A Novel Pentacoordinated Dioxovanadium(V) Salicylaldiminate: Solvent Specific Crystallization of Dimorphs with Contrasting Coordination Geometries, Ligand Conformations and Supramolecular Architectures

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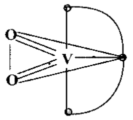
The reaction of the tridentate salicylaldimine of 2-picolylamine, $C_6H_4(OH)CHNCH_2C_5H_4N$ (HL), with bis(acetylacetonato)oxovanadium(IV) at room temperature under oxygen (or with $VOSO_4{\cdot}5H_2O$ plus H_2O_2) furnished crystalline greenish-yellow α-VO_2(L) and green β-VO_2(L) from methanol (or ethanol) and acetonitrile (or dichloromethane), respectively. The dimorphs give rise to the same solution species as revealed by spectroscopic data (UV/Vis, ^{1}H and ^{51}V NMR). Both forms react with 3,5-bis(*tert*-butyl)catechol (H_2dbcat) furnishing the known pseudooctahedral complex VO(L)(dbcat). In the α form the V(L) fragment is planar and the VO_3N_2 coordination sphere is distorted trigonal bipyramidal ($\tau = 0.55$) with the two oxo oxygen atoms and the azomethine nitrogen atom defining the trigonal plane. In β-VO_2(L) the V(L) moiety, like that in VO(L)(dbcat), is not planar but consists of two planar parts rotated away from each other along the C–N single bond. In this case the coordination sphere is distorted square pyramidal ($\tau = 0.20$) with the three donor sites of the L ligand and an oxo oxygen atom defining the tetragonal plane. Both the α and β crystal lattices consist of dimers which associate further to form supramolecules. The noncovalent intradimer and interdimer bonding interactions are predominantly of aromatic π-π stacking (aryl···pyridyl and pyridyl···pyridyl) and C–H···O hydrogen bonding (azomethine···oxo and aryl···phenolato) types in the α and β dimorphs, respectively. It is proposed that the low polarizability of methanol promotes π-π stacking of planar V(L) fragments, resulting in crystallization of the α form. When the polarizability is relatively high, as in acetonitrile, the β form crystallizes. The geometrically isomeric coordination spheres of the α and β forms are sustained by the respective supramolecular architectures. The Schiff base HL′ of 2-hydroxynapthaldehyde and 2-picolylamine has also afforded two forms of VO_2(L′) in the same manner as for VO_2(L).

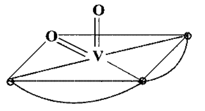
Introduction

The long-standing interest in the structure and properties of mononuclear VO_2^+ complexes[1] has multiplied with the emergence of bioinorganic linkages to the RNase transition state,[2] vanadium dependent haloperoxidase[3,4] and insulin mimicry.[5] The coordination number of the metal in VO_2^+ complexes can be six,[1,6] but the focus of the present work is on pentacoordinate species of type VO_2(tridentate), which have attracted special attention in recent years. The geometry of structurally characterized compounds of the latter type is (relatively rarely) distorted trigonal bipyramidal (dtbp, α form, as shown in **1**),[7] the common geometry being distorted square pyramidal (dsp, β form, as in **2**).[8–10] The latter geometry is particularly relevant in the context of the RNase transition state[2] and haloperoxidase activity.[3]



dtbp (α form)

1



dsp (β form)

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In the present work we report the synthesis and characterization of a remarkable pentacoordinate VO_2^+ system which has been isolated in two distinct crystalline forms by merely varying the solvent employed in the synthesis. The solid-state structural features of the dimorphs (which otherwise display identical chemical composition and solution properties) differ dramatically in coordination geometry, ligand conformation and supramolecular architecture. To the best of our knowledge, structural dimorphism of the present type is unprecedented in VO_2^+ solid-state chemistry.

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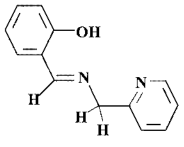
Results and Discussion

Synthesis of Dimorphs

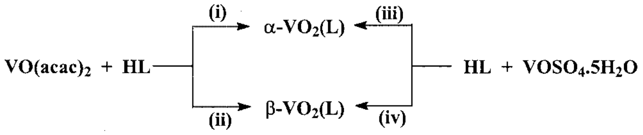
The tridentate ligand concerning us in this work is the salicylaldimine of 2-picolylamine (HL, **3**). It reacted smoothly with $VO(acac)_2$ in methanol solution at room temperature in the presence of oxygen, furnishing in excellent yield a greenish-yellow crystalline complex of composition $VO_2(L)$, designated as the α dimorph.



HL

3

A similar reaction occurred in acetonitrile solution to give the β dimorph; this complex had the same composition, but was green. The same dimorphs were also synthesized by reacting $VOSO_4 \cdot 5H_2O$ with HL using hydrogen peroxide as the oxidant (Scheme 1). The possible role of the solvent in crystallization of specific dimorphs will be considered later.



Scheme 1. Synthesis of dimorphic $VO_2(L)$ at room temperature; (i) MeOH, O_2; (ii) MeCN, O_2; (iii) MeOH, H_2O_2; (iv) MeCN, H_2O_2

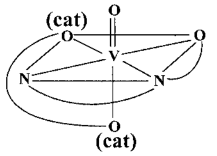
Spectra and Solution Behaviour

Spectral data are given in the Exp. Sect. Both forms display two V=O stretches near 920 and 940 cm^{-1} (KBr disk), consistent with *cis* geometry of the VO_2 moiety. Both dimorphs are insoluble except in solvents like *N*,*N*-dimethylformamide and dimethyl sulfoxide. The pale yellow solutions display identical UV/Vis spectra (within experimental error), and display a band at 395 nm. In dimethyl sulfoxide solutions the two forms give rise to identical ^{51}V NMR spectra, with a signal at $\delta = -535$ ppm. The well-resolved ^1H NMR spectra of both the α and β forms in $[D_6]$dimethyl sulfoxide are also superimposable. Thus, α-$VO_2(L)$ and β-$VO_2(L)$ must give rise to the same species in mobile solution.

Reaction with a Catechol

In dichloromethane suspension, both α and β-$VO_2(L)$ react [as shown in Equation (1)] with aromatic diols such as 3,5-di-*tert*-butylcatechol (H_2dbcat) furnishing the violet complex VO(L)(dbcat) (**4**), which is already known from the reaction of $VO(acac)_2$ with HL and H_2dbcat in air.[11] The conformation of the L ligand in VO(L)(dbcat) has close similarities to that in β-$VO_2(L)$; the significance of this is considered later.

$$VO_2(L) + H_2dbcat \rightarrow VO(L)(dbcat) + H_2O \qquad (1)$$



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Structure

The α and β dimorphs have distinctive crystal, molecular and supramolecular structures. They belong respectively to the monoclinic and triclinic crystal systems. Molecular views are given in Figure 1 and 2; selected bond parameters are listed in Table 1. In both forms, the VO_2 fragment has a *cis* geometry and the tridentate ligand is meridionally disposed. The coordination sphere is of type VO_3N_2. The metal−ligand bond lengths in the two forms are equal to within 0.02 Å. However, there are major differences in the coordination geometry, V(L) conformation and noncovalent intermolecular interactions.

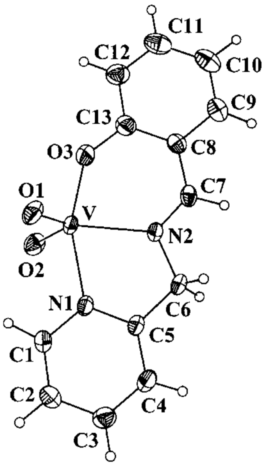


Figure 1. Perspective view and atom labeling scheme of α-$VO_2(L)$. All non-hydrogen atoms are represented by 30% thermal probability ellipsoids

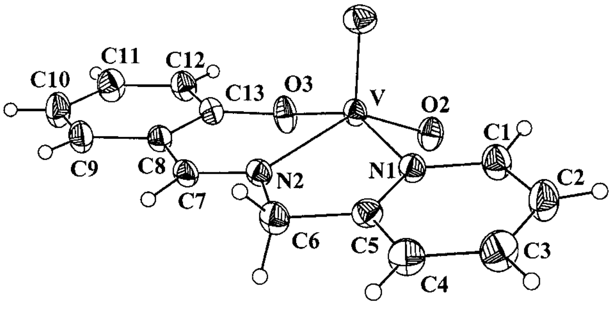


Figure 2. Perspective view and atom labeling scheme of β-$VO_2(L)$. All non-hydrogen atoms are represented by 30% thermal probability ellipsoids

Table 1. Selected bond lengths [Å] and angles [°] for α-VO_2(L) and β-VO_2(L)

	α-VO_2(L)	β-VO_2(L)
V−O(1)	1.617(2)	1.613(2)
V−O(2)	1.615(2)	1.627(2)
V−O(3)	1.901(2)	1.903(2)
V−N(1)	2.113(2)	2.134(2)
V−N(2)	2.129(2)	2.145(2)
O(1)−V−O(2)	109.4(1)	109.2(1)
O(1)−V−O(3)	100.2(1)	105.5(1)
O(2)−V−O(3)	100.7(1)	97.1(1)
O(1)−V−N(1)	90.9(1)	98.2(1)
O(1)−V−N(2)	123.0(1)	109.4(1)
O(2)−V−N(1)	92.3(1)	89.4(1)
O(2)−V−N(2)	125.8(1)	139.7(1)
O(3)−V−N(1)	159.0(1)	151.7(1)
O(3)−V−N(2)	83.8(1)	83.4(1)
N(1)−V−N(2)	75.2(1)	74.2(1)

Coordination Geometry

In the α form, the V(L) fragment constitutes a plane (mean deviation, 0.03 Å), which makes a dihedral angle of 90.5 with the VO_2 plane. The double bonds in the latter fragment constrain the O1−V−O2 angle to about 109°, as is generally observed among pentacoordinated VO_2 complexes.[7−10]

An important feature of the α structure is that the metal atom is shifted only by about 0.1 Å from the O1−O2−N2 plane towards the O3 atom, and the N2 atom is approximately symmetrically positioned with respect to the Ol and O2 atoms, the O1−V−N2 and O2−V−N2 angles being 123.0(1) and 125.8(1)°, respectively [N2···O1, 3.301(7) Å and N2···O2, 3.341(7) Å]. The rigidity of the L ligand constrains the O3−V−N1 angle to 159.0(1)°.

The coordination geometry of α-VO_2(L) is thus best described as dtbp (trigonal plane O1−O2−N2). The τ parameter[12] (equal to Δ/60°, where Δ is the difference between the largest and the next-to-largest ligand−metal−ligand angles) is a useful geometrical discriminator; $\Delta = 60$, $\tau = 1$ for idealized tbp and $\Delta = 0$, $\tau = 0$ for idealized sp).[12] The τ value of α-VO_2(L) is 0.55. In representative structures of VO_2(tridentate) species the τ values generally lie well below 0.50 and in most cases below 0.40.[7−10] Thus α-VO_2(L) approaches the tbp geometry more closely than any other known member of the VO_2(tridentate) family.

The V(L) moiety in the β form is not planar and it actually consists of two highly planar fragments: C1−C6, N1, V (plane A, mean deviation, 0.01 Å) and C7−C13, N2, O3 (plane B, mean deviation, 0.02 Å). Plane A is rotated away from plane B by 11.2° along the C6−N2 bond. The metal atom is shifted from plane B by 0.53 Å, and thus the six-membered chelate ring is folded by 20.4° along the N2···O3 line.

Whereas the rigid O1−V−O2 angle remains virtually unchanged near 109°, V(L) nonplanarity results in major changes in the other angles at the metal compared to those in the α form. Thus, the O1−V−N2 angle decreases by about 14° to 109.4(1)° and the O2−V−N2 angle increases by a similar amount to 139.7(1)°. The O3−V−N1 angle is also contracted by about 7° to 151.7(1)°. The net result of these angular changes is that the O2, O3, N1 and N2 atoms in the β form constitute an approximate tetragonal plane, from which the metal atom is displaced by 0.51 Å towards the O1 atom. Therefore, the coordination geometry in the β form can be aptly described as dsp, which is also consistent with its low τ value of 0.20.

The structure of β-VO_2(L) bears certain qualitative similarities to that[11] of pseudooctahedral V(L)(dbcat) **4**. A significant feature is that the nonplanar V(L) fragment in **4** also consists of two planar fragments of types A and B (dihedral angle 19.7°). The approximate tetragonal plane is again of N_2O_2 type from which the metal atom is displaced towards the oxo atom (by 0.28 Å). The nonplanarity of the V(L) fragment appears to be crucial for achieving a tetragonal equator, be it in β-VO_2(L) or in VO(L)(dbcat).

Aromatic Stacking and Hydrogen Bonding: Dimers and Supramolecules

All the hydrogen atoms in both α-VO_2(L) and β-VO_2(L) were directly located by difference Fourier maps. Both the lattices consist of dimers, which associate further to form supramolecules. The noncovalent intradimer and interdimer bonding interactions are primarily of the π-π stacking and C−H···O hydrogen-bonding type. These interactions can be seen in the partial packing diagrams shown in Figure 3 and 4; the relevant distances are listed in Table 2.

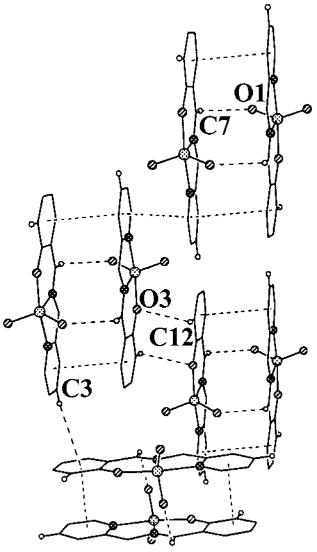


Figure 3. Supramolecular structure of the α-VO_2(L) lattice; hydrogen atoms other than H3, H7 and H12 have been omitted for clarity and noncovalent interactions are indicated by dotted lines

In the α dimers the (virtually parallel) V(L) planes are held together by a pair of aryl···pyridyl π-π interactions and a pair of azomethine···oxo (C7−H7···O1) hydrogen bonding interactions(Figure 3). The distance between the centroids of the overlapping aryl and pyridyl rings (ar···py in Table 2), 3.716(7) Å, is consistent[13,14] with the presence of an attractive π-π interaction. The ar···py line subtends an

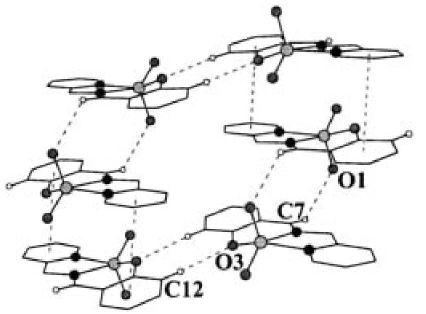


Figure 4. Supramolecular structure of the β-VO_2(L) lattice. Hydrogen atoms other than H7 and H12 have been omitted for clarity and noncovalent interactions are indicated by dotted lines

Table 2. Distances [Å] and angles [°] characterizing aromatic π-π stacking and C−H···O hydrogen bonding in the two dimorphs

	α-VO_2(L)	β-VO_2(L)
ar···py[a]	3.716(7)	3.752(7)
py···py[a]	3.520(6)	–
C(7)···O(1)	3.185(7)	3.063(6)
H(7)···O(1)	2.62(9)	2.51(8)
C(12)···O(3)	3.550(7)	3.431(6)
H(12)···O(3)	2.95(8)	2.56(9)
C(7)−H(7)···O(1)	120(1)	123(1)
C(12)−H(12)···O(3)	123(1)	176(1)

[a] ar = aryl ring centroid; py = pyridyl ring centroid.

angle of 10.4° with the aryl ring normal, and 10.8° with the pyridyl ring normal. The offset of the parallel rings is thus small, signifying strong stacking. In metal complexes of pyridyl ligands π-π stacking is usually associated with a larger offset (about 20°).[13] The bond parameters of the C7−H7···O1 fragment (Table 2) are consistent with the presence of significant hydrogen bonding. The accepted ranges are 3.0−3.5 Å (C···O), 2.3−3.0 Å (H···O) and 100−180° (C−H···O).[15−18]

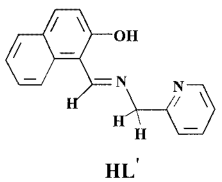
Interdimer bonding in the α form consists of a relatively strong pyridyl···pyridyl π−π overlap [py···py, 3.520(6) Å] with a very small offset (5.6°), and aryl···phenol (C12−H12···O3) hydrogen bonding which is significantly weaker than the intradimer C7−H7···O1 bonding. There is also a weak interdimer edge-to-face interaction[13,17,19] between the pyridyl C3−H3 and aryl fragments, the centroid of the latter being 3.31(9) Å and 3.889(8) Å away from the H3 and C3 atoms, respectively. The C3−H3···ar angle is 124°. The C10 carbon atom of the aryl ring lies closest to H3 [distance 2.91(8) Å].

The nonplanarity of the V(L) fragment in the β form results in increased intradimer aryl···pyridyl separation, marginalizing the π-π interaction [ar···py, 4.086(8) Å]. On the other hand, the azomethine function now lies closer to the O1 atom, thus resulting in stronger intradimer C7−H7···O1 hydrogen bonds than in the α dimer (Table 2). The interdimer association is also dominated by the relatively strong hydrogen bonding which occurs between the aryl and phenolato functions, the site of action being the nearly linear C12−H12···O3 moiety. Interdimer aryl···pyridyl stacking (offset 19.9°) also contributes to supramolecule formation in the β form.

Solvent Specific Crystallization

In summary, π-π stacking and C−H···O hydrogen bonding are the respective dominant features in the supramolecular architectures of the α and β forms of VO_2(L). This provides some insight into the possible nature of the role of solvent in dimorph crystallization. It is known that solvents like water and small alcohols with low polarizability and high cohesive interaction lead to aggregation of lipophilic molecular π surfaces in solutes.[13,20] It is therefore logical to propose that such effects lead to π-π stacking in the case of VO_2(L), with consequent crystallization of the α form from methanol (we have found ethanol to be just as effective). The planar V(L) configuration and the associated dtbp geometry may very well be the consequence of maximization of the π-π stacking interactions in the lattice. The tendency towards lipophilic aggregation is considerably diminished in solvents of significantly higher polarizability such as acetonitrile (dichloromethane is found to behave similarly);[20c] in these cases the β form crystallizes, with a structure dominated by polar interactions (viz. strong C−H···O hydrogen bonding) rather than π-π stacking. This is best achieved when the V(L) configuration is nonplanar and consequently the coordination geometry is dsp. The synthesis of α and β forms of VO_2(L) is an instance of solvent-directed crystal engineering. The two geometrical isomeric coordination spheres are sustained by their characteristic supramolecular architectures.

On the basis of the above logic we expected that 2-hydroxynapthaldimine(HL′, **5**) of 2-picolylamine should also yield dimorphs. Indeed, two forms of VO_2(L′) have been isolated by the same procedures employed for the VO_2(L) dimorphs.



HL′
5

Selected characterization data is given in the Exp. Sect. Unfortunately, neither α-VO_2(L′) nor β-VO_2(L′) afforded single crystals suitable for structure determination. A search for other examples of the VO_2(tridentate) family showing similar dimorphism is continuing.

Conclusions

A remarkable case of solvent-directed crystal engineering has been revealed in the synthesis of VO_2(L) in dimorphic α and β forms, isolated from methanol and acetonitrile, respectively.

The two forms differ strongly in both their coordination geometries (dtbp versus dsp) and supramolecular architecture (aromatic π-π stacking versus C−H···O hydrogen bonding), the former being a consequence of the latter.

This solvent-specific dimorph crystallization is qualitatively consistent with relative polarizability; the $VO_2(L')$ dimorphs appear to be similar to those of $VO_2(L)$.

Experimental Section

General: Bis(acetylacetonato)oxovanadium(IV) was prepared by literature methods.[21] 2-Picolylamine, salicylaldehyde, 2-hydroxynapthaldehyde and acetylacetone were obtained from Aldrich. Vanadyl sulfate pentahydrate was purchased from Loba Chemie (India) and 30% hydrogen peroxide was obtained from S. D. Fine Chem. (India). All other chemicals and solvents were of analytical grade and were used as received. Spectra were recorded using the following equipment: IR (KBr disk), Nicolet Magna 750 Series II spectrometer. UV/Vis, Shimadzu UVPC 1601 spectrometer. ^1H NMR, Bruker FT 300 MHz spectrometer (assignments were based on chemical shifts and spin-spin structures) and ^{51}V NMR, Varian 78.8 MHz spectrometer ($VOCl_3$ external reference). A Perkin−Elmer 240C elemental analyzer was used for microanalysis (C, H, N).

HL: 2-Picolylamine (0.885 g, 8.2 mmol) was added to a solution of salicylaldehyde (1 g, 8.2 mmol) in ethanol (15 mL). After refluxing the mixture for half an hour, the solvent was removed in a rotary evaporator and the yellow oil thus obtained used without further purification.

HL′: Prepared similarly, using 2-hydroxynapthaldehyde in place of salicylaldehyde.

α-VO_2(L): A solution of HL (0.159 g, 0.75 mmol) in methanol (5 mL) was added to a solution of $VO(acac)_2$ (0.2 g, 0.75 mmol) in methanol (50 mL). Pure oxygen was bubbled through the deep red solution for 5 h with stirring. The greenish-yellow precipitate that appeared was filtered off, washed with dichloromethane, and dried in vacuo over fused $CaCl_2$. Yield: 0.171 g (77%). $C_{13}H_{11}N_2O_3V$ (294.18): calcd. C 53.08, H 3.77, N 9.52; found C 53.14, H 3.85, N 9.58. IR (KBr): ṽ = 921, 939 (s, V=O), 1621 (s, C=N) cm^{-1}. UV/Vis (DMF): $\lambda_{max.}$ (ε, $M^{-1}\cdot cm^{-1}$) = 395 nm (1810). ^1H NMR ([D$_6$]DMSO): δ = 5.60 (s, 2 H, $-CH_2-$), 9.06 (s, 1 H, −CH=N), 8.95 (br., 1 H, $-C_6H_4$), 8.15 (t, *J* = 6.0 Hz, 1 H, $-C_6H_4$), 7.80 (d, *J* = 6.0 Hz, 1 H, $-C_6H_4$), 7.52 (t, *J* = 7.5 Hz, 1 H, $-C_6H_4$), 7.64 (t, *J* = 6.0 Hz, 2 H, $-C_5H_4N$), 6.87 ppm (d, *J* = 6.0 Hz, 2 H, $-C_5H_4N$) ppm. ^{51}V NMR ([D$_6$]DMSO): δ = −535 ppm.

Synthesis from $VOSO_4{\cdot}5H_2O$: 30% Hydrogen peroxide (1 mL) was added to a suspension of $VOSO_4{\cdot}5H_2O$ (0.2 g, 0.79 mmol) in methanol (50 mL). 15 min of stirring resulted in the formation of an orange-red solution, to which a solution of HL (0.168 g, 0.79 mmol) in methanol (5 mL) was added. The dark-brown solution was kept undisturbed in air at room temperature. After 24 h, the crystalline product deposited was filtered off, washed with methanol and dried in vacuo under fused $CaCl_2$. This afforded 0.168 g (72%) of α-VO_2(L).

β-VO_2(L): Prepared as for α-VO_2(L), but using acetonitrile instead of methanol. Yield: 0.164 (74%). $C_{13}H_{11}N_2O_3V$ (294.18): calcd. C 53.08, H 3.77, N 9.52; found C 53.19, H 3.82, N 9.57. IR (KBr): ṽ = 918, 939 (s, V= O), 1626 (s, C=N) cm^{-1}. UV/Vis (DMF): $\lambda_{max.}$ (ε, $M^{-1}\cdot cm^{-1}$) = 395 nm (1789). ^1H NMR ([D$_6$]DMSO): δ = 5.60 (s, 2 H, $-CH_2-$), 9.06 (s, 1 H, −CH=N), 8.95 (br., 1 H, $-C_6H_4$), 8.15 (t, *J* = 6.0 Hz, 1 H, $-C_6H_4$), 7.80 (d, *J* = 6.0 Hz, 1 H, $-C_6H_4$), 7.52 (t, *J* = 7.5 Hz, 1 H, $-C_6H_4$), 7.64 (t, *J* = 6.0 Hz, 2 H, $-C_5H_4N$), 6.87 ppm (d, *J* = 6.0 Hz, 2 H, $-C_5H_4N$) ppm. ^{51}V NMR ([D$_6$]DMSO): δ = −535 ppm.

Synthesis from $VOSO_4{\cdot}5H_2O$: Prepared as for α-VO_2(L), but using acetonitrile instead of methanol. Yield: 0.174 g (75%).

α-VO_2(L′): Prepared as for α-VO_2(L), but using HL′ instead of HL. Yield: 0.197 g (76%). $C_{17}H_{13}N_2O_3V$ (344.24): calcd. C 59.32, H 3.81, N 8.14; found C 59.38, H 3.89, N. 8.17. IR (KBr): ṽ = 925, 941 (s, V=O), 1626 (s, C=N) cm^{-1}. UV/Vis (DMF): $\lambda_{max.}$ (ε, $M^{-1}\cdot cm^{-1}$) = 412 nm (2068). ^1H NMR ([D$_6$]DMSO): δ = 5.76 (s, 2 H, $-CH_2-$), 9.89 (s, 1 H, −CH=N), 8.94 (d, *J* = 6.0 Hz, 1 H, $-C_{10}H_6$), 8.42 (d, *J* = 6.0 Hz, 1 H, $-C_{10}H_6$), 8.21 (t, *J* = 6.0 Hz, 1 H, $-C_{10}H_6$), 8.09 (d, *J* = 9.0 Hz, 1 H, $-C_{10}H_6$), 7.42 (t, *J* = 7.5 Hz, 1 H, $-C_{10}H_6$), 7.14 (d, *J* = 9.0 Hz, 1 H, $-C_{10}H_6$), 7.88 (t, *J* = 7.5 Hz, 2 H, $-C_5H_4N$), 7.65 (d, *J* = 9.0 Hz, 2 H, $-C_5H_4N$) ppm.

Synthesis of α-VO_2(L′) from $VOSO_4{\cdot}5H_2O$: Prepared as for α-VO_2(L), but using HL′ instead of HL. Yield 0.193 g (71%).

β-VO_2(L′): Prepared as for α-VO_2(L′), but using acetonitrile instead of methanol. Yield: 0.183 g (71%). $C_{17}H_{13}N_2O_3V$ (344.24): calcd. C 59.32, H 3.81, N 8.14; found C 59.34, H 3.85, N. 8.15. IR (KBr): ṽ = 923, 942 (s, V=O), 1623 (s, C=N) cm^{-1}. UV/Vis (DMF): $\lambda_{max.}$ (ε, $M^{-1}\cdot cm^{-1}$) = 412 nm (2026). ^1H NMR ([D$_6$]DMSO): δ = 5.76 (s, 2 H, $-CH_2-$), 9.89 (s, 1 H, −CH=N), 8.94 (d, *J* = 6.0 Hz, 1 H, $-C_{10}H_6$), 8.42 (d, *J* = 6.0 Hz, 1 H, $-C_{10}H_6$), 8.21 (t, *J* = 6.0 Hz, 1 H, $-C_{10}H_6$), 8.09 (d, *J* = 9.0 Hz, 1 H, $-C_{10}H_6$), 7.42 (t, *J* = 7.5 Hz, 1 H, $-C_{10}H_6$), 7.14(d, *J* = 9.0 Hz, 1 H, $-C_{10}H_6$), 7.88 (t, *J* = 7.5 Hz, 2 H, $-C_5H_4N$), 7.65 (d, *J* = 9.0 Hz, 2 H, $-C_5H_4N$) ppm.

Synthesis of β-VO_2(L′) from $VOSO_4{\cdot}5H_2O$: Prepared as for α-VO_2(L′), but using acetonitrile instead of methanol. Yield: 0.201 g (74%).

Conversion of VO_2(L) to VO(L)(dbcat): 3,5-Bis(*tert*-butyl)catechol (H_2dbcat) (0.076 g, 0.34 mmol) was added to a suspension of either form of VO_2(L) (0.10 g, 0.34 mmol) in dichloromethane (20 mL). The mixture was stirred for 8 h and the violet-coloured solution concentrated and left to evaporate in the air. The crystalline product thus obtained was washed with cold methanol and dried in vacuo over fused $CaCl_2$. Yield: 0.134 g (76%). This complex was found to be identical in all respects with that reported earlier.[11]

Crystal Structure Determination: Single crystals of α-VO_2(L) and β-VO_2(L) were obtained directly during synthesis but without stirring of the oxygen-saturated reaction mixture (vide supra). The undisturbed solution deposited suitable single crystals within a few days. Data were collected with a Nicolet R3m/V four-circle diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) using the ω-scan technique ($3 \le 2\theta \le 48°$ for both the α and β forms). All data were corrected for Lorentz polarization, and an empirical absorption correction[22] was performed on each set of data on the basis of the azimuthal scans of six reflections. All calculations of data reduction, structure solution and refinement were done with the programs of SHELXTL, version 5.03.[23] The two structures were solved by direct methods and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. All the hydrogen atoms in two structures were located in the difference Fourier maps. Significant crystal data are listed in Table 3. Supplementary crystallographic data have been deposited.

CCDC-168305 [for α-VO_2(L)] and -168304 [for β-VO_2(L)] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 3. Crystallographic data for α-VO_2(L) and β-VO_2(L)

	α-VO_2(L)	β-VO_2(L)
Empirical formula	$C_{13}H_{11}N_2O_3V$	$C_{13}H_{11}N_2O_3V$
Mr [g·mol^{-1}]	294.18	294.18
Crystal size [mm]	0.40 × 0.30 × 0.20	0.40 × 0.30 × 0.25
T [K]	293(2)	293(2)
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
a (Å)	10.723(2)	7.798(2)
b (Å)	10.270(2)	8.363(2)
c (Å)	11.944(2)	9.585(2)
α [°]	−	80.92(3)
β [°]	108.36(3)	89.47(3)
γ [°]	−	82.76(3)
V (Å^3)	1248.4(4)	612.3(2)
Z	4	2
Calcd. density [g·cm^{-3}]	1.565	1.596
μ [mm^{-1}]	0.799	0.814
R_{int}	0.0189	0.0085
Reflections measured	2115	1985
Independent reflections	1970	1929
R_1 [$I > 2\sigma(I)$]	0.0336	0.0279
wR_2 [$I > 2\sigma(I)$]	0.0759	0.0766
Goodness of fit on F^2	1.087	1.101

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