands of the infrared spectra for the complexes have been given above. The oxovanadium(IV) exhibit >C=N absorption around 1624-1618 cm⁻¹, which normally appears at 1660 cm⁻¹ in free ligands.¹⁴⁻¹⁶ The lowering of this frequency in the complex [VO(L)]SO₄ indicate the coordination of nitrogen atoms of the azomethine groups to the vanadium.¹⁶⁻¹⁸ The presence of a band around 300 cm⁻¹ may be show ν (V-N) vibration.¹⁹ The presence of >C=N band and the absence of the >C=O band at around 1700 cm⁻¹ indicates the condensation of the o-phenylenediamine with the keto group of 1,1'-oxalyldiimidazoles.¹⁸ The band appearing at 3350 and 3179 cm⁻¹ may be assigned to asymmetrical and symmetrical N-H stretching modes of the coordinated terminal amino group of the o-phenylenediamine.²⁰ The complexes show a band at around 980 cm⁻¹, which is assigned to ν (V=O) vibration.²¹ The presence of SO₄²⁻ group in the complexes is indicated by the appearance of three bands at ca. 1133-1140 cm⁻¹ (ν_3), 955-958 cm⁻¹ (ν_1) and 602-608 cm⁻¹ (ν_4). The absence of a ν_2 band and non-splitting band of ν_3 band indicate the retention of tetrahedral symmetry.²² The IR spectra of the complexes of the type [VO(mac)]SO₄ show the same pattern of bands but the asymmetrical and symmetrical N-H stretching modes of terminal amino groups disappear due to condensation of these amino groups with carbonyl groups of β -diketones in cyclization reactions.

Electronic Spectra

The electronic spectra exhibit bands in the regions 11,080 – 12,020 cm^{-1} , 15,120 – 15,900 cm^{-1} and 21,095–22,030 cm^{-1} . These spectra are similar to other four coordinate oxovanadium(IV) complexes involving nitrogen donor atoms. These spectral bands are evaluated according to an energy level scheme reported by Tsuchimoto et al.²² for distorted, five coordinate square pyramidal oxovanadium(IV) complexes.²³ The observed bands can be assigned to ${}^2B_2 \rightarrow {}^2E$, ${}^2B_2 \rightarrow {}^2B_1$ and ${}^2B_2 \rightarrow {}^2A_1$ transitions, respectively. One band is also observed in the region 35,200 – 35,750 cm^{-1} , which may be due to transition of the azomethine linkages.²⁴

Molar Conductance

The molar conductance values (Λ_M) of the oxovanadium(IV) complexes were measured in DMF and the obtained values are between 80–110 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ indicating their 1:1 electrolytic nature.

Magnetic Moment

Effective magnetic moments (μ_{eff}) values of the complexes were measured at room temperature and the observed values were lie in the range 1.71–1.76 B.M. which are in agreement to a $3d^1$ -system of square-pyramidal oxovanadium(IV) centre.²³

ESR Spectra

The X-band ESR spectra of the complexes were recorded in DMSO at room temperature and at LNT (177 K). ESR spectra of the oxovanadium(IV) complexes were analyzed by the method of Mishra, Tan and Ando et al.^{25–27} The room temperature ESR spectra show eight lines, which are due to hyperfine splitting originating from the interaction of the unpaired electron with a ${}^{51}\text{V}$ nucleus having the nuclear spin, $I = 7/2$. This nuclear spin confirms the presence of a single oxovanadium(IV) cation as the metallic centre in the complexes. The anisotropy is not observed due to rapid tumbling of molecules in solution at room temperature and only g -average values at about 1.902 are recorded. The anisotropy is clearly visible in the spectra at LNT and eight bands each due to g_{\parallel} and g_{\perp} are observed at about 1.920 and 1.985 separately which are corresponds to a square pyramidal structure.^{28–30} The g_{\parallel} , g_{\perp} , A_{\parallel} and A_{\perp} values are recorded from the spectra, which are in good agreement for a square-pyramidal structure. Further, g values of all very close to the spin-only value (free electron value) of 2.0020, suggesting little spin-orbit coupling. On the basis of the above studies, the tentative structures are proposed for these oxovanadium(IV) complexes of the type $[\text{VO}(\text{L})]\text{SO}_4$ and $[\text{VO}(\text{mac})]\text{SO}_4$ is given in the Scheme 1.

Conclusions

The present investigation demonstrates simple synthetic routes to 5 new oxovanadium(IV) complexes with tetraaza macrocyclic ligands. The spectral data suggest that the 1,1'-

oxalyldiimidazole is good chelating agents having two reactive carbonyl groups capable of undergoing Schiff base condensation with *o*-phenylenediamine. Schiff bases prepared by condensation of 1,1'-oxalyldiimidazole with *o*-phenylenediamine behave as tetradentate ligands by bonding to the metal ion through the azomethine nitrogen and amino group. The analytical data show the presence of one metal ion per ligand (1:1 metal and ligand) molecule and suggest a mononuclear structure for the VO^{2+} complexes. The electrical conductance, magnetic moment values, infrared, ESR and electronic spectral data indicated a square pyramidal structure for $\text{VO}(\text{IV})$ complexes. X-ray crystallographic data of the synthesized oxovanadium(IV) complexes, which might have confirmed the tentative structures, could not be possible because suitable crystals were not isolated.

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The author(s) declare(s) that there is no conflict of interest regarding the publication of this paper.

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