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Structural Characterization of (Diphenylhydrazido)vanadium(V) Compounds

Takashi Sakuramoto,[a] Toshikazu Hirao,*[a] and Toshiyuki Moriuchi*^[a]

Abstract: (Diphenylhydrazido)vanadium(V) triisopropoxide was synthesized by the reaction of VO(OPr)3 with N,N-diphenylhydrazine. The μ-isopropoxido-bridged dimeric structure was observed in the molecular structure of (diphenylhydrazido)vanadium(V) triisopropoxide. The near-linear V(1)-N(1)-N(2) angle of 173.7(3)° with the V(1)-N(1) distance of 1.667(4) Å indicates that the imido nitrogen has large participation of an sp-hybridized character. The phenyl substituents of the hydrazido moiety were found to conjugate with the N-N bond. Furthermore, CH-π intermolecular interaction between two benzene rings was observed to induce polymeric structure in a solid state. (Diphenylhydrazido)vanadium(V) nitrilotriethoxide was obtained by the treatment of (diphenylhydrazido)vanadium(V) nitrilotriethanol with 2,2',2''-nitrilotriethanol. The slightly increased imido angle (V(1)-N(1)-N(2), 176.4(5)°) was observed as compared with (diphenylhydrazido)vanadium(V) triisopropoxide probably because of the apical coordination of the nitrogen.

Introduction

Hydrazido compounds (M=N-NR2) with a metal-nitrogen multiple bond are regarded as important intermediates in organic transformations such as hydrohazination and related organic reactions.[1] Considerable attention has been attracted to the structural characterization of hydrazido compounds. Vanadium compounds are known to play a crucial role in a biological process. The insulinomimetic properties of vanadium compounds have been investigated.[2] Also, vanadium haloperoxidases mimicking systems have been reported.[3] However, hydrazido compounds of vanadium have attracted less attention[4] On the other hand, the construction of well-organized molecular arrangements in a solid state has been receiving much interest in the field of crystal engineering.[5] The controlled transition-metal-directed assembly to induce self-organized nanostructures is important for development of functional materials.[6] Alkoxide ligands are known to play an important role in the self-association of vanadium compounds through μ-alkoxido-bridging.[7] Although (imido)vanadium(V) alkoxides with vanadium-nitrogen multiple bond have been demonstrated to dimerize through μ-alkoxido-bridging, self-assembling properties of hydrazido compounds of vanadium(V) with alkoxide ligands have not been studied extensively. Recently, alkoxide ligands of (dimethylhydrazido)vanadium(V) have been demonstrated to regulate the self-association properties through the control of coordination environment, wherein isopropoxide ligands were found to induce a μ-isopropoxido-bridged dimeric structure with a trigonal-bipyramidal geometry although a monomeric tetrahedral structure was observed in the case of tert-butoxide ligands.[8] Substituents on the hydrazido moiety of (hydrazido)vanadium(V) alkoxides is envisioned to affect the electronic and steric properties of the vanadium-nitrogen multiple bond, and self-assembling properties. However, the substituent effect of (hydrazido)vanadium(V) alkoxides on the self-assembling properties has not been investigated so far. We have already performed a unique molecular arrangement of (arylimido)vanadium(V) alkoxides through CH-π interaction.[9] In this context, we embarked upon the elucidation of the aromatic substituent effects on the hydrazido moiety of (hydrazido)vanadium(V) alkoxides in vanadium-nitrogen multiple bond and the self-assembling properties.

Results and Discussion

(Diphenylhydrazido)vanadium(V) triisopropoxide (1) was obtained by the treatment of VO(OPr)3 with N,N-diphenylhydrazine in the presence of NaH as a base in dichloromethane at room temperature (Scheme 1). To reveal the effect of apical coordination, 2,2',2''-nitrilotriethanol, which has three oxygens and one nitrogen working donor sites as a tetradentate ligand, was focused on as a basal ligand. The introduction of 2,2',2''-nitrilotriethanol ligand was performed by the ligand exchange reaction of 1 with 2,2',2''-nitrilotriethanol in dichloromethane at room temperature, resulting in the formation of (diphenylhydrazido)vanadium(V) nitrilotriethoxide (2). The structures of the thus-obtained (diphenylhydrazido)vanadium(V) compounds were elucidated by 1H NMR, 13C NMR, 51V NMR, and X-ray crystallographic analyses.

The structures of the (diphenylhydrazido)vanadium(V) compounds were characterized by a single-crystal X-ray structure analysis to elucidate the effect of alkoxide ligands on the coordination environment of the vanadium metal (Table 1). The selected bond lengths and angles are summarized in Table 2. The molecular structure of 1 with isopropoxide ligands was found to contain a hydrazido structure with the V(1)-N(1) distance of 1.667(4) Å, the N(1)-N(2) distance of 1.349(5) Å, and the almost linear V(1)-N(1)-N(2) angle of 173.7(3)° as depicted in Figure 1a. These results suggest that the nitrogen of the V-N bond has an sp-hybridized character. The N(1)-N(2) distance of 1 is longer...
Scheme 1. Synthesis of the (diphenylhydrazido)vanadium(V) compounds 1 and 2.

Figure. 1 (a) Molecular structure of 1, (b) the $\mu$-isopropoxido-bridged dimeric structure, and (c) a portion of polymeric molecular structure of 1 (hydrogen atoms are omitted for clarity).

than that of (dimethylhydrazido)vanadium(V) isopropoxide (1.321(8) Å), because of conjugation between lone pair on N(2) and the benzene rings. A dihedral angle between the least-squares plane of the benzene ring Aph and the plane of C(16)-N(2)-N(1) is 4.1(1)$^\circ$, indicating that $\pi$ orbital of the N-N bond appears to interact with aryl $\pi$ orbitals. The shorter N(2)-C(16) bond distance of 1.408(5) Å compared with the N(2)-C(10) bond distance of 1.443(4) Å also supports the $\pi$ conjugation between the N-N bond and aryl $\pi$ orbitals of the benzene ring Aph. Another benzene ring Bph adopts an almost perpendicular orientation to the benzene ring Aph, in which a dihedral angle between the least-squares planes of the benzene rings Aph and Bph is 87.6(2)$^\circ$. In the crystal packing, a dimeric structure was formed by self-association through the $\mu$-isopropoxido-bridging, wherein
each vanadium atom is coordinated in a distorted trigonal-bipyramidal geometry ($\tau_5 = 0.77^{10}$) with the hydrazido and bridging isopropoxide ligands in apical positions (Figure 1b). The longer apical V(1)-O(1a) distance of 2.157(2) Å than the equatorial V(1)-O(1) distance of 1.888(3) Å in the bridging isopropoxy group was observed due to the weaker apical coordination of isopropoxide ligand to the vanadium metal. The $^1$H NMR spectrum of 1 in CD$_2$Cl$_2$ showed only one kind of isopropyl resonance, suggesting that 1 is considered to exist in a monomeric structure in a solution state. The V(1)-V(1a) distance of 3.2603(8) Å implies the absence of any bonding interaction. Furthermore, each $\mu$-isopropoxido-bridged dimer is connected by continuous CH-$\pi$ interaction between the benzene ring A of one molecule and B of the adjacent molecule to form one-dimensional polymeric structure in a crystal packing as displayed in Figure 1c. Herein, the distance between the meta hydrogen atom of the benzene ring B and the benzene ring A is 3.0 Å.

A single-crystal X-ray structure analysis of 2 with nitroletriethoxide ligand revealed the hydrazido structure, wherein the compound has a pseudo-trigonal-bipyramidal geometry ($\tau_5 = 0.98^{10}$) at the vanadium metal due to coordination of the nitroletriethoxide nitrogen at an apical site as shown in Figure 2a. In this pseudo-trigonal-bipyramidal geometry, vanadium atom is deviated from the plane constituted by an equatorial nitroletriethoxide oxygen atoms in the direction of the hydrazido moiety. The hydrazido structure showed the near-linear V(1)-N(1)-N(2) angle of 176.4(5)° with the V(1)-N(1) distance of 1.693(5) Å and the N(1)-N(2) distance of 1.333(6) Å, wherein the nitrogen atom of the V-N bond is indicated to be an sp-hybridized character. The donor ability of the apical nitroletriethoxide nitrogen caused the longer V(1)-N(1) bond distance of 2 compared with 1.

![Figure 2](a) Molecular structure and (b) the dimeric structure of 2 (hydrogen atoms are omitted for clarity).
This weakened V(1)-N(1) bond caused somewhat shorter N(1)-N(2) distance compared with that of 1, resulting in the multiple-bond character in the N(1)-N(2) bond of 2. The lone pair of electrons in a nitrogen p orbital of the V-N bond seems to interact with the metal π acceptor orbitals in the (diphenylhydrazido)vanadium(V) compound. Another interesting structural features of (diphenylhydrazido)vanadium(V) compounds are their self-assembling structures through CH–π interactions. Studies on the application of the (hydrazido)vanadium(V) compounds for catalysis are now in progress.

Supporting Information Summary

Experimental procedures and characterization data for the compounds 1 and 2 are available in the Supporting Information. Crystallographic data for 1 and 2 have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1443490 for 1 and CCDC-1443491 for 2.

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Keywords: hydrazido compound • vanadium(V) compound • metal-nitrogen multiple bond • self-association • crystal structure

Conclusions

In conclusion, design and structural characterization of (diphenylhydrazido)vanadium(V) compounds were performed to gain insight into the structural properties of vanadium-nitrogen multiple bond and self-assembling properties. The nitrogen of the V-N bond is suggested to have an sp-hybridized character by the X-ray crystallographic analyses of (diphenylhydrazido)vanadium(V) compounds. The (diphenylhydrazido)vanadium(V) trisopropoxide was demonstrated to dimerize through the π-isopropoxido-bridging. The apical coordination of the nitrogen of 2,2'-2''-nitritoetrioxide ligand to vanadium metal was found to lengthen the V-N bond and cause the multiple-bond character in the N-N bond of the (diphenylhydrazido)vanadium(V) nitritoetrioxide although the lone pair of electrons in a nitrogen p orbital of the V-N bond appears to interact with the metal π acceptor orbitals in the (diphenylhydrazido)vanadium(V) isopropoxide. Another interesting structural features of (diphenylhydrazido)vanadium(V) compounds are their self-assembling structures through CH–π interactions. Studies on the application of the (hydrazido)vanadium(V) compounds for catalysis are now in progress.


[10] The structural parameter \( \tau = (\beta - \alpha)/60 \) for the coordination geometry of the five-coordinated complex proposed by Addison and Readijk where \( \beta \) and \( \alpha \) represent two basal angles (\( \beta > \alpha \)). The parameters for an ideal square pyramidal and trigonal bipyramidal geometries are \( \tau = 0 \) (\( \alpha = \beta = 180^\circ \)) and \( \tau = 1 \) (\( \alpha = 120^\circ \) and \( \beta = 180^\circ \)), respectively. A. W. Addison, T. N. Rao, J. Readijk, J. van Rijn, G. C. Verschoor, J. Chem. Soc. Dalton Trans. 1984, 1349-1356.


(Diphenylhydrazido)vanadium(V) trisopropoxide was present as a $\mu$-isopropoxido-bridging dimeric structure with a distorted trigonal-bipyramidal geometry in a solid state, being in contrast to (diphenylhydrazido)vanadium(V) nitrilotriethoxide possessing a pseudo trigonal-bipyramidal geometry. Another interesting structural features of (diphenylhydrazido)vanadium(V) compounds are their self-assembling structures through CH–π interactions.