

# Catalytic Reduction of Hydrazine to Ammonia by the $VFe_3S_4$ Cubanes. Further Evidence for the Direct Involvement of the Heterometal in the Reduction of Nitrogenase Substrates and Possible Relevance to the Vanadium Nitrogenases

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**Abstract:** The catalytic behavior of synthetic Fe/V/S clusters that structurally resemble the Fe/V/S site of nitrogenase is reported. The  $[(L)(L')(L'')VFe_3S_4Cl_3]^{n-}$  clusters ( $L, L', L'' = DMF, n = 1$ ;  $L = PEt_3, L', L'' = DMF, n = 1$ ;  $L, L' = 2,2'$ -bipyridyl,  $L'' = DMF, n = 1$ ) that contain the  $[VFe_3S_4]^{2-}$  cuboidal core are effective catalysts in the reduction of hydrazine (a nitrogenase substrate) to ammonia in the presence of cobaltocene and 2,6-lutidine hydrochloride as sources of electrons and protons, respectively. Reactivity studies show that V-coordinated terminal ligands have a profound effect on the relative rates of hydrazine reduction. Specifically, as the number of labile solvent molecules coordinated to the V atom decreases, the relative rate of hydrazine reduction decreases. The behavior also is observed with the  $[(HBpz_3)VFe_3S_4Cl_3]^{2-}$  cubane ( $L, L', L'' = \text{hydrotris(pyrazolyl)borate}, n = 2$ ), where all coordination sites on the V atom are "blocked". The latter shows no catalytic or stoichiometric hydrazine reduction and its structure has been determined. To investigate the role of the Fe sites in the  $[VFe_3S_4]^{2+}$  cubanes during catalysis, a series of cubanes  $[(DMF)_3VFe_3S_4X_3]^-$  ( $X = Cl^-, Br^-, \text{ or } I^-$ ) was synthesized. Relative rates of hydrazine reduction with each catalyst were virtually identical, indicating little or no involvement of the Fe atoms during catalysis. The results of this study strongly implicate the heterometal (V) as the site directly involved in the binding and activation of hydrazine. Additionally, reduction of phenylhydrazine to ammonia and aniline is observed in these systems. Importantly, the single cubane  $(Me_4N)[(PhHNNH_2)(bpy)VFe_3S_4Cl_3]$  has been synthesized, indicating the ability of a hydrazine-like substrate molecule to interact directly with the V atom. These reactivity studies are compared to those communicated previously for the reduction of hydrazine by the  $[MoFe_3S_4]^{3+}$  cuboidal core. Additionally, a plausible reaction pathway for the reduction of hydrazine-like substrates by the  $[VFe_3S_4]^{2+}$  core is presented. Implications regarding the function of the Fe/M/S ( $M = V, Mo$ ) center in nitrogenase are discussed.

## Introduction

The synthesis of most molecules in biological systems, such as proteins and nucleic acids, ultimately depends on the availability of nitrogenous species that derive directly from reduced nitrogen. Over 60% of the available reduced nitrogen is produced from the fixation of atmospheric nitrogen,  $N_2$ , by microorganisms referred to as diazotrophs.<sup>1</sup> These bacteria employ any of three (Mo, V, and possibly Fe) nitrogenase enzymes,<sup>2</sup> which catalyze the reduction of  $N_2$  to the metabolically usable form of ammonia. Given the very large activation energy associated with reducing  $N_2$  to ammonia, as illustrated by the extreme conditions employed in the Haber process, the ability of nature to fix dinitrogen at ambient temperature and pressure is remarkable. Hence, it is not surprising that the study of nitrogenase has intensified in the last 25 years.

Through a variety of chemical and spectroscopic techniques, a clearer picture of the structure and function of nitrogenase has developed and been thoroughly reviewed.<sup>1–5</sup> Briefly, nitrogenase is a catalytic system composed of two metallopro-

teins which are commonly referred to as the Fe protein and the MFe protein ( $M = Mo, V$ , and possibly Fe). The Fe protein, common to all three nitrogenases, is a dimer with a single  $Fe_4S_4$  cluster bound between two equivalent subunits. The function of the Fe protein is believed to involve MgATP-activated electron transfer to the MFe protein. The MoFe protein, the most thoroughly studied of all nitrogenase proteins, is known to contain two different types of metal clusters, the so-called "P clusters" and an isolable<sup>6</sup> FeMo cofactor. The function of the P-clusters is thought to involve electron transfer to the FeMo cofactor. The latter is believed to be the site of substrate reduction, as mutant MoFe proteins lacking the FeMo cofactor do not reduce nitrogenase substrates.<sup>6</sup> In addition to  $N_2$ , nitrogenase is known to catalyze the reduction of  $H^+, N_3^-,$  and other small molecules, including  $C_2H_2, N_2H_4, HCN, RCN, RNC,$  and  $N_2O$ . At present, the specific site of substrate binding and reduction on the cofactor is not known, although it has been recently suggested that  $CN^-$  binds to the Mo of the cofactor.<sup>7</sup> In the recently determined structure of the MoFe protein, the FeMo cofactor has been shown to contain  $Fe_4S_3$  and  $MoFe_3S_3$

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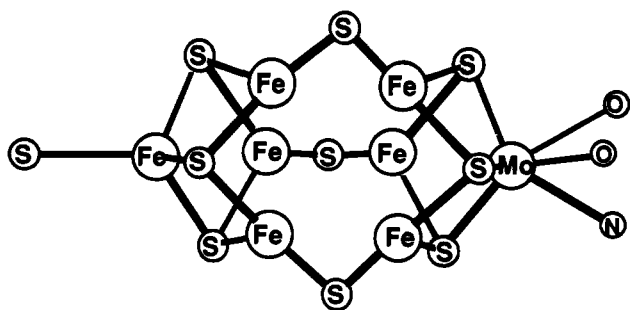


Figure 1. The FeMo cofactor of nitrogenase.<sup>1,4,5</sup>

cuboidal subunits bridged by two<sup>4</sup> or three<sup>5</sup> bridging sulfide ligands and unprecedented, coordinatively unsaturated, FeS<sub>3</sub> units (Figure 1).

An alternative form of the nitrogenase enzyme is produced by certain bacteria grown in molybdenum-deficient environments. This enzyme contains vanadium instead of molybdenum,<sup>8</sup> and is effective in the reduction of N<sub>2</sub> and other nitrogenase substrates, albeit with less activity.<sup>9</sup> Analysis of the X-ray absorption (XAS) spectrum of the V atom for the isolated VFe protein of *Azotobacter chroococcum* suggests that the vanadium is present in an FeV cofactor analogous to the FeMo cofactor,<sup>10</sup> with vanadium substituting in place of the molybdenum. The FeV cofactor is removable from the protein and has been partially characterized.<sup>11</sup>

The unique structural and electronic properties of the FeM cofactors have received considerable attention in recent years and numerous attempts to obtain inorganic synthetic analogs have been reported.<sup>12</sup> Outstanding among the Fe/M/S clusters reported to date are those that contain cuboidal [MFe<sub>3</sub>S<sub>4</sub>]<sup>n+</sup> cores (M = Mo, n = 3; M = V, n = 2). The latter are currently regarded as at least partial structural models for the coordination environment of the heterometal M in the cofactor of nitrogenase,<sup>10,13</sup> in view of their similarity to the recently determined structure of the FeMo center in the protein. Recently we have directed our research efforts toward the structure and reactivity characteristics of Fe/M/S clusters that contain cubane-type [MFe<sub>3</sub>S<sub>4</sub>]<sup>n+</sup> cores in studies that attempt to (i) modify the coordination environment around the heterometal to better approximate that found in the enzyme,<sup>14,15</sup> (ii) assess the ability of the heterometal to bind and/or activate nitrogenase substrates,<sup>16,17</sup> and (iii) chemically link these clusters in order to obtain systems with metal composition similar to that of the cofactor.<sup>16,18</sup>

In the past a major criticism of nitrogenase modeling has been the lack of synthetic clusters that display both structural and

functional relationships to nitrogenase.<sup>2</sup> Recently, however, we have communicated that the single cubanes [(Cl<sub>4</sub>-cat)(CH<sub>3</sub>CN)-MoFe<sub>3</sub>S<sub>4</sub>Cl<sub>3</sub>]<sup>2-</sup><sup>19</sup> and [(citrate)MoFe<sub>3</sub>S<sub>4</sub>Cl<sub>3</sub>]<sup>3-</sup><sup>14,15</sup> may serve as functional analogs for the cofactor of nitrogenase, as these clusters are efficient catalysts in the reduction of hydrazine to ammonia.<sup>20</sup> These reactivity studies have allowed for an indirect investigation of the involvement of the heterometal in the cubane clusters during substrate reduction. As reported previously,<sup>20</sup> the use of substitutionally-inert ligands to "block" the available coordination site on the Mo atom in the [(Cl<sub>4</sub>-cat)(CH<sub>3</sub>CN)-MoFe<sub>3</sub>S<sub>4</sub>Cl<sub>3</sub>]<sup>2-</sup> cubane, results in a decrease in the relative turnover of substrates (either N<sub>2</sub>H<sub>4</sub><sup>20</sup> or C<sub>2</sub>H<sub>2</sub><sup>21</sup>) to products. This result was used to argue in favor of the involvement of the heterometal (Mo) in substrate binding prior to reduction. However, the [MoFe<sub>3</sub>S<sub>4</sub>]<sup>3+</sup> clusters cannot be synthesized without at least a bidentate ligand on the Mo atom, leaving at most one labile site (typically a solvent molecule) bound to the heterometal. This single labile ligand can be replaced by a more substitutionally-inert ligand, and clusters with the formulation [(al<sub>2</sub>cat)(X)MoFe<sub>3</sub>S<sub>4</sub>Cl<sub>3</sub>]<sup>n-</sup> (X = PEt<sub>3</sub>, n = 2; or X = CN<sup>-</sup>, n = 3) have been characterized.<sup>22</sup> Investigations of the role played by the Mo atom in the [MoFe<sub>3</sub>S<sub>4</sub>]<sup>3+</sup> clusters in catalysis, by altering the terminal ligands on the Mo atom, are limited to clusters that differ only in the nature of the monodentate ligand bound to the Mo atom. The reason for this limitation is that the synthesis of [MoFe<sub>3</sub>S<sub>4</sub>]<sup>3+</sup> cubanes with three, two, or no labile sites at the Mo atom has not been realized. The tridentate polycarboxylate and related ligands<sup>14,15</sup> provide a series of Mo cuboidal clusters with all potential coordinating sites on the Mo atom blocked. In protic environments, however, protonation and dissociation of at least one of the coordinated "arms" of the ligand provides a site for substrate binding and reduction.

In this report, we describe the catalytic reduction of N<sub>2</sub>H<sub>4</sub> to NH<sub>3</sub> by the (Me<sub>4</sub>N)[(DMF)<sub>3</sub>VFe<sub>3</sub>S<sub>4</sub>Cl<sub>3</sub>] · 2DMF cubane<sup>23</sup> and derivatives. The substitutional lability of the DMF ligands in the [(DMF)<sub>3</sub>VFe<sub>3</sub>S<sub>4</sub>Cl<sub>3</sub>]<sup>-</sup> cluster allows for synthetic control over the ligating environment around the V atom through the use of bi- and tridentate ligands. Additionally, synthetic manipulation of the Fe terminal ligands can be readily accomplished while maintaining the terminal ligation at the V atom. Consequently, the catalytic function of the [VFe<sub>3</sub>S<sub>4</sub>]<sup>2+</sup> core in the reduction of N<sub>2</sub>H<sub>4</sub> and PhHNNH<sub>2</sub> has been investigated with different coordination environments for the V and Fe atoms.

## Experimental Section

**General Information.** All operations were performed under a pure dinitrogen atmosphere using either standard glovebox or Schlenk techniques. Solvents were dried by distillation from sodium/benzophenone (diethyl ether, tetrahydrofuran) or CaH<sub>2</sub> (acetonitrile, *N,N*-dimethylformamide) and thoroughly degassed prior to use. Potassium hydrotris(1-pyrazolyl)borate (Strem), anhydrous FeBr<sub>2</sub> (Alpha), cobaltocene, 2,6-lutidine, 2,2'-bipyridyl, *p*-(dimethylamino)benzaldehyde, 96% nitromethane, PEt<sub>3</sub>, and 1.0 M HCl in diethyl ether (Aldrich) were purchased and used as received.

Infrared spectra (CsI pellets) were obtained using a Nicolet 740 FT-IR spectrometer (far-IR: 500–150 cm<sup>-1</sup>) or a 5DXB FT-IR spectrom-

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eter (mid-IR: 4000–400  $\text{cm}^{-1}$ ). Electronic spectra were obtained with a Cary 1E spectrophotometer using a 1 mm quartz cell. Electrochemical measurements were performed on a Bioanalytical Systems, Inc. 100A electrochemical analyzer. The electrochemical cell used had platinum working and auxiliary electrodes. A  $\text{Ag}/\text{AgCl}_{(\text{aq})}$  electrode served as the reference. The supporting electrolyte was tetra-*n*-butylammonium perchlorate. Normal concentrations used were of the order of 0.001 M in electroanalyte and 0.1 M in supporting electrolyte. Solutions were degassed thoroughly with Ar before measurement. Detection of hydrogen gas was performed using a Perkin Elmer 8500 GC equipped with a 5 Å molecular sieve (3 ft) column (Hewlett Packard) and a thermal conductivity detector. Elemental analyses were performed by the analytical services laboratory at the University of Michigan.

**Preparation of Compounds.** The compounds  $(\text{Me}_4\text{N})[(\text{DMF})_3\text{VFe}_3\text{S}_4\text{Cl}_3] \cdot 2\text{DMF}$  (**I**),<sup>23</sup>  $(\text{Me}_4\text{N})[(\text{DMF})(2,2'\text{-bpy})\text{VFe}_3\text{S}_4\text{Cl}_3] \cdot 3\text{DMF}$ <sup>23a,b</sup> (**II**),  $(\text{Et}_4\text{N})_2[\text{Fe}_4\text{S}_4\text{Cl}_4]$ ,<sup>24</sup>  $(\text{Et}_4\text{N})_3[\text{VFe}_2\text{S}_4\text{Cl}_4]$ ,<sup>25</sup> and  $(\text{NH}_4)_3\text{VS}_4$ <sup>25</sup> were prepared by slight modifications of literature procedures. The  $[(\text{DMF})_2(\text{PET}_3)\text{VFe}_3\text{S}_4\text{Cl}_3]^-$  cluster<sup>23a</sup> was prepared from **I** *in situ* by the addition of  $\text{PET}_3$  in slight excess over the stoichiometric amount. Analytically pure 2,6-lutidine hydrochloride ( $\text{LutHCl}$ ) was obtained in quantitative yield from the reaction of 2,6-lutidine with 1.0 M ethereal HCl.

$(\text{Me}_4\text{N})[(\text{DMF})_3\text{VFe}_3\text{S}_4\text{Br}_3] \cdot 2\text{DMF}$  (**III**). This compound was prepared from a procedure<sup>23c</sup> similar to that described for **I**, using  $\text{FeBr}_2$  in place of  $\text{FeCl}_2$ . To a stirring solution of 2.77 g (12.8 mmol) of  $\text{FeBr}_2$  in 75 mL of DMF was added 0.75 g (3.2 mmol) of  $(\text{NH}_4)_3\text{VS}_4$ . An immediate color change to an intense red/purple ensured that progressed toward a dark brown as the reaction proceeded. The reaction mixture was stirred for 16 h, after which it was filtered to remove byproducts (primarily  $\text{NH}_4\text{Br}$  and  $\text{NH}_4[\text{FeBr}_4]$ ). The filtrate was layered with 100 mL of diethyl ether and placed in a  $-20^\circ\text{C}$  freezer overnight. Filtration yielded the  $\text{NH}_4^+$  salt of the cluster. This was then dissolved in 100 mL of  $\text{CH}_3\text{CN}$  and 0.38 g (2.6 mmol) of  $\text{Me}_4\text{NBr}$  was added with stirring. After 6 h, the solution was filtered to remove unreacted  $\text{Me}_4\text{NBr}$  and  $\text{NH}_4\text{Br}$ . The filtrate was taken to dryness under vacuum and the brown residue was recrystallized from DMF/diethyl ether. Approximately 2.0 g (60%) of a black microcrystalline solid was obtained. Anal. Calcd for  $\text{C}_{19}\text{H}_{47}\text{N}_6\text{O}_5\text{Br}_3\text{VFe}_3\text{S}_4$ : C, 22.24; H, 4.63; N, 8.19. Found: C, 21.42; H, 4.18; N, 8.16. Mid-IR spectrum (CsI):  $\nu_{\text{asym}}(\text{C}=\text{O}_{\text{DMF}}) = 1650 \text{ cm}^{-1}$ . Far-IR spectrum (CsI): 432 (sh), 408 (s), 390 (sh), 373 (s), 315 (w), 298 (m)  $\text{cm}^{-1}$ . Absorption spectrum ( $\text{CH}_3\text{CN}$ ): a featureless rise from 800 to 270 nm.

$(\text{Me}_4\text{N})[(\text{DMF})_3\text{VFe}_3\text{S}_4\text{I}_3] \cdot 2\text{DMF}$  (**IV**).  $(\text{Me}_4\text{N})[(\text{DMF})_3\text{VFe}_3\text{S}_4\text{Cl}_3] \cdot 2\text{DMF}$  (0.50 g, 0.56 mmol) was dissolved in 30 mL of DMF. To the stirring solution was added 0.25 g (1.7 mmol) of NaI. The reaction mixture was stirred for approximately 1 h, after which it was filtered over a pad of Celite to remove NaCl. The filtrate was then layered with 100 mL of ether and placed in a  $-20^\circ\text{C}$  freezer overnight. The crude product, contaminated with unreacted NaI, was obtained by filtration. The brown solid was extracted from the white crystals with a minimum amount of  $\text{CH}_3\text{CN}$  and filtered over a pad of Celite. The brown filtrate was taken to dryness under vacuum and the resulting brown residue was recrystallized from DMF/diethyl ether. A near quantitative yield of a brown microcrystalline solid was obtained. Anal. Calcd for  $\text{C}_{19}\text{H}_{47}\text{N}_6\text{O}_5\text{I}_3\text{VFe}_3\text{S}_4$ : C, 19.55; H, 4.07; N, 7.20. Found: C, 19.80; H, 3.92; N, 7.28. Mid-IR spectrum (CsI):  $\nu_{\text{asym}}(\text{C}=\text{O}_{\text{DMF}}) = 1650 \text{ cm}^{-1}$ . Far-IR spectrum (CsI): 402 (sh), 386 (sh), 375 (s), 328 (m)  $\text{cm}^{-1}$ . Absorption spectrum ( $\text{CH}_3\text{CN}$ ): a featureless rise from 800 to 270 nm.

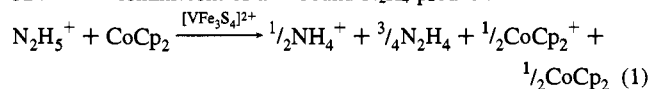
$(\text{Me}_4\text{N})_2[(\text{HBpz}_3)\text{VFe}_3\text{S}_4\text{Cl}_3] \cdot 2\text{CH}_3\text{CN}$  (**V**).  $(\text{Me}_4\text{N})[(\text{DMF})_3\text{VFe}_3\text{S}_4\text{Cl}_3] \cdot 2\text{DMF}$  (0.25 g, 0.28 mmol) was dissolved in 25 mL of  $\text{CH}_3\text{CN}$ . To this stirring solution was added 0.070 g (0.28 mmol) of  $\text{K}[\text{HB}(\text{pz})_3]$  and 0.050 g (0.32 mmol) of  $\text{Me}_4\text{NBr}$ . After stirring overnight, the solution was filtered to remove unreacted  $\text{Me}_4\text{NBr}$  and  $\text{KBr}$ . The filtrate was layered with 60 mL of diethyl ether. A black microcrystalline material was isolated by filtration. Subsequent recrystallizations from  $\text{CH}_3\text{CN}$ /diethyl ether yielded the product as X-ray diffraction-quality crystals in 75% yield. While the crystals contain two  $\text{CH}_3\text{CN}$  molecules of solvation, the solvent molecules are readily

lost and the crystals were dried under vacuum prior to analysis. Anal. Calcd for  $\text{C}_{17}\text{H}_{34}\text{N}_8\text{BCl}_3\text{VFe}_3\text{S}_4$ : C, 25.07; H, 4.22; N, 13.76; V, 6.25; Fe, 20.6. Found: C, 24.90; H, 3.94; N, 13.39; V, 6.74; Fe, 20.1. Mid-IR spectrum (CsI):  $\nu(\text{B}-\text{H}) = 2483 \text{ cm}^{-1}$ ;  $\nu(\text{C}\equiv\text{N}) = 2250 \text{ cm}^{-1}$  for unbound  $\text{CH}_3\text{CN}$ . Far-IR spectrum (CsI): 403 (m), 377 (m), 367 (sh), 354 (sh), 331 (s), 304 (w), 293 (w)  $\text{cm}^{-1}$ . Absorption spectrum: ( $\text{CH}_3\text{CN}$ ): an essentially featureless rise from 800 to 270 nm, with shoulders at 560 and 311 nm.

$(\text{Me}_4\text{N})[(\text{PhHNNH}_2)(\text{bpy})\text{VFe}_3\text{S}_4\text{Cl}_3]$  (**VI**). To 0.2 g of  $(\text{Me}_4\text{N})[(\text{DMF})(\text{bpy})\text{VFe}_3\text{S}_4\text{Cl}_3] \cdot 3\text{DMF}$  (0.2 mmol) in 25 mL of  $\text{CH}_3\text{CN}$  was added 2.0 mL of a 0.5 M solution of phenylhydrazine in  $\text{CH}_3\text{CN}$  (0.5 mmol). The solution was stirred overnight and then filtered. Diethyl ether (100 mL) was layered on the dark purple filtrate. Overnight standing produced a dark purple microcrystalline solid in near-quantitative yield. The material was recrystallized from  $\text{MeNO}_2$ /diethyl ether. Anal. Calcd for  $\text{C}_{20}\text{H}_{28}\text{N}_5\text{Cl}_3\text{VFe}_3\text{S}_4$ : C, 30.34; H, 3.57; N, 8.85. Found: C, 30.08; H, 3.75; N, 8.40. Mid-IR spectrum (CsI):  $\nu_{\text{asym}}(\text{N}-\text{H}) = 3325 \text{ cm}^{-1}$ ;  $\nu_{\text{sym}}(\text{N}-\text{H}) = 3254 \text{ cm}^{-1}$ ;  $\nu(\text{C}-\text{H})_{\text{Ph}} = 3155 \text{ cm}^{-1}$ ;  $\nu(\text{C}-\text{H})_{\text{bpy}} = 3053 \text{ cm}^{-1}$ . Far-IR spectrum (CsI): 423 (w), 400 (m), 377 (m), 343 (s)  $\text{cm}^{-1}$ .

$(\text{Me}_4\text{N})[(\text{NH}_3)(\text{bpy})\text{VFe}_3\text{S}_4\text{Cl}_3]$  (**VII**). To 50 mL of  $\text{CH}_3\text{CN}$  was added 0.090 g of  $\text{NH}_4\text{I}$  (0.62 mmol) followed by 0.090 mL of  $\text{Et}_3\text{N}$  (0.65 mmol). This mixture was allowed to stir until all of the  $\text{NH}_4\text{I}$  was dissolved, after which 0.21 g of  $(\text{Me}_4\text{N})[(\text{DMF})(\text{bpy})\text{VFe}_3\text{S}_4\text{Cl}_3] \cdot 3\text{DMF}$  (0.22 mmol) was added in one portion with stirring. After 3 h, the reaction was filtered to remove a small amount of an insoluble material and the filtrate layered with 100 mL of diethyl ether. A purple powder was obtained in 65% yield (0.1 g). The material was washed thoroughly with  $\text{MeNO}_2$  and  $\text{MeOH}$  before elemental analysis. Anal. Calcd for  $\text{C}_{14}\text{H}_{23}\text{N}_4\text{Cl}_3\text{VFe}_3\text{S}_4$ : C, 24.00; H, 3.32; N, 8.00. Found: C, 23.58; H, 2.58; N, 7.11. Mid-IR spectrum (CsI):  $\nu(\text{N}-\text{H}) = 3328$ ,  $3305 \text{ cm}^{-1}$ ;  $\nu(\text{C}-\text{H})_{\text{bpy}} = 3053 \text{ cm}^{-1}$ . Far-IR spectrum (CsI): 418 (m), 399 (s), 377 (s), 367 (s), 337 (s)  $\text{cm}^{-1}$ .

$[(\text{NH}_2)(\text{bpy})\text{VFe}_3\text{S}_4\text{Cl}_3]^-$  (**C** in Scheme 1). A reaction was carried out in which **II** in  $\text{CH}_3\text{CN}$  solution was allowed to react with 1 equiv of  $\text{N}_2\text{H}_5^+$  (added as the  $\text{BF}_4^-$  salt) for 15 min followed by the addition of 1 equiv of  $\text{CoCp}_2$  and standing for an additional 15 min. An aliquot of this solution was analyzed for  $\text{NH}_4^+$  (*vide infra*) before layering the reaction solution with diethyl ether. The purple powder that was isolated from this reaction rather than being the intermediate **C** (Scheme 1) is believed to be the hydrazine bound cubane obtained in an "all or nothing" reaction (eq 1). This conclusion is based on the following observations: (i) The IR spectrum shows N–H vibrations at 3291 and 3242  $\text{cm}^{-1}$  reminiscent of a V-bound  $\text{N}_2\text{H}_4$  product.



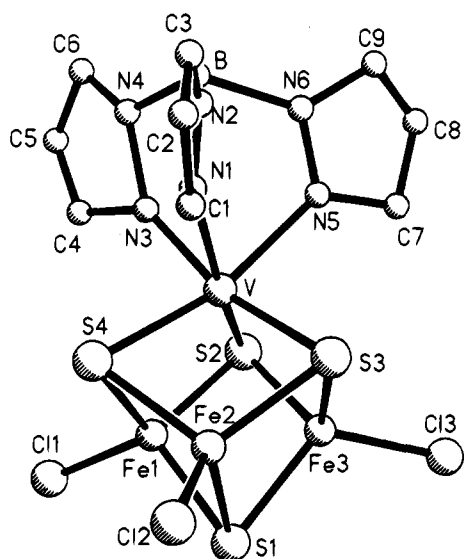
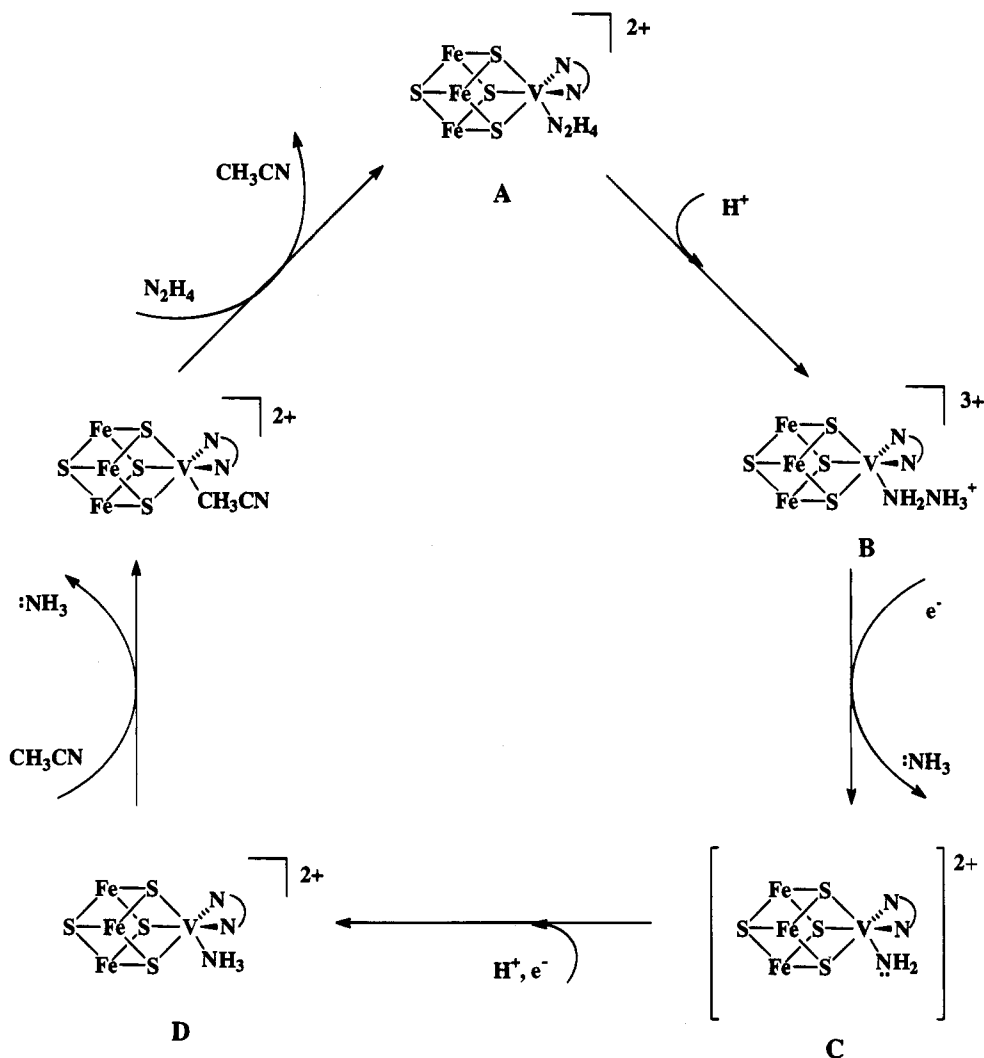
Also present is a stretch at 966  $\text{cm}^{-1}$ , which may indicate an N–N stretch. The mid-IR also shows  $\text{CoCp}_2^+$  (3100, 461  $\text{cm}^{-1}$ ) and  $\text{Me}_4\text{N}^+$  cations. (ii) Quantitative analysis showed approximately 20–30% conversion of hydrazine to ammonia. (iii) The EPR showed an  $S = \frac{3}{2}$  signal, indicative of the cuboidal core in its  $[\text{VFe}_3\text{S}_4]^{2+}$  oxidation state.

**Structure Determination of  $(\text{Me}_4\text{N})_2[(\text{HBpz}_3)\text{VFe}_3\text{S}_4\text{Cl}_3] \cdot 2\text{CH}_3\text{CN}$  (**V**).** Single crystals of (**V**), of marginal diffraction quality, were grown by ether diffusion into an  $\text{CH}_3\text{CN}$  solution of the compound. The protocols followed for the collection and reduction of X-ray data have been deposited as supplementary material. All atoms were located; however, due to the poor quality of the crystals, and limited data, the structure was refined with isotropic temperature factors and even then the data to parameter ratio was only marginally acceptable (6). The final  $R$  and  $R_w$  values were 0.11 and 0.12, respectively. The large standard deviations in the bond distances and angles reflect the problems associated with the data. The core structure in **V** (Figure 2) has been drawn on the basis of crystallographically determined coordinates (PLUTO diagram) and is presented with the intention to show atomic connectivity and more specifically the "blocked" V atom of importance to this report. With a hope that we will be able to obtain high-quality data from better crystals, perhaps with different counterions, we will not deposit crystallographic data at this time.

**Catalytic and Stoichiometric Reductions of Hydrazine and Phenylhydrazine.** Standard solutions of  $\text{N}_2\text{H}_4$  and  $\text{PhHNNH}_2$  (0.2 M) and of cluster (5.6 mM) were prepared in  $\text{CH}_3\text{CN}$  immediately prior

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**Scheme 1.** A Proposed Reaction Pathway for the Reduction of  $N_2H_4$  by the  $[VFe_3S_4]^{2+}$  Core**Figure 2.** PLUTO diagram of the  $[(HBpz_3)VFe_3S_4Cl_3]^{2-}$  anion.

to use. Under an atmosphere of dinitrogen, an aliquot of the cluster solution was added to a Schlenk flask containing a predetermined volume of  $CH_3CN$  (total solution volume was 40.0 mL in all cases). A 0.28 mL aliquot of the 0.2 M substrate solution was then added and the solution was stirred briefly. Cobaltocene ( $CoCp_2$ ) and 2,6-lutidine hydrochloride (LutHCl) were then added in one portion with stirring. The addition of the proton source (4 equiv per mol of substrate) and electron source (2 equiv per mol of substrate) marked  $t = 0$ . Samples

(2.0 mL) were then obtained at  $t = 30, 60,$  and  $120$  min. In all cases,  $[substrate] = 1.4$  mM and the concentrations of cubane,  $CoCp_2$ , and LutHCl were scaled accordingly for 40, 20, 10, and 1 equiv of substrate per mol of cluster.

**Ammonia Analysis.** Samples were analyzed for  $NH_4^+$  by a procedure similar to that previously reported.<sup>26</sup> The 2.0 mL sample obtained from the reaction solution was immediately quenched with 0.5 mL of 1.0 M HCl in diethyl ether. The volatiles were then removed and the residue dried under vacuum. This residue was then extracted with a total of 25.0 mL of DI water and passed through a filter to remove insoluble material. Samples of this standard solution were then tested quantitatively for  $NH_4^+$  by the indophenol method.<sup>27</sup>

**Hydrazine Analysis.** For  $N_2H_4$  reductions, samples were analyzed periodically for hydrazine to ensure N-atom balance. Samples (2.0 mL) were obtained and quenched as described above. The volatiles were then removed and the residue dried under vacuum. This residue was then extracted with 2 mL of DI water. The extracts were passed through a filter into a 50.0 mL volumetric flask containing 10.0 mL of a *p*-(dimethylamino)benzaldehyde (PDMAB) solution (0.80 g in 50.0 mL of 1.0 M HCl in ethanol) and the resulting solution diluted to the mark with 1.0 M HCl in ethanol. Samples of this solution were then tested quantitatively for  $N_2H_5^+$  by the PDMAB method.<sup>28</sup>

**Aniline Analysis.** In the  $PhHNNH_2$  reduction, the presence of aniline was qualitatively determined by GC-mass spectroscopy. A 2.0 mL aliquot from the reaction solution was quenched and worked up as

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described for  $\text{NH}_4^+$  analysis. This standard solution, containing  $\text{C}_6\text{H}_5\text{-NH}_3^+$ , was then made basic and the resulting solution was analyzed for aniline.

**Recovery and Identification of Cluster.** In the case of both  $\text{N}_2\text{H}_4$  and  $\text{PhHNNH}_2$  reduction, the integrity of the  $[\text{VFe}_3\text{S}_4]^{2+}$  cuboidal core prior to and following the catalytic reaction was examined quantitatively. A standard solution (A) of **I** in  $\text{CH}_3\text{CN}$  (6 mM) was freshly prepared. A 4.0 mL aliquot of A was diluted with 20.0 mL of DMF (B). A 1.0 mL aliquot of B was placed in an EPR tube and immediately frozen in  $\text{N}_2(\text{l})$ . The EPR spectrum obtained was that of the  $S = 3/2$  cuboidal core reported previously.<sup>29</sup> A 5.0 mL aliquot of A was then added to 200 mL of  $\text{CH}_3\text{CN}$  and a 10:1 hydrazine–I catalytic reduction reaction was set up as described previously. After 2 h of reaction time (>85% conversion to products), the solvent was removed under vacuum. The residue was then stirred in 100 mL of THF for 30 min in order to remove any unreacted  $\text{CoCp}_2$  ( $S = 1/2$ ). The filtrate was a pale red/brown, which by UV/Vis analysis was shown to correspond to approximately 15% of the  $\text{CoCp}_2$  originally added. The resulting residue was then dissolved in 30.0 mL of DMF and filtered through a fine porosity frit. The residue that remained on the frit was identified as a mixture of  $\text{NH}_4\text{Cl}$ ,  $\text{CoCp}_2\text{Cl}$ , and  $\text{Me}_4\text{NCl}$  from the mid-IR spectrum. A 1.0 mL aliquot of the filtrate was placed in an EPR tube and immediately frozen in  $\text{N}_2(\text{l})$ . The EPR spectrum obtained was qualitatively and, within the detection accuracy of the EPR spectrometer, quantitatively identical to that of the pure catalyst **I**.

Owing to the extremely small amount of cubane in the above reaction system, re-isolation of the cubane for chemical characterization was found impractical. Therefore reactions were performed using relatively large amounts of cubane in the presence of only a small excess of substrate. Described here is the detailed procedure of cluster identification in the phenylhydrazine–I system. A 2:1 phenylhydrazine–cubane reaction was performed with  $[\text{PhHNNH}_2] = 2.2$  mM in 50 mL of  $\text{CH}_3\text{-CN}$ , with all other reagents scaled accordingly. After approximately a 40% conversion of phenylhydrazine to ammonium and anilinium (0.8 turnover, as determined by  $\text{NH}_4^+$  quantification), the reaction solution was filtered through a fine porosity fritted funnel. A small amount of white/grey solid remained on the frit and was identified as  $\text{Me}_4\text{NCl}$ ,  $\text{NH}_4\text{Cl}$ , and some  $\text{CoCp}_2\text{Cl}$ . This solid does not show absorptions in the far-IR spectrum in the 450–300  $\text{cm}^{-1}$  region where cluster vibrations are usually found (a peak at 461  $\text{cm}^{-1}$  is identified as due to  $\text{CoCp}_2^+$  by comparison to the spectrum of pure  $\text{CoCp}_2^+$ ). The dark green/brown filtrate was taken to dryness under vacuum. The brown/black residue was then washed well with THF to remove any unreacted  $\text{CoCp}_2$  ( $S = 1/2$ ). The EPR spectrum obtained from a solution of the residue in DMF showed only the characteristic  $S = 3/2$  spectrum of the V-cubane catalyst. Additionally, the mid- and far-IR spectra of the residue (461, 403, 372, 354, 335, 298  $\text{cm}^{-1}$ ) were identical in all respects to the starting cluster, except for the 461  $\text{cm}^{-1}$  absorption due to  $\text{CoCp}_2^+$ . Due to the solubility of cluster **I** in alcohols, it was impossible to wash away  $\text{CoCp}_2\text{Cl}$  and  $\text{Me}_4\text{NCl}$  from the residue. Therefore, elemental analysis of the re-isolated catalyst was not obtained. Additionally, the above residue was used in a typical reduction reaction in which a “stoichiometric” amount of phenylhydrazine was used, with all other parameters identical to that described previously. While reduction of the substrate occurred to an appreciable extent (40% conversion in 2 h), the turnover was somewhat less than when analytically pure **I** was used. Owing to the presence of additional soluble salts in the residue (i.e.,  $\text{CoCp}_2\text{Cl}$ ) which affect the ionic strength of the medium, such a result may be expected.

## Results and Discussion

**Synthesis.** Given the ability of **I** to catalyze the reduction of  $\text{N}_2\text{H}_4$  to  $\text{NH}_3$  in the presence of an externally added proton source and reducing agent (*vide infra*), it was of interest to obtain two classes of similar compounds, all with the  $[\text{VFe}_3\text{S}_4]^{2+}$  core, in order to investigate the role of the heterometal (V) in substrate reduction. These two classes of catalysts would include clusters containing the following: (A) the  $[\text{VFe}_3\text{S}_4]^{2+}$  core with an identical ligand environment around the V atom but different

**Table 1.** Electrochemistry of the  $[\text{VFe}_3\text{S}_4]^{2+}$  Cores vs  $\text{Ag}/\text{AgCl}$  in  $\text{CH}_3\text{CN}$  Solution<sup>a</sup>

cluster	oxidation (V)	reduction (V)	ref
$(\text{DMF})_3\text{VFe}_3\text{S}_4\text{Cl}_3^-$ ( <b>I</b> )	+0.17 (qr) <sup>b</sup>	−1.20 (irr) <sup>c</sup>	<i>d</i>
$(\text{DMF})(\text{bpy})\text{VFe}_3\text{S}_4\text{Cl}_3^-$ ( <b>II</b> )	+0.30 (irr)	−1.22 (qr) <sup>e</sup>	<i>d</i>
$(\text{DMF})_3\text{VFe}_3\text{S}_4\text{Br}_3^-$ ( <b>III</b> )	+0.12 (qr)	−1.18 (irr)	<i>f</i>
$(\text{DMF})_3\text{VFe}_3\text{S}_4\text{I}_3^-$ ( <b>IV</b> )	+0.14 (qr)	−1.12 (irr)	<i>f</i>
$[\text{HB}(\text{pz})_3\text{VFe}_3\text{S}_4\text{Cl}_3^-]$ ( <b>V</b> )	0.00 (qr)	−0.68 (irr)	<i>f</i>
$(\text{DMF})_3\text{VFe}_3\text{S}_4\text{Cl}_3^- + \text{PEt}_3$ ( <b>VIII</b> )	+0.13 (qr)	−1.20 (irr)	<i>d</i>

<sup>a</sup> See Experimental Section for conditions. <sup>b</sup> qr = quasireversible process under the conditions employed.  $E_{p,c}$  or  $E_{p,a}$  is reported. <sup>c</sup> irr = irreversible process under the conditions employed.  $E_{p,c}$  or  $E_{p,a}$  is reported. <sup>d</sup> Reference 23a. Waves reported here are consistent with those reported vs SCE. <sup>e</sup> First of two reduction waves. <sup>f</sup> This work.

ligation on the Fe atoms, and (B) the  $[\text{VFe}_3\text{S}_4]^{2+}$  core with identical Fe ligation but different ligands on the V atom.

The first class of compounds was realized in the series  $(\text{Me}_4\text{N})[(\text{DMF})_3\text{VFe}_3\text{S}_4\text{X}_3] \cdot 2\text{DMF}$ ,  $\text{X} = \text{Cl}^-$  (**I**),  $\text{Br}^-$  (**III**), or  $\text{I}^-$  (**IV**). While the  $\text{X} = \text{RS}^-$  and  $\text{RO}^-$  are also known,<sup>23a</sup> these clusters could not be utilized in protic media due to the ready protonation of the ligands to RSH and ROH and eventual decomposition of the catalyst. The similarities in reduction potentials (Table 1) for these clusters indicate that the respective LUMO's lack significant contributions from ligand-based orbitals. The slight decrease in potentials for the clusters in the order  $\text{Cl}^- < \text{Br}^- < \text{I}^-$ , while counterintuitive at first, also has been observed in the series  $[\text{Fe}_4\text{S}_4\text{X}_4]^{2-}$ ,<sup>2</sup>  $[\text{Fe}_6\text{S}_6\text{X}_6]^{3-}$ ,<sup>30</sup> and  $[\text{Fe}_6\text{S}_6\text{X}_6(\text{M}(\text{CO})_3)_2]^{3-}$ ,<sup>30</sup>  $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$ , or  $\text{I}^-$  and  $\text{M} = \text{Mo}$  or  $\text{W}$ . With reduction potentials spanning an 8 mV range, these three clusters prove useful in that the only variable between them is the ligation at the Fe atoms.

The known clusters  $(\text{Me}_4\text{N})[(\text{DMF})_3\text{VFe}_3\text{S}_4\text{Cl}_3] \cdot 2\text{DMF}$  (**I**),  $(\text{Me}_4\text{N})[(\text{PEt}_3)(\text{DMF})_2\text{VFe}_3\text{S}_4\text{Cl}_3] \cdot 2\text{DMF}$ <sup>23a</sup> (**VIII**), and  $(\text{Me}_4\text{N})[(\text{DMF})(2,2'\text{-bpy})\text{VFe}_3\text{S}_4\text{Cl}_3] \cdot 3\text{DMF}$  (**II**), with three, two, and one labile solvent molecules at the V atom, respectively, represent three of the clusters in class B. A cluster with no labile sites at the V atom was sought and realized in  $(\text{Me}_4\text{N})_2[(\text{HBpz}_3)\text{VFe}_3\text{S}_4\text{Cl}_3]$  (**V**). This cluster could not be synthesized in DMF due to the oxophilicity of V. The substitution was readily accomplished in  $\text{CH}_3\text{CN}$ , however, and **V** was synthesized and structurally characterized. The synthesis of a cluster similar to **V** has been reported<sup>23c</sup> with  $\text{HB}(\text{pz})_3^-$  coordinated at the V atom and a tridentate “cavitant” ligand coordinated to the Fe sites. The latter cluster was identified exclusively by proton NMR spectroscopy. The reduction potentials of **I**, **II**, and **VIII** are similar (Table 1). The shift in the reduction potential for **V** by approximately +600 mV is indicative of the  $\pi$ -overlap between the V and bound pyrazole N, which results in charge delocalization from the cuboidal core into the ligand.

The crystal structure of  $(\text{Me}_4\text{N})_2[(\text{HBpz}_3)\text{VFe}_3\text{S}_4\text{Cl}_3] \cdot 2\text{CH}_3\text{-CN}$  (**V**) consists of discrete anions and cations. The  $[\text{VFe}_3\text{S}_4]^{2+}$  core of the anion (Figure 2) shows the cubane structure which has several precedents.<sup>23a,b</sup> The three coordination sites of the V atom external to the cubane are occupied by the pyrazolyl nitrogens of the  $\text{HB}(\text{pz})_3^-$  tridentate ligand. The cluster approaches idealized  $C_{3v}$  symmetry with a non-crystallographic  $C_3$  axis passing through the B, V, and S1 atoms. The mean V–Fe, Fe–Fe, V–S, Fe–S, and Fe–Cl interatomic distances of 2.756(12), 2.671(13), 2.302(18), 2.252(17), and 2.332(15) Å, respectively, are unexceptional and similar to those found in identical  $[\text{VFe}_3\text{S}_4]^{2+}$  cores.<sup>23a,b</sup> The mean V–N bond length, 2.196(44) Å, is similar to that reported in **II** (2.200 Å),<sup>23a,b</sup> but the large deviations in interatomic distances for **V**

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**Table 2.** Production of NH<sub>3</sub> by the Catalytic Reduction of N<sub>2</sub>H<sub>3</sub>R (R = H, C<sub>6</sub>H<sub>5</sub>) by the [VFe<sub>3</sub>S<sub>4</sub>]<sup>2+</sup> Core in the Presence of CoCp<sub>2</sub> and LutHCl in CH<sub>3</sub>CN

catalyst	substrate	mol of substrate/ mol of catalyst	NH <sub>3</sub> yield, <sup>a,b</sup> equiv <sup>c</sup>			NH <sub>3</sub> , max	% conversion <sup>d</sup>		
			0.5 h	1.0 h	2.0 h		0.5 h	1.0 h	2.0 h
(DMF) <sub>3</sub> VFe <sub>3</sub> S <sub>4</sub> Cl <sub>3</sub> <sup>-</sup> (I)	N <sub>2</sub> H <sub>4</sub>	1	0.9 (3)	1.0 (4)	1.1 (2)	2	45(4)	51(4)	54(4)
		10	15.2 (3)	17.8 (3)	20.0 (3)	20	76(2)	89(1)	100(1)
		10 <sup>e</sup>			2.0 (2)	20	trace	trace	10(4)
		20	23.2 (3)	28.8 (3)	35.6 (2)	40	58(5)	75(5)	89(2)
		40	36.8 (3)	48.0 (3)	64.8 (2)	80	46(4)	60(5)	81(5)
(DMF) <sub>2</sub> (PEt <sub>3</sub> )VFe <sub>3</sub> S <sub>4</sub> Cl <sub>3</sub> <sup>-</sup> (VIII)	N <sub>2</sub> H <sub>4</sub>	10	5.6 (2)	7.6 (2)	9.4 (2)	20	28(3)	38(2)	47(2)
(DMF) <sub>3</sub> VFe <sub>3</sub> S <sub>4</sub> Cl <sub>3</sub> <sup>-</sup> (I)	N <sub>2</sub> H <sub>3</sub> (C <sub>6</sub> H <sub>5</sub> )	1	0.5 (1)	0.5 (2)	0.6 (2)	1	51(-)	54(1)	63(1)
		10	1.1 (3)	1.5 (3)	2.4 (3)	10	11(1)	15(2)	24(3)
		10		2.2 (2)	3.4 (2)	20	trace	11(1)	17(2)
(DMF)(bpy)VFe <sub>3</sub> S <sub>4</sub> Cl <sub>3</sub> <sup>-</sup> (II)	N <sub>2</sub> H <sub>4</sub>	10							
[HB(pz) <sub>3</sub> ]VFe <sub>3</sub> S <sub>4</sub> Cl <sub>3</sub> <sup>-</sup> (V)	N <sub>2</sub> H <sub>4</sub>	10	0 (2)	0 (2)	0 (2)	20	NR <sup>f</sup>	NR	NR

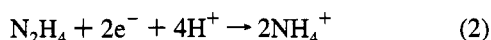
<sup>a</sup> The NH<sub>3</sub> was quantified by the indophenol method.<sup>27</sup> The N<sub>2</sub>H<sub>4</sub> was quantified with *p*-(dimethylamino)benzaldehyde.<sup>28</sup> <sup>b</sup> Hydrazine was quantified in random experiments. In all cases, there was a N atom balance of 100 ± 5%. <sup>c</sup> Number of equivalents reported is an average of *n* trials, where *n* is the number in parentheses. <sup>d</sup> Number in parentheses is the error in the percentage. <sup>e</sup> Reaction ran in DMF. After 24 h, the NH<sub>3</sub> yield was only about 15%, indicating little or no reaction in DMF. <sup>f</sup> Absorbance at 636 nm indistinguishable from baseline measurements.

preclude a detailed comparison. Selected metric data for the anion in **V** have been deposited with the supplementary material. The marginal quality of the structure does not allow for any detailed structural description other than the atomic connectivity shown in Figure 2.

The syntheses of (Me<sub>4</sub>N)[(PhHNNH<sub>2</sub>)(bpy)VFe<sub>3</sub>S<sub>4</sub>Cl<sub>3</sub>] (**VI**) and (Me<sub>4</sub>N)[(NH<sub>3</sub>)(bpy)VFe<sub>3</sub>S<sub>4</sub>Cl<sub>3</sub>] (**VII**) are readily accomplished by reactions of **II** with phenylhydrazine or ammonia in slight excess in CH<sub>3</sub>CN solution. The V site in the [VFe<sub>3</sub>S<sub>4</sub>]<sup>2+</sup> clusters was previously reported to be non-reactive in solvents such as DMF or DMSO.<sup>23</sup> We have observed that in less basic solvents such as CH<sub>3</sub>CN or MeNO<sub>2</sub>, Lewis bases such as phenylhydrazine and ammonia do not compete with the solvent for V coordination sites and readily coordinate to the V atom. The synthesis of **VI** demonstrates the ability of a substrate molecule to interact directly with the V site in the cubanes (*vide infra*). Given that **II** has only one labile site at the V atom, it was used as a starting material to facilitate characterization of the product.<sup>31</sup> Molecules such as VCl<sub>3</sub>(THF)<sub>2</sub>(H<sub>2</sub>NNMe<sub>2</sub>) and VCl<sub>2</sub>[tris(3-(dimethylphosphino)propylphosphine)(H<sub>2</sub>NNMe<sub>2</sub>)] represent examples for the binding of neutral hydrazine-like ligands to V(III) and V(II), respectively.<sup>32</sup>

#### Catalytic and Stoichiometric Reduction of Hydrazine.

Catalytic reductions of N<sub>2</sub>H<sub>4</sub> to NH<sub>3</sub> (eq 2) were carried out using various ratios of hydrazine to cubane (10:1, 20:1, and 40:1) in CH<sub>3</sub>CN solutions at ambient temperature and pressure. Cobaltocene, CoCp<sub>2</sub>, and 2,6-lutidine hydrochloride, LutHCl,



were used as the reducing agent and the proton source, respectively. The results from the catalytic and stoichiometric reductions of hydrazine are collected in Table 2. As was the case with the Mo single cubanes,<sup>20</sup> the [VFe<sub>3</sub>S<sub>4</sub>]<sup>2+</sup> core is an effective catalyst in the reduction of hydrazine, albeit to a lesser extent (*vide infra*).

A number of different reactions were carried out under identical conditions, in CH<sub>3</sub>CN solution, to determine possible NH<sub>3</sub> production in the absence of catalysts containing the

[VFe<sub>3</sub>S<sub>4</sub>]<sup>2+</sup> core. In these reactions the reagents were as follows: (i) N<sub>2</sub>H<sub>4</sub>, CoCp<sub>2</sub>, and LutHCl in the absence of **V** cubane; (ii) CoCp<sub>2</sub> and LutHCl in the absence of **V** cubane and substrate; or (iii) **V** cubane, CoCp<sub>2</sub>, and LutHCl. None of these reactions produced ammonia above the background level. Furthermore, in the absence of substrate, reaction system (iii) demonstrates that NH<sub>4</sub><sup>+</sup> is not produced from reduction of the CH<sub>3</sub>CN solvent in any appreciable amount (<5%) after a 2 h period. In other reactions, solutions that contained N<sub>2</sub>H<sub>4</sub>, CoCp<sub>2</sub>, and LutHCl with the appropriate concentration of either VFe<sub>2</sub>S<sub>4</sub>Cl<sub>3</sub><sup>3-</sup> or FeCl<sub>4</sub><sup>2-</sup> (possible decomposition products of the VFe<sub>3</sub>S<sub>4</sub> cluster) were independently shown to be ineffective in the reduction of N<sub>2</sub>H<sub>4</sub>. It is also important to note at this point that the disproportionation of N<sub>2</sub>H<sub>4</sub> in the absence of externally added protons and reducing agent was not catalyzed by clusters containing the [VFe<sub>3</sub>S<sub>4</sub>]<sup>2+</sup> core after 2 h (*vide infra*). The essentially quantitative production of NH<sub>3</sub> from N<sub>2</sub>H<sub>4</sub> in reaction times not exceeding 2 h (as seen using 10 equiv of N<sub>2</sub>H<sub>4</sub> per cluster, Table 2) appears to be a result of the catalytic activity of **I** in the presence of an externally added proton source and reducing agent.

In order to demonstrate that the cubane core retains its integrity during the reduction of hydrazine and phenylhydrazine, the EPR spectrum of a catalytically active solution was obtained after workup as described previously. The characteristic *S* = 3/2 spectrum of the solution was virtually identical to that of the pure catalyst. In addition, the mid-IR and far-IR spectra of the solid residue isolated from a catalytically active solution were characteristic of the pure cubane. The electronic spectrum obtained from DMF solutions of the residue, while displaying the characteristic absorptions of CoCp<sub>2</sub><sup>+</sup> ( $\nu_{\text{max}}$  = 403, 300, 260 nm), lacked the typical charge-transfer bands in the 400–600 nm range characteristic of species such as VS<sub>4</sub><sup>3-</sup> (544 nm) and VFe<sub>2</sub>S<sub>4</sub>Cl<sub>3</sub><sup>3-</sup> (520 nm),<sup>25</sup> which suggests no decomposition of the cubane to species containing the [V<sup>v</sup>S<sub>4</sub>] unit had taken place. Clusters such as **I**, **III**, and **IV** display featureless electronic spectra between 275 and 800 nm.

The identification of **I** as the species associated with the catalytic reduction process leads to the important question regarding the identity of the sub-site within **I** directly involved in catalysis. Support for the involvement of the V atom in the N<sub>2</sub>H<sub>4</sub> substrate binding and activation is offered by the isolation and characterization of **VI** as a possible intermediate with V-bound substrate.

Additional support for involvement of the V atom is obtained from a comparison in the relative rates of hydrazine reduction between cubanes which differ only in the coordination environment around the V atom (Class B). It is known<sup>23a</sup> that the reaction with **I** and between 1 and 30 equiv of triethylphosphine

(31) A reaction carried out between (Me<sub>4</sub>N)[VFe<sub>3</sub>S<sub>4</sub>Cl<sub>3</sub>(DMF)<sub>3</sub>] · 2DMF and 1 equiv N<sub>2</sub>H<sub>4</sub> in CH<sub>3</sub>CN yielded a brown/black solid with the following characteristics indicative of bound hydrazine: mid-IR— $\nu_{\text{as}}(\text{NH})$  = 3292 cm<sup>-1</sup>,  $\nu_{\text{s}}(\text{NH})$  = 3235 cm<sup>-1</sup>,  $\nu_{\text{twist}}(\text{NH}_2)$  ≈ 1150 cm<sup>-1</sup>,  $\nu(\text{NN})$  = 960 cm<sup>-1</sup>, typical of end-on bound hydrazine,<sup>32</sup>  $\nu_{\text{asym}}(\text{C}=\text{O}_{\text{DMF}})$  = 1650 cm<sup>-1</sup>; far-IR—major absorbances at 440, 415, 380, 342, 296 cm<sup>-1</sup>, consistent with cubane skeletal vibrations. Analysis: V = 5.40%, Fe = 17.3% (Fe:V = 3:1), indicative of cubane. However, CHN analyses were inconclusive, perhaps indicating a statistical distribution of N<sub>2</sub>H<sub>4</sub>-bound cubanes.

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**Table 3.** Production of NH<sub>3</sub> by the Catalytic Reduction of N<sub>2</sub>H<sub>4</sub> by the [(DMF)<sub>3</sub>VFe<sub>3</sub>S<sub>4</sub>X<sub>3</sub>]<sup>-</sup> (X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>) Core in the Presence of CoCp<sub>2</sub> and LutHCl in CH<sub>3</sub>CN<sup>a</sup>

catalyst	mol of N <sub>2</sub> H <sub>4</sub> / mol of catalyst	NH <sub>3</sub> Yield, equiv <sup>b</sup>			
		10 min	20 min	30 min	60 min
(DMF) <sub>3</sub> VFe <sub>3</sub> S <sub>4</sub> Cl <sub>3</sub> <sup>-</sup> (I)	10	11.4	13.6	15.2	17.8
(DMF) <sub>3</sub> VFe <sub>3</sub> S <sub>4</sub> Br <sub>3</sub> <sup>-</sup> (III)	10	14.2	15.4	16.0	18.0
(DMF) <sub>3</sub> VFe <sub>3</sub> S <sub>4</sub> I <sub>3</sub> <sup>-</sup> (IV)	10	14.4	15.8	16.8	18.2

<sup>a</sup> Reaction performed and NH<sub>3</sub> quantified as referenced in Table 2 and in the text. <sup>b</sup> Maximum NH<sub>3</sub> equivalents is 20. Quantitative conversion of N<sub>2</sub>H<sub>4</sub> to 2NH<sub>3</sub> was observed after 2 h.

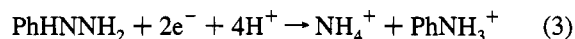
(PEt<sub>3</sub>) results in the formation of only the monosubstituted [(DMF)<sub>2</sub>(PEt<sub>3</sub>)VFe<sub>3</sub>S<sub>4</sub>Cl<sub>3</sub>]<sup>-</sup> cluster (VIII) in solution. Typical catalytic reactions were carried out using 10 equiv of hydrazine in the presence of VIII, with (on average) only 2 labile sites at the V atom. The latter was formed *in situ* by stirring I with a slight excess (1.1 equiv) of PEt<sub>3</sub> for 15 min before the addition of additional reagents. The approximate rate of reduction of N<sub>2</sub>H<sub>4</sub> by VIII, Table 2, was 2-fold slower than the rate with I. Additional experiments using [(DMF)(bpy)VFe<sub>3</sub>S<sub>4</sub>Cl<sub>3</sub>]<sup>-</sup> (II) as catalyst, with only 1 labile site at the V atom, show that the rate of hydrazine reduction also decreased significantly (Table 2). The (Me<sub>4</sub>N)<sub>2</sub>[(HBpz<sub>3</sub>)VFe<sub>3</sub>S<sub>4</sub>Cl<sub>3</sub>] cluster (V) was found to be ineffective in the reduction of N<sub>2</sub>H<sub>4</sub> after a 2 h period. Whether this lack of catalytic activity reflects the lack of labile sites on the V atom or the more positive reduction potential of V at present is difficult to ascertain.

A comparison of rates of N<sub>2</sub>H<sub>4</sub> reduction was made between reductions occurring in CH<sub>3</sub>CN and DMF solutions. After 2 h, the reduction of a 10-fold excess of N<sub>2</sub>H<sub>4</sub> in the presence of I is quantitative (Table 2) in CH<sub>3</sub>CN. In the identical reaction carried out in DMF, NH<sub>3</sub> production is negligible (only 10% conversion after 2 h). Evidently, DMF is a significantly better ligand than CH<sub>3</sub>CN for the V atom in I and competes effectively with hydrazine for the vanadium site, thus rendering the V site relatively unreactive, as reported.<sup>23c</sup> The profound effects of V-bound terminal ligands on the relative rates of hydrazine reduction, given similarities in Fe terminal ligation and reduction potentials for these clusters, strongly suggest the direct involvement of the V atom in the catalytic process. This result also supports observations made previously regarding the Mo cubanes.

In order to establish the role that the Fe atoms may play in these systems, if any, the ability of the [Fe<sub>4</sub>S<sub>4</sub>Cl<sub>4</sub>]<sup>2-</sup> cubane to catalyze the reduction of hydrazine was investigated. In a typical reaction in which hydrazine was present in a 10-fold excess, only a trace amount of NH<sub>3</sub> was present (<5%) after a 2 h period. However, given the significant differences between clusters such as I and [Fe<sub>4</sub>S<sub>4</sub>Cl<sub>4</sub>]<sup>2-</sup> (i.e., electron count, reduction potentials, number of Fe sites), compounds III and IV were synthesized. Including I, these clusters (Class A) are useful because they (i) possess identical terminal ligation at the V atom, (ii) have similar redox properties, (iii) have the same number of available Fe sites, and (iv) possess *different* terminal ligands at the Fe sites. Assuming that the lability of the halide substituents should differ on going from Cl<sup>-</sup> to I<sup>-</sup>, any significant involvement of the Fe atoms in the activation of hydrazine toward reduction should be observed. Typically, reactions involving a 10-fold excess of hydrazine to catalyst were set up as previously described and sampled frequently (10, 20, 30, and 60 min) in order to ascertain differences in the relative rates of hydrazine reduction. As shown in Table 3, the relative rate at which hydrazine is reduced by this series of clusters (I, III, IV) is essentially constant within the inherent errors in the sampling method and quantitative ammonium determination (~±5%). The slight tendency toward a faster

relative rate of hydrazine reduction on going to more substitutionally labile ligands may indicate some Fe involvement in substrate reduction. However, the results in Table 3 and the lack of catalytic activity for the (Me<sub>4</sub>N)<sub>2</sub>[(HBpz<sub>3</sub>)VFe<sub>3</sub>S<sub>4</sub>Cl<sub>3</sub>] cluster support the claim that hydrazine activation and reduction occurs primarily at the heterometal site.

**Stoichiometric and Catalytic Reduction of Phenylhydrazine.** The V cubane is also able to facilitate the reduction of phenylhydrazine (eq 3), albeit at a slower relative rate than that



displayed with hydrazine. This could be due in part to (i) phenylhydrazine being a weaker base than hydrazine and (ii) steric effects, which could result in a slower rate of substitution of phenylhydrazine for solvent molecules on the V atom of the cubane. The fact that PhHNNH<sub>2</sub> is reduced at all suggests that a second cubane is not necessary for the activation and reduction of hydrazine-like substrates. As pointed out previously for the Mo cubanes,<sup>20</sup> coordination of phenylhydrazine to the V atom (for steric reasons) should preclude the formation of either singly- or doubly-bridged double cubanes that contain a μ<sub>2</sub>-PhHNNH<sub>2</sub> ligand between V cubane subunits. The question of whether or not hydrazine is bimetallically activated in a two-cluster arrangement cannot be answered directly due to the unavailability of such vanadium single or double cubanes. However, a bimetallic activation of hydrazine would be at variance with the lack of catalytic function observed with singly- or doubly-bridged Mo cubanes.<sup>20</sup> For the latter, it was concluded that the lack of free lone pairs on the bridging hydrazine (that precluded protonation prior to reduction) was the cause of the lack of reactivity.

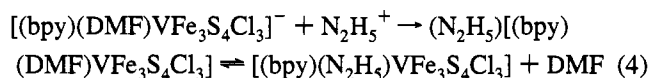
**Reaction Pathway.** The system employed in this report does not readily lend itself to kinetic investigation mainly due to the precipitation of NH<sub>4</sub><sup>+</sup> salts as the reaction proceeds. However, a reasonable reaction pathway can be proposed on the basis of experimental results. The reduction potentials of all of the V cubanes in this discussion (with the exception of V) are on the order of -1.2 V vs Ag/AgCl. Cobaltocene, with a reversible wave corresponding to the Co(II)/Co(III) couple at -0.93 V vs Ag/AgCl, is not a sufficiently strong reducing agent to accomplish reduction of the V cubanes (except of V). In the presence of an excess of N<sub>2</sub>H<sub>4</sub> (2 equiv), the reduction wave of the cubane (I) is virtually unchanged. However, in the presence of excess N<sub>2</sub>H<sub>5</sub><sup>+</sup> (2 equiv, added as the BF<sub>4</sub><sup>-</sup> salt), the reduction wave shifts some +300 mV and broadens significantly, occurring at -0.89 V vs Ag/AgCl. This result indicates that in the presence of protonated substrate, the V cubane cores (as in I) can be reduced by CoCp<sub>2</sub>. In view of this, it is nearly certain that binding and protonation of the substrate occurs prior to the reduction of the cubane. This result further supports the experimental evidence that, in the presence of an acid that is not able to protonate hydrazine (Et<sub>3</sub>N·HCl, pK<sub>a</sub> = 18.3 in CH<sub>3</sub>CN), the reduction of hydrazine (for N<sub>2</sub>H<sub>5</sub><sup>+</sup>, pK<sub>a</sub> = 16.6 in CH<sub>3</sub>CN) to NH<sub>3</sub> (for NH<sub>4</sub><sup>+</sup>, pK<sub>a</sub> = 16.5 in CH<sub>3</sub>CN) does not occur after a 3 h period, as indicated by ammonia analysis. The pK<sub>a</sub> of 2,6-LutHCl in CH<sub>3</sub>CN is approximately 14.1.<sup>33</sup>

It seems likely that the reaction pathway for the reduction of hydrazine-like substrates by the [VFe<sub>3</sub>S<sub>4</sub>]<sup>2+</sup> core is comprised of relatively simple steps, as shown in Scheme 1. This reaction pathway was previously proposed for the [MoFe<sub>3</sub>S<sub>4</sub>]<sup>3+</sup>/hydrazine system and is similar to that discussed for the reduction of

(33) All pK<sub>a</sub> values for acids in acetonitrile are taken from: Izutsu, K. *Acid-Base Dissociation Constants in Dipolar Aprotic Solvents*; Blackwell Scientific Publications: Oxford, IUPAC Chemical Data Ser. No. 35, 1990; pp 17-29.

hydrazine by the FeMo cofactor of nitrogenase.<sup>34</sup> Species A is simply the substrate-coordinated cubane. The phenylhydrazine analog **VI** has been characterized (see the Experimental Section).

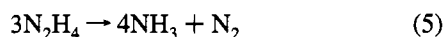
Species B, a hydrazinium-bound adduct of the  $[\text{VFe}_3\text{S}_4]^{2+}$  core, assumes the protonation of the bound substrate prior to reduction. A reaction between **II** and a slight excess of  $(\text{N}_2\text{H}_5^+)(\text{BF}_4^-)$  in  $\text{CH}_3\text{CN}$  yielded a purple solid which, after thorough washing with  $\text{MeOH}$ , showed an IR spectrum that lacked absorptions due to the  $\text{Me}_4\text{N}^+$  cation, showed a significant decrease in the bound-DMF stretch at  $1650\text{ cm}^{-1}$ , and showed N–H stretches at  $3291$  and  $3242\text{ cm}^{-1}$ . In addition, the isolated solid showed a marked decrease in solubility in  $\text{MeNO}_2$  or  $\text{CH}_3\text{CN}$ . These results suggest either of two or a possible mixture of products, as shown in eq 4, in which the relatively poor ligand  $\text{N}_2\text{H}_5^+$  may act as either a cation for the anionic cluster or as ligand for the V atom in equilibrium with DMF.



The external addition of an electron to the cluster followed by a rapid 2-electron intracubane reduction of the substrate would result in a formally oxidized cuboidal core with an amide bound to the V atom and the liberation of one molecule of  $\text{NH}_3$ . A synthetic attempt to obtain the proposed C intermediate (Scheme 1) was unsuccessful (see the Experimental Section). In protic media, the protonation of the amide group in C to ammonia, followed by reduction of the core, would lead to the characterized ammonia-bound cluster **VII**. The catalytic cycle would then continue on the replacement of ammonia for a solvent molecule or hydrazine.

**Comparison between Systems Employing  $[\text{VFe}_3\text{S}_4]^{2+}$  or  $[\text{MoFe}_3\text{S}_4]^{3+}$  as Catalysts.** Based on the results presented thus far, a direct comparison between the rates of reduction of hydrazine by the  $[\text{VFe}_3\text{S}_4]^{2+}$  and  $[\text{MoFe}_3\text{S}_4]^{3+}$  cores cannot be made due to the differences in terminal ligation at the heterometal site and in the redox properties (reduction potential for the reduction of the  $[\text{MoFe}_3\text{S}_4]^{3+}$  cubanes  $\sim -0.90\text{ V}$  vs  $\text{Ag}/\text{AgCl}$ ). A comparison of the data (Table 2 and ref 20) suggests that reduction with the vanadium cubane may occur at a slower relative rate and is based mainly on the observation that the tris-DMF vanadium cubane, **I**, with three labile sites, reduces  $\text{N}_2\text{H}_4$  at a rate essentially the same as the molybdenum cubane with only one labile site. Additionally, a vanadium cubane with only one labile site (i.e., **II**) has a significantly slower relative turnover of substrate to product than  $[\text{MoFe}_3\text{S}_4\text{Cl}_3(\text{Cl}_4\text{-cat})(\text{CH}_3\text{-CN})]^{2-}$ .

A significant difference between the V and Mo cubanes is in the ability to facilitate the disproportionation of hydrazine (eq 5) in the absence of externally added  $\text{H}^+$  and  $\text{e}^-$ . Unlike



the  $[\text{MoFe}_3\text{S}_4]^{3+}$  cluster<sup>20</sup> that catalyzes eq 5, no disproportionation was observed after 2 h for a 10:1 hydrazine–**I** reaction mixture in either  $\text{CH}_3\text{CN}$  or DMF solution. This may be a result of the more negative reduction potentials of the V cubanes ( $-1.2\text{ V}$  vs  $-0.9\text{ V}$  for the Mo cubanes) that preclude reduction by hydrazine that, in the disproportionation reaction, must occur in the absence of cobaltocene as a reducing agent.

Preliminary results indicate that neither  $[\text{VFe}_3\text{S}_4]^{2+}$  nor  $[\text{MoFe}_3\text{S}_4]^{3+}$  catalyze the reduction of  $\text{H}^+$  to  $\text{H}_2(\text{g})$  in the

presence of hydrazine,  $\text{CoCp}_2$ , and  $\text{LutHCl}$ .<sup>35</sup> In the absence of substrate, the Mo core (with terminal chloride on the Fe atoms) with a variety of Mo-bound terminal ligands (i.e., tetrachlorocatecholate, citrate, bis(dimethylphosphino)ethane<sup>36</sup>) facilitates the reduction of protons. This result was previously reported for the  $\text{Mo}_2\text{Fe}_6\text{S}_8(\text{SPh})_9^{4-5-}$  clusters, where two cuboidal cores are bridged by three thiolates, effectively blocking the heterometal.<sup>37</sup>

## Summary and Conclusions

In summary, the following points reflect the significant results of this work: (i) the  $[\text{VFe}_3\text{S}_4]^{2+}$  core, like the  $[\text{MoFe}_3\text{S}_4]^{3+}$  core, is an effective catalyst in the reduction of hydrazine to ammonia; (ii)  $[\text{VFe}_3\text{S}_4]^{2+}$  clusters with identical terminal ligands on the Fe atoms and similar reduction potentials showed a decrease in the relative rate of hydrazine reduction with a decrease in the number of labile sites at the V atom; (iii)  $[\text{VFe}_3\text{S}_4]^{2+}$  clusters with identical terminal ligands on the V atom and similar reduction potentials but different terminal ligands on the Fe atoms showed little change in the relative rates of hydrazine reduction; (iv) results ii and iii above taken together strongly suggest the direct involvement of the V atom in substrate activation and reduction by nitrogenase model compounds. This point is further supported by the synthesis of  $(\text{Me}_4\text{N})-[(\text{PhHNNH}_2)(\text{bpy})\text{VFe}_3\text{S}_4\text{Cl}_3]$ , which has a substrate molecule directly bound to the V atom. To the extent that the synthetic cubane clusters (Mo and V) partially model the coordination environment of the heterometal in the respective nitrogenase cofactors, this study suggests the possibility of active participation of the heterometal in the reduction of hydrazine-like substrates by the nitrogenase enzyme.

In the alternative V nitrogenase,<sup>8</sup> reduction of  $\text{N}_2$  to ammonia also occurs but is not as effective as that observed with the Mo nitrogenase. Furthermore, it has been found that hydrazine is a product of  $\text{N}_2$  reduction by the isolated vanadium nitrogenase.<sup>38</sup> These observations underscore the significance of studies that involve reduction of an N–N bond using partial cofactor model compounds containing either Mo or V. The results reported herein further support the suggestion made previously<sup>20</sup> that the catalytic function of the nitrogenases may rely on the direct involvement of the heterometal, at least in the latter stages of the reduction process.

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**Supplementary Material Available:** Tables listing crystal data, data collection parameters, positional parameters, selected distances and angles for **V** (10 pages); observed and calculated structure factors (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(35) Work in progress.

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