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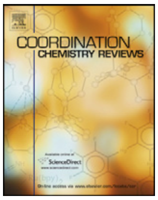

Review

Self-assembling properties of (arylimido)vanadium(V) compounds

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ABSTRACT

(Imido)vanadium(V) complexes have attracted much attention because of their potential applications as catalysts. Compared with oxo ligands, imido ligands can possess a substituent on the imido nitrogen so that the steric and electronic characters of the metal center are considered to be controlled by the properties of the nitrogen substituent. In such a sense, the design of the imido ligands is envisioned to be one of the key factors in the development of efficient catalysts. Furthermore, architectural control of transition metal-directed assembly to create organized nanostructures is of importance for advanced materials. This review highlights self-assembling properties of (arylimido)vanadium(V) compounds.

1. Introduction

The imido ligand coordinates to metals through a metal-nitrogen multiple bond [1], serving as an ancillary or supporting ligand. The imido ligands are a particularly suitable type of ligand for stabilization of transition metal complexes in high oxidation states through extensive ligand-to-metal π donation [2]. Since the initial work by Preuss and Towae [3], Maatta [4], and Horton groups [5], (imido)vanadium(V) complexes have attracted much attention [6] because of the potential application as catalysts for olefin polymerization [7], C–H activation [5c,8], and so on [9]. Introduction of a substituent onto the imido ligands is expected to influence the steric structures and electronic properties of a vanadium center through π conjugation. In such a sense, the design of the imido ligands is considered to be one of the key factors in the development of efficient catalysts. The substituent effect of the imido ligands has been reported only spectroscopically and theoretically [4b]. The design of structurally defined molecular arrangements in a solid state is an area of current interest as crystal engineering [10]. Architectural control of molecular self-organization is of importance for the development of functional materials [11]. The utilization of the transition metal-directed assembly is regarded as a convenient approach to the organized nanostructures [12]. This review describes the self-assembling properties of (arylimido)vanadium(V) compounds.

2. Self-association of (arylimido)vanadium(V) alkoxides to the μ-alkoxido-bridged dimeric structures

According to Scheme 1, (arylimido)vanadium(V) alkoxides are prepared by the reaction of VOX_3 with the corresponding aryl isocyanates. The (p-tolylimido)vanadium(V) triisopropoxides form the μ-isopropoxido-bridged dimeric structure **1**, wherein the V–O bonds of the μ-isopropoxido-bridging are not symmetrical with the V–O distances of 1.8560(13) and 2.2151 (13) Å [6i]. The geometry

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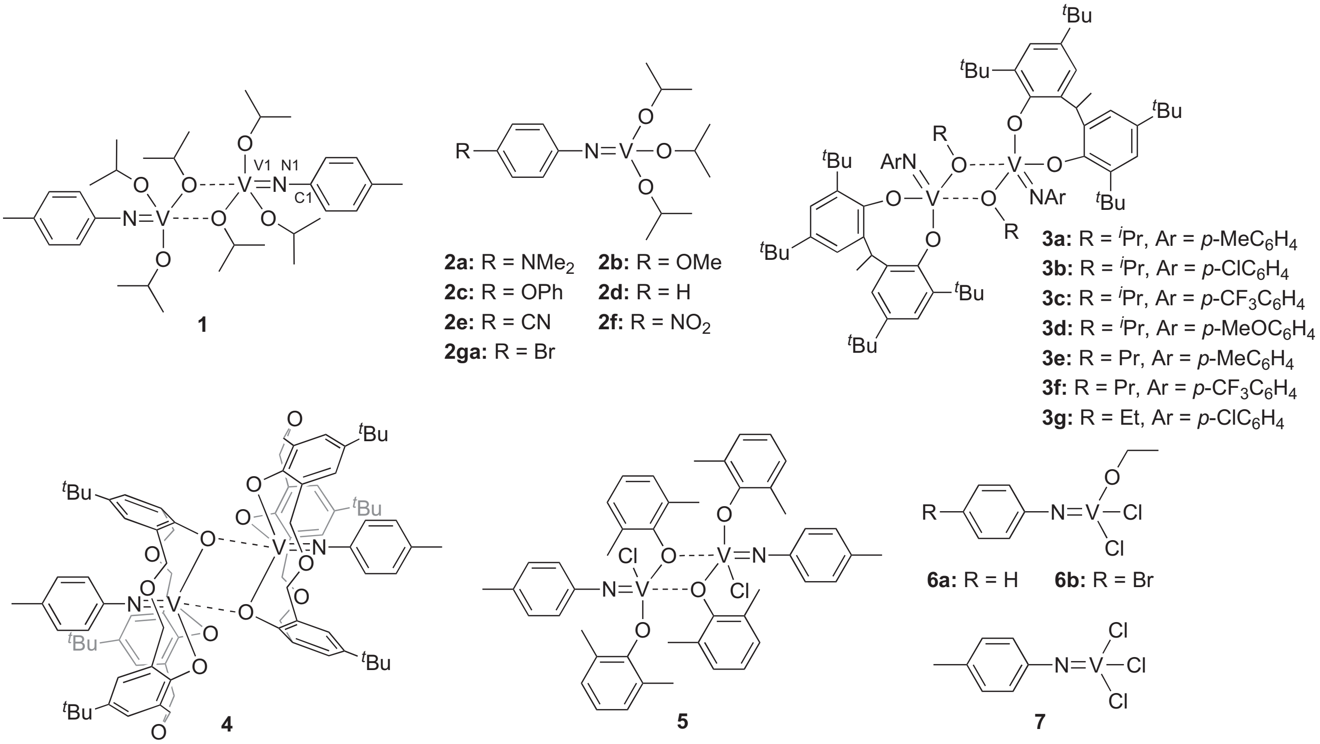


Fig. 1. (Arylimido)vanadium(V) alkoxides [4b,6i,6m,6o,6s,7j,7l,9g].

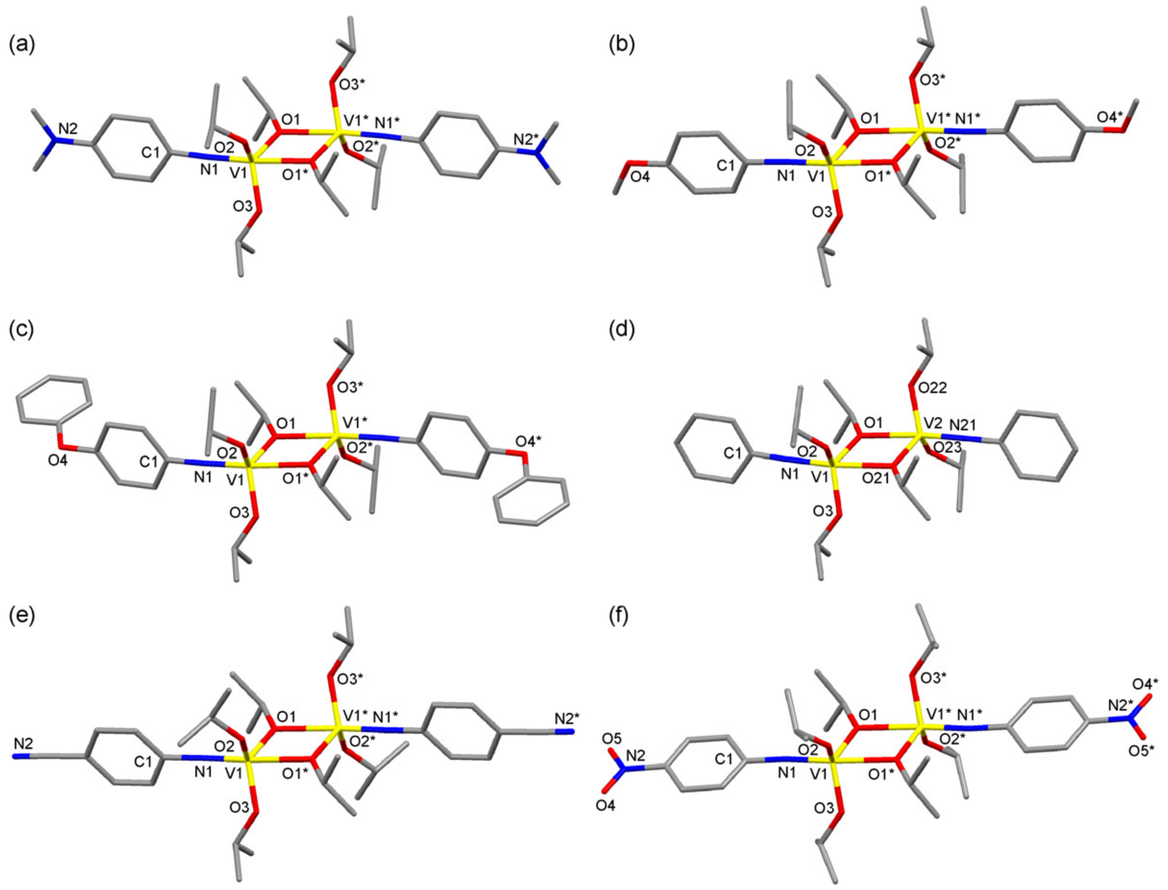


Fig. 2. μ-Isopropoxido-bridged dimeric structures of (a) **2a**, (b) **2b**, (c) **2c**, (d) **2d**, (e) **2e**, and (e) **2f** [6o,6s].

$$\mathrm{VOX_3} + \mathrm{R{-}N{=}C{=}O} \longrightarrow \mathrm{R{-}N{=}VX_3}\quad \mathbf{1}, \mathbf{2}, \mathbf{7}, \text{ or } \mathbf{14}$$

$$\mathrm{R{-}N{=}VX_3} + n\mathrm{L} \longrightarrow \mathrm{R{-}N{=}VL_nX_{3-n}}\quad \mathbf{3}, \mathbf{4}, \text{ or } \mathbf{5}$$

$$\mathrm{VOX_nY_{3-n}} + \mathrm{R{-}N{=}C{=}O} \longrightarrow \mathrm{R{-}N{=}VX_nY_{3-n}}\quad \mathbf{6}$$

Scheme 1. General preparative methods for (arylimido)vanadium(V) alkoxides [4b,6i,6m,6o,6s,7j,7l,9g].

at the imido nitrogen is nearly linear (V(1)–N(1)–C(1), 176.18(16)°) with the V(1)–N(1) distance of 1.6709 (16) Å (Fig. 1).

The effect of the *p*-substituent on the benzene ring of the (arylimido)vanadium(V) triisopropoxides was studied. The reaction of VO(O^{i}Pr)$_3$ with various *para*-substituted aryl isocyanates without solvent at 140 °C affords the corresponding (arylimido)vanadium(V) triisopropoxides, [(*p*-RC$_6$H$_4$N)V(O^{i}Pr)$_3$] (**2a**: R = NMe$_2$; **2b**: R = OMe; **2c**: R = OPh; **2d**: R = H; **2e**: R = CN; **2f**: R = NO$_2$) [6o,6s]. The solid state imido structure of **2b** bearing the electron-donating methoxy group is characterized by the V(1)–N(1) distance of 1.677(2) Å and the nearly linear V(1)–N(1)–C(1) angle of 177.3(2)°, suggesting the higher participation of an sp-hybridized character in the nitrogen of the imido bond (Fig. 2b) [6s]. Furthermore, a μ-isopropoxido-bridged dimeric structure, in which each vanadium atom is coordinated in a trigonal–bipyramidal geometry (τ = 0.96) [13] with the imido and bridging isopropoxido ligands in the apical positions, is observed in the crystal packing. This result is in contrast to the corresponding oxovanadium(V) alkoxides [14] and chloroalkoxides [15], which are distorted from the ideal trigonal bipyramidal structure. A metal-nitrogen multiple bond might lead to such a coordination geometry through ligand-to-metal π donation. The μ-isopropoxido-bridged dimeric structures are also formed in the case of **2a** bearing the electron-donating dimethylamino group, **2c** bearing the electron-donating phenoxy group, and the non-substituted complex **2d** wherein two independent molecules exist in an asymmetric unit in a solid state (Fig. 2a, c and d, respectively) [6o,6s]. Linearity of the imido angles slightly decreases (**2a**: V(1)–N(1)–C(1), 174.3(3)°; **2c**: V(1)–N(1)–C(1), 176.4(2)°; **2d**: V(1)–N(1)–C(1), 175.1(1) and 175.6(1)°) although the V(1)–N(1) distance (1.678(3) Å for **2a**, 1.673(2) Å for **2c**, 1.673(1) and 1.674(1) Å for **2d**) equals to the one observed with **2b**. In these (arylimido)vanadium(V) triisopropoxides, the higher participation of an sp-hybridized character in the nitrogen of the imido bond is suggested, resulting in the formation of the μ-isopropoxido-bridged dimeric structures. The molecular structure of **2e** bearing the electron-withdrawing cyano group is also characterized by the μ-isopropoxido-bridged dimeric structure with the V(1)–N(1) distance of 1.674(2) Å and the nearly linear V(1)–N(1)–C(1) angle of 178.6(2)° (Fig. 2e) [6s]. Linearity of the imido angle increases as compared with **2b**, probably due to the contribution of π-conjugation. The slightly decreased imido angle (V(1)–N(1)–C(1), 172.8(1)°) with the V(1)–N(1) distance of 1.670(2) Å is observed in the case of **2f** bearing the electron-withdrawing nitro group (Fig. 2f) [6s]. The *para*-substituent of the aryl moiety affects the hybridized properties and structures of the (arylimido)vanadium(V) complexes through π-conjugation. The μ-alkoxido-bridged dimeric structures **3** [7l] and **4** [7j] are formed in the (arylimido)vanadium(V) alkoxides.

The association properties of (arylimido)vanadium(V) complexes having chloride ligands were investigated. The molecular structure of the (*p*-tolylimido)vanadium(V) chlorodiaryloxide is characterized by the μ-isopropoxido-bridged dimeric structure **5** with the V–N distance of 1.644(3) Å and the nearly linear V–N–C skeleton (175.8(3)°) [4b]. As observed in the crystal structures of the triisopropoxide and diaryloxide complexes, (phenylimido)vanadium(V) ethoxydichloride **6a** forms the μ-ethoxido-bridged dimeric structure, in which each vanadium atom is coordinated in a trigonal–bipyramidal geometry by bridging the ethoxido group in an apical position (Fig. 3a) [9g]. The V(1)–N(1) distance of 1.6554(14) Å and the nearly linear C(1)–N(1)–V(1) angle of 173.46(13)° suggest the participation of an sp-hybridized character in the imido nitrogen. The crystal structure of **6b** bearing the bromo group on the benzene ring is also characterized by the μ-ethoxido-bridged dimeric structure with the V(1)–N(1) distance of 1.661(3) Å and the nearly linear V(1)–N(1)–C(1) angle of 169.5(2)° (Fig. 3b) [9g]. However, as compared with **6a**, the imido angle is almost 4° bent. This result indicates a smaller contribution of the sp-hybridized character with the imido nitrogen of **6b**. Probably due to the conjugation of the electron-withdrawing group, the bromo group might weaken the sp-hybridized character. Such relationship between the imido bond character and the substituent effect is the similar as the above-mentioned results of the (arylimido)vanadium(V) triisopropoxides. On the other hand, the chlorido-bridged polymeric structure with two chloride bridges to build a chain of edge sharing [(*p*-TolN)VCl(μ-Cl)$_4$] octahedrons is observed in the case of the (*p*-tolylimido)vanadium trichloride **7** [6m].

3. μ-Arylimido-bridged dinuclear complexes from (arylimido)vanadium(V) compounds

Only some examples for the preparation of μ-imido-brigded vanadium(IV) complexes, cyclodivanadazenes, from (imido)vanadium(V) complexes have been reported (Fig. 4) [3d,3e,6d,6e,6s] although the imido nitrogen is considered to participate in the coordination to another metal center. The crystal structures of the μ-imido-brigded dinuclear vanadium(IV) complexes **8**–**12** reveal the formation of almost planar μ-imido-brigded V$_2$N$_2$ core with the V–V distance of 2.907(3) Å for **8** [3d], 2.472(3) Å for **9a** [3e], 2.459(6) Å for **9b** [3e], 2.449(19) Å for **10** [6d], 2.487(1) Å for **11** [6d], 2.5314(9) Å for **12a** [6e], and 2.5095(6) Å for **12b** [6e].

The imido structure of the (arylimido)vanadium(V) triisopropoxides is considered to be an important factor to control the assembly. The imido nitrogen with the larger contribution of an sp^2-hybridized character could coordinate to another metal center by using a lone pair although such coordination is not possible

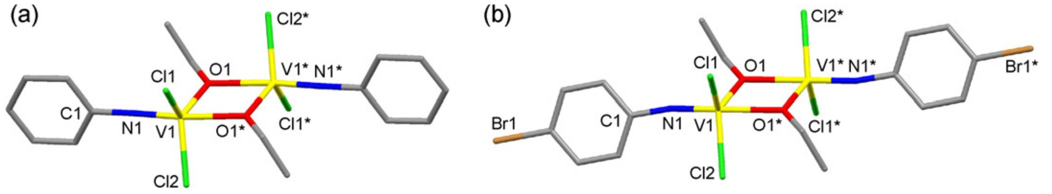
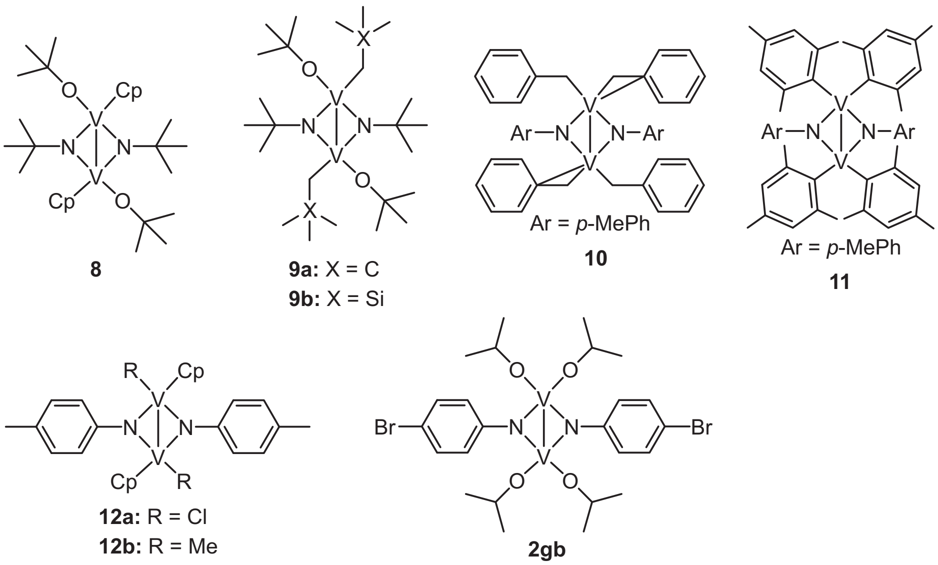


Fig. 3. μ-Ethoxido-bridged dimeric structures of (a) **6a** and (b) **6b** [9g].



8

9a: X = C
9b: X = Si

Ar = *p*-MePh
10

Ar = *p*-MePh
11

12a: R = Cl
12b: R = Me

2gb

Fig. 4. μ-Arylimido-bridged dinuclear complexes [3d,3e,6d,6e,6s].

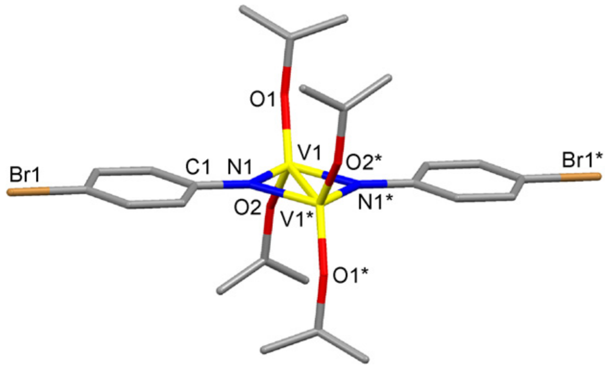
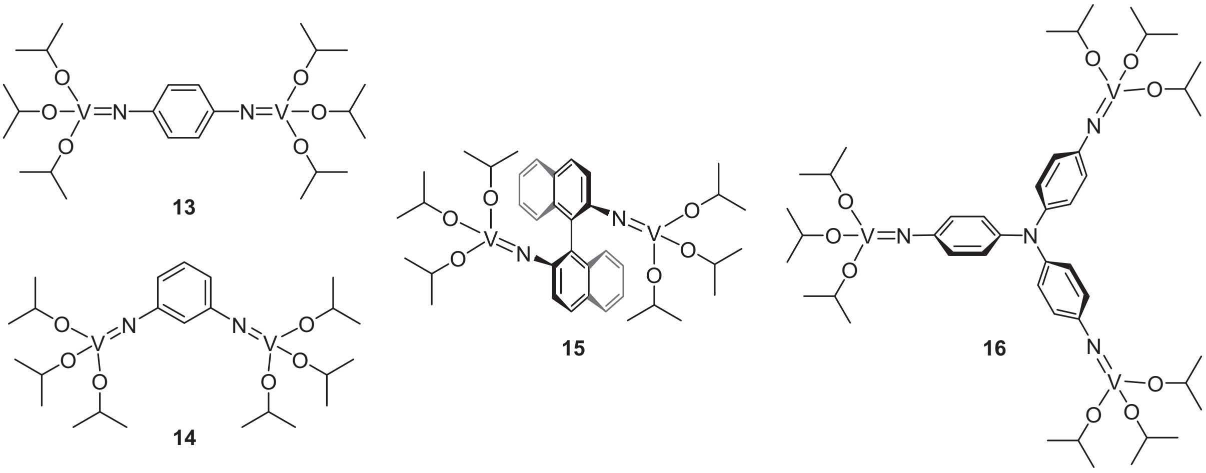


Fig. 5. Molecular structure of **2gb** for the μ-arylimido-bridged dinuclear complex [6s].

with the higher participation of an sp-hybridized character. The self-association is controlled by the characteristics of the V–N imido bond, which depends on the difference in π-conjugation of the *p*-substituent on the benzene ring. The μ-imido-brigded dinuclear vanadium(IV) complex **2gb**, $[V(\mu\text{-N-}p\text{-}C_6H_4Br)(O^iPr)_2]_2$, is obtained by recrystallization of the (arylimido)vanadium(V) complex **2ga**, $[(p\text{-BrC}_6H_4N)V(O^iPr)_3]$, which is initially formed by the reaction of 4-bromophenylisocyanate with $VO(O^iPr)_3$ [6s]. The lone pair on the nitrogen atom coordinates to the vanadium center to afford the cyclodivanadazene **2gb**. The single-crystal X-ray structure determination of the complex **2gb**, wherein two independent molecules exist in an asymmetric unit, reveals a dinuclear structure with two imido ligands bridging two $V(O^iPr)_2$ moieties as shown in Fig. 5 [6s]. Each vanadium atom is coordinated in a distorted tetrahedral geometry. The torsion angles V(1)–N(1)–V(1*)–N(1*) (0.0 and 0.0000(1)°) indicate that the V_2N_2 core is almost planar. The V(1)–V(1*) distances of 2.524(3) and 2.526(3) Å are close to those found in the cyclodivanadazenes so far reported [3d,3e,3h,6b,6d,6e,6j,6p,9e]. The V–N distances (V(1)–N(1) = 1.853(6) and 1.844(6) Å, V(1)–N(1*) = 1.856(6) and 1.850(6) Å) are ca 0.17 Å longer than that of **2b**.

4. Self-association of multinuclear (arylimido)vanadium(V) alkoxides to the highly ordered molecular arrangement in the solid state

Architectural control of well-arranged supramolecular systems based on transition metal directed assembly is a current research area in metal-directed chemistry [12]. A multinu-



13

14

15

16

Fig. 6. Multinuclear (arylimido)vanadium(V) alkoxides [6s,6v].

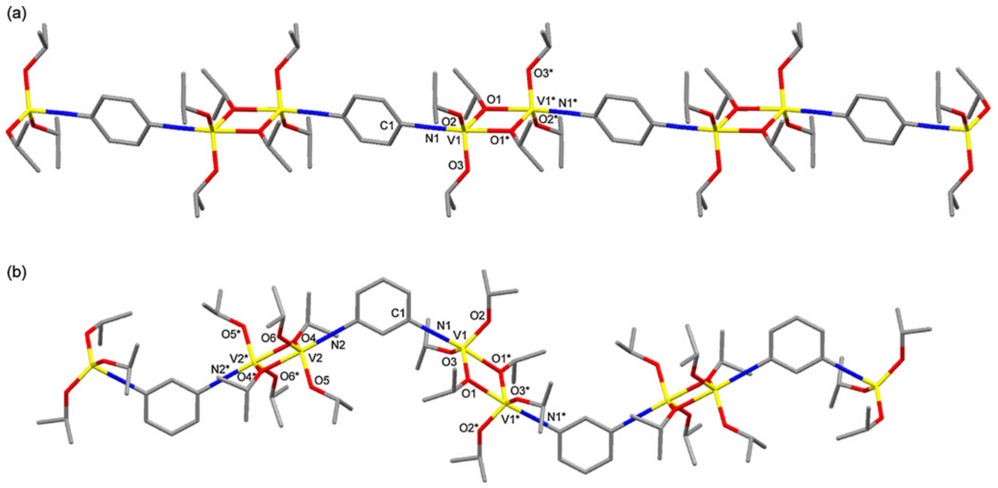


Fig. 7. A portion of a layer containing the one-dimensional linear polymeric structure of (a) **13** and (b) the one-dimensional zigzag polymeric structure of **14** through μ-isopropoxido-bridging in the crystal packings [6s].

clear (arylimido)vanadium(V) complex containing the bridging isopropoxide ligands is envisioned to expand self-association through μ-isopropoxido-bridging in a crystal state. Generally, (imido)vanadium(V) complexes have been prepared by the reaction of (oxo)vanadium(V) complexes with the corresponding isocyanates. However, there are some limitations preventing the design of functional (imido)vanadium(V) complexes because the isocyanates are not necessarily available through an easy synthetic path. One-pot preparation of (arylimido)vanadium(V) triisopropoxides from aniline derivatives is achieved by using NaH as a base (Scheme 2) [6v]. This one-pot preparation of arylimidovanadium(V) triisopropoxides permits the use of a wide range of commercial available aromatic amines in the straightforward synthesis of a variety of arylimidovanadium(V) triisopropoxides. For example, a solution of 1,4-phenylenediamine, $VO(O^iPr)_3$ (2.4 equiv.), and NaH (2.4 equiv.) is heated to reflux in octane to afford the binuclear arylimidovanadium(V) triisopropoxide **13**, $[(^iPrO)_3V(N\text{-}p\text{-}Ph\text{-}N)V(O^iPr)_3]$ (Fig. 6). The structure of **13** is confirmed by X-ray crystallographic analysis. Due to the conjugation, the V–N–Ph–N–V core is almost linear with the V(1)–N(1) distance of 1.678(2) Å and the V(1)–N(1)–C(1) angle of 177.8(1)°. As expected, the one-dimensional linear polymeric structure is formed through μ-isopropoxido-bridging in the crystal packing as shown in Fig. 7a [6s]. The bimetallic complex **14**, $[(^iPrO)_3V(N\text{-}m\text{-}C_6H_4N)V(O^iPr)_3]$, affords the one-dimensional zigzag polymeric structure through μ-isopropoxido-bridging as depicted in Fig. 7b [6s].

The utilization of an axially chiral binaphthyl is expected to induce a helically ordered molecular assembly. The axially chiral dinuclear (arylimido)vanadium(V) triisopropoxide **15**, $[(^iPrO)_3V(N\text{-}(R)\text{-}1,1'\text{-}BN\text{-}N)V(O^iPr)_3]$, is obtained by the reaction of (*R*)-(+)-binaphthyl-2,2′-diamine with 250 mol% of $VO(O^iPr)_3$ in the presence of 240 mol% of NaH. The bimetallic imido structure of **15** is confirmed by X-ray crystallographic analysis (Fig. 8a and b) [6v]. The hydrogen atom on the methine carbon atom almost faces the π-electrons of the naphthalene ring with the distance 2.75 Å, suggesting a CH-π interaction (edge-to-face interaction). As a result of this CH-π interaction, the binaphthyl moiety adopts in a conformation with a dihedral angle of 78.99(9)° between the naphthalene planes. The bent imido structures with the V(1)–N(1)–C(1) angles of 161.7(3), 167.8(3), 167.0(4), and 168.0(4)° are probably due to the CH-π interaction and steric hinderence. The axially chiral binuclear complex **15** exhibits an intermolecular CH-π interaction, wherein two independent molecules exist in the asymmetric unit and are connected alternately through the intermolecular CH-π interaction, creating a left-handed helically ordered arrangement in the crystal packing as depicted in Fig. 8c and d. The (imido)vanadium(V)

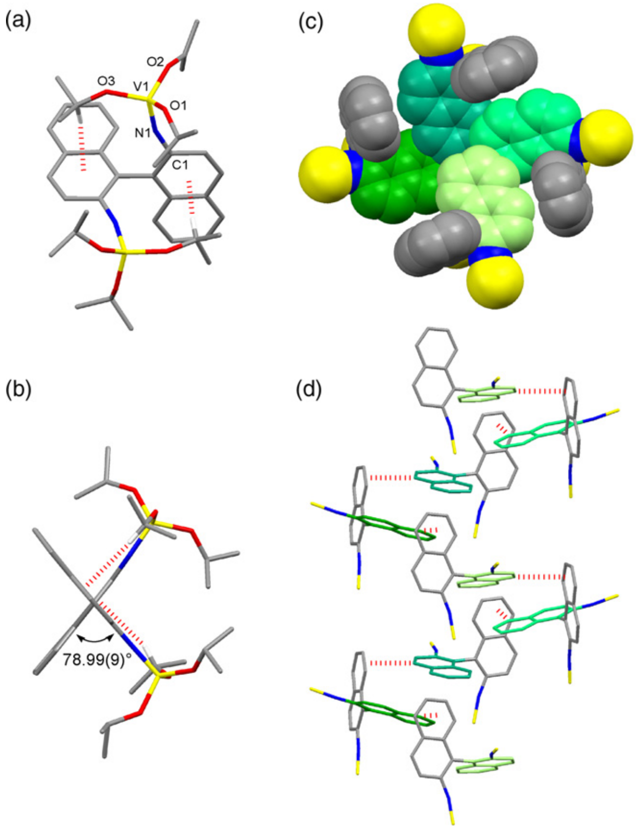
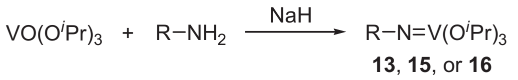


Fig. 8. (a) A top view, (b) a side view of the molecular structure of **15**, (c) space-filling representations of the top view of the crystal packing of **15** (isopropoxy groups are omitted for clarity), and (d) the side view of a portion of a layer containing the helically ordered molecular assembly through CH-π interaction in the crystal packing of **15** (isopropoxy groups are omitted for clarity). The red dotted line represents the intermolecular CH-π interaction [6v].



$$VO(O^iPr)_3 + R{-}NH_2 \xrightarrow{NaH} R{-}N{=}V(O^iPr)_3$$

13, **15**, or **16**

Scheme 2. One-pot synthesis of (arylimido)vanadium(V) alkoxides [6v].

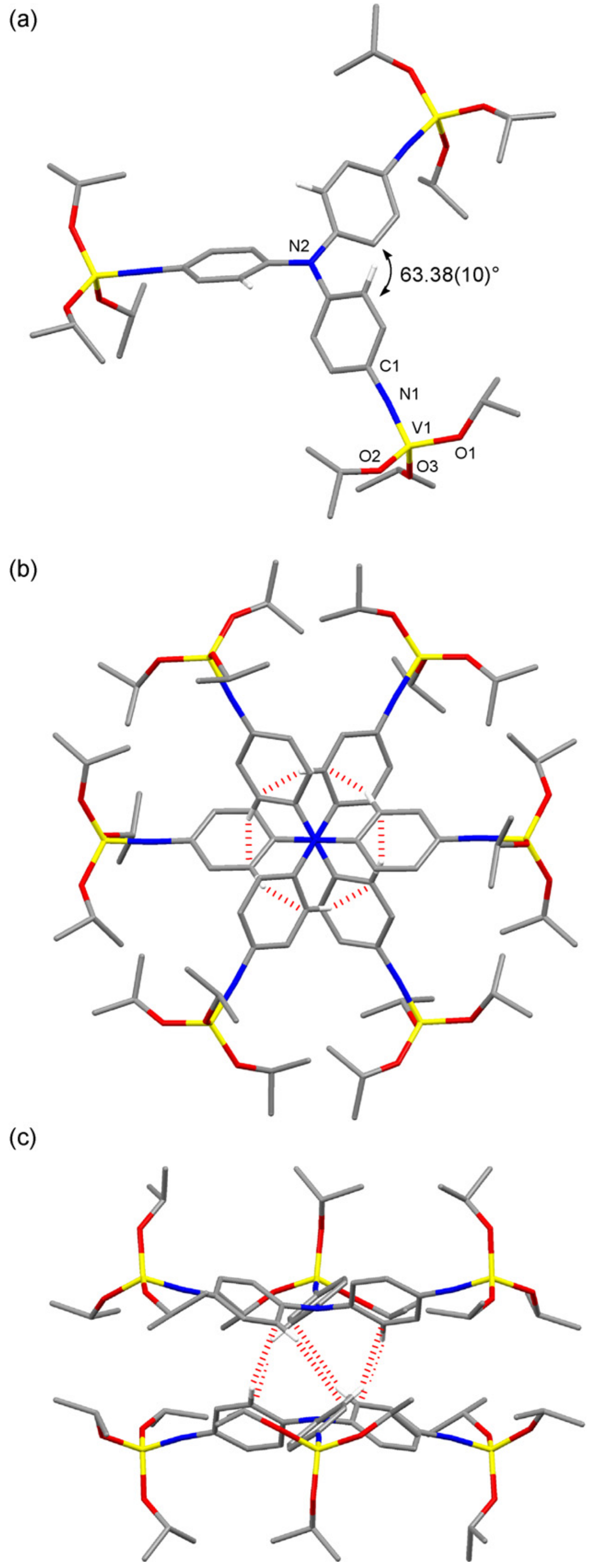


Fig. 9. (a) Molecular structure of **16**, (b) a top view, and (c) a side view of a "gear pair" like dimeric structure of **16** through six intermolecular CH-π interactions. The red dotted line represents the intermolecular CH-π interaction [6v].

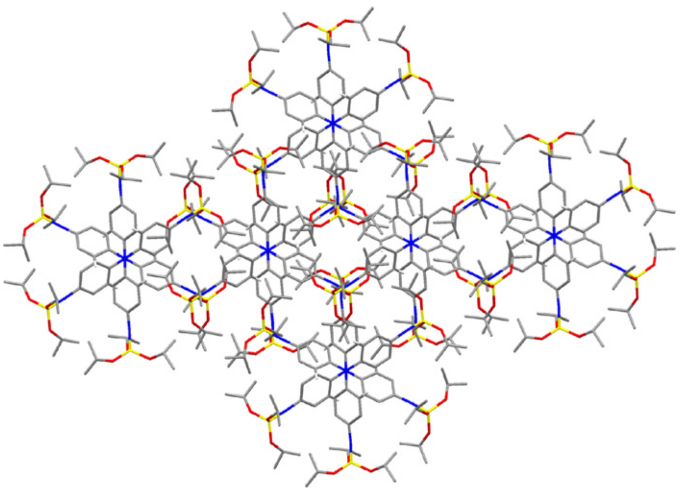


Fig. 10. A portion of a layer containing a hexagonal arrangement in the crystal packing of **16** [6v].

triisopropoxide moieties are assembled around a helical naphthalene core. The circular dichroism spectrum of **15** shows the positive Cotton effect at 326 and the negative Cotton effect at 421 nm around the absorbance region of the (imido)vanadium(V) triisopropoxide moieties, supporting the axially chiral structure.

The trinuclear (arylimido)vanadium(V) triisopropoxide **16**, $[\mathrm{N}[(\text{-}p\text{-Ph-N})\mathrm{V}(\mathrm{O}^i\mathrm{Pr})_3]_3]$, is prepared by the reaction of tris(4-aminophenyl)amine with 600 mol% of $\mathrm{VO}(\mathrm{O}^i\mathrm{Pr})_3$ in the presence of 450 mol% of NaH [6v].The single-crystal X-ray structure determination of **16** reveals a tridendritic centrosymmetric structural motif with a distorted pyramidal geometry at the central nitrogen as depicted in Fig. 9a [6v]. The imido structure with the V(1)–N(1) distance of 1.657(3) Å and the nearly linear V(1)–N(1)–C(1) angle of 173.3(2)° indicate the higher participation of an sp-hybridized character in the nitrogen of the imido bond. The steric interaction between the hydrogen atoms at the *ortho* position of the benzene ring causes a propeller twist of 63.38(10)° between the benzene rings around the central nitrogen. As the trinuclear complex **16** crystallizes in the space group *R*-3 with $Z = 6$, two mirror imaged molecules exist in the asymmetric unit, in which the triphenylamine moieties of these molecules adopt a mirror imaged propeller twist conformation. Instead of the formation of the μ-isopropoxido-bridged polymeric structure as observed in **13** and **14**, these molecules pack in a face-to-face manner to form a "gear pair"-like dimeric structure through six intermolecular CH-π interactions between the aryl moieties (the distance between the hydrogen atom and phenyl C(α) atom is 2.87 Å) in the crystal packing, in which the triphenylamine moieties are surrounded by the (imido)vanadium(V) triisopropoxide moieties as shown in Fig. 9b and c. Each vanadium atom is coordinated in a square pyramidal geometry at the metal center ($\tau = 0.002$) [13]. Another interesting structural feature is that each molecule of **16** is arranged in a hexagonal pattern in the crystal packing, in which the triphenylamine and (imido)vanadium(V) triisopropoxide moieties individually form the columns (Fig. 10).

5. Conclusion

The (arylimido)vanadium(V) alkoxides and the corresponding multimetallic triisopropoxides form the μ-alkoxido-bridged dimeric structures or the μ-imido-bridged one, wherein the *para*-substituent of the aryl moiety controls the assembling properties. The *para*-substituent of the aryl moiety affects the properties and structures of the (arylimido)vanadium(V) compounds through π-conjugation, which is envisioned to control the electronic properties of the vanadium centers. By using the one-pot versatile preparation of the (arylimido)vanadium(V) triisopropoxides from the corresponding anilines and VO(O^{i}Pr)$_3$ in the presence of NaH as a base, the binuclear (arylimido)vanadium(V) triisopropoxide with an axial chirality and the trinuclear (arylimido)vanadium(V) triisopropoxide with a tridendritic centrosymmetric structural motif is synthesized, showing their strong tendency to self-assemble through CH-π interaction to create a unique highly ordered molecular arrangement in a solid state. These architecturally dimensional structures utilizing self-assembling properties of (arylimido)vanadium(V) compounds are allowed to provide a useful approach to artificial organized nanostructures. The precise molecular arrangement is of importance in the development of nano-materials. Furthermore, the design of the imido ligands is considered to permit the development of efficient imidovanadium catalysts.

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