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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R29

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 determination of stability constants from potentiometric titration data: LEAST [1], MINIQUAD [2], MINIQUAD75 [3], MINIQUAD76A [4] and MIQUV [5]. The objective of this research is to develop robust, reliable and fast programs which will enable the solution chemist to specify the composition of any given solution. The last-mentioned program MIQUV was developed to put the model selection process on a sounder statistical basis. Our new program SUPERQUAD is a development of MIQUV designed to be both more efficient and more flexible. The following is a summary of the most important features of the new program.

(1) It uses the method of 'rigorous least squares' in which both e.m.f. (E) and titre values (vol.) are assumed to be subject to experimental error. The data is weighted by a statistically sound weighting scheme. This makes it easier to deal with whole titration curves which include end-points, where measured e.m.f. is very sensitive to variations in volume of titrant added.

(2) The minimization is based on the measured e.m.f. values E_k and all requisite derivatives $\partial E_k/\partial X_j$ are obtained analytically in two stages.

$$\frac{\partial E_k}{\partial X_j} = \frac{\partial E_k}{\partial F_k}\frac{\partial F_k}{\partial X_j} \qquad (1)$$

$$\sum_k \frac{\partial T_i}{\partial F_k}\frac{\partial F_k}{\partial X_j} = \frac{-\partial T_i}{\partial X_j} \qquad (2)$$

This approach was first presented by Nagypál [6]. X_j is the jth parameter; it may be a formation constant, a reactant or titrant concentration or a standard electrode potential. Certain parameters may be constrained to be equal. For example the concentration of added alkali can be refined, but constrained to be the same for a set of titration curves. F_k is the kth concentration of free reactant; for example it may be H^+. T_i is the total concentration of the ith reactant.

(3) The statistical information concerning the distribution of weighted residuals on e.m.f. is expected to be most valuable in the process of model selection. Early trials show that the stastical information supplied by SUPERQUAD is more satisfactory than that of MINIQUAD, and leads more convincingly to selection of the best model. In addition to the errors in e.m.f., the errors in volume can also be back-calculated. Thus, the original titration curve can be totally reconstructed, including calculated errors on all measurements.

(4) Flexibility. There may be 1 or 2 electrodes reading either e.m.f. or $-\log F_k$, 2, 3 or 4 reactants and up to 18 formation constants. The case of 2 reactants and 2 electrodes is included. The computer coding (FORTRAN) has been thoroughly checked for portability onto the widest possible range of computers. Input and output have been oriented towards users having 80 characters video display terminals as the principal input/output device.

(5) Details concerning availability of machine-readable copies of SUPERQUAD and associated text data are available from P.G.

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Thermodynamic Electron Transfer and Catalytic Properties of High-Spin Cobalt(II) Complexes with Dioxygen

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The role of high-spin cobalt(II) complexes with bidentate Schiff bases as oxygen carriers in non-aqueous medium has been investigated.

These complexes have the structure of a distorted tetrahedron, both in the solid and in non-coordinating solvents. In the presence of monodentate ligand (amine) they are transformed into pentacoordinated complexes, with their high-spin character preserved. Such a system is capable of reversible, multicycle oxygen uptake at temperatures below 0 °C. The stability constants and thermodynamic values for pentacoordinated complexes have been determined spectrophotometrically. An interesting correlation between the spacial hindrance in the initial complex and the stability constant of the pentacoordinated complex has been found. The monomeric character of the oxygenated complex formed has been established by volumetric, spectrophotometric and EPR methods. Stability constants and the ΔH and ΔS values for the oxygenated complex have been determined for the series of systems. The rela-