

etching procedure was found that largely removes this remaining damaged layer: Grube and Reindardt¹⁰ reported that dissolution of platinum into hot hydrochloric acid was very efficient when the temperature was kept above 80 °C, the HCl concentration exceeded 7 M, and the current density was less than about 10⁻³ A/cm². When we repeated their experiment using lower current density (10⁻⁵ A/cm²), we found that removal of platinum occurred quantitatively as they reported and produced far fewer etch pits than were observed at higher current densities, judging from optical and scanning electron microscopic examination of the surface. In our experiments, etching was employed to remove about 1000 Å of platinum, based upon four-electron oxidation of the metal to PtCl₆²⁻. Removal of a similar amount of platinum by the conventional procedure involving the use of aqua regia resulted in greater pitting of the surface. The effect of lengthy ion bombardment and annealing after etching was to decrease the size of the LEED spots and the proportion of diffuse intensity somewhat, indicating an increase in the sizes of the ordered domains (for references to reviews of LEED, see ref 1).

Instrumentation and procedures for combined LEED and electrochemistry have been described¹⁻⁵ and reviewed,¹¹ although slight modifications were made for the present work. A diagram of the apparatus appears in Figure 5. The Pt crystal was supported by a pair of fine Pt wires (0.40-mm diameter) spot-welded to one edge. Crystal temperature was measured by means of the thermoelectric voltage generated between a fine (0.25-mm diameter) 90% Pt-10% Rh wire (spot-welded to the crystal) and one of the support wires; this thermocouple voltage was distinguished from the (ac) heating voltage by use of an RC filter.

Electrolytic solutions were prepared from pyrolytically distilled water¹² and reagent grade chemicals. Compressed argon was obtained from Union Carbide Corp. Electrode potentials were measured with respect to a Ag/Ag⁺ half-cell (10⁻³ M AgClO₄ in aqueous 1 M HClO₄) and reported relative to the Ag/AgCl half-cell (1 M NaCl), based

upon direct measurements between the two reference half-cells. Conventional three-electrode potentiostatic circuitry based upon operational amplifiers was employed.

Pt(100)[c(√2×2√2)]R45°-I. Preparation under Vacuum. A clean Pt(100) surface was treated for several minutes at 200 °C with an iodine-vapor beam (Figure 5) equivalent to 3 × 10⁻⁴ torr; the resulting incommensurate structure (Figure 4B) was removed from the iodine beam and heated to 350 °C. After it was allowed to cool to ambient temperature, the crystal was exposed to the iodine-vapor beam until the LEED pattern indicated that the c(√2×2√2)R45°-I structure was present. The LEED pattern and structure are shown in Figures 1A and 4A. Auger spectral intensity for iodine was normalized to this structure, previously shown to contain one I atom per two surface Pt atoms, θ_I = 0.50.^{5e}

Pt(100)[c(√2×5√2)]R45°-I. Preparation at Atmospheric Pressure. The platinum surface (either clean or iodine coated) was blanketed with a flowing argon atmosphere and placed at a distance of about 10 mm from crystals of iodine in a Pyrex glass container (substituted momentarily for the "electrochemical cell" in Figure 5); the distance was adjusted such that the Pt electrode was surrounded by visible I₂ vapor during heating. The electrode was heated electrically to 900 °C for 30 s and 400 °C for 3 min and allowed to cool to ambient temperature. The resulting structure (Figure 4C) contains θ_I = 0.63 (calculated for Pt(100)[c(√2×5√2)]R45°-I: θ_I = 0.60). Programmed heating of this Pt(100)[c(√2×5√2)]R45°-I adlattice under vacuum or iodine-free argon produced the Pt(100)(incommensurate)R45°-I structure (300 °C) and the Pt(100)[c(√2×2√2)]R45°-I structure (365 °C). Both of these iodine adlattices are easily recognized by their distinctive current-potential curves. The other adlattice structures, derived from this "2√2" adlattice by partial desorption of iodine as described in ref 5e, were also obtained.

Acknowledgment. Acknowledgment is made to the National Science Foundation, the Air Force Office of Scientific Research, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. Pt, 7440-06-4; Ag, 7440-22-4; AgI, 7783-96-2; I₂, 7553-56-2.

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A Two-Level Approach to Deconvoluting Absorbance Data Involving Multiple Species. Applications to Copper Systems

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Received June 1, 1983

A least-squares algorithm for obtaining stability constants and molar absorptivities from absorbance data is described. The stability constants are refined by a numerical search method. At each stage in the refinement of the stability constants, conditionally optimum values of the molar absorptivities are estimated by a standard linear least-squares procedure. Treating the parameters on two different levels in this way reduces the guesswork involved and increases the likelihood of converging upon the minimum in the error surface. The method is used to characterize a pentakis complex of imidazole with copper(II) in aqueous solution that exhibits λ_{max} = 650 nm where ε = 118 M⁻¹ m⁻¹. In a second study the mono- and bis-ligand complexes of 2,9-dimethyl-1,10-phenanthroline with copper(I) are characterized in acetonitrile. Here, the most interesting findings are that the mono and bis complexes exhibit charge-transfer absorption maxima at very different wavelengths and that the intensities are not simply related one to the other.

Introduction

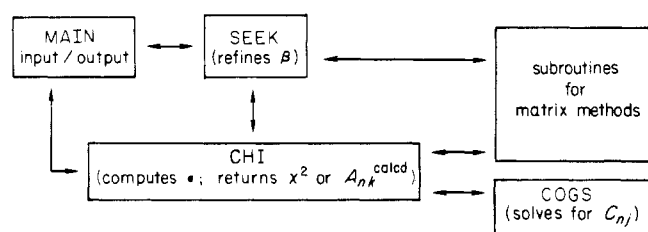
In the course of our work on copper complexes in solution we have often been concerned with speciation and spectral properties.^{1,2} Consequently we have developed a method for deconvoluting stability constants and absorption spectra using absorbance data from solutions containing multiple species.

Here, we describe the program and analyze two systems; in each case it is necessary to qualify previous conclusions drawn in the literature. Whereas previous polarographic studies have suggested that a maximum of four imidazole ligands coordinate to Cu(II),³ we observe a red shift in the visible spectrum at high imidazole/Cu(II) ratios. This result is reminiscent of the well-known pentaamine effect⁴ and shows that at least five imidazole ligands can bind to Cu(II). In studies of com-

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Scheme I



plexes of 2,9-dimethyl-1,10-phenanthroline (dmp) with Cu(I) in acetonitrile we find that the spectra of the 1:1 and 2:1 complexes are not related by the commonly assumed additivity rule.⁵⁻⁷

Although many algorithms have been developed for computing stability constants,⁸ our least-squares method offers some advantages. Most importantly, the program handles the dependent variables on two different levels. The stability constants (β) are refined iteratively by using a modified version of SEEK⁹ while the molar absorptivities (ϵ) are, at each stage in the refinement of the β 's, estimated by a standard *linear* least-squares method. Thus, initial guesses for the ϵ 's are not needed. Moreover, when the values are available, the β and/or the ϵ values of any species can be held constant.

Experimental Section

Materials and Methods. The imidazole studies were carried out with use of reagent grade imidazole that had been recrystallized three times. Copper was added from a stock solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, which was standardized by the method of Felsenfeld.¹⁰ The ionic strength was adjusted to $\mu = 1.0$ by using a stock solution of NaClO_4 ; hydrogen ion was adjusted to pH 8.0 by using a stock solution of HClO_4 . All measurements pertaining to the imidazole system were made in deionized water. Reagent grade acetonitrile was used for the dmp system. The dmp ligand was purchased from Aldrich and was recrystallized from water until the melting point was 160 °C.¹¹ The Cu(I) stock solution was prepared in the same solvent from $\text{Cu}(\text{NCCCH}_3)_4\text{PF}_6$ ¹² and was standardized spectrophotometrically by formation of the $\text{Cu}(\text{dmp})_2^+$ complex in ethanol.¹³ All measurements were made at 25 °C.

Instrumentation. Absorption measurements were carried out with a Cary 17D or a Perkin-Elmer 320 spectrophotometer. The pH was measured on an Orion Model 601A digital ionalyzer. The computer was a CDC 6600.

Computations. The interrelation of the subprograms is depicted in Scheme I. MAIN handles the input and output of data. In addition to the number of solutions involved, the concentrations of reagents in each, etc., formation constants are input for all relevant species, including the free ligand and/or the free metal if either is absorbing. In the case where only one metal and one ligand are involved, the equilibrium concentration of the j th species is expressed by the product

$$E(j)[\text{M}]^{M_j}[\text{L}]^{L_j}[\text{H}^+]^{N_j}$$

where $E(j)$ is the formation constant, M_j denotes the stoichiometry with respect to the metal ion, and L_j and N_j denote the stoichiometry with respect to the ligand and the proton, respectively. Actually, in the present version of the program up to two different metals and two different ligands can be involved. Other input includes the values of the A_{nk} and the ϵ_{ik} , which are stored in arrays ABS and EPS, respectively. A_{nk} denotes the absorbance of the n th solution at the k th

wavelength. ϵ_{ik} denotes the molar absorptivity of the i th species at the k th wavelength. Only known ϵ 's are input; initial guesses are not required for those to be estimated by the program. Finally, various control parameters need to be specified, e.g. an array defining which if any species have fixed β values, the number of cycles of refinement desired, and the fractional change in each parameter to be used by SEEK in sampling the error surface. MAIN then calls SEEK in order to refine the β values, i.e. the $E(j)$. When control returns to MAIN, CHI is called to obtain the final calculated absorbances A_{nk}^{calcd} , and all pertinent data are printed.

The iterative search routine SEEK⁹ has been implemented with only one modification. Briefly, SEEK attempts to fit the error surface to a generalized parabola involving $M = (N + 1)(N + 2)/2$ parameters where N is the number of β 's to be refined. By evaluating the error surface at each of M different points in the neighborhood of the current estimates of the β values, the equations that define the parabola are generated. If, as should be the case near the minimum, the error surface W is well described by the parabola, the true minimum in W should approximately coincide with the extremum of the calculated parabola. The β values associated with the extremum of the parabola then become the current estimators, and the process is iterated until there is no further decrease in the error function. To ensure that progress is made when the parabolic search method fails, we have incorporated a "descent" method into SEEK. In this mode a step is taken in the direction that gave the largest decrease in the error function. Actually, a series of steps are taken, each larger than the one before, until the error function fails to decrease or until the magnitude of any β value changes by a factor of 10. SEEK then reverts to the parabolic fitting mode.

When called by SEEK, CHI returns the error χ^2 (eq 1), which is

$$\chi^2 = \sum_{n,k} [A_{nk} - A_{nk}^{\text{calcd}}]^2 \quad (1)$$

associated with the current set of β values. The A_{nk}^{calcd} are defined in eq 2, which assumes Beer's law and a path length of 1 cm. In eq

$$A_{nk}^{\text{calcd}} = \sum_i C_{ni}\epsilon_{ik} + \sum_j C_{nj}\epsilon_{jk} \quad (2)$$

2, C_{ni} (C_{nj}) denotes the concentration of the i th (j th) species in the n th solution. Index i runs over all species with known ϵ 's; index j runs over species with variable ϵ 's. At each stage in the refinement the ϵ_{jk} that minimize eq 1 are obtained by a least-squares procedure. When CHI is called from MAIN, it returns the A_{nk}^{calcd} .

The C_{ni} are computed in subroutine COGS¹⁴ by a method of successive approximations. The first time through, the free metal and free ligand concentrations are taken to be the total metal and total ligand concentrations, respectively, except that the ligand concentration is corrected for any protonation equilibria. Subsequently, the equilibrium values from the previous cycle serve as initial estimates. Convergence criteria are (1) that the total calculated metal and ligand concentrations agree with the experimental concentrations to 0.01% and (2) that the concentration of no species has changed by more than 0.001% during the last iteration.

Results and Discussion

Computational Method. A number of iterative methods for spectral deconvolution have been described,⁸ but our program, which is denoted SPECDEC, appears to be the first program that (1) is written for generalized species and (2) is designed to refine β 's and ϵ 's by separate algorithms. This is possible because conditionally optimal ϵ 's can be estimated by a *linear* least-squares method at each stage in the refinement of the β values. The fact that the ϵ 's can be treated as linear parameters does not seem to be generally recognized although at least one other group has adopted this approach.¹⁵ As discussed by Lawton and Sylvestre in a more general context,¹⁶ handling linear parameters separately in calculations of this type can be expected to facilitate parameter refinement, the reason being that the number of variables that must be refined

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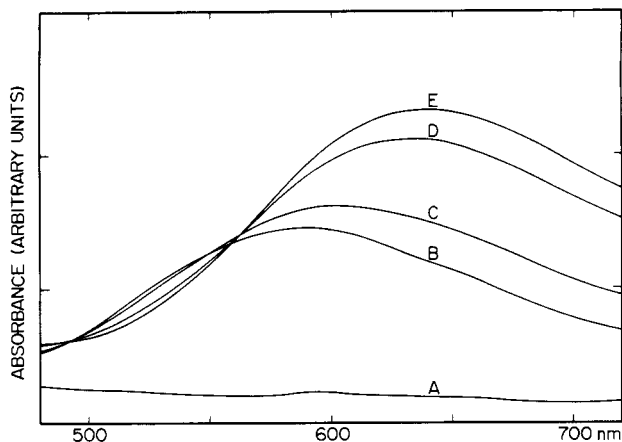


Figure 1. Absorption spectra of aqueous solutions of Cu(II) and imidazole at pH 8.0 and $\mu = 1.0$ M. The concentration of Cu(II) is 2.0 mM in all but A, which is the base line. Total imidazole concentrations: B, 0.1 M; C, 0.5 M; D, 2.0 M; E, 4.0 M.

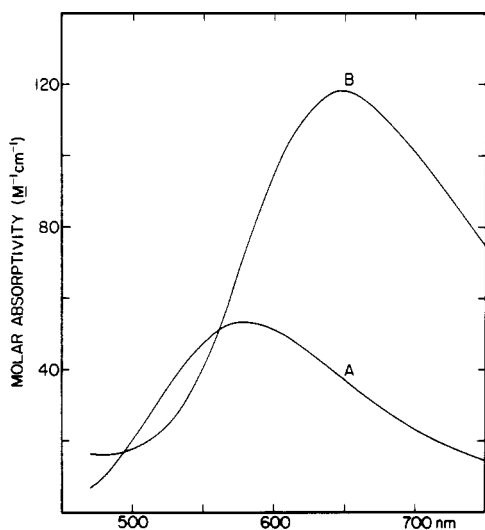


Figure 2. Absorption spectra of $\text{Cu}(\text{Im})_4^{2+}$ (A) and $\text{Cu}(\text{Im})_5^{2+}$ (B). The spectra were resolved by SPECDEC using the data from Figure 1. The standard deviation in the calculated absorbance of the fit was 2.09×10^{-3} .

by an iterative search method is sharply reduced. Convergence is never guaranteed in a nonlinear least-squares refinement and is only probable if good guesses are available for the parameters. Another important advantage of our method, which does not require initial guesses for the ϵ 's, is that preconceived ideas about the absorption spectra do not bias the calculation.

Although as many ϵ 's as desired can be introduced without affecting convergence, the fewer β 's that must be refined the better. Accordingly, SPECDEC is written so that all known β values can be treated as fixed constants. One of the most time-consuming aspects of the calculations is the solution of the mass balance equations. The method of COGS is probably not the most efficient,⁸ but it is reliable. An early version of the program used the method of COGSNR¹⁷ with much less success. Finally we note that, coincidentally, SEEK uses the same principle as LETAGROP.¹⁸

Copper(II) Complexes with Imidazole. Visible absorbance spectra of a series of copper(II) solutions are presented in Figure 1 where pH = 8.0, $\mu = 1.0$ M, and $\text{p}K = 7.3$ for imidazole.¹⁹ At low imidazole-to-copper ratios the absorbance

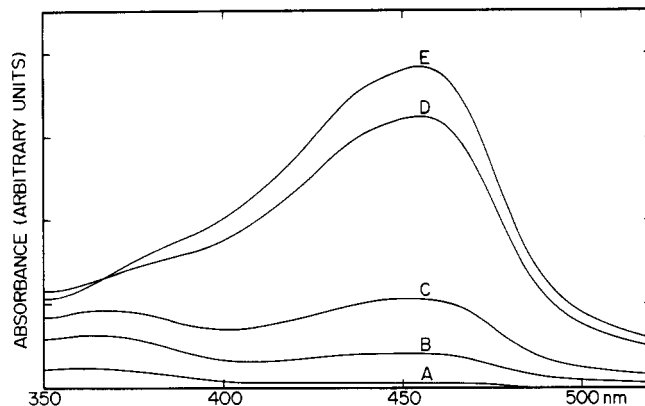
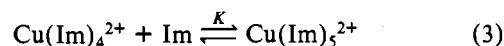


Figure 3. Absorption spectra of acetonitrile solutions of Cu(I) and dmp. The concentration of Cu(I) is 9.787×10^{-5} M. dmp concentrations: A, 2.301×10^{-5} M; B, 6.904×10^{-5} M; C, 1.151×10^{-4} M; D, 2.301×10^{-4} M; E, 4.602×10^{-4} M.

maximum undergoes a steady blue shift as the imidazole concentration increases. This is consistent with Sjöberg's results and can be ascribed to the successive formation of $\text{Cu}(\text{Im})_n^{2+}$ ($n = 1-4$).²⁰ However, as can be seen in Figure 1, the spectrum shifts back toward the red at high levels of imidazole. An analogous reversal occurs as the ammonia ligand is added, and the red shift has been termed the "pentaamine effect".⁴ The generally accepted explanation for the spectral shift to lower energies is that the addition of the fifth ligand decreases the tetragonal character of the ligand field, narrowing the spread in the energies of the d orbitals.^{21,22}

On the basis of the stability constants available,²³ the addition of the fourth imidazole should be essentially complete under the conditions in Figure 1. In fact, isosbestic points are maintained for all but the lowest ligand concentration in Figure 1. Thus, we have fit this data assuming the only copper-containing species present are those in eq 3. An excellent fit



of the data is obtained with $K = 0.8$ (0.1) M. The calculated spectra of $\text{Cu}(\text{Im})_4^{2+}$ and $\text{Cu}(\text{Im})_5^{2+}$ are given in Figure 2. The fact that $\text{Cu}(\text{Im})_5^{2+}$ is only favored at very high imidazole-to-copper ratios probably explains why it was missed in the polarographic studies.³ The fact that the free energy is positive for the addition of the fifth imidazole may reflect an inductive effect of the other imidazole groups and/or a steric effect.²⁴ The importance of the steric interactions is difficult to judge, but it can be noted that $\text{Cu}(\text{Im})_6^{2+}$ has been observed in the solid state.^{25,26} A much poorer fit results if we try to rationalize the data in Figure 1 in terms of $\text{Cu}(\text{Im})_4^{2+}$ and $\text{Cu}(\text{Im})_6^{2+}$. The molar absorptivities also argue in favor of the formation of $\text{Cu}(\text{Im})_5^{2+}$. By analogy with the ammonia system the molar absorptivities are expected to increase with each nitrogen added,^{4,22} but the sharp increase that occurs beyond the fourth nitrogen (Figure 2) is most readily explained in terms of the loss of inversion symmetry that occurs when the fifth ligand is added.²²

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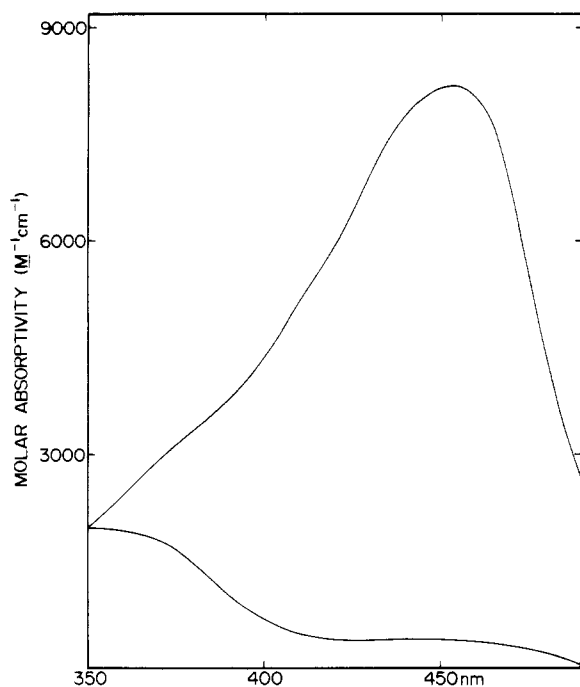


Figure 4. Absorption of Cu(dmp)^+ (lower curve) and Cu(dmp)_2^+ (upper curve). The spectra were resolved by SPECDEC using the data from Figure 3. The standard deviation in the calculated absorbance of the fit was 5.31×10^{-3} . This value is marginally high, possibly because ion-pairing effects have been ignored.

Sjöberg has also studied this system and has reported a similar spectrum for Cu(Im)_4^{2+} .²⁰ His data led him to invoke another imidazole complex that he inferred had a $\lambda_{\text{max}} \approx 595$ nm and that he assigned as Cu(Im)_6^{2+} . Thanks mainly to the larger ligand:metal ratios that have been employed, we believe our analysis is the more reliable. In particular Figure 1 plainly shows that the absorbance maximum shifts well beyond 595 nm as further imidazole combines with Cu(Im)_4^{2+} . In the

crystal the absorption maximum of Cu(Im)_6^{2+} occurs at 617 nm.²⁵

Copper(I) Complexes with dmp. In Figure 3 spectra of the copper(I)/dmp system are shown where the metal:ligand ratio has been varied over a wide range. When the metal is in excess, the major absorption occurs around 360 nm, but as more ligand is added a much stronger absorption band grows in around 454 nm. Analysis of these data using SPECDEC yields formation constants of 1×10^6 and $8 \times 10^{10} \text{ M}^{-1}$ for the 1:1 and 1:2 complexes, respectively, and the calculated spectra are presented in Figure 4. The relative errors in the calculated absorptivities are estimated to 5%; the formation constants are order of magnitude values. The error surface reveals that the fit is relatively insensitive to the value of β_1 and that the best fit always occurs with $\beta_2 \approx 10^5 \beta_1$. Thus, the stepwise formation constant $K_2 = \beta_2/\beta_1$ is known with better precision than $K_1 = \beta_1$.

Contrary to the commonly assumed model, there is no simple relationship between the spectra of the mono- and bis-ligand complexes of dmp and copper(I). Indeed, the molar absorptivity at the charge-transfer maximum has more than doubled with the addition of the second dmp, and the λ_{max} values are well separated (Figure 4). Besides the number of dmp molecules bound, several factors are likely to influence the charge-transfer spectrum, including the geometry about copper and the electronic structure of the other donors that may be involved. A reviewer has reminded us that similar effects are noted with ruthenium(II) systems.^{27,28}

Acknowledgment. We are indebted to the Public Health Service and the National Science Foundation for support of this research via Grants GM 22764 and CHE 81-05003, respectively. We also thank Jon R. Kirchoff for helping develop certain aspects of the program. J.A.B. was the recipient of a David Ross Fellowship administered by the Purdue Research Foundation.

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