

leads to deactivation of the system. GPC analysis of the polymer indicated M_n and M_w values of 21 000 and 47 900 daltons (Da), respectively, and a DSC curve for the polymer exhibited no detectable exotherm prior to the onset of crystalline melting at 131.6 °C. In contrast, the reactions of $(\text{Ph}_3\text{SiO})_3\text{VO}$ and $(n\text{-PrO})_3\text{VO}$ under identical conditions gave no polyethylene; the only observable reaction (by ^{51}V NMR) was metathesis of alkyl ligands on Al for alkoxide ligands on V.^{7d,8} We have not extensively explored the use of other cocatalysts with **2**, but we have observed similar activities with Et_3Al and somewhat lower activities with $(\text{Me}_2\text{SiCH}_2)_3\text{Al}$.

A survey of the catalyst's reactivity indicates that other olefins can also be polymerized or copolymerized, although not as efficiently as ethylene. For example, the reaction of **2** and Me_3Al (3 equiv) in propylene (25 °C, ~8 atm, 3 h) gave a small amount (~125 turnovers) of atactic polypropylene⁹ ($MW < 10\,000$). Similarly, the copolymerization of ethylene (1%) in neat propylene produced small amounts (~350 turnovers) of copolymer, which contained 5–10% propylene (by ^{13}C NMR).⁹ One olefin that is polymerized well by our catalyst is 1,3-butadiene; an ampule containing 50 mL of neat butadiene (bp -4.5 °C) completely solidifies within 30 min to create a partial vacuum inside the ampule. ^1H and ^{13}C NMR spectroscopy¹⁰ indicated that the resulting product was >95% *trans*-1,4-polybutadiene.¹¹

The activity of the catalyst is sensitive to the amount of Me_3Al used. As shown in Figure 1, polyethylene production (1 atm, 25 °C, 3 h) is maximized when approximately 3 equiv of Me_3Al is used as cocatalyst. Large excesses of Me_3Al lead to complete deactivation of the catalyst. Both observations are contrary to the behavior of typical "soluble catalysts"¹² prepared from trialkylvanadates, which typically require large excesses of alkyl-aluminum reagents (15–500 equiv) to initiate olefin polymerization.¹³ In light of the narrow polydispersity measured for our polyethylene sample (2.28), these results suggest that a well-defined catalyst is being formed¹⁴ and that this catalyst is fundamentally different from these conventional soluble V catalysts.

The presence and equilibration of both **2** and **3** in the starting solution greatly complicate mechanistic studies, but several polymerization reactions performed at -30 °C, where the equilibration of **2** and **3** is negligibly slow, indicate that the active catalyst is derived from the reaction of **2** with Me_3Al . Specifically, the addition of Me_3Al to an ethylene-saturated solution of **2** and **3** (~10:90 by ^{51}V NMR) at -30 °C initiates ethylene polymerization by slowly consuming **2**, but does not affect the amount of **3** in solution. Furthermore, ethylene polymerization is only initiated when the ^{51}V NMR resonance for **2** is initially present.

The active polymerization catalyst(s) in our system is (are) currently not known, and it would be inappropriate to speculate about its identity without additional data.¹⁵ It is, however,

important to note that this POMSS-based catalyst is capable of polymerizing olefins when stoichiometrically similar complexes (e.g., $(\text{Ph}_3\text{SiO})_3\text{VO}$ and $(n\text{-PrO})_3\text{VO}$) show little or no reactivity. Since our understanding of surface catalysis is both based upon and inherently limited by known reaction chemistry of solution complexes, the unique chemistry of V-containing POMSS may provide new insights into the chemistry of silica-supported vanadate catalysts. Efforts to elucidate the active polymerization catalyst(s) in this interesting system are currently in progress.

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(15) A referee has suggested that a V(IV) species might be the active catalyst. This is clearly a reasonable hypothesis, but we have prepared $[(\text{C}_6\text{H}_{11})_7\text{Si}_7\text{O}_{12}\text{V}(\text{CH}_2\text{SiMe}_3)]$ and found that it does not initiate ethylene polymerization. The synthesis of this complex and the results from our other efforts to elucidate the identity of the polymerization catalyst(s) will be reported in a subsequent article.

2D Nuclear Magnetic Resonance Study of the Structure of the Fullerene C_{70}

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Geodesic structures were developed by R. Buckminster Fuller² on the basis of his insight into their structural economy and stability. In 1985, similar considerations led Smalley, Kroto, et al.³ to propose that C_{60} , observed in carbon cluster beam experiments,^{3,4} possessed the geometry of a soccer ball, and they named it "Buckminsterfullerene". Their prediction of the stability of this molecule, as well as other fullerenes, has been stunningly verified by the recent synthesis of macroscopic amounts of C_{60} and C_{70} .⁵⁻⁸ This development has sparked intense research activity in the production and characterization of these materials.⁸⁻¹⁸ Raman^{9,18}

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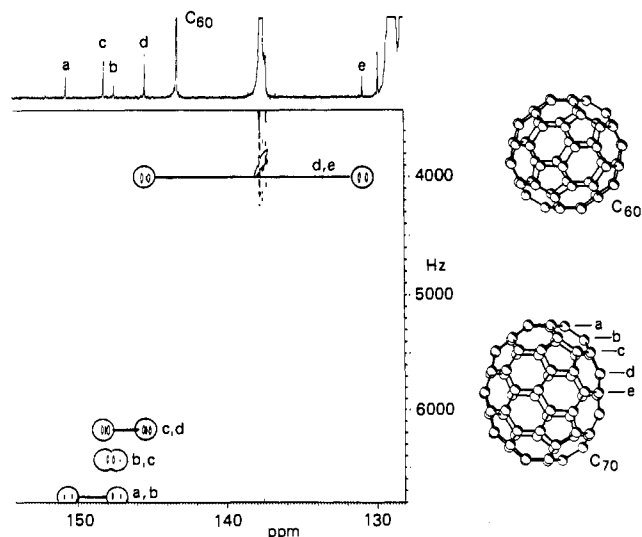


Figure 1. Upper trace: aromatic region of the ^{13}C NMR spectrum of $\sim 300\ \mu\text{g}$ of $\text{C}_{70}/\text{C}_{60}$ in toluene- d_8 without ^1H decoupling, obtained with a Bruker AM-500 NMR spectrometer operating at 125.7 MHz at 25 $^\circ\text{C}$. Lower spectrum: the 2D NMR "INADEQUATE" spectrum of C_{70} . Doublets (circled) are obtained at a common double quantum frequency for the two resonances of a bonded carbon pair. The connectivity obtained is linear and highlighted by lines; the asymmetrical intensity string of 10:10:20:20:10 allows the assignment of polar end cap carbon a and the remaining carbons. The spectrum was obtained in the presence of $\text{Cr}(\text{ac})_3$, by using the pulse sequence of Mareci and Freeman²⁵ with a refocusing delay of 5 ms, a sweep width of 13 000 Hz digitized into 8K-work datasets for the horizontal dimension, and a sweep width of 7000 Hz for the double quantum dimension digitized into 512 blocks, with 512 scans/block.

and infrared^{5,6,17,18} spectroscopy support the proposed C_{60} soccer ball structure, and the single-resonance ^{13}C NMR spectrum of C_{60} is strong evidence for the icosahedral symmetry of this molecule.^{8,10}

NMR spectroscopy is a powerful probe of chemical structure.^{19,20} ^{13}C NMR analysis of fullerenes probes structure, torsional strain, and bonding in these molecules. The ^{13}C NMR spectrum of C_{60} is a single line at 143 ppm (in both liquids^{8,10} and solids^{15,16}), showing that all carbons in the molecule are chemically equivalent. The resonance position for C_{60} is in excellent accord with similar carbons¹⁹ in azulene (140.2 ppm), fluorene (141.6 and 143.2 ppm), and 3,5,8-trimethylaceptylene (146.8 ppm); this is consistent with the soccer ball structure for C_{60} (Figure 1).

The 1D ^{13}C NMR spectrum for C_{70} , shown in the upper trace of Figure 1, consists of five lines with intensities in the ratio 10:20:10:20:10, as reported by Taylor et al.,⁸ which strongly supports the D_{5h} C_{70} structure²¹ shown in Figure 1. This structure has five chemically distinct kinds of carbon atoms and is similar to the C_{60} structure with the insertion of 10 carbons forming a belt around the molecule. Characterization of the bonding of C_{70} is important for understanding its structure, and assignment of

the NMR lines is critical for their interpretation. An assignment of the resonances of C_{70} was proposed by Taylor et al.,⁸ based on model compounds and relative strain in the molecule. However, unequivocal experimental assignment of the lines is clearly desirable.

In this communication we show that it is possible to map the bonding connectivities of C_{70} and obtain definitive resonance assignments by the 2D "INADEQUATE" NMR experiment.²²⁻²⁵ This experiment correlates the ^{13}C NMR line of a carbon to that of its bonded neighbor by excitation of a shared double quantum coherence via scalar J coupling, thus yielding the carbon connectivity map of the molecule. C_{70} samples enriched to $\sim 20\%$ ^{13}C were used to increase the probability of adjacent ^{13}C atoms, reducing the data acquisition time to a feasible 4 days despite low solubility. The enriched clusters were prepared by using cored carbon rods loaded with amorphous ^{13}C powder (Cambridge Isotopes) in an arc fullerene generator.^{6,12,26}

The 2D INADEQUATE NMR spectrum of C_{70} is shown in Figure 1. For this experiment, two bonded carbons share a double quantum frequency in the vertical dimension, and peaks occur at the two respective chemical shifts in the horizontal dimension, allowing the correlation to be made. In addition, each peak will be split into a doublet by the relevant $^1J_{\text{CC}}$ coupling constant. The D_{5h} structure of C_{70} suggests a linear connectivity of the five carbon types, with the polar carbons (labeled a) representing one end of the connectivity and the belt carbons (e) representing the other. The 2D spectrum reveals the four connectivities, showing a single string of connected resonances, with respective intensities 10:10:20:20:10, solidly supporting the D_{5h} structure. The crucial connectivity is obtained between the two intensity 10 lines at 150.8 ppm and 147.8 ppm, forcing the assignment of the line at 150.8 ppm to the polar end cap carbon a, and hence the remaining assignments. We note that the resonances correlating a to b are the least intense, as only one out of the three bonds of an end cap carbon a connects to a carbon b. In contrast, the belt carbons e at 130.8 ppm are each bonded to two type-d carbons at 144.4 ppm, giving cross peaks twice as intense as those revealing the a-b connectivity. The small separation between resonances b and c gives rise to second-order effects in the cross peaks, reducing the outer line of each multiplet.²⁷ These results confirm the assignments of ref 8.

Taylor et al.⁸ noted that the C_{70} chemical shifts indicated torsional strain. Belt carbon e resonating at 130.8 ppm can be contrasted to similar carbons in benzo[a]pyrene (125.5 and 123.8 ppm);²⁸ the downfield position of e is consistent with torsional strain (e.g., the bridgehead carbons in paracyclophane¹⁹ resonate at 140.4 ppm). However, while carbon a has a similar structural environment to those in C_{60} , it resonates 7 ppm further downfield. The origin of this relative shift is not clear, but may be due to differences in ring currents or aromaticity between the two molecules.^{29,30}

One-bond carbon-carbon coupling constants ($^1J_{\text{CC}}$) in polycyclic aromatic compounds generally range from 53 to 63 Hz.³¹ It has been concluded that the size of the coupling is related to the s character of the bond, and a linear correlation between $^1J_{\text{CC}}$ and decreasing bond lengths or increasing π -bond orders has been

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suggested by several groups for polycyclic aromatic compounds.^{28,31-34} A value of $^1J_{9,10}$ of 45 Hz for azulene was interpreted as evidence for this bond being weak.³⁵ For C₇₀, the 2D spectrum gives the $^1J_{CC}$ values: $^1J_{a,b} = 68$, $^1J_{b,c} = 55$, $^1J_{c,d} = 55$, and $^1J_{d,e} = 62$ Hz. These values indicate that the four bonds have substantial s character and π -bond order. Bonds d-e and a-b fuse six-membered rings and may be compared with $^1J_{9,10}$ in 1-methyl- and 2-methylnaphthalene at 52 and 53 Hz, respectively.³³ In analogy with cyclopropane derivatives,^{36,37} the larger value of $^1J_{a,b}$ may arise from both carbons in bond a-b belonging to five-membered rings, whose bonds have greater p character due to smaller internal angles. This should increase the s character of the a-b bond and hence the coupling constant; this effect should be less for bond d-e, as this bond has only carbon d in a five-membered ring. We note that the large values for $^1J_{CC}$ we report are evidence against proposed structures for fullerenes involving three-membered rings,³⁸ as by analogy with cyclopropane derivatives^{36,37} these rings would be expected to have markedly small coupling constants.

The 2D NMR spectrum of C₇₀ yields bonding topology, coupling constants, and a definitive assignment of the ¹³C NMR spectrum. The bonding topology and coupling constants solidly support the "rugby ball" *D*_{5h} structure for this molecule. The resonance assignments confirm those previously proposed.⁸ The $^1J_{CC}$ values are relevant to investigations of reactivity and bonding in fullerenes.

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Evidence from EXAFS for a Copper Cluster in the Metalloregulatory Protein CUP2 from Yeast

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Expression of yeast metallothionein, which binds copper specifically, is regulated by the protein CUP2 (also known as ACE1).^{1,2} CUP2 itself is activated for binding to DNA by

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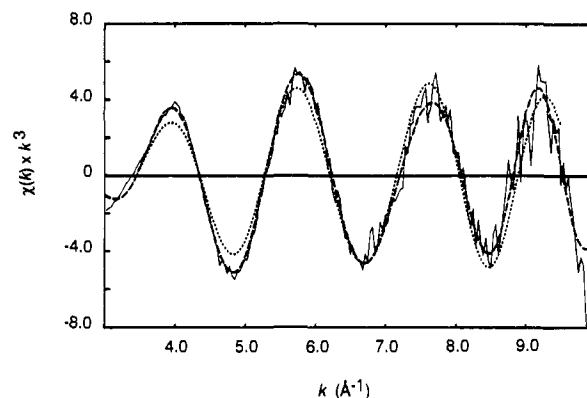


Figure 1. EXAFS data for CUP2. The solid line is the raw data. The dashed line is the data obtained by Fourier transforming the data into *R* space, applying a filter from 0.80 to 3.35 Å, and back-transforming. The dotted line is the calculated EXAFS from two-shell fits described in the text and reported in Table I.

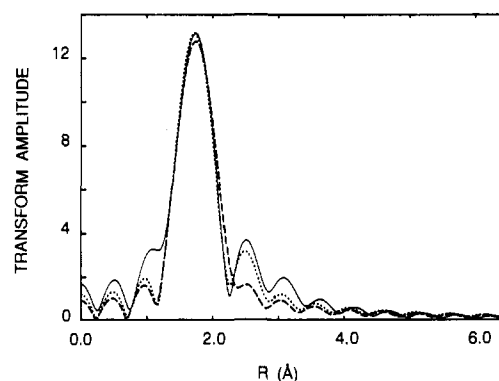


Figure 2. Comparison of the Fourier transform on filtered EXAFS data ($R = 0.80$ – 3.35 Å, k range of 3.0 – 10.0 Å⁻¹) from CUP2 (solid line) with transforms of a one-shell fit containing S (dashed line) and a two-shell fit containing S and Cu (dotted line). Notice the excellent agreement between the fit and data for the first shell in both cases. However, while the second peak is not reproduced by a single S shell, it is well reproduced with the presence of a second shell of Cu.

copper(I).³ Yeast metallothionein contains a cluster of eight copper(I) ions bridged by thiolate ligands that are likely provided by the 12 cysteines of the protein.⁴ How copper is bound to CUP2 is unknown, however. Since stimulation by copper(I) of CUP2 binding to DNA is a cooperative process,⁵ and the DNA binding domain of CUP2 contains 12 cysteines,^{3,6} the presence of a copper cluster in CUP2 is also likely. Here we report that Cu K-edge extended X-ray absorption fine structure (EXAFS) gives strong evidence that the coppers bound to CUP2 are sulfur-coordinated and in close proximity to each other, most likely bridged by thiolate sulfurs. The Cu K-edge X-ray absorption edge structure demonstrates that the coppers in CUP2 are in the +1 oxidation state and furthermore indicates that their electronic environment is closest to 3-fold coordination.

Cu K-edge X-ray absorption spectra were collected at the Stanford Synchrotron Radiation Laboratory on wiggler beam line 4-2 (unfocused) under dedicated ring conditions (3.0 GeV, 70–90 mA) using a Si(220) double-crystal monochromator. Protein⁷

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