Nitrogenase Substrates as Intercluster Bridging Units between the Mo Atoms in Doubly Bridged, Double Cubanes. The Synthesis and Characterization of the \([\text{MFe}_2\text{S}_4\text{Cl}_2(\text{Clcat})_2(\mu_2-S)(\mu_2-L)]^-\) Anions (L = \(\text{N}_2\text{H}_4, n = 4; \text{L} = \text{CN}^-, n = 5\))

P. R. Challen, Sang-Man Koo, C. G. Kim, W. R. Dunham, and D.Coucouvanis.*

Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109-1055

Received July 16, 1990

The enzymatic reduction of dinitrogen to ammonia is catalyzed by the nitrogenase enzymes and is intimately associated with a multimetallic Fe/Mo/S site of unknown structure. This site is characterized by an approximate Fe:Mo:S composition of 7 ± 1, 1, 1 ± 2, and as indicated by Mo and Fe EXAFS analyses it may contain Fe–(μ2-S)–Fe and Mo–(μ2-S)–Fe rhombic structural subunits. In spite of extensive studies in recent years, the synthesis of an acceptable structural analogue for the nitrogenase Fe/Mo/S site still remains an important unfulfilled goal. The recent discoveries of new nitrogenase systems that contain vanadium and perhaps iron in place of molybdenum prompted us to search for a synthetic analogue with a common Fe/S structural framework capable of accommodating different metals and their activation in bimetallic substrate complexes. Thence, the nitrogenase enzymes couple single cubanes with the bimetallic activation of nitrogenase substrates. A composite cluster that contains the known Fe₂S₄ and Fe₂S₃ subunits (M = Mo, V) coupled in a Fe–(μ2-S)–Fe, singly bridged double cube conformation would be in compliance with these proposed requirements. Preliminary results of our attempts to obtain such clusters were reported in recent communications where the synthesis and structural characterization of singly bridged and doubly bridged double cubanes have been described. These clusters have cores that consist of two Fe₂S₄ cubane units coupled by either one Fe–(μ2-S)–Fe bridge (M = Fe) or doubly coupled by the Fe–(μ2-S)–Fe and Mo–(μ2-L)–Mo (L = S²⁻, OH⁻) bridges. In this communication we report on the synthesis and characterization of two new doubly bridged double cubanes that contain Mo–(μ2-L)–Mo bridges with the biologically relevant N₂H₄ ligand and with CN⁻. The synthesis (from [Et₄N⁺][MoFe₂S₄(Cl)₂(μ₂-S)(μ₂-CN)]⁻ and the structural characterization of [Et₄N⁺][MoFe₂S₄(μ₂-S)(μ₂-CN)]⁻ ) have been described previously. The reaction of 1 with \(\text{N}_2\text{H}_4\) in \(\text{CH}_3\text{CN}\) in a 1:1 molar ratio affords in excellent yield the \([\text{MoFe}_2\text{S}_4\text{Cl}_2(\text{Clcat})(\mu_2-S)(\mu_2-N_2H_4)]^-\) salt, II, where the \(\text{N}_2\text{H}_4\) bridge has been introduced following protonation of the μ₂-OH ligand in I. The reactivity of the μ₂-OH ligand in I is manifested in its reactions with \((\text{RSi})\text{X}\) (X = CN⁻, N₃⁻). These stoichiometric reactions that are thermodynamically driven by the formation of the (RSi)OH byproduct result in the introduction of X in place of OH⁻ and occur readily in CH₃CN solution at ambient temperature. The black, microcrystalline \([\text{Et₄N⁺}[\text{MoFe}_2\text{S}_4(\text{Clcat})(\mu_2-S)(\mu_2-CN)]^-\]) also can be obtained in CH₃CN solution by the stoichiometric reaction of [Et₄N⁺][MoFe₂S₄(μ₂-S)(μ₂-CN)]⁻ with Et₄NCl followed by addition of Na₂S₂.

In the infrared spectrum of II, weak vibrations at 3232 and 3287 cm⁻¹ are indicative of \(\text{N}_2\text{H}_4\). The presence of \(\text{N}_2\text{H}_4\) (97.6% of the expected amount) was further substantiated by spectrophotometric quantitative analysis with \(p\)-(dimethylamino)benzaldehyde as a reagent. This procedure has been employed previously for the detection of \(\text{N}_2\text{H}_4\) as a bound intermediate during nitrogenase turnover. The C=N vibration in III at 2322 cm⁻¹ is higher in energy than that in [MoFe₂S₄(μ₂-S)(μ₂-CN)]⁻ (2121 cm⁻¹). This hypsochromic shift is typical of end-to-end bridging cyanide.

The electronic spectra of II and III are nearly featureless and show a steadily increasing absorption from 750 nm to the UV region of the spectrum. The cyclic voltammogram of II and III (in CH₃CN solution vs Ag/AgCl) shows a quasireversible reduction (\(E_{1/2} = 1.06 \text{ V, II}; E_{1/2} = -1.20 \text{ V, III}\)) and two quasireversible oxidation waves (\(E_{1/2} = +0.10, +0.32 \text{ V, II}; E_{1/2} = -0.03, +0.23 \text{ V, III}\)). By comparison, the [MoFe₂S₄(μ₂-S)(μ₂-CN)]⁻ single cube under the same conditions shows a quasireversible reduction at -0.8 V and an irreversible oxidation at +0.4 V. The 37Fe Mossbauer spectra of the EPR silent (21 K) II and III can be fitted satisfactorily by three quadrupole doublets in a 1:1:1 intensity ratio. Two of these doublets have similar isomer shift, IS, and quadrupole splitting, \(\Delta q\), values (for II IS = 0.53, 0.51 mm/s and \(\Delta q = 1.17, 0.98 \text{ mm/s for III IS = 0.51, 0.49 mm/s and } \Delta q = 1.23, 0.98 \text{ mm/s}\)). The third doublet has a considerably smaller IS value (for II IS = 0.33 and \(\Delta q = 1.03 \text{ mm/s for III IS = 0.30 and } \Delta q = 0.96 \text{ mm/s}\)) for the Fe(w)-Fe(w) doublet, consistent with Fe–(μ2-S)–Fe sites where the Fe atoms contain no chloride in their coordination sphere. These data suggest that the two Fe atoms bound to the μ₂-S bridging ligands may be at a higher formal oxidation level (~3) than the remaining four Fe atoms (~2.7). The apparent insensitivity of the Mossbauer spectra to the nature of the bridging ligands in II and III suggests that any ligand-induced changes in the electronic structures of these dimers probably reside on the Mo atoms.

The structure of the anion in II has been determined from

In connection with earlier observations that the variable hapticity of halides plays a "lightly stabilizing" role for coordination sites in some anion-promoted systems based on the complexes [PPN][Ru(μ-Br)(X)(CO)]2 (X = Cl, Br, I; n = 1, 10, 9), we report that amido, mercapto, and alkoxo groups modified by a pyridyl substituent give related activated species [PPN][Ru(μ-(C5H4N))(CO)]2 (PPN)[La-c], n = 10; [PPN][Lb-c], n = 9; PPN* = (C5H5)2PNN(C5H5)2; a: X = N(C5H4); b: X = S; c: X = O) that are involved in the equilibrium shown in eq 1.5,7

Furthermore, the corresponding hydroxy amido complex Ru3(μ-H)[μ-2,3-N(CH3)2CH2CH2NCO]2 (3a) is seen to activate alkynes selectively via the alkynyl complex 5a and to promote an alkyny-ethylene codimerization under mild conditions (Scheme I).

Acknowledgment. This research was supported by a grant from the National Institutes of Health (GM-33080).

Figure 1. Preliminary structure18 of the anion core in [Et4NI4]+(MoFeS6C2(C2)(C2)-C2N(CH3)2CN). The structure has been drawn from crystallographically determined coordinates with use of the program Molecular Editor, and the catecholate phenyl rings have been omitted for clarity.

data obtained from the best obtainable, albeit poor quality, crystals. The core structure in II (Figure 1) has been drawn on the basis of crystallographically determined coordinates and is presented with the intention of showing atomic connectivity. The anion has approximate C2 symmetry and is located on a crystallographic mirror plane that contains the μ2-S and the side-on, bridging N2H2 ligand and bisects the Mo–Mo and Fe–Fe interatomic vectors. Most of the interatomic bond distances and angles in II and III are reasonable. Unfortunately the unacceptably high standard deviations of these values preclude a comparison of II or III to the structures of analogues. A meaningful comparison can be made between the Mo–Mo distance in II (5.22 Å) and that in I (4.248 Å) and demonstrates the remarkable flexibility of the basic structure in accepting bridging ligands with differing steric demands.

The syntheses of II and III demonstrate the feasibility of introducing nitrogenase substrates in an "end-to-end" bridging mode within two μ2-S-bridged cubane subunits and establish a methodology for the rational synthesis of analogous mixed-cubane clusters. Whereas II and III possess Mo–L–Mo bridges (L = CN–, N2H4) and a stoichiometry of no direct consequence to the nitrogenase active site problem, mixed clusters analogous to II and III that contain MoFeS3 and FeMoS3 as subunits could be biologically relevant. The latter will provide the first examples of molecules with Mo–L–Fe bridges, will have a biologically relevant Fe:Mo:S ratio, and will be potentially capable in the heterobi-metallic coordination of nitrogenase substrates. A Mo–μ2-S–Fe unit has been suggested previously19 as a possible site for the activation and reduction of N2 in nitrogenase.

An intriguing question arises as to whether, under strongly reducing conditions, clusters similar to I, II, and III or derivatives (perhaps with homocitrato20 in place of the catechol ligands) can be obtained with N2 as an intercube bridging ligand. Toward this goal the reactivity of I, II, and III, and of analogous "mixed" clusters21 that contain FeS2 and MoFeS3 subunits, currently is under investigation.


(5) (a) Our interest in these ligands is related to our earlier work on phosphido-pyridyl groups. (b) Lugan, N.; Lavigne, G.; Bonnet, J.-J.; Réau, R.; Neibecker, D.; D. in "Metallic Coordination of Nitrogenase Substrates: A New Strategy for the Catalytic Reduction of N2."; Walter, W., Ed.; Springer-Verlag, 1993; pp 221–243.

(6) Experimental details for the preparation and characterization of the compounds are provided in the supplementary material.

(7) (a) [PPN][La-a]: IR (v(CO), cm−1, THF) 2066 (m), 2015 (w), 2007 (vs), 1985 (vs), 1951 (m), 1935 (m), 1925 (sh), 1855 (vw), 1811–1800 (s, br). (b) [PPN][La-b]: IR (cm−1, THF) 2021 (s), 2012 (s), 1975 (sh), 1934 (vs), 1912 (m), 1842 (vw), 1793 (vs).


(18) Black crystals of 1,2-CN (MW 3042) are orthorhombic with space group Pmnn and a = 15.502(6), b = 19.661(4), c = 27.024(6) Å, and Z = 4; α = 1.64 g/cm3; β = 1.63 g/cm3; MW = 2020 ± 20. Single-crystal X-ray diffractometer data were collected for II and the structure was solved by a combination of heavy-atom Patterson techniques, direct methods, and Fourier techniques. All atoms in the anion were located, however, due to the poor quality of the crystal and limited data (II: Mo Ka, 2θ = 35.9°; 1317 data with F > 2σ(F)). A Rietveld-type model for the disordered Et4N+ cations in the structure has not yet been found. At present with a complete anion refined but only parts of the Et4N+ cations included in structure factor calculations R = 0.16. All attempts to obtain better crystalline derivatives of II have failed. With the expectation that it will be possible to obtain high-quality data from better crystals, perhaps with different counterions, deposition of crystallographic data is not warranted at this time.


(20) The presence of the Fe atom at this site has been recently detected. Hoover, T. R.; Imperial, J.; Ludden, P. W.; Shah, V. K. Biochemistry 1989, 28, 2768.