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 C_{70}, 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 C_{70} yields bonding topology, coupling constants, and a definitive assignment of the ^{13}C 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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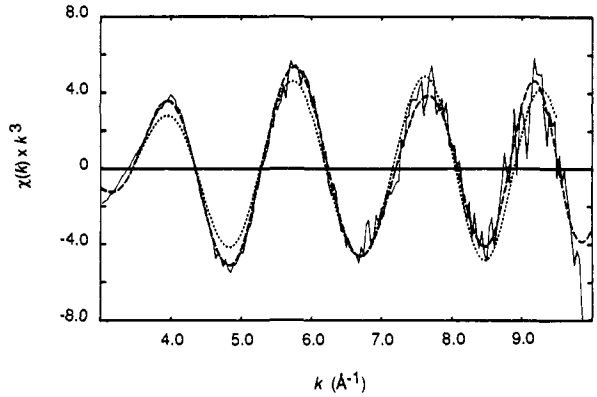

Figure 1. EXAFS data for CUP2. The solid line is the raw data. The dashed line is the data obtained by Fourier transforming the data into R space, applying a filter from 0.80 to 3.35 Å, and back-transforming. The dotted line is the calculated EXAFS from two-shell fits described in the text and reported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

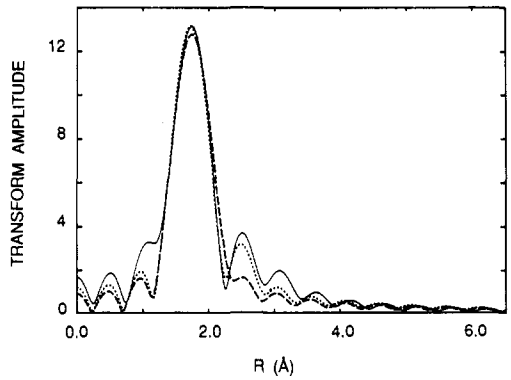

Figure 2. Comparison of the Fourier transform on filtered EXAFS data (R = 0.80-3.35 Å, k range of 3.0-10.0 Å^{-1}) from CUP2 (solid line) with transforms of a one-shell fit containing S (dashed line) and a two-shell fit containing S and Cu (dotted line). Notice the excellent agreement between the fit 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.

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 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. Protein[7]

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Table I. Summary of EXAFS Curve-Fitting Results[a]

Fourier region	filter region,[b] Å	inner S shell		outer Cu shell		outer S shell		
		N	R, Å	N	R, Å	N	R, Å	F[c]
first shell	0.90–2.35	2.34	2.27					0.72
second shell	2.10–3.25			0.80	2.78			0.45
second shell	2.10–3.25			0.70	2.80	0.22	2.62	0.43
wide shell	0.80–3.35	2.39	2.27					0.89
wide shell	0.80–3.35	2.44	2.27	0.66	2.75			0.75
wide shell	0.80–3.35	2.26	2.26	2.66	2.82	2.19	2.84	0.61

[a] Errors in distances (±0.03 Å) and coordination number (±25%) are estimated from variance of fitting results between true values from models of known structure.[9c] [b] Fourier transform filter including a 0.1-width Gaussian window. [c] F is a goodness of fit criterion defined by $F = [\sum k^6(\text{data} - \text{fit})^2/(\text{no. of points})]^{1/2}$.

data were collected at 10 K as Ni-filtered fluorescence excitation spectra monitored by an argon-filled ionization chamber.[8] Data reduction and analysis were performed as previously reported.[9,10] Curve-fitting techniques were applied by using empirical phase and amplitude parameters for various Cu–X scattering pairs from the following models:[11] Cu–S, $Cu[SC(NHC_2H_5)_2]_3 \cdot 0.5SO_4$;[12] Cu–Cu, $Cu_2(C_2H_3CO_2)_2$;[13] Cu–N, $Cu(C_4H_6N_2)_4[ClO_4]$.[14]

The EXAFS ($*k^3$) spectra are shown in Figure 1, and the Fourier transform taken over the k range of 3.0–10.0 Å^{-1} is shown in Figure 2. Curve fitting was performed on filtered first- and second-shell contributions as well as on a wide-shell filter, as indicated. All fits were done with the range k = 3.5–9.5 Å^{-1}. Bond distance and coordination values were allowed to vary during fitting of the protein data.[15] The resulting values are listed in Table I.

The first shell could not be adequately fit with a single low-Z shell, but could be explained sufficiently by a single shell of S atoms. All fits consistently show that the first coordination shell is composed of two to three S at approximately 2.26 Å.

The Fourier transform (Figure 2) shows a second peak ($r + \Delta \approx 2.5$ Å) after the first-shell transition, which is absent in the transform of the fitted first-shell Cu–S wave. Second-shell and wide-shell curve fits consistently showed this to be due to the presence of Cu–Cu interactions at a distance of about 2.75 Å. Fits to this second shell with only a S wave were poor, as were wide-shell fits with two S waves (at 2.26 and 2.75 Å). Attempts were made to establish if the second-shell peak also contains contribution of longer distance Cu–S backscattering. Due to the limited k range of the data (caused by a severe, nonremovable monochromator glitch at 10.2 Å^{-1}), there was high correlation between the Cu and S parameters, in particular for the amplitudes, and the improvement of the fits upon addition of a S wave in the second shell were not significant. The fits thus show a second shell with approximately 0.7–0.8 Cu atom at 2.75–2.78 Å. The determination of the coordination number is less accurate due to the limited k range. Fits were also done to the raw data. Although, as expected, fit values were worse, there were no significant changes in the results compared with those in Table I.

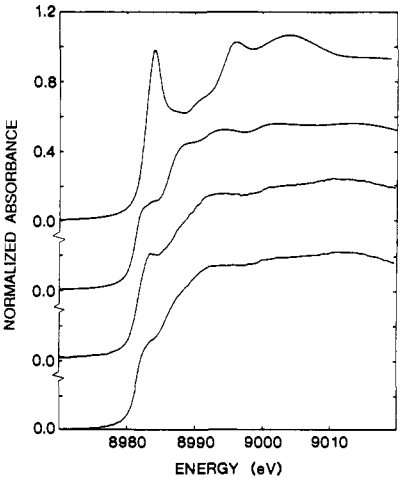

Figure 3. Comparison of the X-ray absorption Cu K-edge spectra. From top to bottom, a two-coordinate linear Cu(I) complex,[18] a three-coordinate Cu_4S_6 model cluster compound,[17] a Cu-metallothionein protein,[16] and the CUP2 protein. Notice the strong similarities in the features of the lower three edges and the distinct difference between the CUP2 and the two-coordinate Cu(I) complex edge.

The Cu K X-ray absorption edge spectrum of CUP2 is shown in Figure 3. Also included are edge spectra of *Neurospora crassa* metallothionein,[16] of a Cu_4S_6 cubane-type cluster, which contains Cu in a distorted-trigonal coordination,[17] and of $[Cu_2(EDTB)](ClO_4)_2$, a two-coordinate linear Cu(I) complex.[18] Each spectrum shows a transition on the rising portion of the edge at 8984 eV. This has been assigned to a 1s → 4p based electronic transition which is very sensitive to the coordination geometry of the Cu(I).[19] The transition is most pronounced when the Cu(I) environment is two-coordinate or T-shaped three-coordinate,[20] and it is absent in a four-coordinate tetrahedral geometry.[21] The edge feature of the protein shows the closest resemblance to the Cu_4S_6 cluster and thus to a trigonal three-coordinate environment. The

(7) CUP2 was expressed and purified as described (see ref 26), with the following exceptions: Buffer E contained 0.05% Nonidet P-40 and 20% glycerol. Following the ammonium sulfate fractionation, the pellet was dialyzed against buffer E containing 0.015 M KCl and passed over a DEAE-Sephacel column. The flow through was applied to a heparin agarose column as described, and the 0.6 M KCl fraction was dialyzed against buffer E (0.15 M KCl) and then run over a DNA cellulose column. The 0.6 M KCl peak was dialyzed against buffer E (0.15 M KCl) and concentrated (Amicon centricon) to 8.0 mg/mL. The number of Cu atoms in the protein was determined, using the EXAFS sample, by combining the results of atomic absorption measurement of Cu and protein determination by acid hydrolysis followed by HPLC in which the valine, proline, and glutamic acid contents were analyzed. The number determined was 5.72 ± 0.49 Cu/CUP2.

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CUP2 spectrum also closely resembles that of the Cu(I) cluster in *N. crassa* metallothionein as well as those of several other metallothioneins,[22-24] most notably the *Saccharomyces cerevisiae* yeast metallothionein itself.[4] The edge energy position, along with the absence of a 1s → 3d transition, further establishes that it is indeed a Cu(I), and not a Cu(II), cluster.[20]

Taken together, the results thus suggest that CUP2 contains Cu atoms arranged in a cluster bridged by S atoms, presumably donated by protein cysteines. The Cu-S distance (2.26 Å) and coordination numbers determined from EXAFS are consistent with the electronic structure indicated by the edge transition. It is furthermore consistent with findings from Cu-S model clusters, where two-coordinate Cu-S distances average 2.16-2.17 Å, trigonal coordination 2.25-2.28 Å, and tetragonal coordination 2.3-2.42 Å.[17,25] CUP2 thus joins the class of Cu-S cluster-containing proteins, established through EXAFS in the metallothioneins of *S. cerevisiae* yeast,[4] *N. crassa* fungus,[16] β-domain of rat liver,[22] a mixed Cu:Zn metallothionein from pig liver,[23] and possibly also canine liver[24] (although in this study, the Cu-S distance was 2.27 Å but the coordination number four).

It is thus remarkable that the CUP2 copper cluster seems to resemble that of the very yeast metallothionein protein[4] that it regulates. What is the functional advantage for CUP2 to be activated by formation of a copper cluster, instead of a simple mononuclear copper center? There are several possibilities. A small amount of copper is necessary for viability of yeast, but high concentrations are deleterious. Induction of metallothionein synthesis could be controlled to a fine degree of cooperative construction of a copper cluster in CUP2 . Thiolate-bridged clusters are characteristic of copper(I) chemistry and offer a way to enforce specificity for copper in metallothionein activation. Effective DNA binding might require more than one structural domain to be formed in a protein. Although the zinc finger is a DNA-binding domain formed around one metal ion, all zinc finger proteins that have been demonstrated to bind to DNA contain more than one finger, which likely act cooperatively. Support for this hypothesis is provided by the analysis of a variant CUP2 protein in which a single cysteine residue was substituted by a tyrosine.[26] This protein, which binds less Cu than the wild-type protein, is capable of interacting with only a part of the DNA sequence recognized by the wild-type protein. These findings were interpreted to suggest that the DNA-binding domain of CUP2 contains at least two functional units involved in sequence recognition.[26] Another possibility is that the metalloregulatory protein CUP2 is evolutionarily related to the protein whose synthesis it controls. The structural similarity of the copper(I) clusters in yeast metallothionein[4] and CUP2, as we have demonstrated in this paper, makes this an attractive prospect.

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"Cation-like" Homogeneous Olefin Polymerization Catalysts Based upon Zirconocene Alkyls and Tris(pentafluorophenyl)borane

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Lewis acid cocatalysts such as aluminum alkyls and methylalumoxane are ubiquitous components of several important classes of highly active group 4 alkyl-based (e.g., titanocene, zirconocene) olefin polymerization catalysts.[1,2] Although electrodialysis,[3] chemical trapping,[4] model synthetic,[5-7] XPS,[8] surface chemical,[9] NMR spectroscopic,[10] and theoretical studies[11] argue indirectly that the role of the Lewis acid is to promote (e.g., by alkide abstraction) the formation of unsaturated "cation-like" active centers (e.g., Cp_2MR^+), the exact structural nature of the catalyst-cocatalyst interaction has remained elusive. We report here the use of the strong Lewis acid tris(pentafluorophenyl)borane[12] for the first synthesis of stoichiometrically precise, isolable/crystallographically characterizable, highly active "cation-like" zirconocene polymerization catalysts.

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