85% under conditions of complete inhibition by the sulfonamides acetazolamide and ethoxzolamide.[5,9] However, the component of the relaxation rate not inhibited by methazolamide also showed a linear dependence on enzyme concentration in the experiments reported here (Figure 2): for $n = 0.10$ the least-squares slope from Figure 2 is 1.1×10^2 M^{-1} s^{-1}; for $n = 0.75$, 46 M^{-1} s^{-1}. From the data in Figure 2, the difference in slopes $1/T_1$ between the uninhibited and inhibited Co(II)-carbonic anhydrase at $n = 0.10$ was $(3.5 \pm 0.3) \times 10^2$ M^{-1} s^{-1} and at $n = 0.75$ was $(3.4 \pm 0.3) \times 10^2$ M^{-1} s^{-1} (least-squares slope and 95% confidence limit). No correction has been made for the contribution of dissolved O_2 to relaxation rates. For these samples in equilibrium with air, the effect on $1/T_1$ of O_2 is about 0.1 s^{-1}, a sizable fraction of the observed rates. This and the small paramagnetic contribution to $1/T_1$ at proton resonance frequencies above 10 MHz compared to lower resonance frequencies[5,9] are disadvantages in these data.

The fractionation factor ϕ for the species of water bound to cobalt expresses the ratio of the preference of this site for deuterium over protium compared with the preference of a solvent site for deuterium over protium:[10]

$$\phi = \frac{[Co(OHD)]/[Co(OH_2)]}{[HOD]/[H_2O]}$$

Here it is assumed that the rule of the geometric mean holds.[11] Gold[3] and Kresge and Allred[4] have described an NMR method for determining fractionation factors based on the fact that when the chemical shift of a rapidly exchanging proton is collapsed into a single peak, its chemical shift is the weighted average, based on mole fraction, of the chemical shifts in the absence of exchange. This and the definition of the fractionation factor is sufficient to determine ϕ from NMR data (for a review see ref 10). The relaxation rate $1/T_1$ of a nucleus exchanging between two sites, in the fast exchange limit, is also a weighted average of the values of $1/T_1$ for each site in the absence of exchange.[12] Hence, the method of Gold[3] and Kresge and Allred[4] is directly applicable to the data of Figure 2. For two experiments using solvents of different deuterium content, the slopes of plots of $1/T_1$ vs. mole fraction of solute are related:

$$\frac{\text{slope 1}}{\text{slope 2}} = \frac{(1 - n + \phi n)_2}{(1 - n + \phi n)_1}$$

Application of this equation to the data in Figures 1 and 2 demonstrates that ϕ is unity for protons exchanging from the inner coordination sphere of cobalt in the aquometal complex, $Co(H_2O)_6^{2+}$, and in bovine Co(II)-carbonic anhydrase $\phi = 1.05 \pm 0.17$ for those protons which are displaced by methazolamide from the inner coordination sphere of cobalt.

A fractionation factor of unity for both the hexaaquo cobalt complex and the cobalt-substituted enzyme is consistent with an exchange of water between the inner coordination sphere of the metal and solvent at pH 8.2, although this experiment does not determine whether protons alone or the entire water molecule is exchanging (see, however, ref 12). The conclusion that the proton exchange observed by NMR occurs from water in the inner coordination site of cobalt in cobalt(II)-carbonic anhydrase was also reached by Fabry et al.[5] on the basis of kinetic arguments and the observed pH dependence of the relaxation rate of the exchanging protons. However, the determination in this report of a fractionation factor of unity is not in itself unambiguous evidence for the existence of a rapidly exchanging water bound to metal. Although the fractionation factor observed for hydroxide ion in aqueous solution is 0.47–0.56,[10] it is believed to arise from the hydrogens of solvating water molecules strongly hydrogen bonded to the hydroxide ion. The fractionation factor of hydrogen in the hydroxide ion itself is estimated to be close to unity.[13,14] Hence, the fractionation factor of unity determined in this study is also consistent with a hydroxide bound to cobalt at the active site which is not as extensively or as strongly solvated as hydroxide ion in solution. Although these fractionation factors cannot be used to distinguish between cobalt-bound water and hydroxide in cobalt(II)-carbonic anhydrase, it can be concluded that fractionation factors for nuclei exchanging rapidly from paramagnetic sites can be determined from nuclear magnetic relaxation rates.

Acknowledgment. It is a pleasure to acknowledge Dr. C. K. Tu, Dr. K. S. Venkatasubban, and Mr. G. C. Wynns for their assistance and helpful discussions. This work was supported by NIH Grant GM-25154.

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Total Synthesis and Stereochemical Identity of the $C_{18}H_{32}O_5$ Degradation Product from Boromycin

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Boromycin **1** is a unique boron-containing antibiotic[1] whose constitutional structure was determined by X-ray studies[2] and shown to be that of a novel macrodiolide containing a D-valine ester and a Böeseken complex of boric acid. Limited chemical degradation studies[2] on des-valine-des-boron-boromycin involving hydroxylation of the double bond followed by periodate oxidation gave acetaldehyde, an acid, $C_{13}H_{24}O_4$, and a neutral compound, $C_{18}H_{32}O_5$, which was assigned structure **2**, on the basis of its mode of formation. As part of our studies directed toward the total synthesis of boromycin[3] and the structurally related aplasmomycin,[4] we report herein a highly stereoselective, total synthesis of **2**, thereby unambiguously confirming its structure. Together with the glycolic acid unit, this constitutes the entire upper half of boromycin. We also describe methodology that allows the attachment of such a unit and hence the generation of a valuable intermediate toward our intended final goal.

Examination of the structure in question (Scheme I) reveals elements of carbohydrate-type symmetry[5] by virtue of the presence of the tetrahydrofuran and tetrahydropyran rings. Clearly, the major synthetic challenges in attaining this structure consist in devising practical routes to appropriately functionalized chiral precursors to the two ring subunits **3** and **4**, in elaborating suitable appendages, and in exploring methods for their union. Among several bond-forming possibilities, it was decided that the formation of the 9′–10′ bond (boromycin numbering), hence the creation of the neopentyl-type alcohol function, would constitute a viable protocol. Following extensive model studies it was also convened that the critical union of the two subunits would utilize a sulfoxide intermediate (**3**) (X = SOPh) and the aldehyde **4**.

Subunit 3. The chiral tetrahydrofuran unit **3** can be envisaged to arise by one of several possible routes formally leading to a

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(3) Portions of this work were communicated previously. See: Hanessian, S. "Abstracts"; 179th National Meeting of the American Chemical Society, Houston, FTX, March 24–28, 1980; American Chemical Society; Washington, DC, 1980; ORGN 47. See, also: White, J. D. "Abstracts"; *Ibid.*, ORGN 48.
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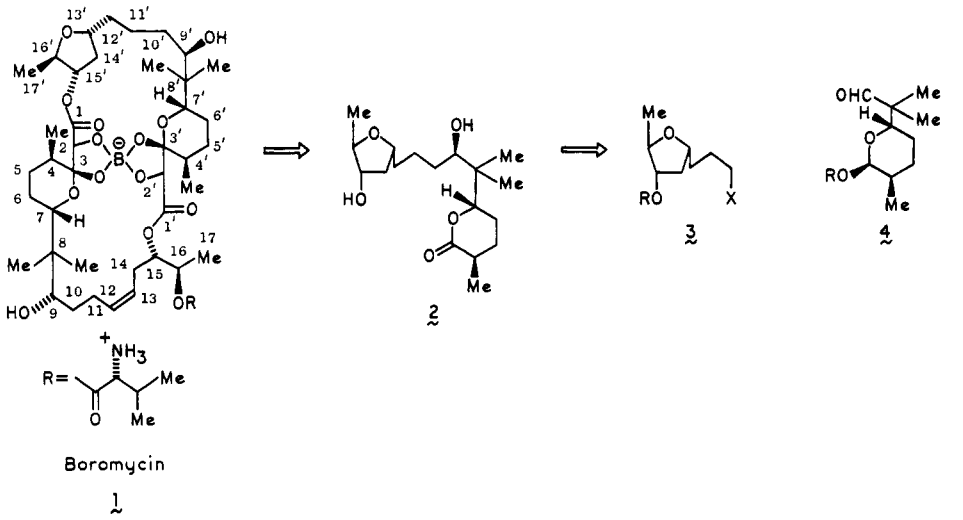
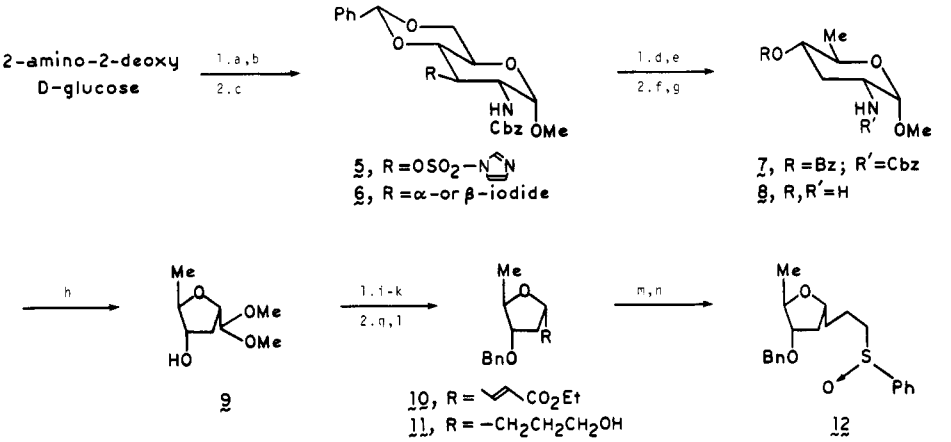
Scheme I



Scheme II[a]



[a] (a) Reference 7; then PhCHO, HCO_2H, 92%. (b) SO_2Cl_2 (2 equiv), DMF, -40 °C; imidazole (10 equiv), 25 °C, 87%. (c) Bu_4NI, benzene, reflux, 4 h, 85%. (d) NBS, CCl_4, $BaCO_3$, reflux. (e) Bu_3SnH, AIBN, toluene, 80-90 °C, 50% (overall 3 steps). (f) NaOMe, MeOH. (g) Pd/C, H_2, EtOAc, ~ quantitative. (h) N_2O_3, H_2O, then MeOH, HCl, reflux, 30 min, 62% overall 4 steps. (i) BnBr, NaH, THF, 83%. (j) aqueous AcOH, THF, quantitative. (k) $Ph_3P{=}CHCO_2Et$, THF, 30 min, 92%. (l) LAH, THF. (m) PhSSPh, Bu_3P, CH_2Cl_2, 25 °C, 2 h, 88% (overall 3 steps). (n) MCPBA, CH_2Cl_2, -40-25 °C, 92%.

C-glycoside.[6] In view of the α orientation of the three carbon appendage we chose a strategy that relied on a key, stereocontrolled ring-contraction process. This proved to be practical as well as rewarding. Thus, commerically available 2-amino-2-deoxy-D-glucose was transformed into the crystalline 3-imidazylate derivative **5**, mp 130 °C dec, $[\alpha]_D$ +17.1°, by well-known processes[7,8] in high yield and without recourse to chromatography (Scheme II). The synthetic utility of the novel imidazolesulfonate group[8] was clearly demonstrated by the efficient displacement by iodide ion to give **6**. Similar reactions with other sulfonates can be complicated by virtue of neighboring groups participation and oxazolidone formation.[9] Treatment of **6** with *N*-bromosuccinimide[10] followed by reduction with tri-*n*-butyltin hydride[11] gave the crystalline 3,6-dideoxy derivative **7**, mp 127-128 °C, $[\alpha]_D$ +80.6°, in good overall yield. Thus the required deoxygenation pattern as well as the correct sense of chirality at two centers in the intended target **3** had been achieved in a few steps. The stage was now set for a stereocontrolled ring contraction to the desired trisubstituted tetrahydrofuran. Thus, debenzoylation followed by hydrogenolysis gave the amino derivative **8** which when treated in water with dinitrogen trioxide[12] followed by methanolic hydrogen chloride gave the dimethylacetal derivative **9** $[\alpha]_D$ +22.7° (62%, 4 steps). The required three-carbon appendage was introduced by routine procedures. Thus, benzylation of **9** followed by acid hydrolysis gave the corresponding aldehyde, $[\alpha]_D$ +40.9°, which was chain extended with [(carbethoxy)methylene]triphenylphosphorane to give a 8.5:1 trans-cis mixture of olefins. Reduction of this mixture gave the alcohol **11**, $[\alpha]_D$ +35.6°, which was transformed into the corresponding sulfide, $[\alpha]_D$ +39.3°, and the sulfoxide derivative **12**, $[\alpha]_D$ +45.3°, by known procedures.

Subunit 4. The highly deoxygenated tetrahydropyran ring in subunit **4** which contains two asymmetric centers was obtained in a number of efficient transformations starting with D-glucose (Scheme III). Thus the readily available crystalline 2-acetoxy-D-glucal derivative **13**[13] was treated with *tert*-butyl alcohol in the presence of boron trifluoride according to Ferrier[14] to give

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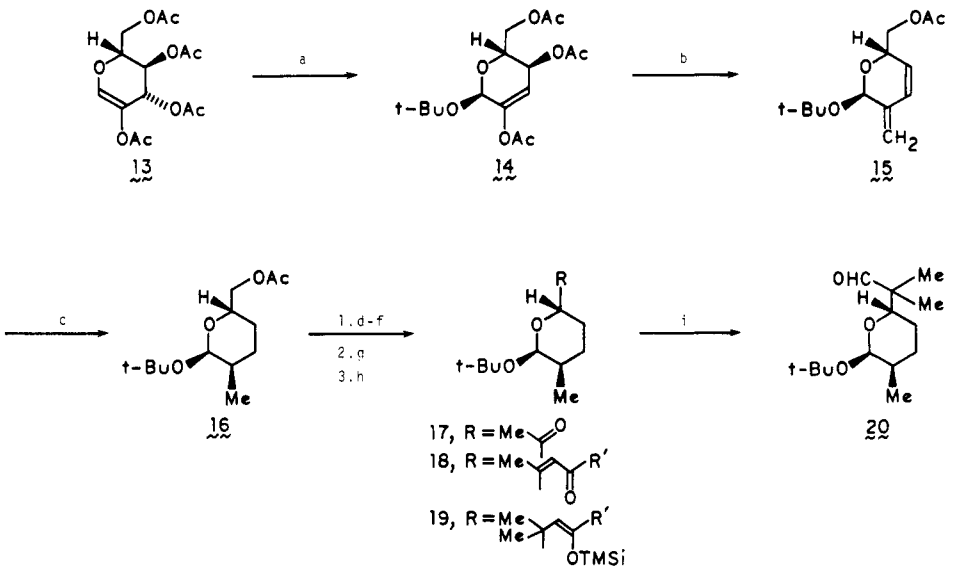
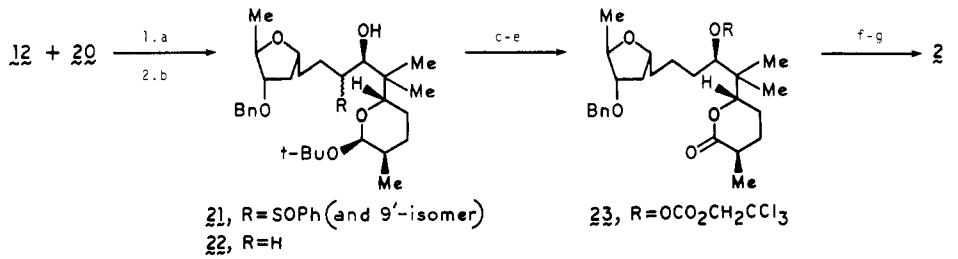
Scheme III[a]



[a] (a) *t*-BuOH, $BF_3 \cdot Et_2O$, toluene, 25 °C, 6 h, 90%. (b) $Ph_3P{=}CH_2$ (2.5 equiv), THF, 25 °C, 2 h; then acetylation, 90% overall. (c) Pd/C, H_2, EtOAc, 95%, 9:1 mixture. (d) NaOMe, MeOH, 98%. (e) Collins, 25 °C, 96%. (f) MeMgBr, ether, 25 °C, 30 min; then Collins ~90% overall, separate 17 from epimer. (g) $(MeO)_2P(O)CH_2COC_5H_{11}$, NaH, DME, reflux, 24 h, 72% (91% based on recovered ketone). (h) Me_2CuLi, ether, -40 °C, 30 min; then Me_3SiCl, Et_3N, HMPA, -40 °C, then 25 °C, 1.5 h, ~quantitative. (i) O_3, CH_2Cl_2, 1% pyridine, -78 °C.

Scheme IV[a]



[a] (a) LDA, THF/10% HMPA, -78 °C, 1 h, 87%. (b) Raney Ni (in portions), hexanes, 25 °C, 89.5%; then Pd/C, H_2, EtOAc (monitor by TLC); then flash chromatography. (c) Cl_3CCH_2OCOCl, pyridine, 25 °C, 18 h. (d) Aqueous HCl, THF, 25 °C, 1-2 days. (e) PCC, NaOAc, CH_2Cl_2, 25 °C, 1 h, 92% (overall, 3 steps). (f) Zn, THF, aqueous KH_2PO_4, 25 °C, 30 min. (g) Pd/C, H_2, EtOAc.

the new crystalline *tert*-butyl glycoside **14**, mp 63–63.5 °C, $[\alpha]_D$ +84.3°. On the basis of previous experience with the reaction of enosides such as **14** with various nucleophiles, it was treated with methylenetriphenylphosphorane whereupon a remarkable reaction took place giving diene **15** $[\alpha]_D$ +108.8°, and a small amount of the corresponding alcohol, $[\alpha]_D$ +146.9°. After acetylation, a combined yield of 90% of **15** could be accounted for. Evidently the Wittig reagent first attacks the enol acetate group generating an enone which is transformed to the diene in the presence of a second equivalent of reagent. By virtue of the presence of a bulky aglycon having an α orientation, it was anticipated that reduction of **15** would lead to a preponderance of the *C*-methyl derivative with the desired sense of chirality. Indeed, catalytic hydrogenation gave a 92% yield of a 9:1 mixture of isomeric products of which the desired **16** was the major component. Thus, an expedient and highly efficient synthesis of the chiral tetrahydropyran ring of the intended subunit had been achieved. The next task was the elaboration of the hydroxymethyl group to the pivalic aldehyde group. Compound **16** and its C-2 epimer were transformed into the corresponding methyl ketone derivatives which could be easily separated at this stage by flash chromatography or HPLC. The desired methyl ketone **17** $[\alpha]_D$ +65.5°, was then converted to the enone **18**, $[\alpha]_D$ +28.6°. The quaternary methyl group was introduced by conjugate addition with lithium dimethylcuprate, and the resulting enolate was trapped as the trimethylsilyl ether which after ozonolysis gave the desired aldehyde derivative **20**, $[\alpha]_D$ +82.3°, in 56% yield (3 steps). Thus, relying on the unique behavior of conformationally biased β-acyloxyenol esters such as **14** toward carbon nucleophiles, the anticipated anomeric stereoselection provided by the *tert*-butoxy group in the reduction step, and the efficient functionalization of the hydroxymethyl group, it was possible to construct the aldehyde derivative **20** from the readily available **14** in six steps and in very good individual yields.

Lactone 2. Initially we had intended to prepared a bormomagnesium derivative corresponding to **3** (R = Bn, X = MgBr) and to effect a Grignard-type reaction with the aldehyde **20**. Such a strategy would have ensured a measure of stereocontrol based on coordination of the reagent with the ring oxygen.[15] However, all attempts to prepare a Grignard reagent from the bromide were unsuccessful, leading to coupling and reduction. We therefore resorted to the formation of the sulfoxide **12**, and studied the reactivity of the corresponding carbanion with model aldehydes and eventually aldehyde **20** (Scheme IV). This resulted in the formation of diastereomeric sulfoxides **21** in high yield. Controlled reductive desulfurization gave a 1.5:1 mixture of alcohols epimeric at C-9′ (boromycin numbering). After reduction with Raney nickel, the desired isomer **22**, $[\alpha]_D$ +89.3°, was preponderant and could be easily separated from its C-9′ epimer, $[\alpha]_D$ +52.1°, by column chromatography. Moreover, it was found that the unwanted isomer could be converted into **22** by a sequence-involving

(14) Ferrier, R. J.; Prasad, N.; Sankey, G. H.; *J. Chem. Soc. C* **1969**, 587–591. See also ref 13.

(15) Wolfrom, M. L.; Hanessian, S. *J. Org. Chem.* **1962**, *27*, 1800–1804. Hanessian, S.; Rancourt, G.; Guindon, S. *Can. J. Chem.* **1978**, *56*, 1843–1846. See also: Cram, D. J.; Kopecky, K. R. *J. Am. Chem. Soc.* **1959**, *81*, 2748–2755.

oxidation (PCC, dichloromethane) and reduction (LAH, ether) giving a mixture rich in **22**. Completion of the synthesis required the selection of an appropriate protecting group that would also be useful for the subsequent steps in our synthesis of boromycin. The *O*-(trichloroethoxy)carbonyl group proved to be useful in this regard. Thus the readily formed trichloroethyl carbonate derivative of **22** was treated with acid and oxidized to the lactone **23**, $[\alpha]_D$ +28.8°. Removal of the protecting groups gave the desired lactone **2**, $[\alpha]_D$ +33°, in high overall yield. Similar treatment of the other isomer gave the C-9′ epimeric lactone, $[\alpha]_D$ +3.4°.[16] Oxidation of des-valine-des-boron-boromycin with periodic acid followed by mild base treatment and chromatographic separation gave a product which was identical with **2** in all respects [$[\alpha_D]$, mass spectrum, ^{1}H NMR (400 mHZ) spectrum, TLC, IR spectrum].

In addition to establishing the correct structure and stereochemical identity of the $C_{18}H_{32}O_5$ degradation product from boromycin by its total synthesis, we have found efficient and virtually regio- and stereospecific routes to the component chiral tetrahydrofuran and tetrahydropyran subunits as well as a practical method for joining them.[17,18]

Acknowledgment. We thank the National Science and Engineering Council of Canada for financial support and the CNRS (France) for fellowships. We would like to particularly thank Professor V. Prelog and Ciba-Geigy, Basel, for a sample of boromycin.

Supplementary Material Available: Infrared and proton magnetic resonance spectra, optical rotations, and other physical constants of the new compounds (9 pages). Ordering information is given on any current masthead page.

(16) The somewhat large change in the value of optical rotation compared to **2** can be ascribed to a change in conformation of the acyclic portion, which is borne out by the difference in chemical shift of the *gem*-dimethyl group in both isomers.

(17) Attachment of the glycolic acid chain in **23** was done by the Meinwald procedure. See: Duggan, A. J.; Adams, M. A.; Brynes, P. J.; Meinwald, J. *Tetrahedron Lett.* **1978**, 4323-4326.

(18) Another approach for the stereoselective synthesis of segments of boromycin has been recently described. See: White, J. D. "Abstracts of Papers"; 179th National Meeting of the American Chemical Society, TX, Houston, March 24-28, 1980; American Chemical Society: Washington, DC, 1981; ORG 48.

Synthesis and Structure of a New Type of Mo-Fe-S Double-Cubane Cluster and Evidence for Formation of Magnetically Uncoupled $S = {}^3/_2$ $MoFe_3S_4$ Subclusters

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In the course of our synthetic approach to the catalytic site(s) of the nitrogenase FeMo proteins we have been encouraged as to the viability of the double-cubane clusters $[Mo_2Fe_6S_9(SR)_8]^{3-}$ (**1**), $[Mo_2Fe_6S_8(SR)_9]^{3-}$ (**2**), $[Mo_2Fe_7S_8(SR)_{12}]^{3-}$ (**3**), and $[Mo_2Fe_7S_8(SR)_{12}]^{4-}$ (**4**)[1-5] as preliminary models by several observations: elements of apparent similarity in Mo coordination

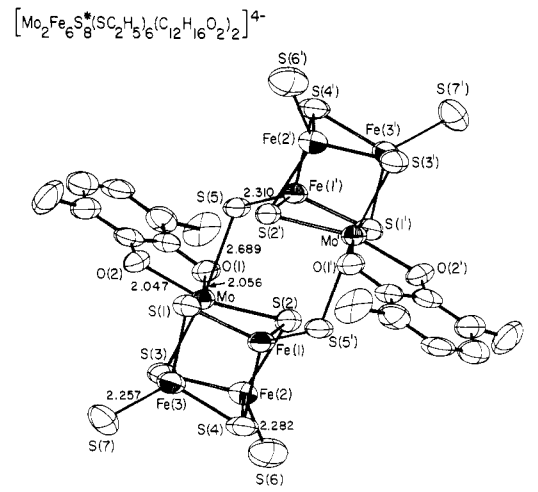

Figure 1. Structure of $[Mo_2Fe_6S_8{}^*(SEt)_6(Pr_2cat)_2]^{4-}$ as its Et_4N^+ salt; shown are 50% probability ellipsoids and bridging and terminal ligand-metal bond distances (Å). Primed and unprimed atoms are related by an inversion center. Mean distances within a cluster: Mo-S*, 2.371 (10); Mo-Fe, 2.737 (32); Fe-Fe, 2.714 (9), Fe-S*, 2.278 (19) Å. Distances between clusters: Mo···Mo′, 6.042 (4); Mo···Fe(1′), 4.380 (4); Fe(1)···Fe(1′), 4.055 (5) Å. Ethyl groups are omitted for clarity.

site environments from comparative EXAFS[1] of clusters and native proteins and their common cofactor[6-8] (FeMo-co) and occurrence of at least one type of substrate reduction (H_2 evolution from protic sources) using reduced forms of **2**.[9] However, clusters **1-4** are likely to prove ineffectual in activation of other nitrogenase substrates if binding at a Mo site is requisite, owing to coordinative saturation completed by strong bridge-sulfur atom ligation as in, e.g., **3**.[2,3] Clusters lacking this structural feature should prove more manipulable chemically. In addition, single clusters or double cubanes having magnetically insulated subclusters would facilitate examination of the electronic properties of individual $MoFe_3S_4$ units for comparison with the spin-quartet cluster present in FeMo-co[8,10] and native enzymes.[11] Such species have not been detected among direct synthesis products[1,3] nor are they accessible from **1-3** by reactions with electrophiles, which afford terminal ligand substitution only.[4] Cleavage of the Fe(III) bridge in **3** with catechol yields **5**,[12] a single cluster but with an appended, paramagnetic $Fe(cat)_3^{3-}$ subunit. The structure of **5** indicates steric destabilization from Et/3-substituent interactions when the latter is methyl or larger, suggesting a different product upon reaction of **3** with an appropriate 3,6-disubstituted catechol.

Reaction of $(Et_4N)_3[Mo_2Fe_7S_8(SEt)_{12}]$[3] (**3**, 3.6 mmol) and 3,6-$(n\text{-}Pr)_2C_6H_2(OH)_2$[13] (22 mmol) in the presence of Et_3N (44 mmol) and Et_4NBr (21 mmol) in acetonitrile (100 mL) for 48 h (N_2 atmosphere) produced a solid which after recrystallization from acetonitrile gave black crystals of composition $(Et_4N)_4[Mo_2Fe_6S_8(SEt)_6(Pr_2cat)_2]$ (**6**-Mo, 32%, λ_{max} 395 nm (ϵ_M 35 000), Me_2SO). The tungsten cluster, **6**-W, was prepared analogously. One form of **6**-Mo[14] crystallizes in monoclinic space group $C2/c$ with a = 31.474 (7) Å, b = 19.544 (5) Å, c = 25.182 (6) Å, β

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(5) Type **2** clusters have been independently investigated by others: (a) Christou, G.; Garner, C. D. *J. Chem. Soc., Dalton, Trans.* **1980**, 2354. (b) Christou, G.; Garner, C. D.; Miller, R. M.; Johnson, C. E.; Rush, J. D. *Ibid.* **1980**, 2364.
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(13) Müller, E.; Günter, F.; Rieker, A. *Z. Naturforsch.* **1963**, *18b*, 1002.
(14) Data were collected on a Nicolet R3m diffractometer with graphite monochromatized Mo Kα radiation. The Mo atom position was determined from a Patterson map; subsequent maps revealed remaining nonhydrogen atoms, all of which in the anion were refined anisotropically. The structure of a second crystalline form (triclinic, space group $P\bar{1}$) has been solved to R = 8.3%; its anion structure is unimportantly different from that reported here.

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