Volume 32

Number 9

April 28, 1993

Inorganic Chemistry

Communications

Oxidative Decoupling of the $MoFe_3S_4$ Clusters and Possible Relevance to the Oxidative Degradation of the Nitrogenase Cofactor. Isolation and Structural Characterization of the $[(Cl_4cat)Mo(O)(\mu\text{-}S)_2FeCl_2]^{2-}$ Anion

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Received October 30, 1992

Certain structural features of the Fe/Mo/S clusters in nitrogenase[1] or of the isolated nitrogenase cofactor[2] were recognized from data available through EXAFS analyses,[3] Mossbauer and EPR spectroscopy,[4] ENDOR spectroscopy,[5] and other techniques.

The available spectroscopic and analytical[6] data have served as a guide for the design and attempted syntheses of numerous speculative models of the nitrogenase cofactor. The intense interest in this area notwithstanding, the realization of a well-characterized, stoichiometrically and/or chemically acceptable model complex still remains an unfulfilled goal. Two recent structure determinations of the MoFe protein of nitrogenase from two different sources[7,8] have revealed the structure of the FeMoS center as a cluster with a $MoFe_7S_{8,9}$ core. The core consists of two cuboidal subunits, $MoFe_3S_3$ and Fe_4S_3, bridged by two[7] or three[8] μ_2-S^{2-} ligands. These recent developments clearly define a target for nitrogenase synthetic analog studies and mark the transition of active site modeling from speculative to corroborative.

Some information regarding the reactivity of the nitrogenase cofactor has been obtained from an examination of the products that form in the oxidative degradation of the cofactor. This information could be useful in a retrosynthetic analysis of the problem and may suggest rational approaches toward the synthesis of acceptable analog complexes.

The first report on the degradation of the Fe/Mo/S center in nitrogenase revealed[9] that thiomolybdates such as MoS_4^{2-} and $MoOS_3^{2-}$ were released following an acid–base treatment of the Fe/Mo protein component of nitrogenase. At a later date, a controlled oxidation of the nitrogenase cofactor in NMF solution and a spectrophotometric investigation[10] indicated that the initial degradation byproducts may have contained binuclear Fe–$[MoOS_3]^{2-}$ complexes. These observations suggest that the extreme sensitivity of the cofactor to oxidation and decomposition may well be due to the irreversible conversion of Mo^{III} or Mo^{IV} ions to thermodynamically stable but nonfunctional $Mo^{VI}{=}O$ groups.

Recently we reported on the syntheses and structural characterization of singly-bridged[11a] and doubly-bridged[11b,c] double-cubanes that contain two Fe_4S_4 or two $MoFe_3S_4$ subunits respectively. We proposed these molecules as conceptually relevant for the design and synthesis of speculative models for the active site of nitrogenase.[12] In this communication, we report on the oxidative degradation of the $MoFe_3S_4$ structural units in the $[[MoFe_3S_4Cl_2(Cl_4cat)]_2(\mu_2\text{-}S)(\mu_2\text{-}L)]^{n-}$ doubly-bridged double-cubane ($L = NH_2OH$; $n = 4$) DBDC-I and the formation of the hetero-dinuclear thiomolybdate complexes $[(Cl_4cat)Mo(O)(\mu\text{-}S)_2FeCl_2]^{2-}$ and $[(S)Mo(O)(\mu\text{-}S)_2FeCl_2]^{2-}$.

Previously we reported[11c] on the synthesis of DBDC-II ($L = N_2H_4$; $n = 4$) by the acid-base reaction of DBDC-III ($L = OH^-$; $n = 5$) with $N_2H_4{\cdot}HCl$. A very similar reaction of DBDC-III with $NH_2OH{\cdot}HCl$ under strictly anaerobic, anhydrous conditions affords the short-lived DBDC-I cluster ($L = NH_2OH$; $n = 4$). On the basis of analytical, and infrared spectroscopic data a

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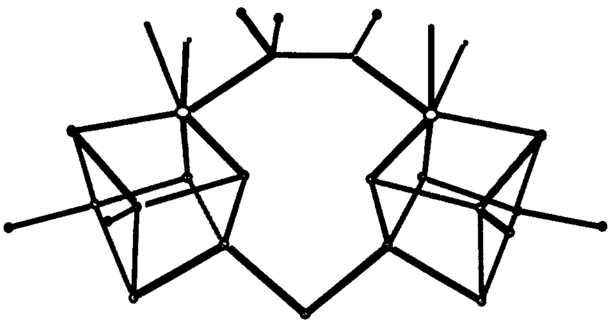

Figure 1. Proposed structure of DBDC-I.

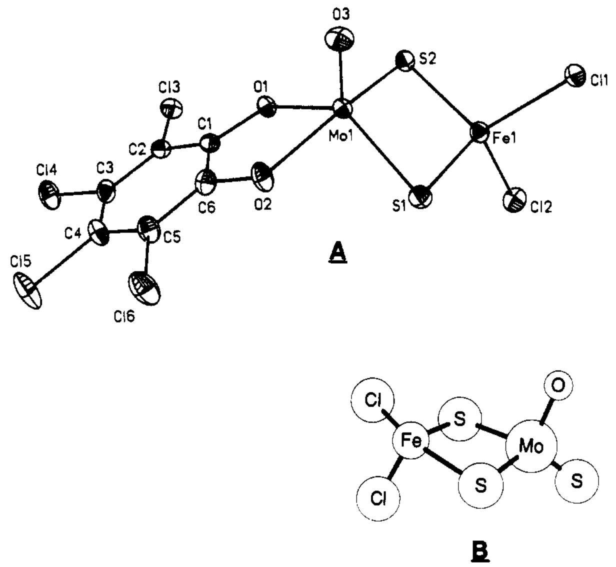

Figure 2. (A) Structures and labeling of the anion in $(Et_4N)_2[(Cl_4cat)Mo(O)(\mu\text{-}S)_2FeCl_2]\cdot{}^1/_2(C_2H_5)_2O$ (IV). Thermal ellipsoids as drawn by ORTEP represent the 40% probability surfaces. Selected distances and angles: Fe—Mo, 2.7642(5) Å; Mo—S(1), 2.292(1) Å; Mo—S(2), 2.311(1) Å; Mo═O, 1.676(3) Å; Mo—O_{cat}, 2.044(2), 2.072(2) Å; Fe—S(1), 2.225(1) Å, Fe—S(2), 2.224(1) Å; Fe—Cl(1), 2.250(1) Å; Fe—Cl(2), 2.237(1) Å; C—O, 1.33 Å; Mo–S(1)–Fe, 75.45(3)°; Mo–S(2)–Fe, 75.08(3)°; S(1)–Mo–S(2), 120.6(3)°; S(1)–Fe–S(2), 106.76(4)°; O(1)–Mo–O(2), 76.09(9)°; O(1)–Mo–O(3), 114.9(1)°; O(2)–Mo–S(2), 155.02(8)°; O(1)–Mo–S(1), 134.78(7)°; O(3)–Mo–S(1), 107.8(1)°; O(3)–Mo–S(2), 102.37(9)°; O(2)–Mo–S(1), 83.29(8)°; O(1)–Mo–S(2), 83.47(6)°. (B) Atomic connectivity in the $[(S)Mo(O)(\mu\text{-}S)_2FeCl_2]^{2-}$ anion in the $(Et_4N)_4\{[(S)Mo(O)(\mu\text{-}S)_2FeCl_2]\cdot[FeCl_4]\}$ (V) "double-salt".[21]

structure similar to that of the N_2H_4 analog[11c] (Figure 1) is proposed for this compound. Upon standing at ambient temperature, in an oxygen and moisture free atmosphere, CH_3CN/diethyl ether solutions of $(Et_4N)_4$ (DBDC-I) decompose and deposit crystals[13] of $(Et_4N)_2[(Cl_4cat)Mo(O)(\mu\text{-}S)_2FeCl_2]$ (IV) and $(Et_4N)_4\{[(S)Mo(O)(\mu\text{-}S)_2FeCl_2]\cdot[FeCl_4]\}$ (V) (Figure 2). Approximately equal amounts of IV and V are obtained and the two types of crystals can be separated manually. The reaction yields of IV and V combined account for approximately half of the molybdenum present in DBDC-I. The perchlorocatecholate ligand is accounted for nearly quantitatively in IV and the $[Fe(Cl_4cat)_3]^{3-}$ complex that also is a product of the degradation. As is the case with the molybdenum, roughly half of the iron atoms are accounted for in the tractable reaction products (i.e. IV, V, $(FeCl_4)^{2-}$, and $[Fe(Cl_4cat)_3]^{3-}$. The unaccounted for Mo, Fe, and Cl very likely are present in the intractable residue that also forms in an appreciable amount. We have been unable to establish the identity of this material or to detect unequivocally the NH_3 (or NH_4^+) byproducts that are expected to form following the reductive cleavage of the NH_2OH molecule.[14] The source of oxygen in IV and V does not appear to be H_2O, but rather the bridging hydroxylamine molecule that apparently has undergone a N–O bond cleavage reaction as the oxygen atom is transferred oxidatively to one of the Mo atoms in DBDC-I. This conclusion is supported by the following observations: (a) The formation of the Mo═O-containing dimers (IV and V combined) *under anaerobic conditions* is quantitative with respect to the amount of NH_2OH present in DBDC-I. (b) The same degradation products are obtained with either DBDC-III (L = OH^-; $n = 5$) or DBDC-II (L = N_2H_4; $n = 4$). While the reaction of $NH_2OH{\cdot}HCl$ with DBDC-III produces H_2O that may be a source of oxygen, the reaction of $NH_2OH{\cdot}HCl$ with DBDC-II forms $NH_2NH_2{\cdot}HCl$ and does not produce H_2O as a possible source of oxygen. Some support for the possible role of bimetallic activation prior to the cleavage of the N–O bond is provided by the reaction of the *uncoupled* $[Fe_3S_4Cl_3(Cl_4cat)Mo(OH)]^{3-}$ cubane with $NH_2OH{\cdot}HCl$. This reaction affords mainly a noncrystalline product with a NO stretch in the infrared at 1740 cm^{-1}. The Mo:Fe:S ratio of this compound as obtained by X-ray fluorescence microprobe analysis is approximately 1:3:4 and suggests that the molecule probably is a NO-substituted Fe_3MoS_4 cubane. No evidence for the NO (or NO^+) chromophore can be found in the products of the reactions of either DBDC-III or DBDC-II with $NH_2OH{\cdot}HCl$.

The structure of IV has been determined.[15] The predominant structural feature in the complex dianion (Figure 2A) is the Fe-$(\mu\text{-}S)_2$Mo rhombic unit. This unit is similar to those found in a plethora of Fe-MoS_4 complexes[16] and is characterized by a Fe–Mo distance of 2.7642(5) Å and a Fe–S–Mo angle of 75.26°. The molybdenum atom is pentacoordinate with a distorted trigonal bipyramidal structure. The equatorial trigonal plane is defined by S(1), O(1), and O(3), and the S(2) and O(2) ligands lie in the "axial" position. The S(2)–Mo–O(2) angle is 155.02(8)°, and the equatorial L–Mo–L angles range from 107.8(1) to 134.78(7)° and add up to 357.5°. The $(\mu\text{-}S)_2FeCl_2$ unit is nearly tetrahedral with a mean L–Fe–L angle of 109.5(2.0)° and a range from 106.76(4) to 112.95(4)°. Unlike the dinuclear Fe-MoS_4 complexes[16] where the formal oxidation state of the Fe atom is between +2 and +3, the oxidation state of the Fe atom in IV is very close to +3 and "fixes" the Mo oxidation state at +5. This argument is supported by the small value of the ^{57}Fe isomer shift (0.304 mm/s relative to iron metal at 125 K) and the Fe–μ-S and Mo–μ-S bond lengths of 2.225 and 2.301 Å, respectively. The structural and Mossbauer spectroscopic parameters of IV resemble those reported for the $[(S_2)Mo(O)(\mu\text{-}S)_2Fe_2Cl_2]^{2-}$ complex[17] (Mo–μ-S, 2.304(4) Å; Fe–μ-S, 2.243(4) Å; IS, 0.40 mm/s). In

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(13) Approximately equal amounts of $(Et_4N)_2[(Cl_4cat)Mo(O)(\mu\text{-}S)_2FeCl_2]$ (IV) and $(Et_4N)_4\{[(S)Mo(O)(\mu\text{-}S)_2FeCl_2]\cdot[FeCl_4]\}$ (V) are obtained, and the two types of crystals can be separated manually. Anal. Calcd for $MoFeCl_6S_2O_3N_2C_{22}H_{40}$ (IV): C, 32.63; H, 4.94; N, 3.46. Found: C, 32.8; H, 4.8; N, 3.5. Calcd for $MoFe_2Cl_6S_3ON_4C_{32}H_{80}$ (V): C, 36.47; H, 7.60; N, 5.32. Found: C, 36.8; H, 7.12; N, 4.51. Electronic spectra: for IV, 640 nm, 470 nm (sh); for V, 422 nm, 350 nm (sh). Infrared spectra: for IV, ν(Mo═O), 936 cm^{-1}; for V, ν(Mo═O), 877 and 902 cm^{-1}.

(14) The fate of the NH_2 group is difficult to ascertain but presumably it accepts the hydroxylamine OH proton to give ammonia that may or may not bind to the second Mo atom. Thus far we have been unable to isolate a Mo complex that contains ammonia. In a few instances the characteristic N-H vibrational frequencies of the NH_4^+ ion were detected in the intractable residue, however they were only in very small amount and apparently not enough to satisfy the stoichiometric requirements.

(15) Crystal and refinement data: Black crystals of $(Et_4N)_2[(Cl_4cat)Mo(O)(\mu\text{-}S)_2FeCl_2]\cdot{}^1/_2(C_2H_5)_2O$ (IV) are monoclinic, space group $P2_1/a$ (No. 14), with $a = 16.907(7)$ Å, $b = 8.489(1)$ Å, $c = 25.19(1)$ Å, $\beta = 97.00(3)°$, and $Z = 4$. Single-crystal X-ray diffraction data were collected on a Siemens R3m/v diffractometer using Mo Kα radiation, at 173 K. The solution of the structure was carried out by direct methods and Fourier techniques. The refinement of the structure by full-matrix least-squares methods was based on 7515 unique reflections ($2\theta_{max} = 55°$, $> \sigma I$). Anisotropic temperature factors were used for all non-hydrogen atoms. At the current stage of refinement on 362 parameters $R = 0.049$.

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the latter complex, the S_2^{2-} ligand occupies the position that the catecholate ligand occupies in IV and does not seem to be as effective in the withdrawal of electron density from the $FeCl_2$ subunit. In the structure of the $[(SCH_2CH_2S)MoS_3]_2Fe]^{3-}$ cluster,[18] which also contains Fe(III) coordinated by the $[(SCH_2CH_2S)MoS_3]^{3-}$ fragment and shows pentacoordinate Mo(V), the Fe–μ-S and Mo–μ-S bonds are found at 2.22(1) and 2.32(2) Å, respectively. In the Fe–MoS_4 complexes,[16] where the delocalization of charge is small and the Fe^{III}–Mo^{V} electronic description is not as important, the ^{57}Fe isomer shifts are found around 0.5 mm/s while the Fe–μ-S bonds range from 2.245(8) to 2.257(8) Å and the Mo–μ-S bonds range from 2.246(6) to 2.259(8) Å. Indeed the $(\mu\text{-}S)_2FeCl_2$ site in IV is quite similar to the $(\mu\text{-}S)_2FeCl_2$ sites in the $[Fe_2S_2Cl_4]^{2-}$ complex.[19] In the latter, the Fe^{3+}–μ-S bond at 2.200 Å and the Fe^{3+}–Cl bond at 2.252 Å are very close to those in IV.[20]

A structure determination of V shows[21] the compound to be a double salt of $(Et_4N)_2FeCl_4$ and $(Et_4N)_2[(S)Mo(O)(\mu\text{-}S)_2FeCl_2]$. A severe positional disorder of the $[(S)Mo(O)(\mu\text{-}S)_2FeCl_2]^{2-}$ dianion did not allow for a satisfactory refinement of the structure; however, the atomic connectivity within the anion is readily apparent.

Both IV and V can be considered as derivative fragments of the $[[MoFe_3S_4Cl_2(Cl_4cat)]$ cubane subunits in the DBDC. The latter apparently collapse following oxidation of the Mo atoms and formation of the $(Mo{=}O)^{3+}$ units. The electronic spectra of IV and V are due to the perturbed thiomolybdato chromophores and resemble the electronic spectra obtained from oxidized solutions of the nitrogenase cofactor. The presence of the $[OMoS_3]^{2-}$ unit in such solutions has been demonstrated previously[9,10] and suggests that the $MoFe_3S_3$ subunit in the FeMo cluster of nitrogenase collapses following oxidation in a similar fashion as the $[MoFe_3S_4Cl_2(Cl_4cat)]$ cubanes. The oxidative "decoupling" of the $[MoFe_3S_4]$ cubanes raises the possibility that the reverse process of reductive coupling, already used in the synthesis of the Fe_4S_4 cubanes,[22] may be an approach to the rational synthesis of cubanes such as $[LMo(\mu\text{-}S)_2\text{-}ML']_2$ and $\{[LMo(\mu\text{-}S)_2ML'][L'Fe(\mu\text{-}S)_2\text{-}FeL']\}$ (M = Fe, Co, Zn) from appropriate dimeric units. The feasibility of such reactions is currently under study in our laboratory.

Acknowledgment. The support of this work by a grant from the National Institutes of Health (GM-33080) is gratefully acknowledged.

Supplementary Material Available: Table S1, containing listings of positional parameters, thermal parameters, and selected distances and angles of $(Et_4N_2)[(Cl_4cat)Mo(O)(\mu\text{-}S)_2FeCl_2]\cdot{}^1/_2(C_2H_5)O$ (IV), and a stereoscopic drawing of the core of IV (10 pages). Ordering information is given on any current masthead page.

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(20) A detailed study of the magnetic, and Mossbauer properties of IV is in progress.

(21) Crystal and refinement data: Orange-brown crystals of $(Et_4N)_4\{[(S)Mo(O)(\mu\text{-}S)_2FeCl_2]\cdot[FeCl_4]\}$ (V) are monoclinic, space group $P2_1/c$, with a = 13.315(3) Å, b = 28.59(1) Å, c = 13.537(4) Å, β = 91.37(7)°, and Z = 4. Single-crystal X-ray diffraction data for both crystals were collected on a Nicolet R3m diffractometer using Mo Kα radiation. The solutions of all structures were carried out by a combination of heavy-atom Patterson techniques, direct methods, and Fourier techniques. The four cations and the two anions $[(S)Mo(O)(\mu\text{-}S)_2FeCl_2]^{2}$ and $[FeCl_4]^{2-}$ were located; however severe disorder problems did not allow for a satisfactory refinement of the structure. A second data set was obtained for VI from crystals grown out of an equimolar solution of $(Et_4N)_2FeCl_4$ and independently synthesized $(Et_4N)_2[(S)Mo(O)(\mu\text{-}S)_2FeCl_2]$. The crystals were identical in all respects to the $(Et_4N)_4$ DBDC-II decomposition product and perhaps not unexpectedly showed the same crystallographic disorder problem. The combination of the available crystallographic data and the independent synthesis of an identical compound from the component anions and four Et_4N^+ leaves no doubt regarding the identity of VI.

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