tion for Cu(II)–(histidine)$_2$ is comparable to that observed for Cu(II)–diethylenetriamine–imidazole. Therefore, at physiological pH, a single imidazole is equatorially coordinated to the metal ion. At pH 3.4, where the predominant species are Cu(II)-aquo and the low pH intermediate, the modulation pattern characteristic of coordinated imidazole is still observed. Thus imidazole remains bound to Cu(II) here as well.

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Resonance Raman Spectroscopy of Binuclear Iron Centers. Hemerythrin, Ribonucleotide Reductase and Iron Phenanthroline Complexes

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Binuclear iron centers are known to be present in the respiratory protein, hemerythrin [1], and in the enzyme, ribonucleotide reductase [2]. These centers are characterized by strong antiferromagnetic coupling ($-J \cong 100$ cm^{-1}) of the two ferric ions, and by one or more intense absorption bands between 320 and 380 nm ($\epsilon \cong 4000\ M^{-1}$ cm^{-1} per Fe atom). These properties have long been ascribed to the presence of a μ-oxo bridge between the iron atoms. Verification of such a bridge was obtained in the 2.2-Å resolution crystal structure of azidomethemerythrin [3].

Resonance Raman spectroscopy provides an additional valuable technique for the detection and characterization of binuclear iron centers. The Fe–O–Fe symmetric stretch, ν_s(Fe–O–Fe), is Raman active and the intensity of this vibration may be enhanced by excitation within the Fe–O–Fe charge transfer band in the near ultraviolet. As a model system, we have investigated the resonance Raman spectra of binuclear 1,10-phenanthroline (phen) complexes of iron(III) [4]. The complex $Fe_2O(phen)_4(NO_3)_4 \cdot 7H_2O$ has a Raman peak at 395 cm^{-1} which can be assigned to ν_s(Fe–O–Fe) on the basis of its frequency being appropriate to an Fe–O–Fe angle of 154°, its absence from the spectrum of mononuclear complex $Fe(phen)_3(ClO_4)_3 \cdot 3H_2O$, and its intensity being dependent upon excitation wavelength. The perchlorate and chloride salts of $[Fe_2O(phen)_4]^{4+}$ have similar resonance-enhanced modes close to 400 cm^{-1}, and in all three cases the enhancement is maximized using 363.8 nm excitation.

Confirmatory evidence for an Fe–O–Fe vibration can be obtained from oxygen isotope exchange with $H_2^{18}O$ solvent. For example, in the μ-oxo bridged dimer, $[Fe_2O(Cl)_6]^{2-}$, ν_s(Fe–O–Fe) at 458 cm^{-1} shifts to 400 cm^{-1} in $H_2^{18}O$ [5]. Similarly, the resonance-enhanced band at 507 cm^{-1} in the Raman spectrum of azidomethemerythrin shifts to 490 cm^{-1} for a sample which has been formed from oxyhemerythrin in $H_2^{18}O$ [6]. We have now found evidence for the corresponding Fe–O–Fe vibration at 489 cm^{-1} in the resonance Raman spectrum of oxyhemerythrin, through the use of near-ultraviolet excitation [7]. Furthermore, this band shows an isotope dependence on solvent ($H_2^{18}O$), and appears to be in resonance with the 360 nm electronic transition of oxyhemerythrin. The resonance enhancement of the ν_s(Fe–O–Fe) peak intensity with ultraviolet excitation has also been observed for azidomethemerythrin [7] and for ribonucleotide reductase [2]. In contrast to hemerythrin, however, where the oxo group only exchanges during exogenous ligand replacement, the oxo group in ribonucleotide reductase undergoes facile exchange with solvent ($k_{obs} = 8.3 \times 10^{-4}$ s^{-1}), indicating it is located in a more accessible site.

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SUPERQUAD – A New Computer Program for Determination of Stability Constants of Complexes by Potentiometric Titration

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We have developed, separately and together, a sequence of computer programs for the determina-