

Syntheses and Structures of Divanadium Complexes Bearing Triamidoamine Ligands with Bulky Substituents

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Keywords: Vanadium Complex; Dinitrogen Complex; Dinitrogen Activation; Dinuclear Complex; Triamidoamine Ligand

The catalytic conversion reaction of atmospheric dinitrogen into ammonia using dinitrogen complexes has been attracted attention. We previously reported syntheses and characterizations of some dinitrogen-divanadium complexes with triamidoamine ligands bearing bulky substituents ($[\{V(L^R)\}_2(\mu-N_2)]$ ($R = iBu$ (**1**), $EtBu$ (**2**), iPr_2Bn (**3**), Bn (**4**), and $MeBn$ (**5**)).^{1,2} Their crystal structures revealed to be a divanadium complex with a bridging N_2 ligand. The protonation reactions of these complexes in the presence of reductant and proton source showed ammonia generation. However, the substituent effect for ammonia generations was not observed. Therefore, we have synthesized three triamidoamine ligands with isopropyl (**6**), 3-pentyl (**7**) or dicyclohexyl (**8**) groups as a bulkier substituent in order to examine the substituent effect on the coordinated N_2 . And we prepared three novel divanadium complexes by reacting $[VCl_3THF_3]$ with these ligands in Et_2O under N_2 . These complexes were obtained as dark green crystals by recrystallization from Et_2O or hexane under N_2 . Also, we carried out ammonia generation reactions using these complexes. For complex **6**, the crystal structure revealed a divanadium complex with a bridging N_2 ligand. The coordination geometry around each vanadium center is trigonal bipyramidal and the τ -value is 1.00. The $V-N_{N_2}$ and $N-N$ bond lengths are 1.7655(18) and 1.218(4) Å, respectively, whose bond lengths, when compared with those of **2** ($V-N_{N_2}$ (1.768(2) Å) and $N-N$ (1.221(4) Å)), indicated similar values despite a smaller number of C atoms. In the same way, complexes **7** and **8** were characterized by NMR, IR, and UV-vis spectroscopic and X-ray structure analyses. In this presentation, the syntheses and characterizations of divanadium complexes with a bulkier triamidoamine ligand will be described in detail.

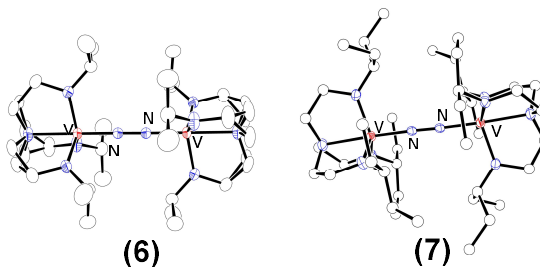
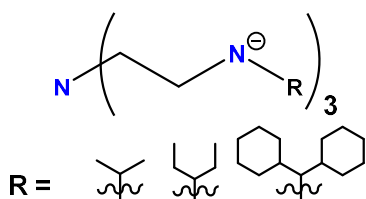


Figure 1. Structures of ligands prepared

Figure 2. Crystal structures of complexes **6** and **7**

1) Y. Kokubo et al., *Inorg. Chem.* **2018**, 57, 11884-11894. 2) Y. Kokubo et al., *Eur. J. Inorg. Chem.* **2020**, 15, 1456-1464.