relative to water).[82] The initial interaction of ammonia with the catalytic Mn cluster certainly occurs through the NH_3 form. Upon formation of such a $Mn{\cdot}NH_3$ complex, the pK_α of the NH_3 ligand will be reduced due to the electron affinity of the metal Lewis acid.[83] It is possible that NH_3 forms a transient, weakly bound complex with the Mn cluster in the S_1 state, but only a small fraction of the binding sites are occupied by NH_3 due to competition with 55 M H_2O. The electron affinity of the Mn cluster in the S_1 state is apparently insufficient to effect the NH_3 deprotonation necessary to form the amido bridge. However, the Mn cluster undergoes oxidation during the $S_1 \rightarrow S_2$ transition.[84] This oxidation apparently increases the electron affinity of the cluster sufficiently to trigger deprotonation and metal cation substitution of the NH_3 ligand following binding to the Mn cluster in the S_2 state. The resultant amido bridging ligand is tightly bound and only slowly exchangeable, and water is effectively blocked from reentering the substrate binding site.

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Conclusions

We have demonstrated via electron spin-echo envelope modulation experiments that a single NH_3-derived ligand binds to the PSII Mn complex during the $S_1 \rightarrow S_2$ transition of the S-state cycle. The NH_3-derived ligand binding appears to be correlated with the formation of the previously described "altered" multiline signal.[24-31] The ESEEM study has determined the magnetic and electric quadrupole coupling parameters for the ^{14}N isotope of nitrogen coordinated to the Mn complex ($A(^{14}N)$ = 2.29 MHz, e^2qQ = 1.61 MHz, and η = 0.59). The hyperfine result is consistent with that measured for the ^{15}N isotope ($A(^{15}N)$ = 3.22 MHz). The electric quadrupole data are interpreted to favor an amido (NH_2) bridge between metal ions as the molecular identity of the NH_3-derived ligand, and a mechanism for the formation of this bridge involving the deprotonation of NH_3 by the Mn cluster in the S_2 state is discussed.

Acknowledgment. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Division of Biological Energy of the Department of Energy, under Contract DE-AC03-76SF00098, and by a grant from the U.S. Department of Agriculture (85-CRCR-1-1847). J.-L.Z. is supported by the Commissariat â l'Energie Atomique (France).

Relaxation of the Electronic Spin Moment of Copper(II) Macromolecular Complexes in Solution

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Abstract: The magnetic field dependence of the longitudinal relaxation rate ($1/T_1$) of solvent protons (NMRD profile) was measured for solutions of Cu^{2+}-substituted transferrin and native (copper-zinc) superoxide dismutase as a function of solvent viscosity, the latter adjusted with sucrose. Similar measurements were made on demetalated transferrin and reduced superoxide dismutase to obtain the diamagnetic background. Both sets of data are found to be dependent on the viscosity of the solvent, as expected. Subtraction of the two sets of data gives the paramagnetic contribution to the NMRD profiles, which is insensitive to solvent viscosity. This indicates that the correlation time for the magnetic interaction of protons with the paramagnetic Cu^{2+} centers is insensitive to thermal (Brownian) rotational motion of the protein. From this it is argued that the longitudinal relaxation time of the electronic spin moment of the Cu^{2+} ions, including the correlation time for its coupling to the thermal motions of the protein, is also insensitive to the rotational thermal motion of the protein. Possible implications for the mechanism of electron relaxation in copper systems in solution are discussed.

Clarification of the mechanisms of magnetic relaxation of the electronic spin moments of paramagnetic metal ions at room temperature, in both small and macromolecular solute complexes, is difficult. ESR, an ostensibly straightforward and direct spectroscopic approach, has many limitations. In particular, measuring the electronic longitudinal relaxation time can be difficult for many reasons: (1) room-temperature ESR spectra may not be detectable either because the electronic relaxation rate is too fast and the lines are too broad or because large zero-field splittings in manifolds with $S > {}^1/_2$ make transitions unobservable at the usual microwave energies; (2) direct measurements of electronic relaxation are restricted, for technical reasons, to the case of very long relaxation times ($\geq 10^{-8}$ s, normally uncommon at room temperature for metal ions); (3) linewidth analyses are often complicated by broadenings unrelated to longitudinal relaxation. An indirect method, however, has been very successful, particularly for Mn^{2+} and Gd^{3+} (S-state ions with half-filled inner shells): inferences about electronic relaxation mechanisms can be drawn from interpretation of the magnetic field dependence of the nuclear magnetic relaxation rate (NMRD—for Nuclear Magnetic Relaxation Dispersion—profile[2]) of solvent protons.[2-5] In such experiments, the NMRD profile of $1/T_1$, the longitudinal

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relaxation rate of solvent water protons, is measured over a broad range of magnetic field, typically 0.01–50 MHz proton Larmor frequency (corresponding to about 0.0025–1.2 T). It is often the case that the electronic relaxation time τ_s dominates the fluctuations in the interactions between solvent water protons and the paramagnetic ions; τ_s then becomes the correlation time for the interaction and appears in the data as a characteristic inflection in the NMRD profiles. This allows one to compare electronic relaxation in both small and macromolecular solute complexes.[3-5] For S-state ions, the existence of a strong magnetic field dependence of the electronic relaxation plays an important role in determining the form of the observed NMRD profiles; as a consequence, the correlation time τ_v, which characterizes this field dependence, can often be obtained from analysis of these profiles. An important result from analyses of many small and large complexes of Mn^{2+} and Gd^{3+} ions is that, except for characteristic differences in the magnitude of τ_v, electronic relaxation processes for these S-state ions are very similar in small and macromolecular solute complexes, a conclusion from which insight into mechanism can be obtained.

The experimental and theoretical situation is quite different for Cu^{2+} ions, which have one hole in the d shell. It was shown quite early[6] that the magnetic field dependence of the electronic properties of Cu^{2+} ions, though in principle rather complex,[7] in practice can be ignored because of fortuitous near-cancellations of competing effects. These same effects, however, complicated the theory for relaxation of solvent protons, a complication that has now been successfully overcome.[8] As a result, the NMRD profiles of macromolecular complexes of Cu^{2+} ions are particularly tractable for measurement and analysis.[8,9] A significant question that arises in this connection is the role of molecular tumbling, arising from Brownian motion, in mediating energy exchange between the Zeeman energy of the electronic moment and the solvent (the thermal reservoir), a role stressed in the past by many authors.[7] Modulation of the anisotropies of g and A by this rotational motion may be expected to contribute substantially to electronic relaxation for small complexes (as can spin–rotation interactions[10]), but it is unclear to what extent this is important in macromolecular complexes of Cu^{2+} ions. It is also unclear to what extent the rotation of Cu^{2+}–macromolecular complexes enters into the correlation time for the water proton–solute ion interaction. Absence of a field dependence of τ_s contributes to the first uncertainty, whereas the comparable numerical values of the electronic relaxation time and the Brownian orientational relaxation time contribute to the second.

In the present work, we attempt to clarify some of these issues by measuring the paramagnetic contribution to the NMRD profiles of two Cu^{2+}–proteins, at a single temperature as a function of solvent viscosity (adjusted by addition of sucrose), and by comparing the data with the theory. The major result is that τ_r has no effect on the paramagnetic contribution to solvent proton relaxation and, by extension, none on the electronic parameters of the Cu^{2+} ions as well.

Theoretical Background

The paramagnetic contribution to the NMRD profiles of solvent protons contains information about the electronic relaxation mechanisms of the solute paramagnetic ions: the water protons relax at a rate that is influenced by the correlation time τ_c of the magnetic dipolar interaction between the moments of the protons and the unpaired electrons of the paramagnetic ions, which is given by

$$\tau_c^{-1} = \tau_s^{-1} + \tau_r^{-1} + \tau_m^{-1} \qquad (1)$$

where τ_s, the electronic relaxation time, may be either transverse, longitudinal, or a combination of the two;[11] τ_r is the rotational correlation time; τ_m is the lifetime of the ion–water complex in which relaxation occurs. It is known that for small Cu^{2+} complexes (MW < 1000) the correlation time is dominated by τ_r, which is in the range 10^{-10}–10^{-11} s at room temperature. For macromolecular complexes (MW > 10000), $\tau_r \geq 10^{-8}$ s whereas τ_c is typically of the order of a few nanoseconds. Since τ_m for a typically coordinated water molecule is usually 10–100-fold longer,[12] τ_c is therefore determined by τ_s. Moreover, the temperature dependence observed for τ_c is generally not consistent with a dominant τ_m.[4,13] Previous analyses of $1/T_1$ NMRD profiles have yielded $\tau_s = 5.7 \times 10^{-9}$ s for Cu^{2+}-substituted transferrin[9] (Cu_2TRN, MW = 77000), 1.8×10^{-9} s for native bovine erythrocyte superoxide dismutase[8] (Cu_2Zn_2SOD, MW = 31000), 1.9×10^{-9} s for Cu^{2+}-substituted bovine carbonic anhydrase II[14] (CuBCA II, MW = 30000), and 4.0×10^{-9} s for Cu^{2+}-substituted alkaline phosphatase[15] (Cu_2AP, MW = 94000). The corresponding calculated values for τ_r at 25 °C for these proteins, assumed spherical, are 20.0, 8.0, 7.8, and 24.3×10^{-9} s, respectively.

As a consequence of the variation of τ_r, the overall shape of the paramagnetic contribution to the NMRD profiles changes dramatically upon going from small complexes, for which τ_c is dominated by τ_r, to macromolecular complexes, for which τ_s dominates. That this transition occurs for molecular weights not too much greater than those of the small complexes is demonstrated by the fact that the NMRD profiles of small complexes dissolved in viscous solvents, e.g., ethylene glycol somewhat below room temperature, become much like those of macromolecular complexes.[16] Thus, there is good reason to expect that the paramagnetic contribution to the NMRD profiles of Cu^{2+}–proteins should be insensitive to rotation of the macromolecular complexes, but the arguments are inferential and the point has not been demonstrated directly.

For paramagnetic macromolecular systems, the diamagnetic part of the solute protein contributes substantially (particularly at low fields) to the total NMRD profile, as an additive background. This diamagnetic effect has been well documented, and its phenomenology is well understood.[17] The diamagnetic contribution is very sensitive to the molecular weight of the protein, and the temperature and viscosity of the solvent. It can be well represented by[2,17]

$$\frac{1}{T_1} = \frac{1}{T_{1w}} + D + A(\tau_d)\ \mathrm{Re}\left[\frac{1}{1 + (i\nu\tau_d)^{\beta/2}}\right] \qquad (2)$$

where Re means "the real part of", $1/T_{1w}$ is the contribution of the solvent, D and A are the amplitudes of constant and dispersive contributions to the NMRD profile, ν is the magnetic field in units of the Larmor frequency, and β is a parameter that determines the slope of the profile at its inflection point, determined by the condition

$$\nu\tau_d = 1 \qquad (3)$$

τ_d is $2\pi\sqrt{3}\tau_r$, so that the inflection point condition can also be expressed as $\sqrt{3}\omega\tau_r = 1$. τ_r, the rotational relaxation time, can be computed from Stokes' law[17] by

$$\tau_r = 4\pi\eta a^3/(3kT) \qquad (4)$$

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where a is the radius of the protein molecule (assumed spherical), and η is the microscopic viscosity of the solvent. A highly simplified model of diamagnetic relaxation[2,17] would give $\beta = 2$, which produces a Lorentzian NMRD profile and makes A linear in τ_d. The experimental data do not deviate much from this model view.

Experimental Section

Demetalated (apo) protein was prepared as previously reported;[18,19] reconstituted Cu_2Zn_2SOD was prepared by addition of copper at pH 3.8 followed by addition of zinc at pH 5.3.[20] Demetalated human transferrin was purchased from Sigma Chemical Co., St. Louis, MO, and further purified by standard methods.[21] Dicopper transferrin was prepared by adding slightly less than stoichiometric 2:1 copper–protein to a solution of apotransferrin containing 44 mM HCO_3^- at pH 8.3.

The NMRD measurements were taken using a field-cycling relaxometer, as previously described.[22] The paramagnetic contributions to the NMRD profiles were obtained by subtraction of the appropriate diamagnetic background, measured either on solutions of the demetalated protein or the protein with the paramagnetic ions reduced to Cu^+. In each case, the viscosity-dependent solvent contribution is included with that of the diamagnetic protein. For comparison of the diamagnetic profiles with the theory in eq 2–4, a least-squares analysis was performed with the four parameters as adjustable parameters. The fit of the paramagnetic contribution to theory was done as previously described.[8,9] The macroscopic viscosity of the sucrose–water solvent is taken from the literature.[23]

Results

Figure 1A shows the measured NMRD profiles for solutions of (diamagnetic) apoTRN for five solvent viscosities at 25 °C. Figure 1B shows comparable profiles, for four viscosities, for reduced CuSOD. The solid lines through the data points in parts A and B of Figure 1 result from a least-squares comparison of the data with eq 2. For apoTRN, τ_r varies from 10.7 to 21.9 × 10^{-8} s for η/η_0 ranging from 1.0 to 2.2; for reduced SOD, the analogous ranges are from 2.45 to 13.4 × 10^{-8} s for η/η_0 ranging from 1.0 to 5.9. The excellent agreement with the predictions of eq 2 and 4, i.e., the shift in inflection field with viscosity, which gives τ_d, is clear. In addition, from the low field rates, the near-linear dependence of $A(\tau_d)$ on τ_d is also apparent. This is the first time that the explicit dependence of diamagnetic NMRD profiles on viscosity (rather than implicitly through a change of temperature) has been reported. Its importance in the present work is that it confirms that the (microscopic) Brownian rotational motion of the protein molecules is indeed influenced by the presence of sucrose as anticipated from measurements of macroscopic viscosity,[23] so that the paramagnetic contributions to the NMRD profiles can be interpreted with confidence.

The data in Figure 1 indeed demonstrate that the rotational correlation times of the proteins increase linearly with the macroviscosity of the solutions, i.e. that the microviscosity sensed by the proteins according to eq 4 is the same as the macroviscosity. This is a fundamental aspect of the present experiment, in that it provides an independent and reliable estimate of the rotational correlation times of the systems. Even the fact that both sets of curves are interpreted on the basis of eq 2 and 4, by varying only the molecular weight, indicates that proton relaxation is indeed monitoring the molecular rotation.

Parts A and B of Figure 2 show the paramagnetic contribution of the Cu^{2+} macromolecular complexes to the NMRD profiles, derived by subtracting the diamagnetic NMRD profiles (including the solvent contribution) from the measured profiles of the paramagnetic complexes. For Cu_2TRN, this meant subtracting

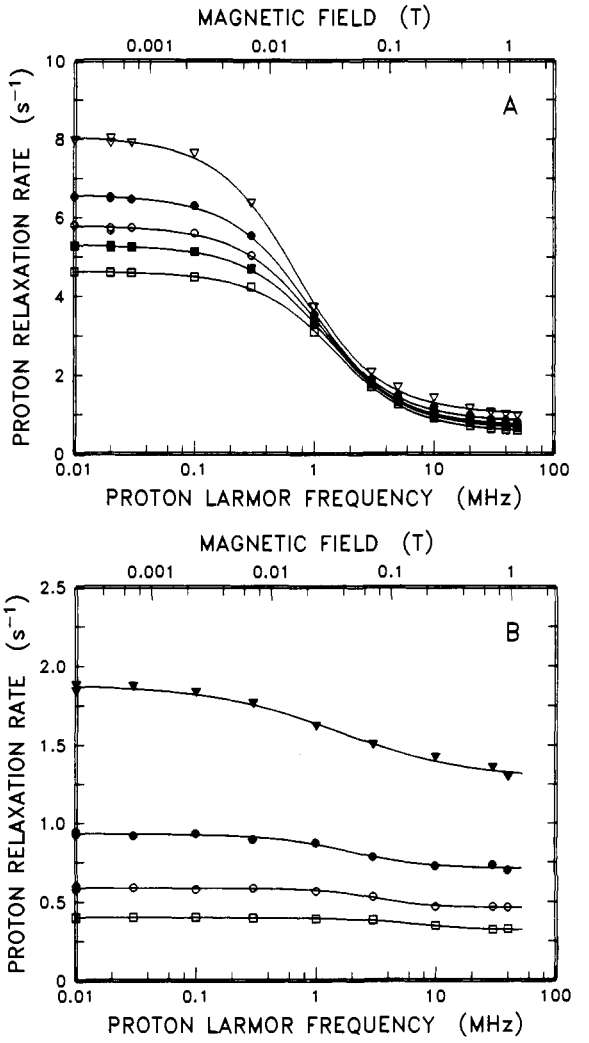

Figure 1. (A) $1/T_1$ NMRD profiles of solvent protons at 25 °C of a 1 mM solution of (diamagnetic) apotransferrin at pH 8.3, 44 mM HCO_3^-, with 0.0 (□), 7.1 (■), 11.4 (○), 17.0 (●), and 22.7 (▽) weight percent sucrose, corresponding to η/η_0 = 1.0, 1.2, 1.4, 1.7, and 2.2, respectively.[23] (The profiles include the viscosity-dependent solvent contribution in each case.) The solid curves through the data are from a least-squares comparison of the data with eq 2. (B) $1/T_1$ NMRD profiles at 25 °C of a 0.44 mM solution of superoxide dismutase reduced with dithionite at pH 5.1, unbuffered, with 0.0 (□), 15.1 (○), 27 (●), and 39.4 (▼) weight percent sucrose, corresponding to η/η_0 = 1.0, 1.6, 2.7, and 5.9, respectively. The solid curves are from a fit to eq 2.

the data shown in Figure 1A, since the same solvent viscosities and protein concentrations were used for the diamagnetic and paramagnetic proteins. For Cu_2Zn_2SOD, appropriate interpolations had to be made from the data in Figure 1B since the set of solution viscosities used was different. The paramagnetic contribution of copper (II) to water proton relaxation is in any case as large as the diamagnetic contribution or more, and therefore its separation can be easily and accurately accomplished. Fitting the theory of relaxation by Cu^{2+} centers[8] to the data of parts A and B of Figure 2 for the extremes of sucrose concentration gives the solid curves shown in the Figures. For TRN, τ_c varies from 6.4 to 6.0 ns for η/η_0 ranging from 1.0 to 2.2, and for SOD, the variation is comparably small, from 2.4 to 2.9 ns for η/η_0 ranging from 1.0 to 5.9.[23] The detailed results are collected in Table I.

Discussion

The small, essentially negligible, changes of τ_c for large variations in solvent viscosity (almost 6-fold for Cu_2Zn_2SOD) rule out any significant contribution of rotational motion of the macromolecular complexes to the correlation time for the Cu^{2+}–proton dipolar interaction. This means that (i) τ_r is not the

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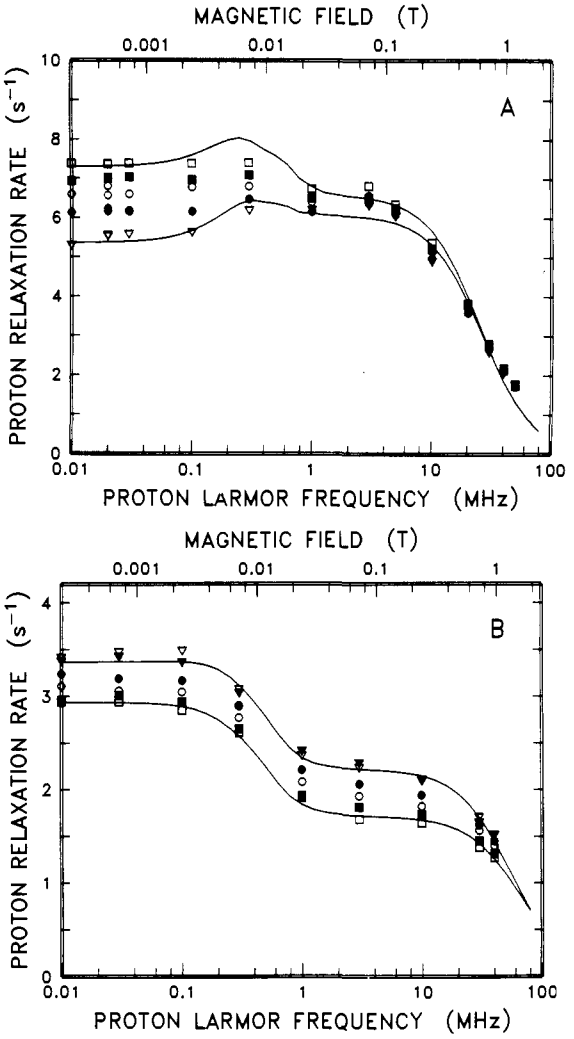

Figure 2. (A) Paramagnetic contributions to the NMRD profiles of dicopper transferrin, 1.8 mM in Cu^{2+}. The values[23] of η/η_0 are 1.0 (□), 1.2 (■), 1.4 (○), 1.7 (●), and 2.2 (▽). The curves are a best fit of the data at the extremes of the viscosity range to the theory[8] of proton relaxation by hyperfine-coupled Cu^{2+} ions. (B) Paramagnetic contributions to the NMRD profiles of Cu_2Zn_2SOD, 0.88 mM in Cu^{2+}. The values[23] of η/η_0 are 1.0 (□), 1.3 (■), 1.9 (○), 2.6 (●), 3.7 (▽), and 5.9 (▼). The curves are a best fit of the data at the extremes of the viscosity range to theory.[8] In all cases, the diamagnetic background was subtracted using data from Figure 1.

dominant correlation time for the Cu^{2+}–proton dipolar interaction; hence, (ii) the electronic relaxation time, τ_s, is the relevant correlation time, and (iii) the electronic relaxation processes (including both the magnitudes of the interactions and their correlation times) do not depend on rotational motions. The latter is the main result of the present work.

Electronic relaxation in Cu^{2+}–proteins is dominated by fluctuations of the hyperfine interaction of the Cu^{2+} ions with the Cu^2 nuclei below $\simeq 1$ MHz and of both the electronic g value and its anisotropy at higher field.[7,10] The theoretical analyses of McConnell[7] and Atkins and Kivelson[10] compute the above modulations to molecular rotation and yield the following equation, which includes spin rotational mechanisms

$$T_{1e}^{-1} = \frac{8\pi^2}{15}\left[\frac{(\Delta g)\mu_B B_0 + (\Delta A)I_z}{\hbar}\right]^2\left[\frac{\tau_c}{1+\omega_e^2\tau_c^2}\right] + \frac{\delta g^2}{9\tau_r} \quad (5)$$

where $\Delta g = g_{\parallel} - g_{\perp}$, B_0 is the external magnetic field, $\Delta A = A_{\parallel} - A_{\perp}$, and $\delta g^2 = (g_{\parallel} - g_e)^2 + 2(g_{\perp} - g_e)^2$, and τ_c is taken equal to τ_r. This equation was derived assuming that A anisotropy be smaller than g anisotropy[7] and therefore, strictly speaking, should not be valid at low fields. Furthermore, the correlation time τ_s obtained from NMRD data is only equal to T_{1e} at high field.

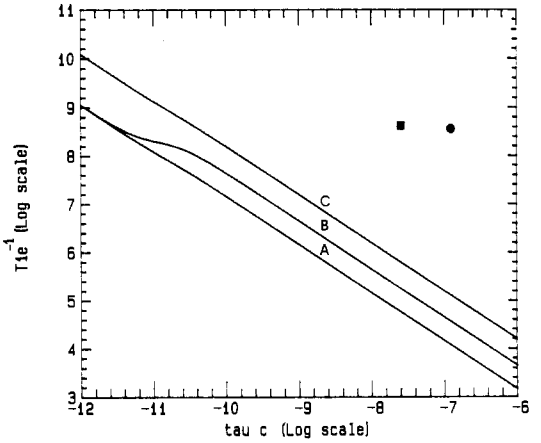

Figure 3. Calculated dependence of the electronic longitudinal relaxation time of copper(II) complexes as a function of τ_c (equal to τ_r) at 0.32 T for three different choices of spin Hamiltonian parameters: (A) Δg = 0.1, $\Delta A = 50 \times 10^{-4}$ cm^{-1}, and $\delta g^2 = 0.01$; (B) $\Delta g = 0.3$, $\Delta A = 200 \times 10^{-4}$ cm^{-1}, and $\delta g^2 = 0.01$; (C) $\Delta g = 0.3$, $\Delta A = 200 \times 10^{-4}$ cm^{-1}, and δg^2 = 0.11. Curves A and C delimitate a range of values where most copper(II) complexes with nitrogen and oxygen donors would fall. The T_{1e}^{-1} values of Cu_2Zn_2SOD from Table I at $\eta/\eta_0 = 1$ (■) and 5.9 (○) are also shown.

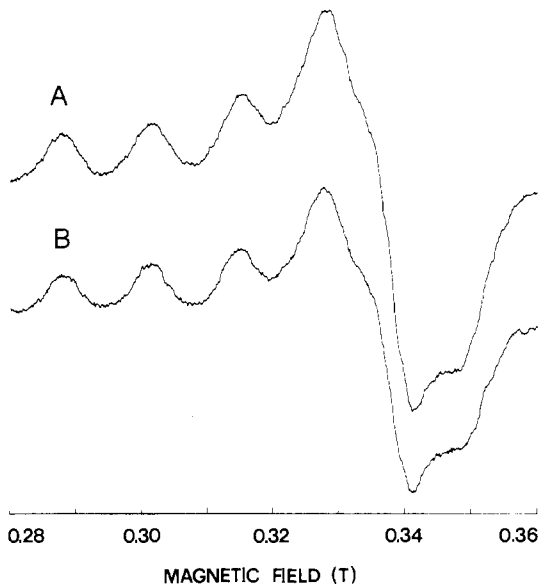

Figure 4. 25 °C X-band EPR spectra of Cu_2Zn_2SOD, 0.88 mM in Cu^{2+}. The values[23] of η/η_0 are 1.0 (A) and 5.9 (B). The spectra can be reproduced with standard simulation programs using Gaussian lines and linewidths of about $(60 \pm 3) \times 10^{-4}$ T for spectrum A and $(52 \pm 3) \times 10^{-4}$ T for spectrum B.

Therefore, the predictions of eq 5 should be tested with a high-field measurement of T_{1e}. Our τ_s values are, indeed, strongly determined by the high-field inflection of the NMRD profiles and field independent within the experimental error.

The T_{1e} values expected from eq 5 are shown in Figure 3 at 9-GHz electron resonance frequency (0.33 T, $\simeq$14 MHz for protons) as a function of τ_r for typical values of g anisotropy, A anisotropy, and deviations from g_e (see caption to the figure). The electronic relaxation times estimated through the fitting of our NMRD data (Table I), which essentially are T_{1e} values, are also shown in Figure 3. The striking disagreement confirms that another mechanism for longitudinal electron relaxation, by far more efficient than rotational mechanisms, must be operative in macromolecular complexes.

The linewidth of the EPR signals of tetragonal copper complexes at room temperature, both of small complexes as diluted solids or as macromolecules in solution at the same temperature, are consistent with T_2 values in a narrow range around 2×10^{-9} s.

Table I. Results of Comparisons of Relaxation Theory for Hyperfine-Coupled[a] Cu^{2+} Ions with the 25 °C NMRD Profiles of Various Cu^{2+}-Protein Complexes, at Different Solvent Viscosities Adjusted by Sucrose

protein	η/η_0	r_{Cu-H},[a] Å	τ_c,[b] ns	θ,[c] deg
Cu_2TRN[d]	1.0	3.6	6.4	42
Cu_2TRN[d]	2.2	3.6	6.0	53
Cu_2Zn_2SOD[e,f]	1.0	3.4	2.4	15
Cu_2Zn_2SOD[e]	5.9	3.4	2.9	26

[a] Calculated assuming a single water molecule, in rapid exchange, interacting with each Cu^{2+} with its protons equidistant from the ion. [b] It is assumed, as in other Cu^{2+}-protein systems, that τ_s can be equated to the derived correlation time. The estimated uncertainty on τ_c is ±10%. [c] θ is the angle between the direction of r_{Cu-H} and the unique axis of the hyperfine tensor for the interaction of a Cu^{2+} ion with its nucleus. This parameter is required by the theoretical treatment, but the results are relatively insensitive to its value. [d] Samples in 44 mM HCO_3^{-1} buffer at pH 8.3. Fitting done using $A_\parallel = 168 \times 10^{-4}$ cm^{-1} and $A_\perp = 20 \times 10^{-4}$ cm^{-1}. [e] Samples, unbuffered, at pH 5.1. Fitting done using $A_\parallel = 143 \times 10^{-4}$ cm^{-1} and $A_\perp = 20 \times 10^{-4}$ cm^{-1}. [f] The data for the superoxide dismutase for $\eta/\eta_0 = 1$ yield a somewhat longer τ_c and larger r_{Cu-H} than do earlier data[13] taken near neutral pH and also required a smaller $A_\perp$ value for a satisfactory fit. This could indicate that at lower pH the ligand field of the copper chromophore becomes somewhat more axial; the conclusions drawn in the present paper, however, remain unaffected.

Even if there are no explicit estimates, a variation of more than a factor of 2 in linewidth would provide linewidths either at the limit of detection or extraordinarily sharp, which is rare. As suggested by a reviewer, we also measured the EPR spectra of SOD in the presence and absence of sucrose. The EPR data, shown in Figure 4, are consistent with T_{2e} values of 1.8×10^{-9} or 2.1×10^{-9} s for the $\eta/\eta_0 = 1$ and the $\eta/\eta_0 = 5.9$ samples, respectively; these values compare exceedingly well with the T_{1e} values reported in Table I. It should be pointed out, however, that T_{2e}^{-1} is not expected to decrease with increasing τ_r as T_{1e}^{-1} does outside the so-called fast motion regime, even in the presence of rotational mechanisms. Therefore T_{2e} data cannot be easily used to prove or disprove any particular mechanism.

The present NMRD experiments demonstrate that τ_r has no influence on the electronic relaxation processes. Therefore, the modulation of the interaction energy between the electron and the lattice[24] has to occur through nonrotational mechanisms, such as vibration distribution of phonon type in a "microcrystal" formed by the metal and the protein as suggested by Kivelson,[25] although he concluded from his data that vibrational mechanisms might not be the major source of relaxation in solution. For small complexes ($\tau_r < 10^{-10}$ s) rotational mechanisms related to eq 5 have been shown to account for the observed T_{1e}^{-1}. However, the similar splitting of the d orbitals in small and large molecules of similar geometry (which determine g and A anisotropy) and the similar EPR linewidth may suggest that also in small complexes the nonrotational mechanism here proposed can concur to determine electron relaxation.

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Structural Models for Non-Oxide Chalcogenide Glasses. Atomic Distribution and Local Order in the System Phosphorus–Selenium Studied by ^{31}P Dipolar NMR Spectroscopy

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Abstract: Homonuclear dipolar coupling information encoded in solid-state NMR spectra affords a quantitative criterion for the test of structural hypotheses for non-oxide chalcogenide glasses. Using a selective spin–echo sequence, ^{31}P–^{31}P dipolar second moments have been measured for glasses in the system phosphorus–selenium (10–50 atom % P) and related model compounds. The results are in striking contrast to the preliminary structural hypotheses raised with the aid of competing spectroscopic techniques. The NMR results can be simulated quantitatively in terms of a random distribution of P and Se atoms over a cubic lattice with a decidedly preferential formation of P–Se over P–P bonds. Up to 25 atom % P, the phosphorus atoms are entirely coordinated to selenium, whereas in glasses with higher P contents, P–P bonds are introduced in less than purely statistical proportions. The NMR results show no indication of units with intermediate-range order, such as the P_4Se_n clusters inferred from neutron diffraction and EXAFS work.

1. Introduction

Non-oxide chalcogenide glasses, which are based on the sulfides, selenides, and tellurides of the main group III–V elements, have recently gained much interest for semiconductors, photoconductors, solid electrolytes, and low-frequency waveguide materials.[1] Because of these technologically attractive properties, the structural arrangement in these systems has recently received considerable attention. In spite of considerable efforts, there is still no good microscopic structural model that provides a comprehensive description of the principles of glass formation, the atomic environments, and their distribution in these systems. The various models developed for different, but chemically related, systems diverge dramatically in their fundamental concepts. As an example, the chaos implied in the "model of broken chemical order" postulated for As–Se and Ge–Se glasses[2,3] is in sharp contrast to

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0002-7863/89/1511-3536$01.50/0