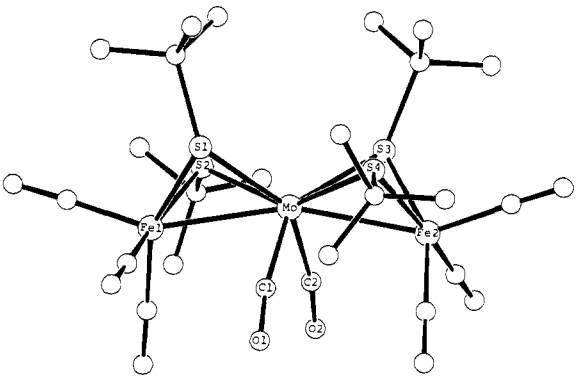

Figure 1. Molecular structure of $MoFe_2(\mu\text{-}t\text{-}BuS)_4(CO)_8$, a view perpendicular to the C_2 axis. Important bond distances are as follows: Mo-Fe1 2.754, Mo-Fe2 2.759, Mo-S1 2.517, Mo-S2 2.448, Mo-S3 2.537, Mo-S4 2.441, Fe1-S1 2.294, Fe-S2 2.266, Fe-S3 2.293, and Fe2-S4 2.268 Å, esd's are 0.001 Å for these distances. The nonbonded S1···S2 and S3···S4 distances are 2.961 (2) and 2.989 (2) Å, respectively.

temperature (δ 1.38 at 110 °C), indicating equilibration of two *t*-Bu substituents of the bridging *t*-BuS groups. The temperature variant behavior is reversible. The spectrum was also examined in toluene-d_8 with added *t*-BuSLi (**1**:*t*-BuS^- = 1:1). The two singlets due to **1** coalesce at the same temperature (~70 °C) without affecting the signal due to *t*-BuS^- (δ 1.19), a result implying an intramolecular site-exchange mechanism. A similar conformational equilibration was reported for syn and anti configurations of *t*-BuS bridged dinuclear complex $(t\text{-BuS})_4Mo(\mu\text{-}t\text{-BuS})_2CuBr$.[2e] The ^{13}C signals for both methyl carbon and tertiary-carbon atoms of *t*-Bu groups also split into two at room temperature (δ (Me_4Si) 34.36 and 35.77 for $(CH_3)_3C$; 48.48 and 53.28 for $(CH_3)_3C$). The signals for CO ligands are not observed.

The molecular structure of **1** was determined by X-ray crystallography.[6] The molecule possesses a noncrystallographic C_2 axis passing through the Mo atom and approximately bisecting the ClMoC2 angle (77.0°) (Figure 1). Selected structural parameters are also indicated in Figure 1. The Fe1-Mo-Fe2 angle is 160.43 (3)° and the dihedral angle between Mo-S1-S2 and Mo-S3-S4 is 120.89 (4)°. This molecular framework may remind one of chiroptera or bat. The Mo coordination geometry cannot be described in terms of simple symmetry. At the best the geometry (neglecting the Fe atoms) may be approximated as a highly distorted and flattened trigonal prism. This open structure can be rationalized in terms of the formal electron count (Lauher rule[7]). Electron-precise trinuclear carbonyl cluster $M_3(CO)_{12}$ has 48 cluster valence electrons (CVE), whereas **1** has 50 CVE regarding each *t*-BuS group as a four-electron donor.

The Mo-Fe distances (2.754 (1) and 2.759 (1) Å) are somewhat longer than those in triply thiolate bridged Mo-Fe bonds (2.559 and 2.309 Å) in the double cubane cluster $(Et_4N)_3[Mo_2Fe_7S_8(SEt)_{12}]$,[8] reflecting the lower oxidation states of the metal ions in **1**. There are two distinct Mo-S distances, one pair (Mo-S2 and -S4) is short and the other (Mo-S1 and -S3) long (Figure 1).[9] Another salient feature in the structure is the coordination geometry of CO ligands on the Mo atom. The reason for the bent CO coordination (169.5 (4) and 170.8 (4)°) may be ascribed to the interaction with the Fe atoms (C1-Fe1 = 2.734 (5) vs. C1-Fe2 = 3.499 (5) Å and C2-Fe2 = 2.810 (5) vs. C2-Fe1 = 3.580 (5) Å). The CO ligands may then be classified as a semibridging CO, and the low stretching frequencies are consistent with this view.

Despite the open structure, the molecule shows remarkable thermal stability as manifested in its mass spectrum and solution NMR data described above. This Mo-Fe thiolato compound adds an example of a novel structure to the Fe-Mo cofactor model chemistry of current interest.

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Registry No. 1, 87803-90-5; $Mo(t\text{-BuS})_4$, 74656-39-6; $Fe_2(CO)_9$, 15321-51-4.

Supplementary Material Available: Tables of structural amplitudes, atomic coordinates, thermal parameters, bond lengths, and bond angles and structural figure (15 pages). Ordering information is given on current masthead page.

(6) Single crystals grown from toluene are monoclinic, space group $P2_1/n$ with a = 21.694 (6) Å, b = 15.828 (4) Å, c = 9.892 (2) Å, β = 94.53 (2)°, and Z = 4 (d_{calcd} = 1.546 g cm^{-3}); μ(Mo Kα) = 15.01 cm^{-1}. Three-dimensional X-ray diffraction data were collected for 5950 independent reflections on a Philips PW1100 automatic four-circle diffractometer with graphite-monochromatized Mo radiation. The structure was solved by using the heavy-atom technique for 4460 reflections having $I > 3\sigma(I)$ and $2\theta < 50°$. Structural parameters have been refined to convergence [R(unweighted, based on F) = 0.038] in cycles of weighted cascade-blocked least-squares refinement that employed anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for all hydrogen atoms. See also supplementary material.

(7) Lauher, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 5305-5315.

(8) Wolf, T. E.; Berg, J. M.; Power, P. P.; Hodgson, K. O.; Holm, R. H. *Inorg. Chem.* **1980**, *19*, 430-437.

(9) A referee has asked a rationale for the difference. The molecular model of **1** based on this X-ray results suggests a possibility that the lone pair orbitals of S2 and S4 atoms lie in a more favorable orientation in making p_π-d_π interaction compared to those of S1 and S3. A definite comment, however, will be deferred until we obtain information from MO calculations, which are now under way.

^{15}N Spin Exchange in a Protein

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The observation of through-space interactions among nuclear spins provides a general method for molecular structure determination. These interactions are most conveniently observed with two-dimensional homonuclear spin-exchange experiments.[1] The best known of these is the NOESY sequence used in high-field ^1H NMR on molecules as complex as proteins and nucleic acid in solution.[2] Recently, related methods have been found to detect through-space dipolar interactions among ^{13}C sites in the solid state.[3-5] The acquisition of data concerning spin interactions over reasonably long molecular distances is an important new capability in NMR spectroscopy.

We have adapted the solid-state dilute-spin-exchange experiments described by Maciel[3,4] and Ernst[5] for ^{15}N NMR of biopolymers. High levels of ^{15}N enrichment increase the probabilities for through-space spin interactions via homonuclear dipolar couplings among nearby sites. In order to observe off-diagonal cross peaks, the sites must be in close proximity and have resolved resonances. In the previous solid-state spin-exchange experiments, magic-angle sample spinning[3,4] and molecular reorientation[5] resulted in isotropic chemical shift spectra where resolution was based on different chemical environments. Here magnetic

(1) Jeener, J.; Meier, B. H.; Bachmann, P.; Ernst, R. R. *J. Chem. Phys.* **1979**, *71*, 4546-4553.

(2) Kumar, A.; Ernst, R. R.; Wuthrich, K. *Biochem. Biophys. Res. Commun.* **1980**, *95*, 1-6.

(3) Szeverenyi, N. M.; Sullivan, M. J.; Maciel, G. E. *J. Magn. Reson.* **1982**, *47*, 462-475.

(4) Szeverenyi, N. M.; Bax, A.; Maciel, G. E. *J. Am. Chem. Soc.* **1983**, *105*, 2579-2582.

(5) Caravatti, P.; Deli, J. A.; Bodenhausen, G.; Ernst, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 5506-5507.

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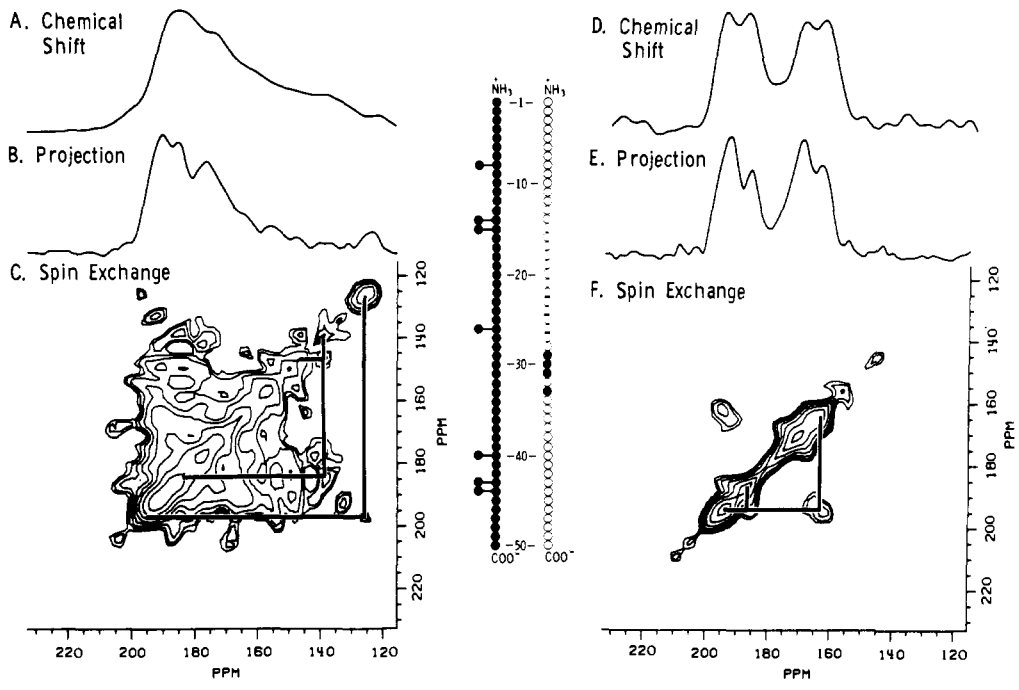

Figure 1. ^{15}N NMR spectra of the coat protein in oriented fd. (A–C) The data on the left are from a sample where all nitrogen sites are uniformly labeled with ^{15}N as indicated with the dark dots in the left schematic drawing of the coat protein. (D–F) The data on the right are from a sample where only the amide nitrogen sites of the four valine residues (29, 30, 31, 33) are specifically labeled with ^{15}N as indicated with the dark dots in the right schematic drawing of the coat protein. (A and D) ^{15}N chemical shift spectra. (B and E) Projections of 2D data. (C and F) Contour plots of 256 × 256 point 2D spin exchange: mix times—C, 5 s; F, 3 s. t_1 was incremented in 64 steps of 50 μs. Each t_1 value was signal averaged 32 times in C and 384 times in F. All spectra were obtained at 25.2 MHz on a home-built double-resonance spectrometer. The virus samples were 45 mg/mL at 63 °C and pH 8.

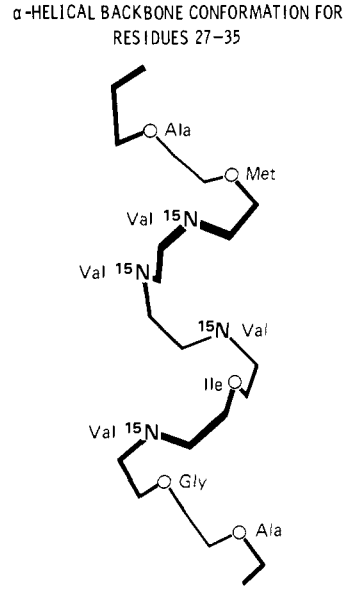

Figure 2. α-Helical backbone conformation for residues 27–35 of the viral coat protein demonstrating the variation in distances between valine nitrogens.

alignment of the molecules results in resolution among chemically similar sites on the basis of orientation with respect to the field.

The filamentous bacteriophages are of considerable interest as simple and tractable models for nucleoprotein complexes. Many aspects of the viruses and their coat proteins are being studied by NMR; in particular, the structure of the coat protein in the virus is being determined by NMR methods.[6-7] Results from spin-exchange experiments, such as those described here, are playing an important role in these studies. The experimental strategy involves the use of ^{15}N-labeled virus samples.[8] Two different samples of the filamentous bacteriophage fd are compared here, one of which is uniformly labeled in all nitrogen sites and the other of which has only four labeled sites, The schematic drawing of the 50-residue coat protein on the left in Figure 1 shows all backbone amide linkages and the seven nitrogen-containing side chains uniformly labeled with ^{15}N. The coat protein labeled only in the amide nitrogens of the four valine residues had four ^{15}N sites in close proximity as shown in the sequence diagram on the right in Figure 1. Spin exchange among ^{15}N sites in both uniformly and selectively labeled fd coat proteins is used here to demonstrate the method, to locate nearby nitrogen sites, to enhance spectral resolution by spreading the resonance in two dimensions, and to make resonance assignments.

The long filament axis of fd orients parallel to the applied magnetic field because of the net diamagnetic anisotropy of the α-helical coat proteins. Figure 1A is the chemical shift spectrum from uniformly ^{15}N-labeled fd oriented in the magnetic field. This spectrum has been described and interpreted previously;[7] nearly all of the amide nitrogen resonances are in the relatively narrow band near σ_{33} of the amide chemical shift tensor where the N–H bonds are approximately parallel to the filament axis and the magnetic field. The two-dimensional spin-exchange experiment yields the complex contour plot in Figure 1C. Intensity along the diagonal is from the chemical-shift frequencies, while the off-diagonal intensity results from spin exchange among nitrogens with different chemical shifts that are close enough to have dipole–dipole couplings. In the projection of the two-dimensional spectrum (Figure 1B) the effective resolution has been enhanced, primarily by selecting for resonances with relatively long T_1, as seen in the comparison to the normal chemical shift spectrum

(6) Cross, T. A.; Opella, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 306–308.
(7) Cross, T. A.; Tsang, P.; Opella, S. J. *Biochemistry* **1983**, *22*, 721–726.
(8) Cross, T. A; DiVerdi, J. A.; Opella, S. J. *J. Am. Chem. Soc.* **1982**, *104*, 1759–1761.

(Figure 1A). The number and intensity of cross-peaks, and the resolution apparent in the projection, can be varied by changing the fixed mix time in the pulse sequence. It is frequently useful to be able to select for resonances from, and interactions among, defined populations of spins. There are several clearly resolved cross-peaks in this two-dimensional spin-exchange spectrum despite the large number of labeled nitrogen sites. Correlations for a few cross–peaks have been drawn in the lower half of the contour plot. The indole nitrogen of Trp-26 has a chemical shift of 127 ppm[6] and gives a well-defined cross-peak to 198 ppm, which is most likely from a peptide nitrogen. The resonance at 140 ppm has cross-peaks to resonances at 147 and 187 ppm.

The spectral data become much simpler when the number of labeled sites is decreased. The four valine residues of the fd coat protein are in close proximity in the sequence (Figure 1) and in space (Figure 2). All four sites give resolved resonances in the chemical-shift spectrum (Figure 1D) and the projection (Figure 1E) from the two-dimensional spin-exchange spectrum. Therefore, there is the possibility of detecting the interactions among all the valine peptide nitrogen sites. There is a well-defined cross-peak between the valine ^{15}N resonances at 197 and 165 ppm. The shoulder off the diagonal between the resonances at 197 and 189 ppm is suggestive of a second cross-peak. The cross-peaks due to nitrogens with very similar chemical shifts are difficult to detect because of the width of the diagonal ridge due to T_2 relaxation. The coat protein is almost entirely α-helical and both the ^{15}N chemical shifts and ^{15}N–^{1}H dipolar couplings for the valine residues correspond to peptide bonds in an α-helix. Figure 2 shows this segment of protein as an α-helix. Val-30 is only about 2.8 Å from Val-29 or Val-31. The results in Figure 1 are consistent with cross-peaks occuring from Val-30 to Val-29 and Val-31; certainly one of the cross-peaks is present with some doubt about the second. The nitrogens of Val-29 and Val-33 are more than 6 Å apart and are unlikely to give rise to a cross-peak. Spin exchange between the backbones of neighboring protein subunits is unlikely because the distance of closest appraoch is approximately 8 Å.

The simple applications of ^{15}N spin-exchange demonstrated for the coat protein in fd provide distance information with cross-peaks occurring only for nearby sites. In the uniformly labeled virus spectrum in Figure 1C the cross-peak between the Trp-26l ring site and an amide site shows the closeness of a side chain to the backbone. The presence of cross-peaks can be used in making resonance assignments. If there are indeed two cross-peaks off of one nitrogen resonance in Figure 1F, then the resonance at 197 ppm is assigned to Val-30.

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Registry No. Nitrogen-15, 14390-96-6.

Poly[1-(trimethylsilyl)-1-propyne]: A New High Polymer Synthesized with Transition-Metal Catalysts and Characterized by Extremely High Gas Permeability

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Though the polymerization of acetylenes has been attempted by various methods, the products are often not high polymers but linear oligomers and cyclotrimers.[1] It is known that acetylene and monosubstituted acetylenes are selectively cyclotrimerized by the pentachlorides and pentabromides of niobium (Nb) and tantalum (Ta), group 5 transition metals.[2] We have recently found that these metal halides polymerize disubstituted hydrocarbon acetylenes.[3] The present communication reports that 1-(trimethylsilyl)-1-propyne is polymerized by these metal halides to give a new high-molecular-weight polymer. Polymers from aliphatic acetylenes such as *tert*-butylacetylene have been found to exhibit fairly high gas permeabilities.[4] Thus we further examined the permeability of the present polymer to oxygen to observe the highest value among those ever known.

Table I. Polymerization of 1-(Trimethylsilyl)-1-propyne by Halides of Nb and Ta[a]

run	catalyst	polymer yield, %	"$\bar{M}_n$"[b] 10^4	"$\bar{M}_w$"[b] 10^4	$[\eta]$,[c] dL/g
1	$NbCl_5$	100	23	32	0.99
2	$NbBr_5$	100	13	27	0.63
3	$TaCl_5$	100	61	85	5.43
4	$TaBr_5$	95	26	61	3.60

[a] Polymerized under dry nitrogen in toluene at 80 °C for 24 h; $[M]_0$ = 1.0 M. [Cat] = 20 mM. [b] Number- and weight-average molecular weights ("$\bar{M}_n$" and "$\bar{M}_w$", respectively) determined by gel permeation chromatography using a calibration curve for polystyrene. [c] Measured in toluene at 30 °C.

Table II. Gas Permeability of Poly[1-(trimethylsilyl)-1-propyne][a]

polymer sample[b]	P_{O_2}[c]	P_{N_2}[c]	P_{O_2}/P_{N_2}
1	72×10^{-8}	42×10^{-8}	1.7
2	83×10^{-8}	49×10^{-8}	1.7
3	61×10^{-8}	34×10^{-8}	1.8
4	63×10^{-8}	37×10^{-8}	1.7

[a] Measured at 25 °C. [b] Corresponding to the run numbers in Table I. [c] In units of cm^3 (STP)/cm/(cm^2 s cmHg).

Under the conditions shown in Table I, the chlorides and bromides of Nb(V) and Ta(V) yielded poly[1-(trimethylsilyl)-1-propyne] virtually quantitatively. The molecular weights of the polymers, determined tentatively by gel permeation chromatography, ranged from 1×10^5 to 1×10^6. The high molecular weights are endorsed by the high intrinsic viscosities, $[\eta]$. This polymerization proceeded in hydrocarbons (toluene, cyclohexane, etc.) and halogenated hydrocarbons [CCl_4, $(CH_2Cl)_2$, etc.] but not in oxygen-containing solvents (anisole, acetophenone, etc.). Similarly, some homologues such as 1-(dimethylpropylsilyl)-1-propyne and 1-(dimethyl-*n*-butylsilyl)-1-propyne polymerized with $NbCl_5$ and $TaCl_5$.

The fluorides and iodides of Nb(V) and Ta(V) did not polymerize 1-(trimethylsilyl)-1-propyne at all. $MoCl_5$–Ph_4Sn (1:1) and WCl_6–Ph_4Sn (1:1) work as effective polymerization catalysts for mono- and disubstituted acetylenes,[5] Fe(III) complexes–Et_3Al (1:3) for monosubstituted acetylenes,[6] and Ti(O-*n*-Bu)$_4$–Et_3Al (1:4) for acetylene.[7] None of these catalysts, however, polymerized 1-(trimethylsilyl)-1-propyne. Thus the high efficiency toward disubstituted acetylenes with large steric hindrance is a characteristic of the Nb and Ta catalysts.

(1) For reviews, see: (a) Simionescu, C. I.; Percec, V. *Prog. Polym. Sci.* **1982**, *8*, 133. (b) Chauser, M. G.; Rodionov, Yu. M.; Misin, V. M.; Cherkashin, M. E. *Russ. Chem. Rev. (Engl. Transl.)* **1976**, *45*, 348; *Usp. Khim.* **1976**, *45*, 695.

(2) (a) Dändliker, G. *Helv. Chim. Acta* **1969**, *52*, 1482. (b) Masuda, T.; Mouri, T.; Higashimura, T. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1152. (c) Masuda, T.; Deng, Y.-X.; Higashimura, T. *Ibid.* **1983**, *56*, 2798.

(3) Masuda, T.; Takahashi, T.; Higashimura, T. *J. Chem. Soc., Chem. Commun.* **1982**, 1297.

(4) Higashimura, T.; Masuda, T.; Okada, M. *Polymn. Bull.* **1983**, *10*, 114.

(5) Masuda, T.; Higashimura, T. *Acc. Chem. Res.*, in press.

(6) (a) Ciardelli, F.; Lanzillo, S.; Pieroni, O. *Macromolecules* **1974**, *7*, 179. (b) Kern, R. J. *J. Polym. Sci., Polym. Chem. Ed.* **1969**, *7*, 621.

(7) (a) Ito, T.; Shirakawa, H.; Ikeda, S. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 11.

0002-7863/83/1505-7473$01.50/0