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COMMUNICATION

 C_3 Symmetric vanadium(III) complexes with *O,N*-chelating hexadentate tripodal ligands of pyrazoloneSanjay Parihar,^a R. N. Jadeja^{*a} and Vivek K. Gupta^b

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Novel C_3 Symmetric vanadium(III) complexes of tripodal ligands of pyrazolones were synthesized and characterized by various spectroscopic and analytical techniques including single crystal XRD. This is the first report on the C_3 symmetric propeller-shaped vanadium(III) complexes of tripodal ligands of pyrazolones. The complex $[VL^1]$ forms rare triple-stranded helicate having λ (Λ) and δ (Δ) isomers.

Metallosupramolecular chemistry deals with the design of highly organized architectures, based upon metal-ion-directed self-assembly processes.¹ The synthesis of metallohelicates, by twisting multidentate organic ligands (helicands), through interaction with the appropriate metal ions, played a key role in the development of supramolecular chemistry.² The key step for the design of metallohelicates is the choice of ligands. The ligands should be capable of bridging metal atom in certain directions and should also contain steric information that can be interpreted by the arrangement of the bound metal centres, resulting in the formation of helical structures.³ With respect to these requirements tripodal ligands of pyrazolones, with their high functionality, can represent a promising class of ligands for the synthesis of metallohelicates.

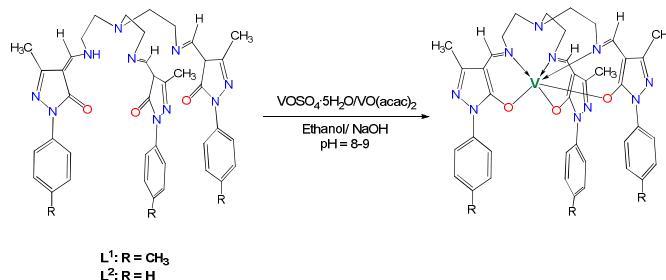
Vanadium has long been an attractive transition metal for study due to its wide range of oxidation states (usually, +3, +4 and +5 oxidation states) and associated beautiful colours of its complexes.⁴ Among these oxidation states, V^{III} has traditionally been less studied than V^{IV} or V^V , which have better defined biological/physiological and catalytic roles.⁵ High-valent V^{IV} complexes of pyrazolones are an important structural motif that has been extensively studied due to their geometrical properties and catalytic applications. However, no attention was paid to the study of low-valent V^{III} complexes of pyrazolones.⁶⁻¹⁰ Currently our group^{8,10} in parallel with the others^{7,9} have embarked on the studies of the oxidovanadium(IV) complexes of pyrazolones and their catalytic applications towards the oxidation of styrene and benzylic alcohols. The present work has originated from our continued interest in this area.

Herein we report the synthesis and structural characterization of a new class of vanadium(III) complexes $[V(L^1/L^2)]$ with tripodal ligands of pyrazolones having interesting geometrical features. These complexes are remarkable because of the following: (i) this is the first report on the C_3 symmetric propeller-shaped V^{III} complexes of pyrazolones. (ii) V^{III}

complexes were synthesized by the *in situ* reduction of $V^{IV}O$ into V^{III} (iii) crystal structure of $[VL^1]$ was obtained and revealed that three helical chains interlink one another to form rare triple-stranded helicate.

Tripodal ligands of pyrazolones were synthesized by refluxing a 1:3 ratio of tris(2-aminoethyl)amine and 4-formyl pyrazolones in dry methanol in N_2 . Vanadium(III) complexes of tripodal ligands L^1 and L^2 were synthesized by refluxing equimolar amount of tripodal ligand (L^1/L^2) and $VOSO_4 \cdot 5H_2O/VO(acac)_2$ in the presence of NaOH and ethanol as a solvent. During the reaction oxidovanadium(IV) get reduced to vanadium(III) and afforded green V^{III} complex with the ligand in 1:1 ratio (*see* Scheme 1). The reduction is facilitated by the ligand as well as base, in *in situ* complexation reaction.^{4a,11} There is no apparent change in the colour of the reaction medium during such reduction. However, the same has been confirmed from magnetic moment measurement after isolation of the solid complex. Both the complexes are stable to air and moisture, without any kind of decomposition also after several months.

Ligands were characterized by routine spectral and chemical analysis such as 1H & ^{13}C NMR, ESI-MS and elemental analyses along with their low temperature (273°C) crystal structure determination. 1H NMR and crystal structure suggests that the ligands exist in an amine-one form.¹² The solid-state structure of $[VL^1]$ has been established by single crystal X-ray diffraction analysis (at 293°C). However, we could not get good quality crystals of the complex $[VL^2]$ suitable for single crystal XRD. The green crystals of complex $[VL^1]$ suitable for X-ray structure analysis were grown in DMF at 35 °C. An ORTEP view of the complex is depicted in Fig. 1.

Scheme 1. Synthetic procedure for $[VL^1]$ and $[VL^2]$.

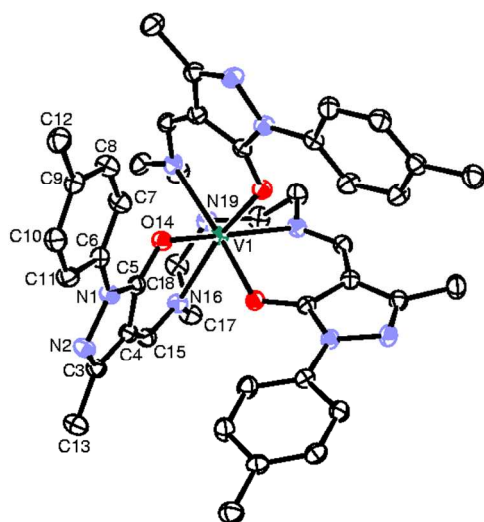


Fig 1. ORTEP view of the complex $[VL^1]$. H atoms and solvent molecule were omitted for clarity. Selected bond lengths (Å): V(1)—O(14), V(1)—O(14_i) and V(1)—O(14_{ii}) 2.0631 (17); V(1)—N(16), V(1)—N(16_i) and V(1)—N(16_{ii}) 2.164(2). Selected bond angles (°): O(14)—V(1)—N(16), O(14_i)—V(1)—N(16_i), and O(14_{ii})—V(1)—N(16_{ii}) 84.91 (7); N(16)—V(1)—N(16_i), N(16)—V(1)—N(16_{ii}) and N(16_i)—V(1)—N(16_{ii}) 109.52 (6); O(14)—V(1)—O(14_i), O(14)—V(1)—O(14_{ii}) and O(14_i)—V(1)—O(14_{ii}) 83.26 (8); O(14)—V(1)—N(16_{ii}), O(14_i)—V(1)—N(16_{ii}) and O(14_{ii})—V(1)—N(16_{ii}) 159.02 (8); O(14)—V(1)—N(16_i), O(14_i)—V(1)—N(16_i) and O(14_{ii})—V(1)—N(16_i) 78.15 (8).

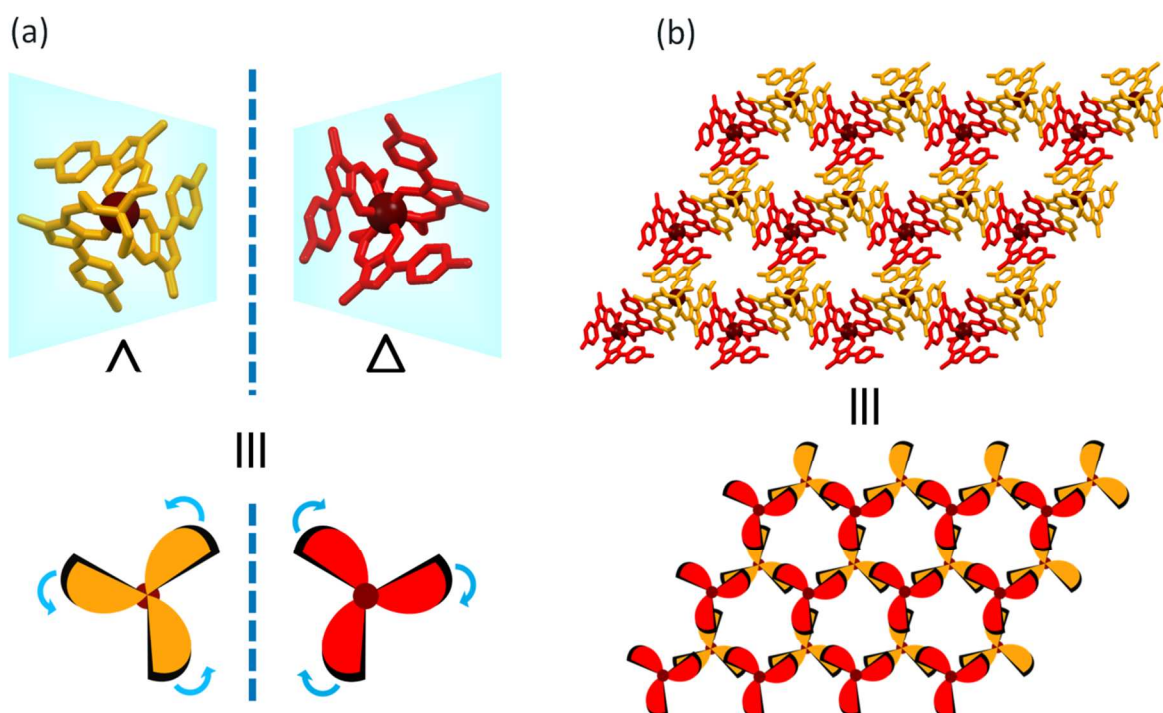


Fig 2. (a) Crystal structure and cartoon depiction of propeller shaped C_3 symmetric λ - and δ - isomers of vanadium complex observed in $[VL^1]$; (b) packing diagram down c -axis depicts the alternate arrangement of λ - and δ - isomers which is attributable to the racemic (achiral) nature of the compound.

The ligand coordinated to central metal atom to give a mononuclear complex $[VL^1]$, resembling a three-bladed propeller, in which each blade is derived from a pyrazolone

X-ray crystallographic characterization revealed that $[VL^1]$ crystallizes in trigonal system with space group $P-3$ and one pyrazolone moiety in asymmetric unit. The ligand L^1 is coordinated with vanadium as a hexadentate N_3O_3 donor creating three six-membered chelate rings. The coordination around the vanadium is distorted from ideal octahedral geometry. The bond lengths of V(1)—O(14), V(1)—O(14_i) and V(1)—O(14_{ii}) were found to be similar 2.0631 (17) Å, which have been increased from the previous reported bond lengths (V—O) in vanadium complexes of pyrazolones from 1.969(3)–2.018(2).^{2,3,5} The bond lengths of V(1)—N(16), V(1)—N(16_i) and V(1)—N(16_{ii}) were also found to be similar 2.164(2) Å in the $[VL^1]$. The bite angles O(14)—V(1)—N(16), O(14_i)—V(1)—N(16_i) and O(14_{ii})—V(1)—N(16_{ii}) were also identical and found to be 84.91°. The crystal structure suggests that the structure of $[VL^1]$ approximates to C_3 symmetry with the axis passing through the tertiary N atom and the central V^{3+} ion. Usually, in the C_3 symmetric mononuclear complexes vanadium is four or five coordinated, while in this case vanadium is roughly six coordinated.¹³ However, the intramolecular distance of V(1)...N(19) is 2.53 Å, which suggests that the coordination around vanadium is not exactly 6-fold, but is half way between 6- and 7-fold.

moiety and each blade is piled to the next blade in either clockwise or counter clockwise direction by 32.38° to the C_3 axis to form helical chains. The C_3 symmetric λ and δ

(Δ) isomers of $[\text{VL}^1]$ are depicted in the Fig 2. It is interesting that three such helical chains intertwine one another to result in a rare triple-stranded helicate. The helical assemblies form an achiral compound, a racemic mixture of alternating clock and anticlockwise spinning helices has been found (Fig 3). Helical vanadium complexes have been reported in numerous reports,¹⁴ however as per our knowledge this is the first example of triple-stranded helical complex of vanadium.

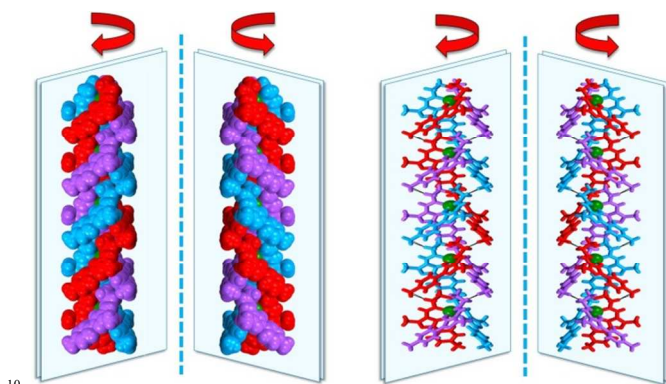


Fig 3. Mirror image relation of right and left handed helical motifs composed of achiral building blocks in $[\text{VL}^1]$.

Crystal structural analysis indicates no significant intermolecular interactions among three strands; however, there exist supramolecular interactions between the adjacent helices. As depicted in Fig. 4, every single strand of the triple helix forms weak $\text{C-H}\cdots\pi$ interaction (Hydrogen-to-centroid distance 3.594 Å) with a neighbouring strand belonging to the adjacent triple helix. This causes closely interdigitating packing and hence directs the handedness of the neighbouring triple helices. The right-handed and left-handed triple helices are aligned alternately by such $\text{C-H}\cdots\pi$ interactions to result in 2D racemic layers.

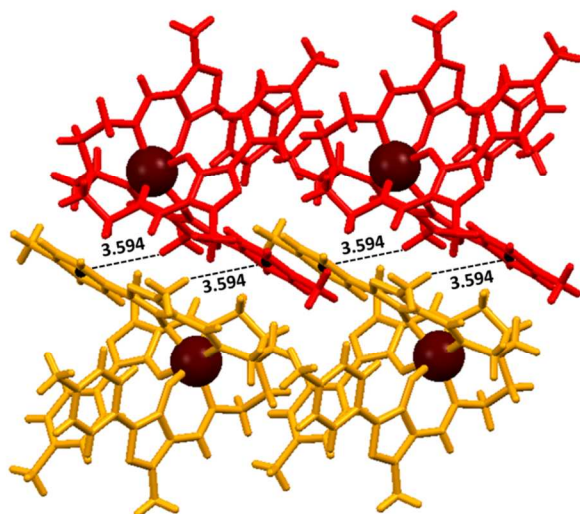


Fig 4. $\text{C-H}\cdots\pi$ interactions between the single strands belonging to the adjacent triple-stranded helices.

The LC-MS of complexes $[\text{VL}^1]$ and $[\text{VL}^2]$ show molecular ion peaks at 788.41 $[\text{M}]^+$ and 746.45 $[\text{M}]^+$, respectively, which confirm that both the complexes are mononuclear and oxido-group is not present in the complexes. The removal of oxido

group is also supported by the absence of the band for V-O stretching in the FT-IR spectra of the complexes. Electronic spectrum of $[\text{VL}^1]$ shows three $d-d$ transition bands (592 nm, 670 nm and 760 nm) and one LMCT band (473 nm) confirming the presence of vanadium in +3 oxidation state (Figure S12).^{4a} A shoulder band at 530 nm also appeared in the electronic spectrum of complex $[\text{VL}^1]$. Magnetic susceptibility measurements showed that both the complexes are paramagnetic with the effective magnetic moment (μ_{eff}) 3.12 BM and 2.94 BM for the $[\text{VL}^1]$ and $[\text{VL}^2]$, respectively, which corresponds to the +3 oxidation state of vanadium ($3d^2$) in these complexes.

In summary, two new vanadium(III) complexes of tripodal ligands of pyrazolones were synthesized and their structures were experimentally confirmed. The single-crystal XRD structure of the complex $[\text{VL}^1]$ reveals that it is a C_3 symmetric propeller shaped mononuclear complex which forms triple-stranded helical chains in which each blade is stack with the next blade in either clockwise or counter clockwise direction to form λ - and δ - isomers of the vanadium complex.

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Notes and references

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‡ Crystal data for ligand L^1 : $\text{C}_{42}\text{H}_{48}\text{N}_{10}\text{O}_3$, MW = 740.90, crystal system triclinic, space group $P-1$, $a = 10.5266$ (5) Å, $b = 13.6775$ (7) Å, $c = 14.9717$ (6) Å, $\alpha = 65.299$ (4)°, $\beta = 89.444$ (5)°, $\gamma = 84.799$ (5)°, $V = 1949.35$ (16) Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.262$ g cm⁻³, $F(000) = 788$, total reflections 14834, unique reflections 7623, Final R = 0.0595, GOF = 1.006, Final residual electron density (eÅ⁻³) = -0.151 < $\Delta\rho$ < 0.152. (CCDC 869325)

Crystal data for ligand L^2 : $\text{C}_{39}\text{H}_{42}\text{N}_{10}\text{O}_3$, MW = 698.83, crystal system triclinic, space group $P-1$, $a = 10.5310$ (11) Å, $b = 12.2330$ (12) Å, $c = 14.8664$ (15) Å, $\alpha = 113.201$ (2)°, $\beta = 91.722$ (2)°, $\gamma = 92.732$ (2)°, $V = 1755.8$ (3) Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.316$ g cm⁻³, $F(000) = 740$, total reflections 6610, unique reflections 5475, Final R = 0.1013, GOF = 1.147, Final residual electron density (eÅ⁻³) = -0.365 < $\Delta\rho$ < 0.478. (CCDC 994250)

Crystal data for complex $[\text{V}(L^1)]$: $\text{C}_{42}\text{H}_{45}\text{N}_{10}\text{O}_3 \cdot \text{C}_3\text{H}_9\text{N}$, MW = 847.93, crystal system trigonal, space group $P-3$, $a = 15.5913$ (4) Å, $b = 15.5913$ (4) Å, $c = 10.1470$ (3) Å, $\alpha = 90$ °, $\beta = 90$ °, $\gamma = 120$ °, $V = 2136.16$ (10) Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.318$ g cm⁻³, $F(000) = 896$, total reflections 4383, unique reflections 2413, Final R = 0.0458, GOF = 1.046, Final residual electron density (eÅ⁻³) = -0.32 < $\Delta\rho$ < 0.52. (CCDC 994251).

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