influenced by the number of type of substituent atoms in the side chain. However, these isotropic shifts, which result primarily from Fermi hyperfine contact interactions,[24] are not readily interpreted in terms of currently developed theory. Further work may determine the relative magnitudes of the steric and electronic contributions to the isotropic shifts.

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Supplementary Material Available: A listing of anisotropic thermal parameters and a stereoview and packing diagram for *α-cis*-[Cr(edda)(gly)]·2H$_2$O (2 pages); a listing of observed and calculated structure factors for the same compound (7 pages). Ordering information is given on any current masthead page.

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Structural Study of the Cu Sites in Metallothionein from *Neurospora crassa*

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The structure of the Cu centers in the low-molecular-weight metallothionein (MT) from *Neurospora crassa* has been investigated by X-ray absorption edge and EXAFS spectroscopy. Analysis of the EXAFS data by curve-fitting procedures yields results most consistent with an average Cu environment of 3–4 S atoms at 2.20 Å, and 1–2 Cu atoms at 2.71 Å. Comparison of the Cu–MT X-ray absorption edge with that of a structurally characterized Cu$_4$S$_6$ inorganic cluster reveals distinct similarities, suggesting significant congruence between the protein and the compact cluster structure found in the model. When they are taken together, the edge and the EXAFS data of Cu–MT are most consistent with three- or four-coordinate geometry around Cu and do not support the previously proposed two-coordinate linear-chain structure.

Introduction

Metallothioneins (MT) are low-molecular-weight, cysteine-rich proteins, binding high amounts of metal ions such as Zn, Cd, and/or Cu.[1] The mammalian proteins are characterized by a single polypeptide chain of 61 amino acids, with a total of 20 cysteine residues. On the basis of recent chemical, spectroscopic, and structural studies, mammalian MT's are thought to bind IIB (12)[23] metal ions in the form of two clusters with each ion tetrahedrally coordinated to four cysteinyl residues.[2–5] In contrast to the MT's of higher eucaryotic organisms that bind different metal ions, fungal MT's contain exclusively Cu.[6,7] *Neurospora* Cu–MT consists of only 25 amino acids and binds 6 Cu ions to 7 cysteinyl residues.[8] A recent spectroscopic study has indicated that the metal ions are coordinated in the form of a single Cu(I)–thiolate cluster.[9] To obtain further insight into the structure of this unique Cu(I) complex, an X-ray absorption study was undertaken.

In this paper, the edge, near-edge, and extended X-ray absorption fine structure (EXAFS) spectra of *Neurospora* Cu MT are presented and compared to those of a Cu$_4$S$_6$ cluster complex. The data are indicative of a compact and rigid cluster structure for *Neurospora* Cu MT.

Experimental Section

A solution of *Neurospora crassa* metallothionein (Cu–MT) was prepared in an inert-atmosphere glovebox by dissolving $\sim$2 mg of a lyophilized powder of the protein[8] in 0.5 mL of degassed 60 mM phosphate buffer (pH 7.2). The resulting solution was $\sim$10 mM in Cu. A 250-mL sample of the solution was loaded into an anaerobic, Mylar-lined cell and then frozen in dry ice.

Cu K-edge X-ray absorption spectra were collected at the Stanford Synchrotron Radiation Laboratory under dedicated ring conditions (3.5-GeV electron energy, 30–60-mA current) with use of a Si(220) two-crystal monochromator. Data were measured on the frozen solution, kept at −45 °C by a thermoelectric cooling module. EPR spectra taken before and after X-ray irradiation to monitor any sample degradation did not reveal any significant differences, each giving a Cu(II) signal consistent with $\sim$0.7% Cu(II) impurity in the Cu MT solution.

The Cu K-edge absorption was monitored as the Kα excitation fluorescence signal detected by six NaI(Tl) scintillation detectors. Sixteen data scans, collected from 300 eV below to 600 eV above the absorption edge, were averaged to give the reported spectra. The spectra were energy-calibrated relative to the first inflection point (8980.3 eV) of a Cu-foil spectrum collected simultaneously.[10a] Established methods of data averaging, background removal, Fourier transformation, and curve fitting were used, which have been described previously in detail.[10] The edge spectrum presented has been normalized by fitting the smooth postedge region (9050–9650 eV) with a linear function and scaling the data to give a value of 1.0 for this smooth background absorption extrapolated to 9000 eV.

Results and Discussion

EXAFS Results. The EXAFS data are shown in Figure 1 and the Fourier transform of these data taken over the k range of 3.5–12.5 Å^{-1} in Figure 2. The Fourier transform is characterized by a major peak at 1.75 Å and a peak on the high-R side of this main peak at 2.28 Å that is smaller in amplitude. Two peaks at higher R (3–4 Å) may also be above the noise level of the data. The peak positions in the Fourier transforms are shifted to lower R by an average of 0.35–0.4 Å from the true interatomic distance as a result of the pairwise atom phase shift. In order to obtain more accurate distances and coordination numbers, the EXAFS data were fit with use of S and Cu parameters obtained from

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Table I. Summary of EXAFS Curve-Fitting Results

		refined parameters[a]						
		inner S shell		outer S shell		outer Cu shell		
Fourier region	filter region, Å[b]	*N*	*R*, Å	*N*	*R*, Å	*N*	*R*, Å	*F*[c]
first shell[d]	1.31–2.10	3.1 S1	2.20					0.20
first shell	1.31–2.10	1.8 S	2.23					0.37
second shell	2.09–2.52			1.0 S1	2.81			0.23
second shell	2.09–2.52					0.6 Cu	2.69	0.11
second shell	2.09–2.52			1.2 S1	2.73	0.8 Cu	2.69	0.05
two shell	1.31–2.48	3.6 S1	2.20					0.64
two shell	1.31–2.48	3.7 S1	2.20			0.7 Cu	2.65	0.39
two shell[e]	1.31–2.48	3.0 S1	2.20	2.2 S1	2.72	1.6 Cu	2.71	0.20

[a] Errors in distances (±0.02 Å) and coordination number (±25%) are estimated by comparison of values calculated from EXAFS and compared with crystal structure results for a number of copper complexes. [b] Fourier transform filter including a 0.1 width Gaussian window. [c] *F* is a goodness of fit criterion defined by $F : [\sum k^6(\text{data-fit})^2/(\text{no. of points})]^{1/2}$. [d] Visual comparison for this fit with filtered-FT data for this region is shown in Figure 3a. [e] Visual comparison for this fit with filtered-FT data for this region is shown in Figure 3b.

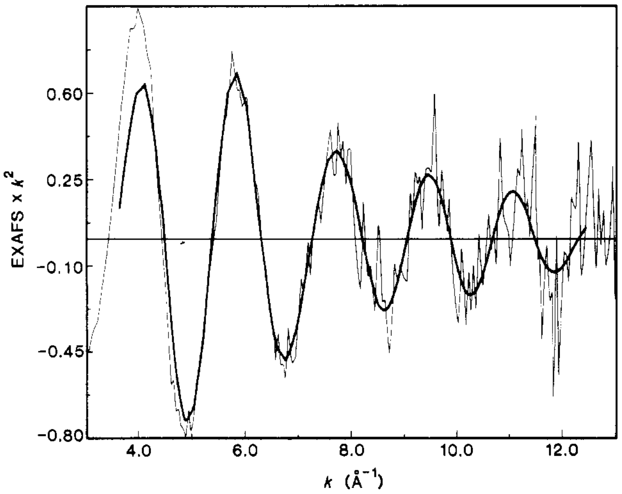

Figure 1. EXAFS data for Cu–MT. The light line is the raw data. The dark line is the data obtained by Fourier transforming the data into *R* space, applying a filter from 1.31 to 2.48 Å, and back-transforming. These filtered data were used for the two-shell fits described in the text and reported in Table I.

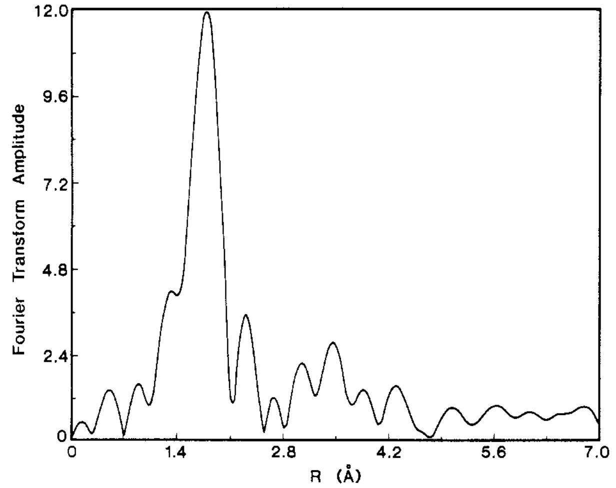

Figure 2. Fourier transform of the unfiltered EXAFS data shown in Figure 1. The data were transformed over the *k* range of 3.5–12.5 Å^{-1}.

model compounds of known structure. Two different sets of Cu–S parameters were investigated: S1 parameters from a Cu(I) bis(2,5-dithiohexane) model and S2 parameter from a Cu(II) bis(dithiocarbamate) model. The Cu–Cu parameters were obtained from Cu(II) acetate dimer. A summary of the results of EXAFS curve fitting is given in Table I.

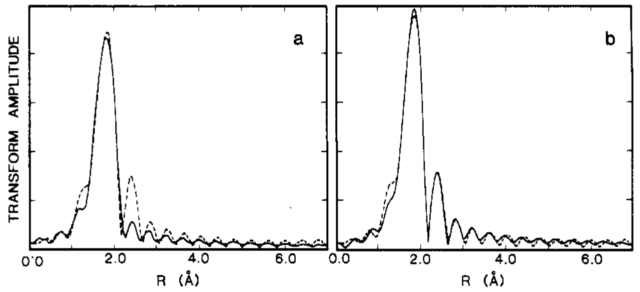

Figure 3. (a) Comparison of the Fourier transform of filtered EXAFS data (*R* = 1.31–2.48 Å) from Cu–MT (dashed line) with transform of the one-shell fit that contained 3 sufur atoms at 2.20 Å (solid line). Notice the excellent agreement between the fit and the data for the first shell but the lack of reproduction for the peak to higher *R*. (b) Comparison similar to that in (a) but with wider filter (*R* = 1.31–2.48 Å). In this case, the fit included three shells of atoms (3 sulfur atoms at 2.20 Å, 1.6 Cu atoms at 2.71 Å and 2.2 sulfur atoms at 2.72 Å). The improvement in the agreement for the higher *R* feature is dramatic.

First-Shell Fits. With use of a narrow filter (1.31–2.1 Å), the major peak in the Fourier transform was isolated and back-transformed to give EXAFS data that were fit with a single shell of S atoms. The refined distances and amplitudes for the two sets of S parameters are 3.5 atoms at 2.20 Å with use of the S1 parameters or 2.0 atoms at 2.23 Å with use of the S2 parameters. A comparison of the fits from these two different S parameter sets showed that the S1 (Cu(I)) parameters give a slightly better fit to the phase of the filtered data. The phase error resulting from using the S2 (Cu(II)) parameters could be corrected by allowing E_0 (the $k = 0$ energy) to float during the fitting procedure, giving a refined ΔE_0 value of −6.4 eV, although optimization of E_0 did not produce any significant changes in the refined *R* and *N* values.

In a study of S1 and S2 fits to a series of Cu(I) and Cu(II) models, the EXAFS spectra from single-shell models were better fit with Cu–S parameters of the same Cu model oxidation state. The phase error in the fit with the other oxidation state S parameters was correctable by optimizing E_0, which shifted negatively for Cu(I) models fit with S2 parameters and positively for Cu(II) models fit with S1 parameters. In all single-ligand models, shifting E_0 had a negligible effect on the refined distances and amplitudes. In all model studies, the S1 parameters gave more accurate refined amplitudes (within 15% of the known value), while the refined distances were slightly low (0.02–0.04 Å).

In models with mixed-ligand shells, smaller E_0 shifts produced measurable changes in the refined amplitudes in a somewhat unpredictable fashion and resulted in an insignificant change in the quality of the fit. Comparison of the results of the first-shell analysis of Cu–MT with the model study is consistent with the major peak in the Fourier transform being attributable predominantly to a single S shell.

Second-Shell Fits. A Fourier transform of an inner S shell including three S1 atoms at 2.20 Å shows essentially no contribution to the FT amplitude in the region of the 2.28-Å peak in the experimental data as illustrated in Figure 3a. The EXAFS spectrum of this second peak isolated with use of a narrow Fourier filter (2.09–2.52 Å) was first fit with one atom in the shell. The fit is poor with only S. Replacing S by Cu results in a two-fold lower fit function value (giving a 2.69-Å Cu–Cu distance) and a significantly improved agreement over the entire *k* range. The function value is further lowered by a factor of 2 on including both Cu–Cu and Cu–S shells. The S distance in the Cu–S and Cu–Cu fit is, however, 0.09 Å shorter than with Cu–S alone (whereas the Cu–Cu distances do not change). This magnitude of change in frequency, together with observation of the fits compared to the data, raises some question as to the actual presence of the long-distance Cu–S shell. It could be the case that the Cu–S shell is around 2.7 Å, compensating for small inaccuracies in the Cu–S parameters.

Two-Shell and Unfiltered Data Fits. Using a wide Fourier filter (1.31–2.48 Å) to include the contribution of both Fourier transform peaks, the filtered EXAFS spectra were fit with an inner S shell and an outer shell consisting of Cu and/or S. Two-shell fits with either Cu or S in the outer shell gave fits that matched well the observed phase of the data but that had amplitude errors, particularly at high *k*. The fit with an outer Cu shell alone was somewhat better than the outer S shell fit over the entire *k* range, and the Fourier transform comparison of the fit with the filtered data revealed that a Cu in the outer shell was required to reproduce the observed amplitude of the high-*R*-side peak. A three-shell fit of both Fourier transform peaks including Cu and S in the outer shell resulted in a noticeably improved fit to the filtered data (Figure 3b) and its Fourier transform with an insignificant change in the refined inner shell. This fit resulted in refined parameters of: 3.0 S at 2.20 Å, 1.6 Cu at 2.71 Å, and 2.2 S at 2.72 Å. It is unusual that a S shell at a distance as large as 2.7 Å would produce a noticeable change in the fitted EXAFS; however, as with the filtered second-shell fits described above, the inclusion of the second S shell resulted in almost a factor of 2 improvement in the function value, *F* (see Table I). This magnitude of improvement does in fact appear to be real and suggests that the longer S shell is present, though as expected over this data range there is some correlation in the three-wave fits between the longer Cu–S and Cu–Cu waves, particularly in amplitude. In any event, the fitting results demonstrate a compact and rigid structure for the Cu centers. Attempts to include low-*Z* atoms (O, N) in either the inner or outer shell did not produce an improvement in the fit and/or a consistent set of refined distances and positive amplitudes.

A number of curve fits were also carried out on the full range of unfiltered data. These were done to examine the effects of noise on the results reached from the filtered fits (described above) and to see if the higher *R* features in the Fourier transform could be attributed to any significant molecular features. Fits with Cu–S and Cu–Cu in the first two shells gave results that were not significantly different from the filtered fits reported in Table I (with, of course, higher overall function values). Fits including longer distances shells of Cu–C (which could arise from the cysteine ligation) in some cases gave reasonable distances and number of carbons but resulted in higher correlation and more convergence problems in the fitting procedures. Given the range of data available, it did not seem worthwhile to pursue the four- or five-shell fits further as it appeared that statistically significant results could not be obtained.

Discussion of the Structure. The average Cu environment most consistent with the above EXAFS data analysis results in 3–4 S atoms at 2.20 Å and 1–2 Cu atoms at 2.71 Å. It also appears that there may be 2 S at 2.72 Å. Cu–thionein has a Cu:S ratio of 6:7, with S ligation through cysteine groups.[8] The only type of structure that can account for three- or four-coordinate Cu centers is a Cu_6S_7 cluster. A linear-chain model previously proposed[5] is clearly not consistent with the EXAFS results. Cu(I) is known to form a number of stable thiolate cluster compounds with a range of Cu:S stoichiometries of Cu_4S_6 to Cu_8S_{12}.[11-19] Previous structural studies on mammalian MT's demonstrate,[2-5] and for yeast Cu-thionein[20] provide evidence for, the presence of metal–sulfur clusters in the proteins.

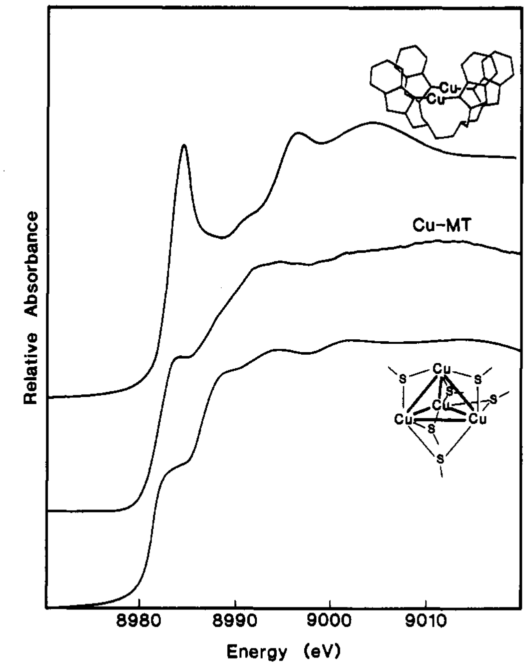

Figure 4. Comparison of the X-ray absorption edge spectra for a two-coordinate linear Cu(I) complex (top), Cu–MT (middle), and a Cu_4S_6 model cluster[12] compound (bottom). The distinct similarity in the features of the lower two edges as well as the intensity of the feature at 8984 eV are only consistent with three- or four-coordinate Cu (see text for discussion).

For comparison, we collected EXAFS data on a Cu_4S_6 cubane-type cluster model (the structure is shown in Figure 4) with Cu–S(av) = 2.29 Å and Cu–Cu(av) = 2.7 Å.[12] These data gave a Fourier transform (not shown) that was very similar to that of Cu–MT with a major peak at 1.80 Å and a second lower amplitude peak at 2.36 Å. EXAFS data filtered from the major peak could be fit with a single S shell (3 S1 at 2.24 Å or 2 S2 at 2.27 Å). As was observed for Cu–MT, an outer Cu shell was required to reproduce the second, higher *R* FT peak. A good fit to the entire EXAFS region including both peaks was obtained with 3 S1 at 2.24 Å and 1 Cu at 2.67 Å. As expected, a second longer Cu–S shell was not required to fit the model complex. The model structure would predict that 3 Cu atoms be refined at 2.7 Å but only 1 Cu in the outer shell is sufficient to reproduce the second FT peak in this model as well as in the Cu–MT data. The low amplitude of the Cu shell can result from several effects, including interference from multiple scatterers in outer shells or from Debye–Waller effects. It is not surprising that the amplitude parameters derived from the first-shell Cu–Cu interactions in the Cu acetate dimer are not completely transferable in fitting the second shell in the Cu_4S_6 cluster or in the Cu–MT cluster.

The results from the model study thus provide further evidence for a similar cluster-type environment in the Cu–MT protein and indicate that the refinement of only one Cu in the outer shell is

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not inconsistent with the expected presence of additional Cu atoms in a compact cluster structure.

Edge and Near-Edge Structure (XANES). The energies and intensities of fine-structure features in the edge and near-edge region of the absorption spectrum (0–50 eV above the threshold energy) are also useful probes of the electronic and geometric environment of the absorbing Cu atom. The expanded edge spectra of Cu thionein, the aforementioned Cu_4S_6 cluster model, and a linear two-coordinate Cu complex are shown in Figure 4. Each of the spectra reveal a feature on the rising portion of the edge at 8984 eV. For the two-coordinate complex, this feature is very intense and much better resolved. Polarized edge studies on a series of Cu(I) and Cu(II) model compounds revealed that this type of feature of the rising portion of the edge (found at 8983–8984 eV for Cu(I) and 8986–8987 eV for Cu(II)) is most readily assigned to a 1s → 4p transition.[21] It is most intense in highly anisotropic ligand fields such as linear and square-planar geometries and is strongly polarized along the direction of minimum ligand interaction. Linear Cu(I) models typified by the complex shown in Figure 4 exhibit 1s → 4p transitions in the 8983–8987-eV region that appear as resolvable edge features more intense than the observed shoulder in the edge of Cu–MT or the three-coordinate Cu_4S_6 model complex.[22] This observation is consistent with three- or four-coordinate geometry around Cu in Cu–MT and a more symmetric Cu environment than that indicated by the previously proposed two-coordinate linear-chain structure. Comparison of the Cu–MT and Cu_4S_6 model edge data reveals similar edge features between the two spectra and provides further evidence for a Cu cluster moiety in Cu–MT. A more quantitative treatment of these effects in Cu(I) and Cu(II) edges for inorganic complexes and proteins will be soon forthcoming.[22]

When they are taken together, these X-ray absorption edge and EXAFS results indicate that the Cu atoms are contained in a compact polynuclear cluster with sulfur (thiolate cysteine) ligation. From EXAFS analysis on solutions, it is not possible to determine geometry, and thus, a detailed structure cannot be proposed. It is worthwhile to note that as the Cu:S ratio approaches 1 in such a compact structure, there will, of necessity, be nonbonded S ligands in closer proximity to Cu atoms if a coordination number of 3–4 is maintained. The alternative for approaching a coordination number of 2 is a more linear, extended structure, the presence of which is shown to be unlikely on the basis of, in particular, the edge results and the EXAFS results described above. Thus, in a compact cluster, the nonbonded contacts could account for the second shell of S atoms possibly present in Cu–MT.

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Registry No. Cu, 7440-50-8; S, 7704-34-9.

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(23) The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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Single-Crystal Optical Spectral Studies of Tetrabutylammonium Bis(maleonitriledithiolato)nickelate(II)

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A detailed optical spectral study of $[(n\text{-Bu})_4N]_2[Ni(mnt)_2]$ carried out in solution and single-crystal media is reported. Polarized optical spectral measurements at 298 K and temperature-dependent spectral measurements with unpolarized light in the range 18–298 K have been carried out. Using the 12 transitions observed in single crystals, we could deconvolute the solution spectrum of this complex to locate all of them. The polarization and allowedness of all the bands have been determined. Vibronic progressions have been resolved on some of the bands at 50 K, where maximum resolution occurred. An unusual temperature dependence of spectral intensities has been observed above and below 50 K and is attributed to changes in the lattice. All the d → d transitions have been identified unlike in the earlier works and the assignments based on the energy level scheme proposed in this work are compared with those of earlier reports. Energy level schemes proposed earlier by WHMO, simple MO, and discrete variational $X\alpha$ calculations and EPR results have been comprehensively compared with the present spectral data of crystals.

Introduction

During the 1960s there had been a great deal of progress on the synthesis, electronic structures, and reaction mechanisms of square-planar metal complexes involving dithiolenes.[1–16] In the systems RC(=S)C(=S)R the tendency of the sulfur atoms to form covalent bonds with metals is uniquely combined with a high electron affinity of the ligand, leading to metal complexes char-

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