

# Supporting Text

**Stereospecific Assignment of the Cys-89  $\beta$ -protons.** The stereospecific assignment of the Cys-89  $\beta$ -protons was made on the basis of NOEs and the NMR solution structure of reduced *A.v.* plastocyanin (see Table 3). The assignment obtained here for *A.v.* plastocyanin is in agreement with the assignment obtained previously for spinach plastocyanin (1), i.e. Cys-89 H $^{\beta_1}$  has a chemical shift of 3.33 ppm in the reduced protein and gives a saturation transfer at  $\approx 700$  ppm, while Cys-89 H $^{\beta_2}$  has a chemical shift of 2.89 ppm in the reduced protein and gives a saturation transfer at  $\approx 440$  ppm.

**Structure Calculation.** The structure calculations included distance geometry (DG), simulated annealing (SA), and restrained energy minimization. The paramagnetic restraints were included only in the SA, and the restrained energy calculations (REM), while the applied NOE and dihedral angle restraints were included in all parts of the calculations.

A total of 100 structures were calculated. Only the backbone nitrogen, carbon, and hydrogen atoms, and the  $\beta$  and  $\gamma$  carbons were included in the initial DG calculations of substructures using the protocol `dg_sub_embed` (2). In the following SA calculations, the structure of the apo-protein was fixed in the first step while the copper(II) ion was positioned roughly in the catalytic site by the relaxation restraints, assuming that  $r_{\text{eff}} = r$  in Eq. 1. The restraints were included using a flat-bottomed squared potential with a force constant of  $10 \text{ kcal}\cdot\text{\AA}^{-2}$ .

Subsequently, the structures were run through 200 cycles of restrained Powell energy minimization (REM) followed by 9 ps of restrained molecular Verlet dynamics at a temperature of 3,000 K in time steps of 3 fs. The paramagnetic relaxation restraints were included with the square potential and a force constant of  $100 \text{ kcal}\cdot\text{\AA}^{-2}$ , and the paramagnetic relaxation enhancements were calculated in the point dipole approximation, that is  $r_{\text{eff}} = r$  in Eq. 1. The high-temperature dynamics was followed by 6 ps of cooling to 100 K in time steps of 3 fs and subsequently by 200 cycles of REM.

Finally, the structures were refined using the simulated annealing refine protocol (2). At this stage the unpaired electron spin distribution was gradually changed from a point dipole at the copper atom to the final spin distribution described in Table 2. The structures were initially heated to 3,000 K and hereafter cooled to 100 K over 20 ps in time steps of 2 fs. The unpaired electron spin was described by a two-center model with 70% at the copper 3d orbital and 30% at the Cys S $\gamma$  orbital for temperatures between 3,000 and 800 K. From 800 to 100 K the full electron spin distribution shown in Table 2 was used. Finally, 200 cycles of REM calculations were

applied. The force constants,  $k_{\text{prlx}}^{\pm}$ , of the paramagnetic relaxation restraints were  $500 \text{ kcal} \cdot \text{\AA}^{-2}$  and  $500 \text{ kcal}$ , respectively. In general, the contribution to the total energy from the paramagnetic relaxation restraints was  $\approx 0.3\%$ , which indicates a good agreement between the paramagnetic relaxation restraints and the conventional inter-proton distances and dihedral angle restraints.

The van der Waals energy function was represented by a simple repel function in the SA calculations. The van der Waals interactions were increased by varying the force constant of the repel function from  $0.003$  to  $4 \text{ kcal} \cdot \text{mol}^{-1} \cdot \text{\AA}^{-4}$ . During all calculations the force constant used for the NOE and the dihedral angle restraints were  $50 \text{ kcal} \cdot \text{mol}^{-1} \cdot \text{\AA}^{-2}$  and  $200 \text{ kcal} \cdot \text{mol}^{-1} \cdot \text{rad}^{-2}$ , respectively. Finally, the 10 structures with lowest total energy were selected for further analysis.

It should be noted that the protein structure beyond the metal bound residues is unaffected by the inclusion of the paramagnetic restraints in the structure calculations and is defined entirely by the conventional NOEs and dihedral restraints used in the structure determination. Thus, the root mean square deviation (RMSD) of the backbone atoms of the 10 structures with the lowest energies (the metal sites structures of which are shown in Fig. 1) was  $0.67 \text{ \AA}$ , whereas the RMSD of the 10 structures with lowest energies derived from conventional diamagnetic restraints alone was  $0.73 \text{ \AA}$  (3). In both cases the N- and C-terminal residues were excluded in the RMSD calculations. Finally, the RMSD of the two average structures, that is, the average of the 10 structures here and the average of the 20 previous structures (3), was  $0.59 \text{ \AA}^2$ , excluding the N- and C-terminals and the ligand residues. Finally, it should be noted that the use in the structure determination of NOEs from reduced plastocyanin together with paramagnetic restraints from oxidized plastocyanin is justified by the fact that  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  plastocyanin have nearly identical structures with only minor differences in the first coordination sphere (4–7). Also, as mentioned in the main text the NOEs between side chain atoms of the ligand residues (His-39, Cys-89, His-92 and Met-97) were excluded, to allow the metal site to be defined exclusively by the paramagnetic restraints.

**Evaluation of the Dipole Integral.** To calculate the paramagnetic relaxation enhancements and the effective distance in Eq. 6 for the protons close to the paramagnetic metal site, we want to solve the dipole integral

$$\mathcal{D}_{\nu}(\psi; \mathbf{R}) = \int_V d\mathbf{r} \psi_{n'l'm'}(\mathbf{r}) \widehat{\mathcal{F}}_2^{\nu}(\mathbf{r}') \psi_{n'l'm'}(\mathbf{r})^*. \quad [\text{S1}]$$

The integral describes the dipole interaction between the magnetic moment of a nucleus, N, and an unpaired electron described by the wave function  $\psi(\mathbf{r})$ . The orbital of the unpaired electron,  $\psi(\mathbf{r})$ , is described by a Slater type hydrogen-like atomic orbital in the coordinate system  $\mathcal{O}$ . The

dipole operator  $\widehat{\mathcal{F}}_2^\nu(\mathbf{r}') = \|\mathbf{r}'\|^{-3} Y_2^\nu(\mathbf{r}'/\|\mathbf{r}'\|)$  is described in the coordinate system  $\mathcal{O}'$ , which has the nucleus,  $\mathbf{N}$ , at the origin. Here,  $Y_\rho^\nu(\mathbf{r}/\|\mathbf{r}\|)$  is the solid spherical harmonic. Furthermore, the coordinates of the nucleus are described by the translation vector  $\mathbf{R}$  in the coordinate system  $\mathcal{O}$ , i.e.,  $\mathbf{r}' = \mathbf{r} - \mathbf{R}$ . Finally, an asterisk denotes complex conjugation.

The operator  $\widehat{\mathcal{F}}_2^\nu(\mathbf{r}')$  can be described in the coordinate system  $\mathcal{O}$  by a translation of the irregular solid spherical harmonics (8–11):

$$\widehat{\mathcal{F}}_2^\nu(\mathbf{r}') = \sum_{l=2}^{\infty} \sum_{m=-l}^l (-1)^{\nu+m} \xi(2, \nu, l, m) F_l^m(\mathbf{R}) \Upsilon_{l-2}^{\nu-m}(\mathbf{r}) \quad \text{for } \|\mathbf{r}\| < \|\mathbf{R}\|, \quad [\text{S2}]$$

$$\widehat{\mathcal{F}}_2^\nu(\mathbf{r}') = \sum_{l=2}^{\infty} \sum_{m=-l}^l (-1)^{\nu+m} \xi(2, \nu, l, m) F_l^m(\mathbf{r}) \Upsilon_{l-2}^{\nu-m}(\mathbf{R}) \quad \text{for } \|\mathbf{r}\| > \|\mathbf{R}\|, \quad [\text{S3}]$$

where

$$\xi(\rho, \nu, l, m) = \left\{ \frac{4\pi(2\rho+1)}{(2l-2\rho+1)(2l+1)} \frac{(l-m)!(l+m)!}{(\rho-\nu)!(\rho+\nu)!(l-\rho-m+\nu)!(l-\rho+m-\nu)!} \right\}^{1/2}, \quad [\text{S4}]$$

and  $\Upsilon_l^m$  and  $F_l^m$  are the regular solid spherical harmonics and irregular spherical harmonics, respectively. That is:

$$\Upsilon_l^m(\mathbf{r}) = \|\mathbf{r}\|^l Y_l^m(\mathbf{r}/\|\mathbf{r}\|), \quad [\text{S5}]$$

$$F_l^m(\mathbf{r}) = \|\mathbf{r}\|^{-(l+1)} Y_l^m(\mathbf{r}/\|\mathbf{r}\|). \quad [\text{S6}]$$

For  $\|\mathbf{r}\| \rightarrow \|\mathbf{R}\|$  the operator  $\widehat{\mathcal{F}}_2^\nu(\mathbf{r}')$  approaches a Dirac delta function. That is, even though the volume of integration of the shell  $\|\mathbf{r}\| = \|\mathbf{R}\|$  is zero the integral may still have a nonzero contribution to the total integral in Eq. **S1** (10, 12)

$$\widehat{\mathcal{F}}_2^\nu(\mathbf{r}') = -\frac{4\pi}{3} Y_2^\nu(\mathbf{R}/\|\mathbf{R}\|) \delta(\mathbf{r} - \mathbf{R}) \quad \text{for } \|\mathbf{r}\| = \|\mathbf{R}\|. \quad [\text{S7}]$$

The hydrogen-like atomic orbitals can be separated in an angular part and a radial part:

$$\psi_{n'l'm'}(\mathbf{r}) = R_{n'l'}(Z_{\text{eff}}, \|\mathbf{r}\|) Y_l^{m'}(\mathbf{r}/\|\mathbf{r}\|), \quad [\text{S8}]$$

where  $R_{n'l'}(Z_{\text{eff}}, \|\mathbf{r}\|)$  and  $Y_l^{m'}(\mathbf{r}/\|\mathbf{r}\|)$  are the normalized radial and solid spherical harmonic function, respectively. Furthermore,  $Z_{\text{eff}}$  is the effective charge of the nucleus at which the hydrogen-like atomic orbital is centered. According to the equations for the translated dipole operator, Eqs. **S2**, **S3**, and **S7**, the dipole integral, Eq. **S1**, splits into three parts:

$$\mathfrak{D}_\nu(\psi; \mathbf{R}) = \underbrace{\overleftarrow{\mathfrak{D}}_\nu(\psi; \mathbf{R})}_{\|\mathbf{r}\| < \|\mathbf{R}\|} + \underbrace{\overrightarrow{\mathfrak{D}}_\nu(\psi; \mathbf{R})}_{\|\mathbf{r}\| > \|\mathbf{R}\|} + \underbrace{\overline{\mathfrak{D}}_\nu(\psi; \mathbf{R})}_{\|\mathbf{r}\| = \|\mathbf{R}\|}. \quad [\text{S9}]$$

Below, the three cases:  $\|\mathbf{r}\| < \|\mathbf{R}\|$ ,  $\|\mathbf{r}\| = \|\mathbf{R}\|$ , and  $\|\mathbf{r}\| > \|\mathbf{R}\|$  will be described separately.

$$\|\mathbf{r}\| < \|\mathbf{R}\|$$

Since the hydrogen-like atomic orbitals,  $\psi_{n'l'm'}(\mathbf{r})$ , can be separate in an angular part and a radial part, the integral  $\hat{\mathcal{D}}_\nu(\psi; \mathbf{R})$  can according to Eq. **S2** be calculated as:

$$\hat{\mathcal{D}}_\nu(\psi; \mathbf{R}) = \sum_{l=2}^{\infty} \sum_{m=-l}^l (-1)^{\nu+m} \xi(2, \nu, l, m) \hat{\mathbf{a}}_\nu(\psi; \mathbf{R}; m, l) \hat{\mathbf{r}}_\nu(\psi; \mathbf{R}; m, l), \quad [\text{S10}]$$

where  $\hat{\mathbf{a}}_\nu(\psi; \mathbf{R}; m, l)$  and  $\hat{\mathbf{r}}_\nu(\psi; \mathbf{R}; m, l)$  are the angular part and radial part, respectively.

*Angular part.* From Eq. **S2** it is seen that the angular part is given by:

$$\hat{\mathbf{a}}_\nu(\psi; \mathbf{R}; m, l) = Y_l^m(\mathbf{R}/\|\mathbf{R}\|) \int d\Omega Y_{l-2}^{\nu-m}(\Omega) Y_{l'}^{m'}(\Omega) [Y_{l'}^{m'}(\Omega)]^*, \quad [\text{S11}]$$

where  $\Omega$  is the solid spherical angle:  $\Omega = \mathbf{r}/\|\mathbf{r}\|$ , and

$$\int d\Omega = \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta. \quad [\text{S12}]$$

Angular integrals of the type in Eq. **S11** can be solved using the Clebsch-Gordan series (13):

$$\int d\Omega Y_{l_1}^{m_1}(\Omega) Y_{l_2}^{m_2}(\Omega) [Y_{l_3}^{m_3}(\Omega)]^* = \left\{ \frac{(2l_1 + 1)(2l_2 + 1)}{4\pi(2l_3 + 1)} \right\}^{1/2} \langle l_1 l_2 0 0 | l_1 l_2 l_3 0 \rangle \langle l_1 l_2 m_1 m_2 | l_1 l_2 l_3 m_3 \rangle. \quad [\text{S13}]$$

Here, the Clebsch-Gordan coupling coefficients  $\langle l_1 l_2 m_1 m_2 | l_1 l_2 l_3 m_3 \rangle$  vanish, unless:

- $m_1 + m_2 = m_3$
- $|l_1 - l_2| \leq l_3 \leq l_1 + l_2$

Therefore, the sum in Eq. **S2** only has a finite number of nonvanishing terms. The nonvanishing Clebsch-Gordan coupling coefficients are tabulated in standard tables or can be calculated using angular momentum theory. For the angular integral in Eq. **S11** the nonvanishing conditions are:

- $\nu - m + m' = m' \Leftrightarrow \nu = m$
- $|l - 2 - l'| \leq l' \leq l + l' - 2$

*Radial part.* The radial part of the dipole integral,  $\hat{\mathbf{r}}_\nu(\psi; m, l)$ , is given by:

$$\hat{\mathbf{r}}_\nu(\psi; \mathbf{R}; m, l) = \|\mathbf{R}\|^{-(l+1)} \int_0^{\|\mathbf{R}\|} dr r^2 r^{l-2} |R_{n',l'}(Z_{\text{eff}}, r)|^2, \quad [\text{S14}]$$

where  $r = \|\mathbf{r}\|$ . For the hydrogen-like atomic orbitals the radial part is given by the well-known associated Laguerre polynomials (13), that is, the radial integral can be evaluated analytically.

$$\|\mathbf{r}\| > \|\mathbf{R}\|$$

The integral  $\overset{\triangleright}{\mathcal{D}}_\nu(\psi; \mathbf{R})$  can according to Eqs. **S3** and **S10** be calculated as:

$$\overset{\triangleright}{\mathcal{D}}_\nu(\psi; \mathbf{R}) = \sum_{l=2}^{\infty} \sum_{m=-l}^l (-1)^{\nu+m} \xi(2, \nu, l, m) \overset{\triangleright}{\mathbf{a}}_\nu(\psi; \mathbf{R}; m, l) \overset{\triangleright}{\mathbf{r}}_\nu(\psi; \mathbf{R}; m, l), \quad [\text{S15}]$$

where  $\overset{\triangleright}{\mathbf{a}}_\nu(\psi; \mathbf{R}; m, l)$  and  $\overset{\triangleright}{\mathbf{r}}_\nu(\psi; \mathbf{R}; m, l)$  are the angular part and radial part, respectively.

*Angular part.* From Eq. **S3** and the above-mentioned properties, it is seen that the angular part,  $\overset{\triangleright}{\mathbf{a}}_\nu(\psi; \mathbf{R}; m, l)$ , is given by:

$$\overset{\triangleright}{\mathbf{a}}_\nu(\psi; \mathbf{R}; m, l) = Y_{l-2}^{\nu-m}(\mathbf{R}/\|\mathbf{R}\|) \int d\Omega Y_l^m(\Omega) Y_{l'}^{m'}(\Omega) [Y_{l'}^{m'}(\Omega)]^*, \quad [\text{S16}]$$

which can be evaluated using the Clebsch-Gordan series as shown above. The nonvanishing conditions are:

- $m + m' = m' \Leftrightarrow m = 0$
- $|l - l'| \leq l' \leq l + l'$

*Radial part.* The radial part,  $\overset{\triangleright}{\mathbf{r}}_\nu(\psi; \mathbf{R}; m, l)$ , of the dipole integral  $\overset{\triangleright}{\mathcal{D}}_\nu(\psi; \mathbf{R})$ , is given by:

$$\overset{\triangleright}{\mathbf{r}}_\nu(\psi; \mathbf{R}; m, l) = \|\mathbf{R}\|^{l-2} \int_{\|\mathbf{R}\|}^{\infty} dr r^2 r^{-(l+1)} |R_{n',l'}(Z_{\text{eff}}, r)|^2. \quad [\text{S17}]$$

$$\|\mathbf{r}\| = \|\mathbf{R}\|$$

The contribution;  $\overset{=}{\mathcal{D}}_\nu(\psi; \mathbf{R})$  is trivially calculated from the operator described in Eq. **S7** and the wave function:

$$\overset{=}{\mathcal{D}}_\nu(\psi; \mathbf{R}) = -\frac{4\pi}{3} Y_2^\nu(\mathbf{R}/\|\mathbf{R}\|) |\psi_{n',l',m'}(\mathbf{R})|^2. \quad [\text{S18}]$$

**Real Hydrogen-Like Atomic Orbitals.** Most often the orbital involved in the dipole integral Eq. **S1** is not a pure hydrogen-like atomic orbital, that is, an eigenfunction of the operator  $\widehat{L}_z$ . As an example, the  $2p_x$  and  $2p_y$  orbitals are linear combinations of the hydrogen-like atomic orbitals  $\psi_{211}(\mathbf{r})$  and  $\psi_{21-1}(\mathbf{r})$ . However, the radial function  $R_{n',l'}(Z_{\text{eff}}, \|\mathbf{r}\|)$  is independent of the quantization along the  $z$ -axis.

We now consider the following atomic orbital:

$$\psi(\mathbf{r}) = \widehat{\mathcal{R}}(\alpha, \beta, \gamma) \psi_{nlm}(\mathbf{r}), \quad [\text{S19}]$$

where  $\widehat{\mathcal{R}}$  is the rotational operator and  $\alpha$ ,  $\beta$ , and  $\gamma$  are the three Euler angles of rotation. Since the set of spherical harmonics:  $\{Y_l^m\}_{-l \leq m \leq l}$  forms a basis in the  $(2l + 1)$ -dimensional irreducible rotation group, the angular part of the wave function  $\psi(\mathbf{r})$  in Eq. **S19** is entirely given by a linear combination of the spherical harmonics in the basis  $\{Y_l^m\}_{-l \leq m \leq l}$ . That is:

$$Y_l^m(\theta', \phi') = \widehat{\mathcal{R}}(\alpha, \beta, \gamma) Y_l^m(\theta, \phi) \quad [\text{S20}]$$

$$= \sum_{m'=-l}^l Y_l^{m'}(\theta, \phi) \mathbf{D}_{m',m}^{(l)}(\alpha, \beta, \gamma), \quad [\text{S21}]$$

where  $\mathbf{D}_{m',m}^{(l)}(\alpha, \beta, \gamma)$  denotes the elements of the representation matrix of the rotation  $(\alpha, \beta, \gamma)$ , if the  $2l + 1$  complex spherical harmonics  $\{Y_l^m\}_{-l \leq m \leq l}$  form the basis for this representation. The  $\mathbf{D}_{m',m}^{(l)}(\alpha, \beta, \gamma)$  matrix elements are given by:

$$\mathbf{D}_{m',m}^{(l)}(\alpha, \beta, \gamma) = \langle lm' | \widehat{\mathcal{R}}(\alpha, \beta, \gamma) | lm \rangle \quad [\text{S22}]$$

$$= \langle lm' | \exp(-i\alpha \widehat{L}_z) \exp(-i\beta \widehat{L}_y) \exp(-i\gamma \widehat{L}_z) | lm \rangle \quad [\text{S23}]$$

$$= e^{-i\alpha m'} \mathbf{d}_{m',m}^{(l)}(\beta) e^{-i\gamma m}, \quad [\text{S24}]$$

where  $|lm\rangle = Y_l^m(\theta, \phi)$  and  $\widehat{L}_y$  and  $\widehat{L}_z$  are the Cartesian components of the angular momentum operator. Furthermore (11),

$$\mathbf{d}_{m',m}^{(l)}(\beta) = \langle lm' | \exp(-i\beta L_y) | lm \rangle \quad [\text{S25}]$$

$$= \{(l+m)!(l-m)!(l+m')!(l-m')!\}^{1/2} \times \sum_j \frac{(-1)^{j+m+m'} \cos^{2l+m-m'-2j}(\beta/2) \sin^{m'-m+2j}(\beta/2)}{j!(l-m'-j)!(l+m-j)!(j+m'-m)!}. \quad [\text{S26}]$$

Here, the summation index,  $j$ , runs over all values for which the factorials exist, i.e., the factorial arguments are greater than or equal to zero.

As an example, consider that we want to calculate the dipole integral, Eq. **S1**, when  $\psi$  is a  $2p_y$  orbital. The  $2p_y$  orbital can be described as a rotation of the  $2p_z$  orbital with the following Euler angles:  $\alpha = \pi/2$ ,  $\beta = \pi/2$  and  $\gamma = 0$ , i.e.,

$$2p_y(\mathbf{r}) = \widehat{\mathcal{R}}(\pi/2, \pi/2, 0) \psi_{210}(\mathbf{r}). \quad [\text{S27}]$$

From the equations above, the representation matrix  $\mathbf{D}^{(1)}(\pi/2, \pi/2, 0)$  can be calculated:

$$\mathbf{D}^{(1)} = \begin{pmatrix} i/2 & i/\sqrt{2} & i/2 \\ -1/\sqrt{2} & 0 & 1/\sqrt{2} \\ -i/2 & i/\sqrt{2} & -i/2 \end{pmatrix}. \quad [\text{S28}]$$

Thus,

$$2p_y(\mathbf{r}) = \frac{i}{\sqrt{2}} (\psi_{21-1}(\mathbf{r}) + \psi_{211}(\mathbf{r})). \quad [\text{S29}]$$

The dipole integral in Eq. **S1** can now be written as:

$$\begin{aligned} \mathfrak{D}_\nu(2p_y; \mathbf{R}) = & \frac{1}{2} \left\{ \int_V d\mathbf{r} \psi_{21-1}(\mathbf{r}) \widehat{\mathcal{F}}_2^\nu(\mathbf{r}') \psi_{21-1}(\mathbf{r})^* + \int_V d\mathbf{r} \psi_{21-1}(\mathbf{r}) \widehat{\mathcal{F}}_2^\nu(\mathbf{r}') \psi_{211}(\mathbf{r})^* \right. \\ & \left. + \int_V d\mathbf{r} \psi_{211}(\mathbf{r}) \widehat{\mathcal{F}}_2^\nu(\mathbf{r}') \psi_{21-1}(\mathbf{r})^* + \int_V d\mathbf{r} \psi_{211}(\mathbf{r}) \widehat{\mathcal{F}}_2^\nu(\mathbf{r}') \psi_{211}(\mathbf{r})^* \right\}. \quad [\text{S30}] \end{aligned}$$

Again, each integral in Eq. **S30** can be calculated by the method described above. The same strategy can be applied when other real hydrogen-like atomic orbitals are considered in the dipole integral, Eq. **S1**, e.g.,  $3d_{x^2-y^2}$ ,  $3d_{xz}$ ,  $\dots$ . Also, arbitrary rotations of these atomic orbitals can be evaluated by the methodology described above. Alternatively, since the set  $\{\widehat{\mathcal{F}}_2^\nu\}_{-2 \leq \nu \leq 2}$  forms a spherical tensor operator, the operator  $\widehat{\mathcal{F}}_2^\nu$  can be rotated by the second order representation of the rotation matrix,  $\mathbf{D}^{(2)}(\alpha, \beta, \gamma)$ , instead of a rotation of the orbitals. This last approach does not require the evaluation of extra integrals.

In conclusion, the solution of the dipole integral, Eq. **S1**, makes it feasible to take the delocalization of the unpaired electron spin into account in a structural refinement procedure.

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