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Structural Control of (Arylimido)vanadium(V) Compounds through π Conjugation

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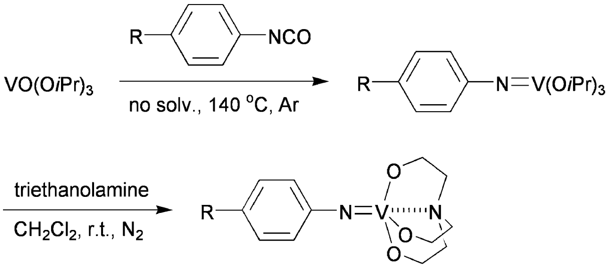
(Arylimido)triethanolaminatovanadium(V) compounds, [V(p-RC_6H_4N)(TEA)] (R = NMe_2, OMe, Me, H, Cl, Br, CN), were synthesised by ligand exchange reaction of the corresponding (arylimido)triisopropoxidovanadium(V) complexes, [V-$(OiPr)_3$(p-RC_6H_4N)], which were prepared by the reaction of $VO(OiPr)_3$ with various p-substituted aryl isocyanates without solvent. Structural characterisation of the (arylimido)triethanolaminatovanadium(V) products was carried out by single-crystal X-ray diffraction in order to elucidate the substituent effect on the imido structures, in which the imido structures were found to be controlled through π conjugation by the *para* substituents of the aryl moieties.

Introduction

The imido ligand coordinates through a metal–nitrogen multiple bond[1] in which the imido ligand can serve as an ancillary or supporting ligand. Imido ligands are known to be particularly suitable for stabilisation of complexes containing metals in high oxidation states through extensive ligand-to-metal π donation.[2] (Imido)vanadium(V) complexes have attracted much attention[3] because of their potential applications as a catalysts for olefin polymerisation,[4] C–H activation[5] and other related processes.[6] Introduction of a substituent onto the imido ligands can be expected to influence the steric and electronic properties of a vanadium centre. In such a sense, design of the imido ligands can be considered to be one of key factors in the development of efficient catalysts. The substituent effect of the imido ligands has been reported based only on spectroscopic and theoretical evidence.[3e] The systematic correlation between the properties and the imido structures has yet to be investigated. We herein report the structural characterisation of (arylimido)triethanolaminatovanadium(V) compounds for the purposes of elucidating the substituent effect of the aryl moieties on the imido structures.

Results and Discussion

(Arylimido)triisopropoxidovanadium(V) compounds are considered to dimerise through oxo-bridging in the crystalline state.[3e,3r] To prevent the dimerisation, triethanolamine was used as a basal ligand.[7] The reaction of $VO(OiPr)_3$ with various p-substituted aryl isocyanates without solvent at 140 °C afforded the corresponding (arylimido)triisopropoxidovanadium(V) complexes, [$V(OiPr)_3$(p-RC_6H_4N)]. The ligand exchange reaction with triethanolamine in CH_2Cl_2 at room temperature led to the desired (arylimido)triethanolaminatovanadium(V) complexes, [V(p-RC_6H_4N)(TEA)] (Scheme 1; **1**: R = NMe_2, **2**: R = OMe, **3**: R = Me, **4**: R = H, **5**: R = Cl, **6**: R = Br, **7**: R = CN).



1: R = NMe_2 **2**: R = OMe **3**: R = Me **4**: R = H
5: R = Cl **6**: R = Br **7**: R = CN

Scheme 1. Preparation of the (arylimido)triethanolaminatovanadium(V) complexes **1**–**7**.

^{51}V NMR spectroscopic measurements were performed in order to clarify the substituent effect on the electronic environment of the vanadium species. The ^{51}V chemical shift of the unsubstituted (phenylimido)vanadium(V) complex **4** was detected at –327 ppm. In the ^{51}V NMR spectra of the (arylimido)triethanolaminatovanadium(V) species, ^{51}V chemical shifts were observed at the lower field with an increase in the electron-donating capability of the *para* substituent (**1**: –224 ppm, **2**: –292 ppm, **3**: –314 ppm). In

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contrast, the electron-withdrawing substituent, in which the nitrogen atom of the imido bond becomes more electronegative and increases the ^{51}V nuclear shielding, causes the higher field shift (**5**: –328 ppm, **6**: –328 ppm, **7**: –340 ppm). These results are consistent with those of the (arylimido)trichloridovanadium(V) compounds reported by Maatta and co-workers.[3e]

Structural characterisation of the (arylimido)triethanolaminatovanadium(V) complexes was carried out by single-crystal X-ray diffraction in order to elucidate the substituent effect on the imido structures (Figure 1). The important bond lengths and angles are listed in Table 1.

The non-substituted (phenylimido)vanadium(V) complex **4** revealed an imido structure with a V(1)–N(1) distance of 1.686(2) Å and a V(1)–N(1)–C(1) angle of 166.7(2)° in which a monomeric structure with a pseudo-trigonal bipyramidal geometry at the metal centre was observed and this is depicted in Figure 1.

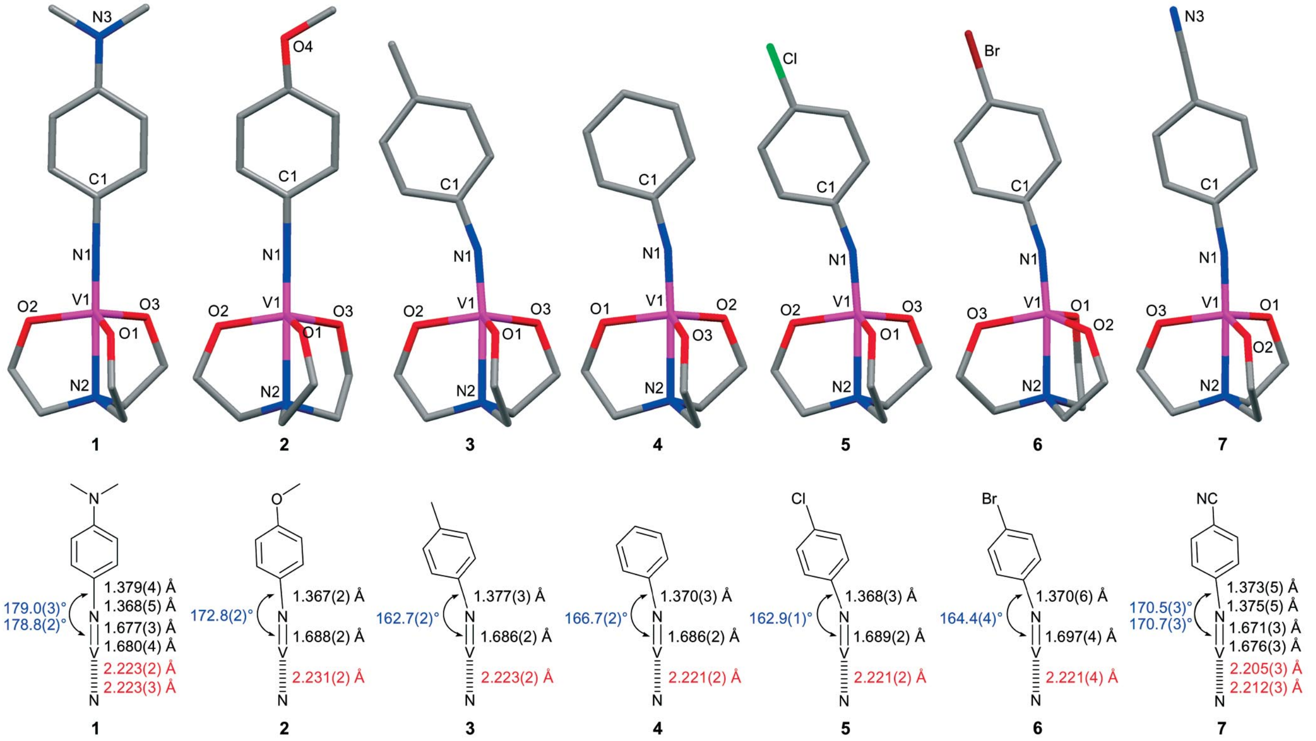

Figure 1. Molecular structures and schematic representations of **1**–**7**.

Table 1. Selected bond lengths [Å] and angles [°] for **1**–**7**.

	1[a]		**2**	**3**	**4**	**5**	**6**	**7**[a]	
Bond lengths									
V1–N1	1.677(3)	1.680(4)	1.688(2)	1.686(2)	1.686(2)	1.689(2)	1.697(4)	1.671(3)	1.676(3)
V1–N2	2.223(2)	2.223(3)	2.231(2)	2.223(2)	2.221(2)	2.221(2)	2.221(4)	2.205(3)	2.212(3)
V1–O1	1.838(2)	1.833(2)	1.830(1)	1.829(2)	1.834(2)	1.826(1)	1.826(3)	1.811(3)	1.819(3)
V1–O2	1.824(3)	1.828(2)	1.828(1)	1.830(2)	1.815(2)	1.827(1)	1.817(4)	1.824(3)	1.816(3)
V1–O3	1.835(3)	1.834(2)	1.829(1)	1.821(2)	1.831(2)	1.812(2)	1.833(3)	1.809(3)	1.806(3)
C1–N1	1.379(4)	1.368(5)	1.367(2)	1.377(3)	1.370(3)	1.368(3)	1.370(6)	1.373(5)	1.375(5)
Bond angles									
C1–N1–V1	179.0(3)	178.8(2)	172.8(2)	162.6(2)	166.7(2)	162.9(1)	164.4(4)	170.5(3)	170.7(3)
N1–V1–N2	179.1(1)	179.2(1)	178.20(8)	175.46(8)	177.48(7)	175.52(7)	175.2(2)	178.4(2)	178.4(2)
N1–V1–O1	98.7(1)	99.1(1)	97.79(8)	100.43(8)	97.04(8)	99.86(7)	100.0(2)	100.0(1)	100.6(1)
N1–V1–O2	99.6(1)	99.7(2)	100.14(7)	95.60(8)	100.46(9)	95.84(7)	102.7(2)	100.4(1)	98.0(2)
N1–V1–O3	99.5(1)	99.1(1)	100.18(7)	102.10(9)	100.50(8)	102.28(8)	95.5(2)	97.8(2)	100.1(1)
O1–V1–O2	116.1(1)	118.0(1)	118.04(6)	117.53(8)	118.32(8)	118.78(6)	115.6(2)	118.7(1)	115.2(1)
O1–V1–O3	118.1(1)	117.6(1)	117.09(6)	116.52(8)	117.14(7)	115.73(7)	118.4(1)	118.4(1)	118.5(1)
O2–V1–N2	80.6(1)	80.5(1)	80.42(6)	80.48(7)	80.44(6)	80.69(6)	80.7(2)	80.6(1)	80.3(1)
O2–V1–O3	118.2(1)	116.8(1)	117.08(6)	118.16(8)	116.80(8)	117.81(7)	118.2(2)	115.1(1)	118.2(1)
O3–V1–N2	81.16(10)	81.1(1)	80.61(6)	80.10(8)	80.66(7)	80.07(6)	81.1(2)	80.6(1)	80.4(1)
O3–V1–N2	80.5(1)	80.5(1)	80.86(5)	81.32(8)	80.91(6)	81.36(7)	80.1(2)	80.6(1)	80.6(1)

[a] Two independent molecules exist in the asymmetric unit.

The vanadium atom is pulled out of the plane formed by triethanolaminato oxygen atoms in the direction of the imido nitrogen. The three equatorial vanadium–oxygen bond lengths are statistically identical.

In the case of the (arylimido)vanadium(V) complex **2** with the electron-donating methoxy group, linearity of the imido angle has increased [V(1)–N(1)–C(1), 172.8(2)°] although the V(1)–N(1) distance of 1.688(2) Å is equal to that observed in **4** (Figure 1). Furthermore, the imido angle is greater in the (arylimido)vanadium(V) complex **1** bearing the dimethylamino group. V(1)–N(1)–C(1) angles of 179.0(3) and 178.8(2)° and V(1)–N(1) distances of 1.677(3) and 1.680(4) Å were observed in the crystal structure (Figure 1). Since **1** crystallises in the space group $P2_1/a$ with $Z = 8$, two independent molecules exist in the asymmetric unit. It is noteworthy that the triethanolamine moieties of these independent molecules adopt a mirror image windmill-like conformation (Figure 2). In the crystal, these molecules pack in a face-to-face manner with an interplanar distance of ca. 3.6 Å between the aryl moieties which form a π stacked dimer as depicted in Figure 3. However, a bent imido bond was observed in the case of the (arylimido)vanadium(V) complex **3** bearing the methyl group [Figure 1, V(1)–N(1)–C(1) 162.6(2)°; V(1)–N(1) 1.686(2) Å]. From these results, the structures of the imido bonds are likely to depend on π conjugation contributions rather than inductive effects. This contribution is supported by the following findings. The crystal structure of the (arylimido)vanadium(V) complex **7** with the cyano group, in which two independent molecules exist in the asymmetric unit, exhibits almost linear V(1)–N(1)–C(1) angles of 170.5(3) and 170.7(3)° with V(1)–N(1) distances of 1.671(3) and 1.676(3) Å, probably due to the π-conjugation contribution as shown in Figure 1. On the contrary, the introduction of the halo group led to a more bent imido bond [**5**: V(1)–N(1)–C(1) 162.9(1)°; V(1)–N(1) 1.689(2) Å; **6**: V(1)–N(1)–C(1) 164.4(4)°; V(1)–N(1) 1.697(4) Å] than in **4** (Figure 1).

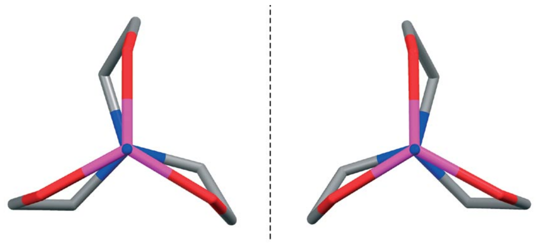

Figure 2. Two independent molecules, which are conformational enantiomers, exist in the asymmetric unit of **1**. Projection down from the imido nitrogen of the conformational enantiomers of **1** (only the molecular structure of the triethanolamine moiety is depicted); the triethanolamine moiety adopts a windmill-like conformation and the enantiomorphs are related by the mirror plane.

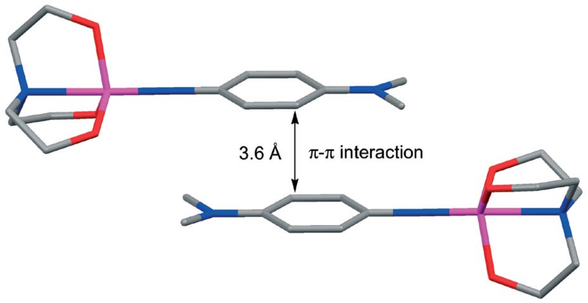

Figure 3. The π-stacked dimer in the crystal packing of **1**.

In the (arylimido)vanadium(V) complexes described in this paper, the structures of the triethanolamine moieties are almost the same and any notable differences were not observed in the V(1)–N(1) and C(1)–N(1) distances. It should be noted that the *para* substituent of the aryl moiety was also found to affect the twist angle *β* defined as the angle between the least-squares plane of the benzene ring and the C(*ipso*)–imido bond (Figure 4 and Table 2) which is considered to correlate to the properties of the imido bond. An almost perpendicular twist angle *β* was observed in the case of the complexes with the π-conjugating electron-donating substituent [43.11(9)° and 101.82(9)° for **1**; 95.92(5)° for **2**]. However, the benzene rings of other (arylimido)vanadium(V) complexes are nearly parallel to the least-squares plane of the corresponding C(*ipso*)–imido bonds [8.69(6)° for **3**; 8.35(6)° for **4**; 9.27(5)° for **5**; 11.2(1)° for **6**; 9.2(1)° and 10.4(1)° for **7**]. The linear imido angle and the almost perpendicular twist angle *β* of the (arylimido)vanadium(V) complexes with the π-conjugating electron-donating substituent might be due to greater participation of sp hybrid character in the nitrogen of the imido bond (Figure 5). The lone pair of electrons is likely to be localised in a nitrogen p orbital, the latter being likely to interact with the metal π acceptor orbitals and aryl π orbitals. In

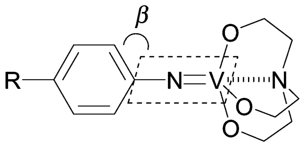

Figure 4. The twist angle *β* defined as the angle between the least-squares plane of the benzene ring and the C(*ipso*)–imido bond.

Table 2. The twist angle *β* defined as the angle between the least-squares plane of the benzene ring and the C(*ipso*)–imido bond of **1**–**7**.

	1[a]	**2**	**3**	**4**	**5**	**6**	**7**[a]
β	43.11(9), 101.82(9)	95.92(5)	8.69(6)	8.35(6)	9.27(5)	11.2(1)	9.2(1), 10.4(1)

[a] Two independent molecules exist in the asymmetric unit.

contrast, the larger contribution of sp^2 hybrid character in the nitrogen of the imido bond can be suggested because of the bent imido bond and the nearly parallel twist angle β in the case of the (arylimido)vanadium(V) complexes bearing no π-conjugating electron-donating substituent, wherein the filled imido π orbital seems to interact with the aryl π orbitals.

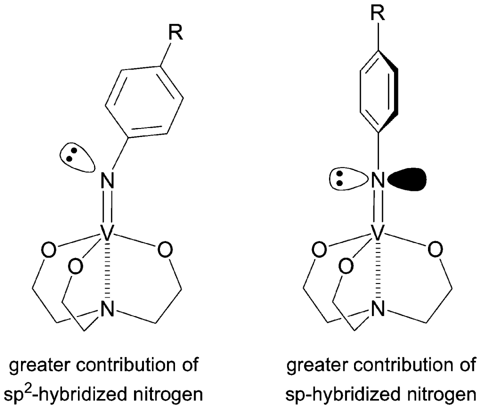

Figure 5. Proposed valence bond structures for a vanadium bound imido ligand.

Conclusions

A variety of (arylimido)triethanolaminatovanadium(V) complexes, [V(p-RC_6H_4N)(TEA)], were synthesised by the ligand exchange reaction of the corresponding (arylimido)triisopropoxidovanadium(V) species, [V(O*i*Pr)$_3$(p-RC_6H_4N)], which were prepared by the reaction of VO(O*i*Pr)$_3$ with various *p*-substituted aryl isocyanates without solvent. Structural characterisation of the (arylimido)triethanolaminatovanadium(V) compounds was carried out by single-crystal X-ray diffraction in order to elucidate the substituent effect on the imido structures. The *para* substituent of the aryl moiety was found to affect the properties and structures of the (arylimido)vanadium(V) compounds through π conjugation which can be envisioned as controlling the electronic properties of the vanadium centres. Regulation of redox properties of the vanadium centres is considered to be one of key factors in the development of an efficient vanadium catalytic system.[8] Further characterisation of the imido structures and the application of the (arylimido)vanadium(V) complexes for catalysis based on the redox control of the vanadium centres are now in progress.

Experimental Section

General: All manipulations were carried out under nitrogen in a vacuum atmospheres drybox or using standard Schlenk techniques. All reagents and solvents were purchased from commercial sources and were further purified by standard methods, if necessary. Solvents employed were dried by heating to reflux in the presence of appropriate drying reagents, distilled under nitrogen and stored in the drybox. (Arylimido)triisopropoxidovanadium(V) was prepared by the reaction of VO(O*i*Pr)$_3$ with the corresponding *p*-substituted aryl isocyanate. ^{1}H NMR spectra were recorded on JEOL JNM-ECP 400 (400 MHz) and Varian MERCURY 300 (300 MHz) spectrometers. The chemical shifts were referenced to the residual resonances of the deuterated solvents. ^{51}V NMR spectra were obtained with a JEOL JNM-ECP 400 (105 MHz) spectrometer with $VOCl_3$ as an external standard.

General Procedure for the Preparation of (Arylimido)triethanolaminatovanadium(V) Complexes: To a stirred dichloromethane (5 mL) solution of the (arylimido)triisopropoxidovanadium(V), [V(O*i*Pr)$_3$(p-RC_6H_4N)] (0.2 mmol) was added a dichloromethane (5 mL) solution of triethanolamine (45 mg, 0.3 mmol) under nitrogen at room temperature. The mixture was stirred at room temperature for 3 h. The solvent was removed in vacuo and the resultant residue was washed with acetonitrile. The desired (arylimido)triethanolaminatovanadium(V) complex was isolated by recrystallisation from dichloromethane/hexane.

1: NMR yield 85%. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.11 (d, J = 9.1 Hz, 2 H), 6.49 (d, J = 9.1 Hz, 2 H), 4.62 (t, J = 5.6 Hz, 6 H), 3.02 (t, J = 5.6 Hz, 6 H), 3.00 (s, 6 H) ppm. ^{51}V NMR (105 MHz, CD_2Cl_2): δ = –224 ppm.

2: NMR yield 95%. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.17 (d, J = 9.1 Hz, 2 H), 6.74 (d, J = 9.1 Hz, 2 H), 4.64 (t, J = 5.6 Hz, 6 H), 3.78 (s, 3 H), 3.06 (t, J = 5.6 Hz, 6 H) ppm. ^{51}V NMR (105 MHz, CD_2Cl_2): δ = –292 ppm.

3: NMR yield quantitatively. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.07 (d, J = 8.7 Hz, 2 H), 7.05 (d, J = 8.7 Hz, 2 H), 4.65 (t, J = 5.6 Hz, 6 H), 3.07 (t, J = 5.6 Hz, 6 H), 2.35 (s, 3 H) ppm. ^{51}V NMR (105 MHz, CD_2Cl_2): δ = –314 ppm.

4: NMR yield 98%. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.25 (dd, J = 8.4, 7.3 Hz, 2 H), 7.19 (d, J = 8.4 Hz, 2 H), 7.02 (t, J = 7.3 Hz, 1 H), 4.67 (t, J = 5.6 Hz, 6 H), 3.10 (t, J = 5.6 Hz, 6 H), 3.00 (s, 6 H) ppm. ^{51}V NMR (105 MHz, CD_2Cl_2): δ = –327 ppm.

5: NMR yield 71%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.22 (d, J = 9.0 Hz, 2 H), 7.14 (d, J = 9.0 Hz, 2 H), 4.67 (t, J = 5.7 Hz, 6 H), 3.11 (t, J = 5.7 Hz, 6 H) ppm. ^{51}V NMR (105 MHz, CD_2Cl_2): δ = –328 ppm.

6: NMR yield 73%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.37 (d, J = 9.0 Hz, 2 H), 7.08 (d, J = 9.0 Hz, 2 H), 4.67 (t, J = 5.7 Hz, 6 H), 3.11 (t, J = 5.7 Hz, 6 H) ppm. ^{51}V NMR (105 MHz, CD_2Cl_2): δ = –328 ppm.

7: NMR yield 72%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.54 (d, J = 9.0 Hz, 2 H), 7.25 (d, J = 9.0 Hz, 2 H), 4.70 (t, J = 5.7 Hz, 6 H), 3.15 (t, J = 5.7 Hz, 6 H) ppm. ^{51}V NMR (105 MHz, CD_2Cl_2): δ = –340 ppm.

X-ray Structure Analysis: All measurements for **1**–**7** were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite-monochromated Mo-K_α radiation. The structures of **1**–**7** were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The H atoms were placed in idealised positions and allowed to ride with the C atoms to which each was bonded. Crystallographic details are summarised in Table 3.

CCDC-656911 (for **1**), -656912 (for **2**), -656913 (for **3**), -656914 (for **4**), -656915 (for **5**), -656916 (for **6**) and -656917 (for **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 3. Crystallographic data for **1**–**7**.

	1	**2**	**3**	**4**	**5**	**6**	**7**
Empirical formula	$C_{14}H_{22}N_3O_3V$	$C_{13}H_{19}N_2O_4V$	$C_{13}H_{19}N_2O_3V$	$C_{12}H_{17}N_2O_3V$	$C_{12}H_{16}ClN_2O_3V$	$C_{12}H_{16}BrN_2O_3V$	$C_{13}H_{16}N_3O_3V$
Formula weight	331.29	318.25	302.25	288.22	322.66	367.12	313.23
Crystal system	monoclinic	monoclinic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	triclinic
Space group	$P2_1/a$ (No. 14)	$P2_1/n$ (No. 14)	*Pbca* (No. 61)	*Pbca* (No. 61)	*Pbca* (No. 61)	*Pbca* (No. 61)	$P\bar{1}$ (No. 2)
a [Å]	20.1234(4)	7.8878(3)	10.8886(4)	10.2721(7)	11.1021(4)	11.3257(8)	6.5936(1)
b [Å]	6.5842(1)	9.6141(3)	13.2292(4)	13.182(1)	13.2196(5)	13.2396(6)	10.2657(2)
c [Å]	25.2351(5)	18.7779(7)	19.2607(6)	19.0852(7)	18.8345(4)	18.871(1)	20.3733(2)
α [°]	–	–	–	–	–	–	89.907
β [°]	112.5650(5)	94.103(2)	–	–	–	–	96.997(1)
γ [°]	–	–	–	–	–	–	90.072(1)
V [Å^3]	3087.6(1)	1420.35(8)	2774.4(2)	2584.3(3)	2764.2(2)	2829.6(3)	1368.77(3)
Z	8	4	8	8	8	8	4
$D_{\text{calcd.}}$ [g cm^{-3}]	1.425	1.488	1.447	1.481	1.551	1.723	1.520
μ(Mo-K_α) [cm^{-1}]	6.55	7.12	7.20	7.69	9.15	35.38	7.35
T [°C]	23	23	4	4	23	2	23
λ(Mo-K_α) [Å]	0.71069	0.71069	0.71069	0.71069	0.71069	0.71069	0.71069
$R1$[a]	0.052	0.044	0.049	0.046	0.047	0.044	0.046
$wR2$[b]	0.163	0.134	0.150	0.175	0.138	0.151	0.142

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

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