

Synthesis, characterization and redox properties of some O,N,O-pincer complexes of oxovanadium species.

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Abstract :

Dipicolinic acid (H_2L^1) is found to act as a pincer ligand towards oxovanadium (IV) species in presence of another ligand like bipyridine (L^2) or phenanthroline (L^3) in refluxing ethanol to produce mixed ligand complexes, i.e., complex **1** and complex **2** respectively. Both the complexes are found to be one-electron paramagnetic and hence show axial ESR spectra at 77 K. X-ray crystallographic study of complex **1** could be achieved and it is found here dipicolinic acid acts as a O,N,O- donor and the neutral ligands act as N,N donor. These complexes show intense MLCT transitions in the visible region. Cyclic voltammetry on both the complexes show that vanadium (IV)/ vanadium(V) oxidation occurs around 1.04 to 1.10 V vs SCE and a bipyridine/phenanthroline reduction occurs around -1.21 to -0.84 V vs SCE.

Keywords :

Oxovanadium complexes, dipicolinic acid, ESR, cyclic voltammetry and X-ray crystallography. Pincer ligands are a family of organic compounds which are tridentate generally mono-anionic compounds. These ligands bind to metal ions to produce robust complexes having adjacent chelate rings. Synthesis, characterization and study of reactivity have been done extensively with pincer complexes [1]. In pincer ligands the donor atoms may show a lot of variation as N, O, P, S, C etc.

The chemistry of vanadium compounds have been well known due to their catalytic activity [2] as well as biological activity [3]. Synthesis of vanadium compounds to study the chemical behaviour of various oxidation states (+2 to +5) has also been performed with great interest [4]. Oxovanadium(IV) complexes have the potential to act as redox catalyst since the central metal atom can readily undergo one-electron oxidation or reduction [5].

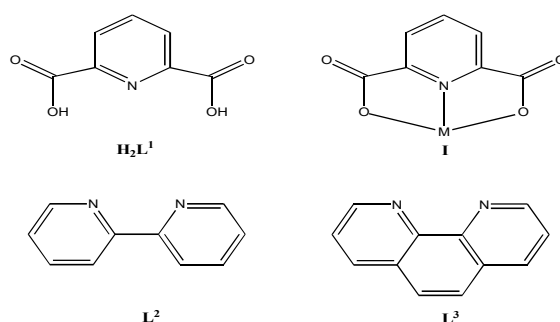


Figure 1

For the present study dipicolinic acid (H_2L^1) (where H stands for the dissociable carboxylic proton) is chosen which has the potential to act as a O,N,O-donor ligand. Along with dipicolinic acid; 2,2'- bipyridine (L^2) and 1,10-phenanthroline (L^3) is taken as two neutral N,N-donor ligand. Ligand L^1 has the potential to bind as a pincer ligand while binding to a metal ion and thereby can form two adjacent five-membered chelate rings.

Bis(acetylacetonato)oxovanadium(IV) was made to react with H_2L^1 and one of the neutral N,N- ligand to form two mixed ligand oxovanadium (IV) complexes.

Experimental Materials :

Commercial vanadyl sulphate and 2,6-dipicolinic acid were obtained from LobaChemie; 2,2'-bipyridine and 1,10-phenanthroline were obtained from Merck and acetylacetonone (acac) was obtained from SRL, India. All other chemicals and solvents were reagent grade commercial materials and were used as received. Tetrabutylammonium hexafluorophosphate (TBHP) for cyclic voltametric study was procured from Sigma Aldrich.

Preparations [VO(acac)₂] :

This preparation was done following a reported method [6]. $VOSO_4 \cdot 5H_2O$ (1 gm, 0.0039 mmol) was dissolved in 15 ml warm water and was added to a solution of anhydrous Na_2CO_3 (1 gm, 0.2170 mmol) and acetylacetonone (1 gm, 0.01 mmol) in 15 ml water. The resulting solution was warmed at 70° C and was then allowed to cool on an ice-bath. $[VO(acac)_2]$ separated as a green crystalline precipitate which was collected by filtration, washed thoroughly with little ice-cold water (5 ml) followed by two 5 ml portions of ice-cold ethanol, and dried in vacuo. Yield: 90%.

Preparation of complex 1 :

To a solution of 2,6-dipicolinic acid (63 mg, 0.38 mmol) and 2,2'- bipyridine (49 mg, 0.38 mmol) in ethanol (40 ml) was added $VO(acac)_2$ (100 mg, 0.38 mmol). The mixture was then refluxed for 3 hours to yield a greenish-yellow solution. The solvent was evaporated to yield a greenish-yellow residue. This product was purified to obtain complex **1** by crystallising from dichloromethane-acetonitrile solution. Complex **1** was obtained as a crystalline greenish-yellow solid. Yield: 104 mg (77%).

Preparation of complex 2 :

To a solution of 2,6-dipicolinic acid (63 mg, 0.38 mmol) and 1,10-phenanthroline (68 mg, 0.38 mmol) in ethanol (40 ml) was added $VO(acac)_2$ (100 mg, 0.38 mmol). The mixture was then refluxed for 3 hours to yield a yellow solution. The solvent was evaporated to yield a yellow residue. This product was purified to obtain complex **2** by crystallising from dichloromethane-acetonitrile solution. Complex **2** was obtained as a crystalline yellow solid. Yield: 115 mg (74%).

Physical measurements :

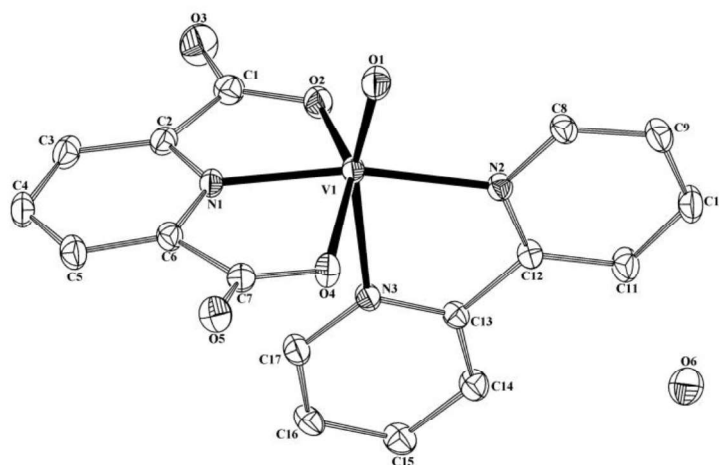
ESR spectra were recorded with JEOL JES-FA200 X-band spectrometer filled with a quartz Dewar for measurements at 77 K (liquid dinitrogen). All ESR spectra were calibrated with an aid of DPPH ($g = 2.0037$). Electronic spectra were recorded on a JASCO V-570 UV-VIS-NIR spectrophotometer. IR spectra a PAR were obtained on a Perkin-Elmer (Paragon) FT spectrometer with samples prepared as KBr pellets. Electrochemical measurements were made using a CH Instruments model 600A electrochemical analyzer. A platinum disc working electrode, a platinum wire auxiliary electrode and an aqueous saturated calomel reference electrode (SCE) were used in the cyclic voltammetry experiments. All electrochemical experiments were performed under dinitrogen atmosphere at 298 K.

X-ray crystallography :

Data for single crystal of complex **1** was obtained from Bruker SMART APEX CCD diffractometer using graphite monochromated and Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). X-ray data reduction, structure solution and refinement were done using SHELXS-97 and SHELXL-97 programs [7]. The structure was solved by the direct methods. Selected crystal data and data collection parameters are given in **Table S1** in supplementary material provided.

Results and discussion Synthesis and crystal structure :

Two mixed ligand complexes of oxovanadium(IV), complexes **1** and **2**, were produced by reacting VO(acac)₂ with 2,6-dipicolinic acid (**H₂L¹**) and a neutral N,N-donor ligand (**L²/L³**). Spectral analysis of these two complexes suggested that **H₂L¹** is probably coordinated to the oxovanadium centre as dianionic tridentate O,N,O-pincer ligand along with coordinated 2,2'-bipyridine or 1,10-phenanthroline. To authenticate the structure of these complexes X-ray crystallographic study of complex **1** was done. The structure is shown in **Figure 2** and the bond parameters are enlisted in **Table 1**. From **Figure 2** it can be observed that the structure of complex **1** is indeed as expected with two adjacent five-membered chelate rings formed by **L¹** with bite angle 77.24° and 76.80°. The overall structure is found to be distorted octahedron where other three coordination sites being occupied by 2,2'-bipyridine and an oxo group. The observed V-O and V-N distances are normal [8]

**Figure 2**

Bond distance (Å)			
V1-O1	1.6009(11)	V1-N2	2.1361(14)
V1-O2	2.0161(10)	V1-N3	2.0293(12)
V1-O4	2.0524(10)	V1-N1	2.0269(13)
Bond angles (°)			
O1-V1-N1	106.49(6)	O4-V1-N1	76.80(4)
O1-V1-N3	163.20(6)	N2-V1-N3	72.69(5)
O2-V1-N1	77.24(4)		

Table 1: Selected bond distances (Å) and bond angles (°) for complex **1**

Spectral properties :

Magnetic susceptibility measurements show that both the vanadium complexes are one electron paramagnetic, which correspond to the +4 oxidation state of vanadium (d^1 , $S = \frac{1}{2}$) in these complexes. ESR spectra of both complex **1** and **2** have been recorded in 1:1 dichloromethane-toluene solution at room temperature and also at 77K. The room temperature spectra of both the complexes shows a typical eight-line spectra for vanadium(IV). Complex **1** and **2** show axial ESR spectra at 77K, where two signals are split into eight components each. Though all sixteen signals could not be identified due to overlap but still thirteen signals could be distinctly found for both the complexes as shown in **Figure S1** and **Figure S2** for complex **1** at 77K and complex **2** at room temperature respectively.

Infrared spectra of the complexes show many bands within 400-4000 cm^{-1} of varying intensities. It was observed in the spectra of both the complexes that the stretching frequency for the O-H group of the carboxylic acid group present in the uncoordinated ligand around 3000 cm^{-1} was absent. This indicated that the proton associated with the carboxylic acid group got dissociated during formation of the complex. Also, a sharp and strong band at 1681 cm^{-1} in both the complexes was due to the presence of carboxylate (C=O) stretching. Another sharp and strong band at 978 cm^{-1} is associated with oxovanadium (V=O) stretching [8]. Infrared spectrum of complex **1** is shown in **Figure S3**. The ESR and infrared spectral data of both the complexes are consistent with their structure.

The oxovanadium complexes are found to be readily soluble in common organic solvents producing greenish-yellow solutions. The electronic spectra of the complexes recorded in dichloromethane solution show several absorption peaks in visible and ultraviolet region. The absorptions in ultraviolet region can be assigned to the transitions within the ligand. It is expected that the HOMO of the complex is mainly based on the metal centre while the LUMO is mainly centred on bipyridine or phenanthroline. Hence absorption in visible region for complexes **1** and **2** can be assigned to transition from HOMO to LUMO of the complex. The data for the electronic spectra of the two oxovanadium complexes are given in **Table 2** and a sample spectrum is shown in **Figure S4**.

Compound	Electronic spectral data λ_{max} , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$)
Complex 1	417 (530), 300 (8900), 242 (8800)
Complex 2	451 (620), 362 (960), 272 (25900)

Table 2 : Electronic spectral data of complex **1** and **2**

Electrochemical properties :

Electrochemical properties of complexes **1** and **2** have been studied by cyclic voltammetry in acetonitrile solution (0.1 M TBHP). Complexes **1** and **2** show one oxidative response on the positive side of the SCE and one reductive response on the negative side (**Table 3**). Here both the oxidative and reductive responses are irreversible in nature and show non-stoichiometric current. Since in these two complexes HOMO is located over metal orbital and LUMO over bipyridine/phenanthroline hence oxidative response may be attributed to oxidation of vana-

dium(IV) to vanadium(V) and the reductive response to the reduction of ligand, i.e., bipyridine / phenanthroline.

Compound	Cyclic voltammetric data E (V) vs SCE
Complex 1	1.1011, -0.8409
Complex 2	1.0485, -1.2117

Table 3: Cyclic voltammetric data of complex 1 and 2

Cyclic voltammogram of complex 2 in 1:9 dichloromethane-acetonitrile solution (0.1 M TBAP) at a scan rate of 50 mVs^{-1} is shown in **Figure 3**.

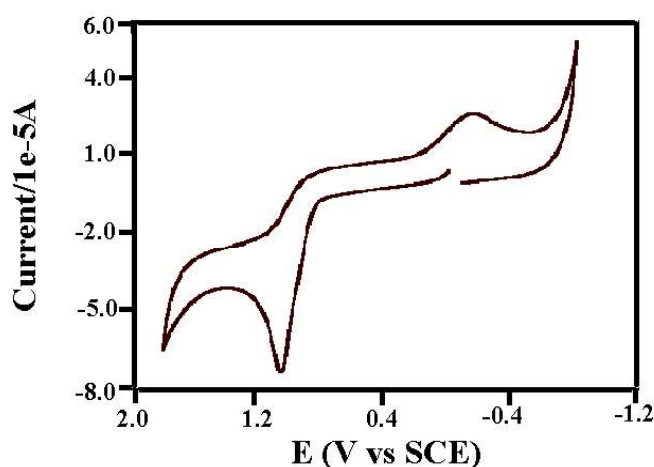


Figure 3

Conclusions :

The present study shows that dipicolinic acid (H_2L^1) can form stable, octahedral mixed ligand oxovanadium (IV) complexes along with neutral N,N-donor ligands. Here dipicolinic acid coordinate to the metal centre as dianionic, tridentate O,N,O-pincer ligand and thereby form two five membered chelates.

References :

1. Singh, A. and Gelman, D. (2020) "Cooperative Reactivity in Carbometalated Pincer-Type Complexes Possessing an Appended Functionality" *ACS Catalysis* 10; 2, 1246-1255.
2. Alig, L.; Fritz, M. and Schneider, S. (2019), "First-Row Transition Metal (De)Hydrogenation Catalysis Based On Functional Pincer Ligands" *Chemical Reviews* 119; 4, 2681-2751
3. Yang, X-Y.; Tay, W. S.; Li, Y.; Pullarkat, S. A. and Leung, P-H. "Versatile Syntheses of Optically Pure PCE Pincer Ligands: Facile Modifications of the Pendant Arms and Ligand Backbones" (2015) *Organometallics* 34; 8, 1582-1588
4. Morales-Morales, D. and Jensen, C. (2007) "The Chemistry of pincer compounds" Elsevier Science: Amsterdam, ISBN: 044531386
5. Gryca, I.; Czerwińska, K.; Machura, B.; Chrobok, A.; Shul'pina, L. S.; Kuznetsov, M. L.; Nesterov, D. S.; Kozlov, Y. N.; Pombeiro, A, J. L.; Varyan, I. A. and Shul'pin, G. B.

- (2018), “High Catalytic Activity of Vanadium Complexes in Alkane Oxidations with Hydrogen Peroxide: An Effect of 8-Hydroxyquinoline Derivatives as Noninnocent Ligands” *Inorg. Chem.* 57; 4, 1824–1839
6. Nishibayashi, Y. (2018), “Development of catalytic nitrogen fixation using transition metal–dinitrogen complexes under mild reaction conditions” *Dalton Trans.* 47; 11290–11297
 7. Miceli, C.; Rintjema, J.; Martin, E.; Escudero-Adán, E. C.; Zonta, C.; Licini, G. and Kleij, A. W. (2017), “Vanadium(V) Catalysts with High Activity for the Coupling of Epoxides and CO₂: Characterization of a Putative Catalytic Intermediate”. *ACS Catal.* 7; 4, 2367–2373
 8. Roy, S.; Böhme, M.; Dash, S. P.; Mohanty, M.; Buchholz, A.; Plass, W.; Majumder, S.; Kulanthaivel, S.; Banerjee, I.; Reuter, H.; Kaminsky, W. and Dinda, R. (2018), “Anionic Dinuclear Oxidovanadium(IV) Complexes with Azo Functionalized Tridentate Ligands and μ -Ethoxido Bridge Leading to an Unsymmetric Twisted Arrangement: Synthesis, X-ray Structure, Magnetic Properties, and Cytotoxicity”. *Inorg. Chem.* 5; 10, 5767–5781
 9. Hosseini, M-J.; Shaki, F.; Ghazi-Khansari, M. And Ghazi-Khansari, J. P. (2013) “Toxicity of vanadium on isolated rat liver mitochondria: a new mechanistic approach” *Metallomics*, 5; 152-166
 10. Boynton, J. N.; Guo, J-D.; Fetting, J. C.; Melton, C. E.; Ngase, S. And Power, P. P. (2013) “Linear and Nonlinear Two-Coordinate Vanadium Complexes: Synthesis, Characterization, and Magnetic Properties of V(II) Amides” *J. Am. Chem. Soc.* 135; 29, 10720–10728
 11. Schmidt, A-C.; Hermsen, M.; Rominger, F.; Dehn, R.; Teles, J. H.; Schafer, A.; Trapp, O. and Schaub, T. (2017) “Synthesis of Mono- and Dinuclear Vanadium Complexes and Their Reactivity toward Dehydroperoxidation of Alkyl Hydroperoxides” *Inorg. Chem.* 56; 3, 1319–1332
 12. Parihar, S.; Pathan, S.; Jadeja, R. N.; Patel, A. and Gupta, A. K. (2012) “Synthesis and Crystal Structure of an Oxovanadium(IV) Complex with a Pyrazolone Ligand and Its Use as a Heterogeneous Catalyst for the Oxidation of Styrene under Mild Conditions” *Inorg. Chem.* 51; 2, 1152–1161
 13. Ogunlaja, A. S.; Chidawanyika, W.; Antunes, E.; Fernandes, M. A.; Nyokong, T.; Torto, N. and Tshentu, Z. R. (2013) “Oxovanadium(IV)-catalysed oxidation of dibenzothiophene and 4,6-dimethyldibenzothiophene” *New J. Chem.* 37; 4220-4229
 14. Bryant, B. E.; Fernelius, W. E., Bausch, D. E.; Stoufer, R. C. and Stratton, W. (1957), “Vanadium(IV) Oxy(acetylacetonate)”. *Inorg. Synth.* 5; 113-116.
 15. G. M. Sheldrick, SHELXS-97 and SHELXL-97, Fortran programs for crystal structure solution and refinement, University of Gottingen, 1997.
 16. Carter, E.; Fallis, I. A.; Kariuki, B. M.; Morgan, I. R.; Murphy, D. M.; Tatchell, T.; van Doorslaer, S. and Vinck, E. (2011), “Structure and pulsed EPR characterization of *N,N'*-bis(5-*tert*-butylsalicylidene)-1,2-cyclohexanediamino-vanadium(IV) oxide and its adducts with propylene oxide”. *Dalton Trans.* 40; 7454-7462
 17. Hitchcock, P. B.; Lee, T. H. and Leigh, G. J. (2003) “*N,N,N',N'*-tetramethylethane-1,2-diamine complexes of vanadium chlorides”. *Inorg. Chim. Acta.* 349; 159-162
 18. Liu, S-X.; Gao, S. (1998) “Synthesis, crystal structure and spectral properties of VO(acetylacetonone benzoylhydrazone)(8-quinolinol)” *Polyhedron.* 17; 81-84