

## Redetermination of bis(acetylacetonato)-oxidopyridinevanadium(IV)

Rubia M. S. da Silva,<sup>a</sup> Cristiano C. Spiazzi,<sup>b</sup> Ricardo Bortolotto<sup>b</sup> and Robert A. Burrow<sup>a\*</sup>

<sup>a</sup>Laboratório de Materiais Inorgânicos, Departamento de Química, Universidade Federal de Santa Maria, 97105-900 Santa Maria, RS, Brazil, and <sup>b</sup>Departamento de Química, Universidade Federal de Santa Maria, 97105-900 Santa Maria, RS, Brazil  
Correspondence e-mail: rburrow@ewald.base.ufsm.br

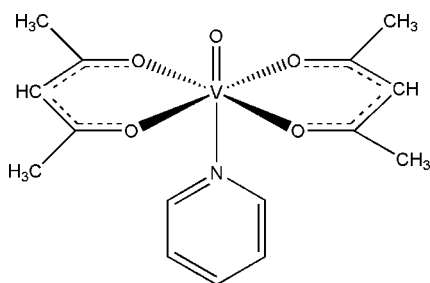
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Key indicators: single-crystal X-ray study;  $T = 296$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.039;  $wR$  factor = 0.116; data-to-parameter ratio = 25.0.

The crystal structure of the title compound,  $[\text{VO}(\text{C}_5\text{H}_7\text{O}_2)_2(\text{C}_5\text{H}_5\text{N})]$ , has been reported previously [Meicheng, Lifeng & Youqi (1984). *Kexue Tongbao*, **29**, 759–764], with an  $R$  value of 0.13. The current redetermination shows a significant improvement in the precision of the geometric parameters. The V atom binds five O atoms and one N atom from the pyridine ligand in a distorted octahedral configuration; the acetylacetonate anions act as bidentate ligands. A crystallographic twofold axis passes through the V, vanadyl O, and pyridine N and *para*-C atoms.

### Related literature

For a related structure, see: Meicheng *et al.* (1984). For related literature, see: Allen (2002).



### Experimental

#### Crystal data

$[\text{V}(\text{C}_5\text{H}_7\text{O}_2)_2(\text{C}_5\text{H}_5\text{N})]$   
 $M_r = 344.25$   
 Monoclinic,  $C2/c$   
 $a = 7.9121$  (3) Å  
 $b = 15.5258$  (7) Å  
 $c = 14.2523$  (6) Å  
 $\beta = 103.621$  (3)°  
 $V = 1701.54$  (12) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.60$  mm<sup>-1</sup>  
 $T = 296$  (2) K  
 $0.35 \times 0.35 \times 0.25$  mm

#### Data collection

Bruker APEX II area-detector diffractometer  
 Absorption correction: multi-scan (SADABS; Bruker, 2006)  
 $T_{\min} = 0.903$ ,  $T_{\max} = 1$   
 (expected range = 0.776–0.860)  
 11650 measured reflections  
 2595 independent reflections  
 1837 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.032$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$   
 $wR(F^2) = 0.116$   
 $S = 1.05$   
 2595 reflections  
 104 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\max} = 0.23$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.31$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

|                       |             |                        |             |
|-----------------------|-------------|------------------------|-------------|
| N1–V1                 | 2.422 (2)   | O2–V1                  | 1.9918 (11) |
| O1–V1                 | 1.5976 (18) | O3–V1                  | 1.9997 (11) |
| C3–O2–V1              | 127.66 (11) | O1–V1–O3               | 98.30 (4)   |
| C1–O3–V1              | 127.44 (11) | O2–V1–O3               | 89.55 (5)   |
| O1–V1–O2              | 99.92 (4)   | O2 <sup>i</sup> –V1–O3 | 87.60 (5)   |
| O2–V1–O2 <sup>i</sup> | 160.16 (8)  | O1–V1–N1               | 180         |

Symmetry code: (i)  $-x + 1, y, -z + \frac{3}{2}$ .

Data collection: APEX2, COSMO and BIS (Bruker, 2006); cell refinement: SAINT (Bruker, 2006); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: DIAMOND (Brandenburg, 2007); software used to prepare material for publication: SHELXL97.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2476).

### References

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 Meicheng, S., Lifeng, W. & Youqi, T. (1984). *Kexue Tongbao*, **29**, 759–764.  
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**supplementary materials**

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## Redetermination of bis(acetylacetonato)oxidopyridinevanadium(IV)

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### Comment

The crystal structure of the title compound,  $\text{VO}(\text{C}_5\text{H}_7\text{O})_2\text{C}_5\text{H}_5\text{N}$ , was determined previously by (Meicheng *et al.*, 1984). The original structure refinement converged with  $R_I = 0.13$  [CUCWUS; Cambridge Structural Database (CSD, Version 5.28, update of January 2007; Allen, 2002)]. The current redetermination shows a significant improvement in the precision of the geometric parameters. A low temperature experiment was attempted, but the crystal quickly powders under a cold nitrogen stream. One half-molecule is found in the asymmetric unit; the complete molecule is generated by a crystallographic 2 fold axis which passes through atoms O1, V1, N1 and C8. The geometry of the hexacoordinate V atom can be regarded as distorted octahedral with the two acetylacetonato ligands chelating in the equatorial plane, and the vandy O and the pyridinal N atoms in axial positions (Fig. 1). The V1 atom is centered 0.3160 (10) Å out of the plane formed by four coordinated oxygen atoms, in the direction of the apical O1 atom. The V=O distance is 1.5976 (18) Å in good agreement with ranges observed for other  $\text{VO}_5\text{N}$  octahedral found in the Cambridge Structural Database (CSD, Version 5.28, update of January 2007; Allen, 2002)] (V=O 1.598 (11) Å for 21 observations), the *cisoid* angles (O–V–O and O–V–N) being 80.08 (4) – 99.92 (4)°, and *transoid* angles (O–V–O and O–V–N) being 160.16 (8) – 180° (Table 1). The molecules packs around a crystallographic twofold screw axis, parallel to the crystallographic *b*-axis (Fig. 2).

The thermal gravimetric analysis (TGA) of **1** shows a loss of one molecule of pyridine (exp. 22.03%, calc. 22.97%) at 334.98 K, followed by the loss of  $\text{C}_{10}\text{H}_{16}\text{O}_5$  (exp. 64.41%, calc. 62.23%) at 438.45 K. The residual weight for the whole process (exp. 13.56%, calc. 14.80%) is in good agreement assuming V as the final end product.

### Experimental

The title compound was synthesized by refluxing  $\text{VO}(\text{acac})_2$  (1.00 g, 3.68 mmol) dissolved pyridine (15 ml) for 2 h. After cooling to room temperature, 80 ml of diethyl ether was added. Light green single crystals of the compound were obtained by slow evaporation of the solution at room temperature over several days in a desiccator. Yield (crystals): 0.13 g (10.15%).

### Refinement

All H atoms on were refined using a riding model, with C—H = 0.93 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for the methine C atoms and C—H = 0.96 Å and  $U_{\text{iso}} = 1.5U_{\text{eq}}(\text{C})$  for the methyl C atoms.

## Figures

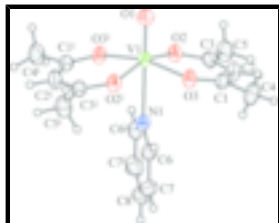


Fig. 1. The molecular structure with 30% probability ellipsoids. [Symmetry code: (i)  $1 - x, y, 1.5 - z.$ ]

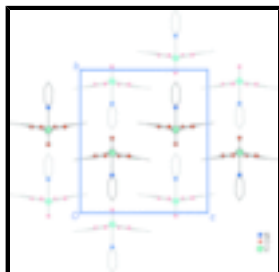


Fig. 2. Part of the crystal structure viewed perpendicular to the  $bc$  plane. The phenyl groups are represented as solid grey lines. Hydrogen atoms omitted for sake of clarity.

## bis(acetylacetonato)oxidopyridinevanadium(IV)

### Crystal data

$[\text{V}(\text{C}_5\text{H}_7\text{O}_2)_2\text{O}(\text{C}_5\text{H}_5\text{N})]$

$M_r = 344.25$

Monoclinic,  $C2/c$

Hall symbol:  $-C\ 2yc$

$a = 7.9121\ (3)\ \text{\AA}$

$b = 15.5258\ (7)\ \text{\AA}$

$c = 14.2523\ (6)\ \text{\AA}$

$\beta = 103.621\ (3)^\circ$

$V = 1701.54\ (12)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 716$

$D_x = 1.344\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 2628 reflections

$\theta = 2.9\text{--}24.1^\circ$

$\mu = 0.60\ \text{mm}^{-1}$

$T = 296\ (2)\ \text{K}$

Trapezoid, blue–green

$0.35 \times 0.35 \times 0.25\ \text{mm}$

### Data collection

Bruker APEX II area-detector diffractometer

Monochromator: graphite

$T = 296\ (2)\ \text{K}$

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan (SADABS; Bruker, 2006)

$T_{\min} = 0.903, T_{\max} = 1$

11650 measured reflections

2595 independent reflections

1837 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.032$

$\theta_{\text{max}} = 30.4^\circ$

$\theta_{\text{min}} = 2.9^\circ$

$h = -11 \rightarrow 11$

$k = -22 \rightarrow 20$

$l = -20 \rightarrow 20$

Refinement

|  |  |
|--|--|
| Refinement on $F^2$  | Secondary atom site location: difference Fourier map     |
| Least-squares matrix: full                                     | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.039$                                | H-atom parameters constrained                            |
| $wR(F^2) = 0.116$  | $w = 1/[\sigma^2(F_o^2) + (0.0608P)^2 + 0.0762P]$        |
| $S = 1.05$   | where $P = (F_o^2 + 2F_c^2)/3$                           |
| 2595 reflections   | $(\Delta/\sigma)_{\max} = 0.001$                         |
| 104 parameters   | $\Delta\rho_{\max} = 0.23 \text{ e } \text{\AA}^{-3}$    |
| Primary atom site location: structure-invariant direct methods | $\Delta\rho_{\min} = -0.31 \text{ e } \text{\AA}^{-3}$   |
|  | Extinction correction: none                              |

Special details

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

|     | $x$        | $y$          | $z$          | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|------------|--------------|--------------|----------------------------------|
| C1  | 0.8337 (2) | 0.61290 (12) | 0.88998 (13) | 0.0543 (4)                       |
| C2  | 0.7518 (2) | 0.62217 (15) | 0.96641 (14) | 0.0663 (5)                       |
| H2  | 0.8226     | 0.6322       | 1.0275       | 0.08*                            |
| C3  | 0.5742 (2) | 0.61768 (12) | 0.95867 (12) | 0.0525 (4)                       |
| C4  | 1.0287 (2) | 0.61760 (18) | 0.91047 (17) | 0.0838 (7)                       |
| H4A | 1.0753     | 0.5607       | 0.9086       | 0.126*                           |
| H4B | 1.0731     | 0.6421       | 0.9733       | 0.126*                           |
| H4C | 1.0623     | 0.6529       | 0.8627       | 0.126*                           |
| C5  | 0.5044 (3) | 0.62994 (17) | 1.04695 (13) | 0.0761 (6)                       |
| H5A | 0.4164     | 0.6738       | 1.0348       | 0.114*                           |
| H5B | 0.5972     | 0.647        | 1.1001       | 0.114*                           |
| H5C | 0.4551     | 0.5768       | 1.0624       | 0.114*                           |
| C6  | 0.6215 (2) | 0.78243 (13) | 0.71999 (13) | 0.0592 (5)                       |
| H6  | 0.707      | 0.7525       | 0.6985       | 0.071*                           |
| C7  | 0.6260 (3) | 0.87100 (15) | 0.71941 (14) | 0.0755 (6)                       |
| H7  | 0.7133     | 0.9          | 0.6985       | 0.091*                           |
| C8  | 0.5        | 0.91579 (19) | 0.75         | 0.0835 (10)                      |
| H8  | 0.5        | 0.9757       | 0.75         | 0.1*                             |

## supplementary materials

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|    |              |              |             |              |
|----|--------------|--------------|-------------|--------------|
| N1 | 0.5          | 0.73721 (13) | 0.75        | 0.0495 (4)   |
| O1 | 0.5          | 0.47833 (11) | 0.75        | 0.0607 (4)   |
| O2 | 0.46038 (14) | 0.60333 (8)  | 0.88081 (8) | 0.0530 (3)   |
| O3 | 0.75487 (14) | 0.59983 (9)  | 0.80249 (9) | 0.0544 (3)   |
| V1 | 0.5          | 0.58123 (3)  | 0.75        | 0.04534 (15) |

### Atomic displacement parameters ( $\text{\AA}^2$ )

|    | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$     | $U^{13}$     | $U^{23}$     |
|----|-------------|-------------|-------------|--------------|--------------|--------------|
| C1 | 0.0421 (8)  | 0.0563 (10) | 0.0592 (11) | 0.0013 (7)   | 0.0014 (7)   | -0.0033 (8)  |
| C2 | 0.0509 (10) | 0.0910 (15) | 0.0500 (10) | -0.0003 (10) | -0.0018 (8)  | -0.0085 (10) |
| C3 | 0.0576 (9)  | 0.0538 (10) | 0.0444 (9)  | 0.0013 (8)   | 0.0087 (7)   | 0.0035 (7)   |
| C4 | 0.0411 (9)  | 0.115 (2)   | 0.0879 (16) | 0.0009 (11)  | 0.0001 (9)   | -0.0218 (14) |
| C5 | 0.0798 (14) | 0.1023 (18) | 0.0470 (10) | -0.0041 (13) | 0.0163 (9)   | -0.0046 (10) |
| C6 | 0.0488 (9)  | 0.0674 (12) | 0.0609 (11) | -0.0088 (8)  | 0.0119 (8)   | 0.0019 (9)   |
| C7 | 0.0876 (15) | 0.0694 (15) | 0.0654 (13) | -0.0281 (12) | 0.0101 (10)  | 0.0034 (10)  |
| C8 | 0.126 (3)   | 0.0495 (17) | 0.0649 (19) | 0            | 0.0016 (19)  | 0            |
| N1 | 0.0413 (9)  | 0.0547 (12) | 0.0520 (11) | 0            | 0.0101 (8)   | 0            |
| O1 | 0.0631 (10) | 0.0560 (11) | 0.0623 (11) | 0            | 0.0133 (8)   | 0            |
| O2 | 0.0448 (6)  | 0.0710 (8)  | 0.0430 (6)  | -0.0021 (5)  | 0.0095 (5)   | 0.0021 (5)   |
| O3 | 0.0360 (6)  | 0.0735 (8)  | 0.0519 (7)  | 0.0035 (5)   | 0.0069 (5)   | -0.0015 (5)  |
| V1 | 0.0375 (2)  | 0.0560 (3)  | 0.0412 (2)  | 0            | 0.00648 (15) | 0            |

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

|          |             |                        |             |
|----------|-------------|------------------------|-------------|
| C1—O3    | 1.272 (2)   | C6—C7                  | 1.376 (3)   |
| C1—C2    | 1.400 (2)   | C6—H6                  | 0.93        |
| C1—C4    | 1.503 (2)   | C7—C8                  | 1.368 (3)   |
| C2—C3    | 1.386 (2)   | C7—H7                  | 0.93        |
| C2—H2    | 0.93        | C8—C7 <sup>i</sup>     | 1.368 (3)   |
| C3—O2    | 1.273 (2)   | C8—H8                  | 0.93        |
| C3—C5    | 1.500 (2)   | N1—C6 <sup>i</sup>     | 1.339 (2)   |
| C4—H4A   | 0.96        | N1—V1                  | 2.422 (2)   |
| C4—H4B   | 0.96        | O1—V1                  | 1.5976 (18) |
| C4—H4C   | 0.96        | O2—V1                  | 1.9918 (11) |
| C5—H5A   | 0.96        | O3—V1                  | 1.9997 (11) |
| C5—H5B   | 0.96        | V1—O2 <sup>i</sup>     | 1.9918 (11) |
| C5—H5C   | 0.96        | V1—O3 <sup>i</sup>     | 1.9997 (11) |
| C6—N1    | 1.339 (2)   |                        |             |
| O3—C1—C2 | 124.71 (15) | C8—C7—H7               | 120.5       |
| O3—C1—C4 | 116.22 (16) | C6—C7—H7               | 120.5       |
| C2—C1—C4 | 119.06 (17) | C7 <sup>i</sup> —C8—C7 | 118.9 (3)   |
| C3—C2—C1 | 125.41 (17) | C7 <sup>i</sup> —C8—H8 | 120.6       |
| C3—C2—H2 | 117.3       | C7—C8—H8               | 120.6       |
| C1—C2—H2 | 117.3       | C6—N1—C6 <sup>i</sup>  | 116.8 (2)   |
| O2—C3—C2 | 125.04 (16) | C6—N1—V1               | 121.61 (11) |
| O2—C3—C5 | 115.39 (15) | C6 <sup>i</sup> —N1—V1 | 121.61 (11) |

|                          |              |  |              |
|--------------------------|--------------|--|--------------|
| C2—C3—C5                 | 119.57 (16)  | C3—O2—V1                               | 127.66 (11)  |
| C1—C4—H4A                | 109.5        | C1—O3—V1                               | 127.44 (11)  |
| C1—C4—H4B                | 109.5        | O1—V1—O2                               | 99.92 (4)    |
| H4A—C4—H4B               | 109.5        | O1—V1—O2 <sup>i</sup>                  | 99.92 (4)    |
| C1—C4—H4C                | 109.5        | O2—V1—O2 <sup>i</sup>                  | 160.16 (8)   |
| H4A—C4—H4C               | 109.5        | O1—V1—O3                               | 98.30 (4)    |
| H4B—C4—H4C               | 109.5        | O2—V1—O3                               | 89.55 (5)    |
| C3—C5—H5A                | 109.5        | O2 <sup>i</sup> —V1—O3                 | 87.60 (5)    |
| C3—C5—H5B                | 109.5        | O1—V1—O3 <sup>i</sup>                  | 98.30 (4)    |
| H5A—C5—H5B               | 109.5        | O2—V1—O3 <sup>i</sup>                  | 87.60 (5)    |
| C3—C5—H5C                | 109.5        | O2 <sup>i</sup> —V1—O3 <sup>i</sup>    | 89.55 (5)    |
| H5A—C5—H5C               | 109.5        | O3—V1—O3 <sup>i</sup>                  | 163.39 (8)   |
| H5B—C5—H5C               | 109.5        | O1—V1—N1                               | 180          |
| N1—C6—C7                 | 123.16 (19)  | O2—V1—N1                               | 80.08 (4)    |
| N1—C6—H6                 | 118.4        | O2 <sup>i</sup> —V1—N1                 | 80.08 (4)    |
| C7—C6—H6                 | 118.4        | O3—V1—N1                               | 81.70 (4)    |
| C8—C7—C6                 | 119.0 (2)    | O3 <sup>i</sup> —V1—N1                 | 81.70 (4)    |
| O3—C1—C2—C3              | 0.7 (4)      | C3—O2—V1—O3 <sup>i</sup>               | -166.86 (15) |
| C4—C1—C2—C3              | -178.7 (2)   | C3—O2—V1—N1                            | -84.87 (15)  |
| C1—C2—C3—O2              | 1.0 (4)      | C1—O3—V1—O1                            | -95.23 (15)  |
| C1—C2—C3—C5              | -179.3 (2)   | C1—O3—V1—O2                            | 4.73 (15)    |
| N1—C6—C7—C8              | -0.6 (3)     | C1—O3—V1—O2 <sup>i</sup>               | 165.09 (15)  |
| C6—C7—C8—C7 <sup>i</sup> | 0.28 (12)    | C1—O3—V1—O3 <sup>i</sup>               | 84.77 (15)   |
| C7—C6—N1—C6 <sup>i</sup> | 0.30 (13)    | C1—O3—V1—N1                            | 84.77 (15)   |
| C7—C6—N1—V1              | -179.70 (13) | C6—N1—V1—O2                            | 133.93 (10)  |
| C2—C3—O2—V1              | 1.2 (3)      | C6 <sup>i</sup> —N1—V1—O2              | -46.07 (10)  |
| C5—C3—O2—V1              | -178.52 (13) | C6—N1—V1—O2 <sup>i</sup>               | -46.07 (10)  |
| C2—C1—O3—V1              | -4.3 (3)     | C6 <sup>i</sup> —N1—V1—O2 <sup>i</sup> | 133.93 (10)  |
| C4—C1—O3—V1              | 175.11 (14)  | C6—N1—V1—O3                            | 42.93 (10)   |
| C3—O2—V1—O1              | 95.13 (15)   | C6 <sup>i</sup> —N1—V1—O3              | -137.07 (10) |
| C3—O2—V1—O2 <sup>i</sup> | -84.87 (15)  | C6—N1—V1—O3 <sup>i</sup>               | -137.07 (10) |
| C3—O2—V1—O3              | -3.22 (15)   | C6 <sup>i</sup> —N1—V1—O3 <sup>i</sup> | 42.93 (10)   |

Symmetry codes: (i)  $-x+1, y, -z+3/2$ .

Fig. 1

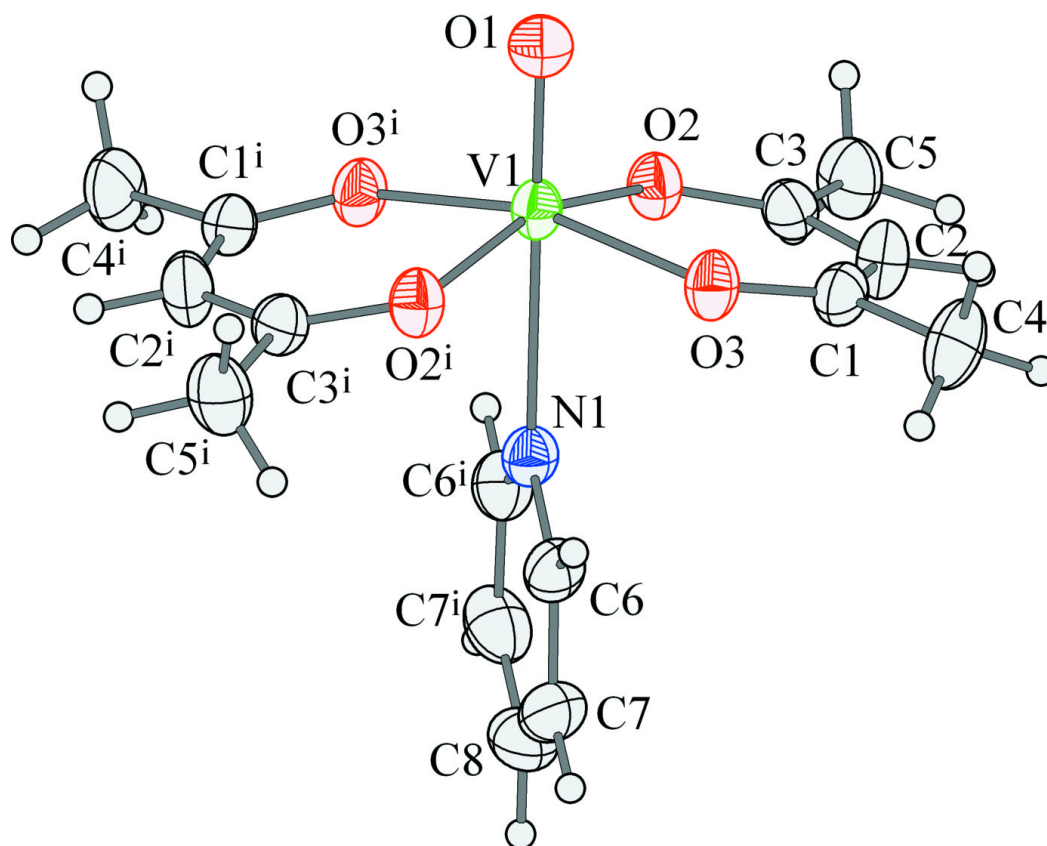




Fig. 2

