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The First Example of a Seven-Coordinate Vanadium(III) Thiolate Complex Containing the Hydrazine Molecule, an Intermediate of Nitrogen Fixation

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The first example of a seven-coordinate vanadium(III) thiolate complex, $[V(PS3'')(N_2H_4)_3]$ (**1**), where PS3″ = $[P(C_6H_3\text{-}3\text{-}Me_3Si\text{-}2\text{-}S)_3]^{3-}$, has been synthesized and characterized. Compound **1** contains a tetradentate ligand (PS3″) and three hydrazine molecules, forming a capped octahedral geometry. A five-coordinate vanadium(III) complex, [V(PS3)(1-Me-Im)] (**2**), where PS3 = $[P(C_6H_4\text{-}2\text{-}S)_3]^{3-}$ and 1-Me-Im = 1-methyl-imidazole, was also obtained. Compound **2** adopts a trigonal bipyramidal geometry, in which the vanadium is ligated by the title ligand, PS3, and one 1-Me-Im molecule.

There has been an increased interest in the studies of vanadium chemistry in a sulfur-rich ligation environment due to the effort of understanding vanadium nitrogenase.[1,2] The enzyme that catalyzes the reduction of dinitrogen to ammonia has not been understood as much as its analogy, Mo-nitrogenase, which has been characterized by X-ray crystallography.[3,4] The genetic and spectroscopic data indicate that the vanadium site in V-nitrogenase has a coordination environment similar to the molybdenum site in Mo-nitrogenase in which Mo binds to three sulfides, His_{442}, and homocitrate.[5] To elucidate the role of the vanadium site in V-nitrogenase, we are prompted to explore the basic coordination chemistry of vanadium, especially in the ligation environment relevant to the enzyme. In this particular research, we studied V(III) chemistry by utilizing tristhiolatophosphine ligands which have the potential to create a S3 coordination environment similar to that of the vanadium site in the enzyme. Davis et al. have used the same strategy to generate several five-coordinate V(III) complexes, [V(NS3)L] (NS3 = $N(CH_2CH_2S)_3^{3-}$, L = NCMe, NH_3, N_2H_4, and Cl^-).[6,7] Compared to the NS3 ligand, the merit of tristhiolatophosphine ligands is that the electronic and steric effects of the complex can be tuned by adding different substituents on the phenyl ring of the ligand. In our effort to investigate the reactivity of vanadium thiolate complexes with the substrates, intermediates, or products of nitrogenase, we have obtained a novel compound, $[V(PS3'')(N_2H_4)_3]$ (**1**). Compound **1** is one of a very few structurally characterized vanadium hydrazine complexes and is the second example of vanadium binding to hydrazine, an intermediate of nitrogen fixation, in a S-rich ligation environment.[7,8] As far as we know, compound **1** is the first report of a seven-coordinate V(III) thiolate complex. In addition, we have synthesized a five-coordinate vanadium(III) complex, [V(PS3)-(1-Me-Im)] (**2**). Herein, we detail our results.

The addition of excess N_2H_4 to a 1:1 molar mixture of $VCl_3(THF)_3$ [9] and PS3″[10] in THF/methanol generated a green solution, in which the crystalline solid of **1**·3THF was obtained in 65% yield at −35 °C after a few weeks.[11] The structure of **1** was characterized by X-ray crystallography, and its ORTEP picture is shown in Figure 1.[12] The vanadium center in **1** adopts a capped octahedral geometry, in which three S donor atoms of PS3″ and three hydrazine molecules

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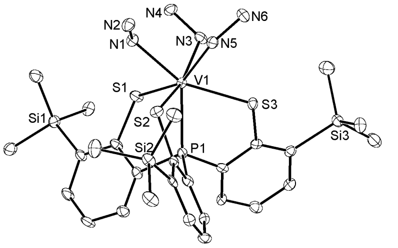

Figure 1. ORTEP diagram of **1** shown with 35% thermal ellipsoids. H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): V1−S1 2.508(2), V1−S2 2.504(2), V1−S3 2.494(2), V1−P1 2.397(2), V1−N1 2.232(4), V1−N3 2.215(4), V1−N5 2.229(4), N1−N2 1.433(5), N3−N4 1.476(5), N5−N6 1.456(5), N2···S2 3.100, N4···S1 3.138, N6···S3 3.204. P1−V1−S1 73.31(5), P1−V1−S2 75.27(5), P1−V1−S3 72.75(5), P1−V1−N1 132.3(1), P1−V1−N3 125.2(1), P1−V1−N5 134.0(1), S1−V1−S2 113.16(6), S1−V1−S3 118.27(5), S1−V1−N1 79.1(1), S1−V1−N3 77.4(1), S1−V1−N5 152.7(1), S2−V1−S3 105.81(5), S2−V1−N1 81.0(1), S2−V1−N3 159.5(1), S2−V1−N5 80.7(1), S3−V1−N1 154.7(1), S3−V1−N3 82.3(1), S3−V1−N5 76.9(1), N1−V1−N3 84.1(2), N1−V1−N5 80.3(2), N3−V1−N5 82.9(2)

form two triangular faces of the octahedron. The P donor atom of PS3″ is located on the top of the triangular face formed by three S atoms. The V−P bond can be considered as a noncrystallographic pseudo-3-fold axis in the molecule. The geometry of the capped octahedron in **1** is very similar to that of $[V(nta)(H_2O)_3]$ (nta = triaqua(nitrilotriacetato)),[13] in which nta is also a 3-fold tetradentate ligand. The average N−N distance of 1.46(2) Å and the mean V−N distance of 2.26(2) Å in **1** are in the range of the N−N single bond and V−N single bond, respectively, found in other V(III)−N_2H_4 complexes.[7,8] Compound **1** has the average V−S distance of 2.502(6) Å, which is significantly longer than those of reported V(III)−thiolate complexes (2.29−2.32 Å for five-coordinated complexes and 2.32−2.39 Å for six-coordinated complexes).[2,7,14−20] The distances of N2···S2 (3.100 Å), N4···S1(3.138 Å), and N6···S3(3.204 Å) are in the range of hydrogen bonds, indicating intramolecular hydrogen bonding interactions between three hydrazine molecules and thiolate donors of PS3″, shown in Figure 2. In addition, the ligated hydrazine molecules in **1** also interact with crystallized solvents, THF, through hydrogen bonds (Figure S1).

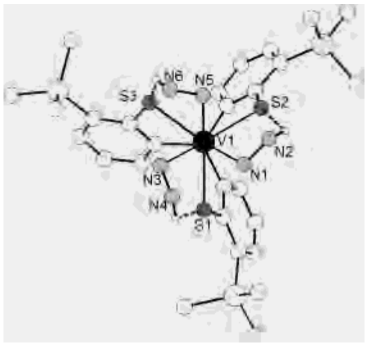

Figure 2. Perspective drawing of **1** showing the NH...S hydrogen bonding interactions, viewed along the V−P axis.

Compound **2** was generated by adding excess 1-methylimidazole to 1:1 molar mixtures of $VCl_3(THF)_3$ and PS3[10] in THF/methanol. Following the addition of hexane to the solution mixture, the X-ray quality crystals were produced in 52% yield after a few days.[11] The X-ray crystallographic data of **2** show that the structure adopts a distorted trigonal bipyramidal geometry. The vanadium is coordinated by the tetradentate ligand, PS3, and 1-Me-Im which is *trans* to the P donor atom of PS3 (Figure 3). The vanadium atom is 0.293(1) Å above the S3 plane. The average V−S bond distance of 2.302(4) Å in **2** is much shorter than that of **1** but comparable to those of five coordinate V(III) thiolate complexes.[7] The average P−V−S angle of 82.7(2)° in **2** is larger than that in **1** (73.8(2)°), showing the flexibility of the geometry supported by the PS3 ligand system.

It is noteworthy that seven-coordinate V(III) complexes are rare, and they all contain aminopolycarboxylate or aminopolypyridine ligands with the exception of $[V_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3]^+$.[13,18,21−23] It was suggested that the unusual coor-

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(11) Complex **1**: A THF solution of $VCl_3(THF)_3$ (0.325 g, 0.87 mmol) was added to a methanol solution of $PS3''Li_3$ which was produced by reacting PS3″H3 (0.499 g, 0.87 mmol) with Li (0.019 g, 2.74 mmol) in methanol to generate a green solution. The reaction mixture changed to dark green upon the addition of excess anhydrous N_2H_4 (ca. 10 equiv). From the reaction mixture, the crystalline solid was precipitated at −35 °C after one week and recrystallized from dichloromethane and methanol to give 0.410 g (65%) of product. The X-ray quality crystals of **1**·3THF were grown from a solvent mixture of THF and methanol. Anal. Calcd for $C_{27}H_{48}N_6Si_3PS_3V$: C, 45.10; H, 5.80; N, 11.70; S, 13.40. Found: C, 45.78; H, 5.80; N, 12.03; S, 12.57. UV−vis in CH_2Cl_2 (λ, nm; ϵ, M^{-1} cm^{-1}): 444(4596), 566(1596), 967(829). IR in CH_2Cl_2 (ν_{N-H}, cm^{-1}): 338, 3286, 3251, 3166. Complex **2**·CH_3OH: A THF solution of $VCl_3(THF)_3$ (0.310 g, 0.83 mmol) was reacted with a methanol solution of $PS3''Li_3$ which was obtained by reacting PS3″H3 (0.297 g, 0.83 mmol) with Li (0.018 g, 2.60 mmol) in methanol to generate a green solution. The reaction mixture changed to dark green upon the addition of excess anhydrous 1-methylimidazole (ca. 10 equiv). The solution was layered with hexane immediately, and the brown X-ray quality crystals were precipitated after 2 days. The compound was further purified by recrystallization from dichloromethane and methanol to give 0.210 g (52%) of product. Anal. Calcd for $C_{23}H_{22}N_2OPS_3V$: C, 53.03; H, 4.23; N, 5.38; S, 18.44. Found: C, 51.55; H, 4.10; N, 5.13; S, 17.86. UV−vis in CH_2Cl_2 (λ, nm; ϵ, M^{-1} cm^{-1}): 467(2652), 880(457).

(12) Crystal data for **1**·3THF: $C_{39}H_{72}N_6O_3PS_3Si_3V$, M = 935.39, T = 150(2) K, triclinic, $P\bar{1}$, a = 11.2441(10) Å, b = 11.2607(10) Å, c = 19.5312(17) Å, α = 86.032(2)°, β = 88.291(2)°, γ = 75.138(2)°, V = 2384.3(4) Å^3, Z = 2, D_c = 1.303 g cm^{-3}, μ = 0.490 mm^{-1}; 15187 reflections collected of which 10574 independent (R_{int} = 0.0512). Final R indices [$I > 2\sigma(I)$]: R1 = 0.0563, wR2 = 0.1136, GOF = 1.029. The hydrogen atoms on N_2H_4 molecules were generated by calculation using the SHELXTL program. However, the electron densities of the hydrogen atoms can be clearly identified from the electron density map, and their coordinates are comparable to the calculated sites. For **2**: $C_{22}H_{18}N_2PS_3V$, M = 488.47, T = ambient temperature, orthorhombic, $P2_12_12_1$, a = 10.297(19) Å, b = 12.886(2) Å, c = 16.690(3) Å, V = 2210.8(7) Å^3, Z = 4, D_c = 1.468 Mg m^{-3}, μ = 0.816 mm^{-1}; 13328 reflections collected of which 5186 independent (R_{int} = 0.0746). Final R indices [$I > 2\sigma(I)$]: R1 = 0.0462, wR2 = 0.0839, GOF = 0.964.

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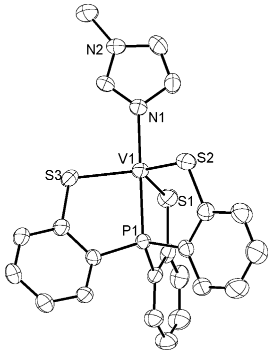

Figure 3. ORTEP diagram of **2** shown with 35% thermal ellipsoids. H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): V1−S1 2.311(1), V1−S2 2.302(2), V1−S3 2.293(1), V1−P1 2.368(1), V1−N1 2.120(4), P1−V1−S1 82.53(5), P1−V1−S2 82.61(5), P1−V1−S3 82.96(5), P1−V1−N1 178.6(1), S1−V1−S2 117.30(5), S1−V1−S3 119.26(6), S2−V1−S3 118.67(6), N1−V1−S1 96.1(1), N1−V1−S2 98.0(1), N1−V1−S3 97.8(1).

dination number in those complexes is related to the insufficiently large chelate ring of the title ligand or bidentate coligand.[22−24] The PS3 ligand system forms the five-membered chelate rings while binding to the metal. However, the finding of seven coordination in **1** versus five coordination in **2** indicates that the geometry of the V(III)−thiolate complex is not dictated by the size of the chelate ring. The space-filling models elucidate that the trimethylsilyl substituents of PS3″ do not impose a significant steric effect that might result in different geometries of these two complexes (Figure S2). It is likely that the presence of three intramolecular N−H···S hydrogen bonding interactions in **1** play an important role for the stabilization of the unusual geometry.

The IR spectrum of **1** in CH_2Cl_2 exhibits stretches at 3338, 3286, 3251, and 3166 cm^{-1}, indicating the binding of N_2H_4 molecules.[7] The UV−vis spectrum of **1** in the region of 400−1100 nm in CH_2Cl_2 displays distinct features from those of **2**, reflecting the difference of the geometry in solution state (Figure S3). Dissolving **1** in DMF resulted in a different UV−vis spectrum from that in CH_2Cl_2, implying that **1** is not stable in DMF (Figure S3). The magnetic properties of the complexes were studied by the SQUID measurements. The effective magnetic moment for **1** and **2** at 300 K is 2.80 and 2.90 μ_B, respectively, close to the spin-only value for two unpaired electrons ($\mu_{eff} = 2.83\ \mu_B$). The $S = 1$ ground state agrees with d^2 complexes which have capped octahedral or trigonal bipyramidal geometries.

In conclusion, **1** constitutes the first example of a seven-coordinate V(III) thiolate complex. The finding of different structures in **1** and **2** demonstrates the versatile coordinate chemistry of V(III) complexes in a sulfur-rich ligation environment. The flexibility of the geometry adopted in V(III) thiolate complexes implies that the vanadium site in V-nitrogenase might play an important role for binding the substrate, intermediate, or product of nitrogen fixation in the catalytic cycle. Further investigation for this chemistry is ongoing in our laboratory.

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Supporting Information Available: Crystallographic data in CIF format, the structure of **1**·3THF showing the hydrogen bonding interaction between hydrazine molecules and crystallized solvents (Figure S1), the space-filling pictures of **1** and **2** (Figure S2), and the UV−vis spectra of **1** and **2** (Figure S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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