A NEW METHOD FOR SIMULATING ESR SPECTRA OF COPPER COMPLEXES IN SOLUTION BASED ON FAST FOURIER TRANSFORM AND MONTECARLO APPROACH

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INTRODUCTION

It is clear from our recent multi-frequency ESR studies that cupric ion in the presence of excess histidine will bind to four equivalent nitrogen donor atoms from the imidazole moiety of histidine in frozen solutions(1). The binding of four histidines was surprising because histidine in solution is a tridentate ligand which acts as a bidentate ligand, $\log K_1 = 10.2$ and $\log K_2 = 7.9$. Thus there appears to be large changes in coordination for cupric ion in the presence of excess histidine as the solution freezes. In this report we have reinvestigated the bidentate binding of excess histidine to cupric ion in solution using the ESR method and have tried to reconcile the change in ligand binding upon freezing.

In order to determine whether the imidazole and the amine are bound to cupric ion ESR spectra for cupric ion in the presence of excess histidine in which ^{15}N is substituted for ^{14}N only in the imidazole ring are compared to ESR spectra for cupric ion in the presence of excess histidine where naturally abundant ^{14}N exists in both the amine and the imidazole ring. The nitrogen hyperfine structure for cupric ion in the presence of excess histidine is not as well resolved as expected because the ^{15}N lines fold back on the ^{14}N lines. Fourier Transfom analysis of ESR spectra for cupric ion in the presence of excess histidine with ^{15}N in the imidazole ring and ^{14}N in the amine helped determine that both

^{14}N and ^{15}N are bound to cupric ion in solution but only ^{15}N is bound in the frozen state. Thus it is reassuring that histamine-like or mixed histamine-like and glycine-like complexes are formed in solution.

COMPUTER SIMULATION

The X-band ESR spectrum for Cu(Histidine)$_2$ was simulated using a program for a fast tumbling copper complex in an isotropic environment. The program is based on Kivelson's theory taking into account the line-width equations of Kivelson, the second order frequency shift equation and the further assumption of Lorentzian line shapes(2). ESR spectra were simulated using a Montecarlo method. Selected spectral parameters were randomly varied within defined limits and chi square was calculated with respect to the experimental spectrum for each set of parameters. The initial ESR parameters were taken from the literature and spectral inspection. Fourier Transforms of ESR spectra were calculated using a swift Fourier Transform program, SFFT, on the IBM 9000 computer. Real and imaginary parts of the Fourier transformed spectra were interchanged and their amplitude (significant plots) were calculated (3). A graphic terminal was used to manipulate the spectra in the Fourier Transform space. Lines due to the hyperfine coupling constant for copper in the amplitude spectrum were cut off in order to examine only the nitrogen splittings.

ESR SPECTRA

Well resolved spectra for ^{63}Cu in the presence of excess histidine in D_2O were simulated for three models: four equivalent ^{14}N donor atoms, $Cu-^{14}N$; three equivalent ^{14}N donor atoms, $Cu-3^{14}N$; or a mixture of $Cu-^{14}N$ and $Cu-3^{14}N$ (Fig.1).

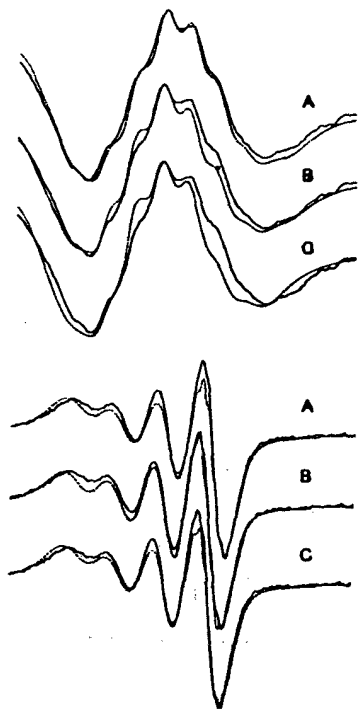
Fig. 1 – Top three spectra: Second derivative, X-band ESR spectra (solid) for M_I =+3/2 line for $^{63}Cu^{2+}$ (2 mM) in the presence of excess histidine(20mM) in D_2O at room temperature. Simulated spectra (dashed) assuming four nitrogen donor atoms, $^{63}Cu-4N(C)$; three nitrogen donor atoms, $^{63}Cu-3N(B)$; and 80% relative concentration for a com- plex with four nitrogen donor atoms super- imposed with 20% for a complex with three nitrogen donor atoms (A).
Bottom three spectra: first derivative X-band ESR (solid) and simulated spec- tra (dashed) showing full display.

A good fit was obtained for the entire spectrum for the model with two complexes using the first derivative display (Fig.1A bottom) and for the three high field lines using the se- cond derivative display (Fig.1A top). This fit consists of a superposition of the spectrum for $Cu-4^{14}N$ (80%) and $Cu-3^{14}N$ (20%) where the τ_R value is 85 psec for both complexes. The same three models were tested for the ESR spectrum of copper in the presence of excess histidine in which ^{15}N is sub- stituted for ^{14}N only in the imidazole ring. The best fit was obtained for the model having two complexes: $Cu-2^{14}N\,2^{15}N$ (80%) and $Cu-2^{14}N\,1^{15}N$ (20%) with τ_R = 65 ps (Fig.2A').
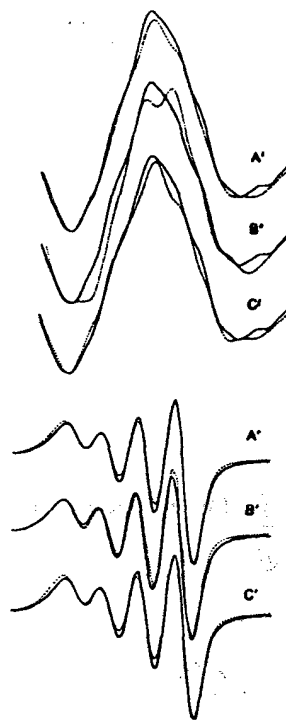

Fig.2- Top three spectra: Second deri- vative, X-band ESR spectra (solid) at room temperature for M_I =+3/2 line for $^{63}Cu^{2+}$ (2mM) in the presence of excess histidine 1,3 $^{15}N_2$ for which the ^{15}N isotope is substituted for ^{14}N in the imidazole ring in D_2O. Simulated spec- tra (dashed) assuming two ^{14}N donor atoms plus two ^{15}N donor atoms, $^{63}Cu-2^{14}N2^{15}N$ (C); two ^{14}N donor atoms plus one ^{15}N donor atom, $^{63}Cu-2^{14}N1^{15}N$ (B); and 80% relative concentration for

$^{63}Cu-2^{14}N2^{15}N$ superimposed with 20% for $^{63}Cu-2^{14}N1^{15}N$ (C).
Bottom three spectra: first derivative, X-band, ESR spectra (solid) and simulated spectra (dashed) showing full display.

These results are consistent with the interpretation of the data for cupric histidine complexes for which all the nitrogen atoms in histidine are ^{14}N.

FT ESR SPECTRA

That the nitrogen hyperfine coupling pattern for cupric ion in the presence of excess histidine arises from predominantly a single complex both ^{15}N and ^{14}N donor atoms is even more apparent from the Fourier Transform of ESR spectra (Figs. 3 and 4). In the Fourier Transform domain, the model spectra differ with respect to the positions of the lines according to a change in the hyperfine pattern (Fig. 3 and Table).
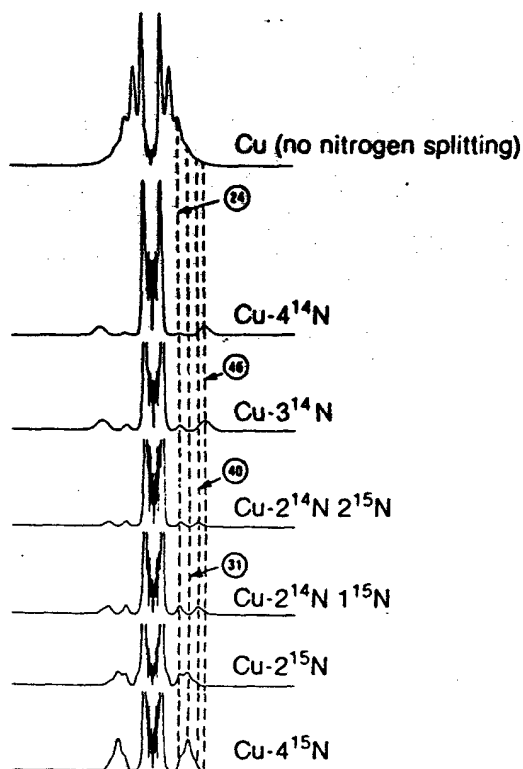
Fig.3 - Fourier Transforms for simula-

ted spectra for which ESR parameters are the same of Figure 1. The spectra represent intensity versus frequencies which represent the Fourier Transform counterpart of the magnetic field. In this figure there are 256 positions for the magnetic field which correspond one to one to frequency space. Transforms from top to bottom are for the following simulations: Cupric complex with no nitrogen donor atoms; with four ^{14}N donor atoms; with three ^{14}N donor atoms; with two ^{14}N plus two ^{15}N donor atoms; with two ^{14}N plus one ^{15}N donor atoms; with two complexes, one with two ^{15}N and one with one ^{15}N donor atoms; and with four ^{15}N donor atoms. Note, the four vertical dashed lines from left to right indicate the 24th, 31st, 40th and 46th positions. Also the 8th position is cut off after the first two transforms.

Table ^{14}N and ^{15}N Hyperfine Coupling Constants for the $M_I = -^1/_2$ Line in the g_1 Region

donor atoms	pattern[a]
1 ^{14}N	1-1-1
2 ^{14}N	1-2-3-2-1
3 ^{14}N	1-3-6-7-6-3-1
4 ^{14}N	1-4-10-16-19-16-10-4-1
1 ^{15}N	1--1
2 ^{15}N	1--2--1
3 ^{15}N	1--3--3--1
4 ^{15}N	1--4--6--4--1
1 ^{14}N + 1 ^{15}N	1--1--1-1--1--1
2 ^{14}N + 1 ^{15}N	1--2-1-3-2-2-3-1-2-1
1 ^{14}N + 2 ^{15}N	1--1-2--1-2-1--2-1--1
2 ^{14}N + 2 ^{15}N	1--2-2-3-4-1-2-6-2-1-4-3-2-2--1

[a] The ratio of the moment for ^{15}N to that for ^{14}N is about 1.4.

Patterns for ^{14}N, which have an 11 G hyperfine coupling constant, correspond to the outermost lines at the 46th position in frequency space. Patterns for ^{15}N, which have a 15.5 G hyperfine coupling constant, correspond to the line at the 31st position. The ^{63}Cu, with a hyperfine splitting of 61 G, corresponds to the 8th position. The higher harmonics of the copper line at the 16th and 24th positions (see the top spectrum in Fig.3). If a mixture of ^{14}N and ^{15}N donor atoms form the square planar

configuration, the lines at the 64th and 31st positions in the frequency domain are absent and a line at the 40th position appears.

Several points can be drawn from the Fourier Transforms in Fig. 3. First, there is little overlap between the position for ^{14}N and positions for ^{15}N or Cu. Second, there is some overlap between the positions for ^{15}N and the 3rd harmonic for copper. Third, there is a shift to a lower position (position 40) if a mixture of ^{14}N and ^{15}N donor atoms contribute to the square planar configuration. If the spectra for a mixture of two complexes one with only ^{14}N donor atoms and one with only ^{15}N donor atoms, are superimposed, lines at the 46th and 31st positions (not at 40th position) confirm the absence of a complex with both ^{14}N and ^{15}N donor atoms.

In the Fourier Transform domain the ESR spectrum for ^{63}Cu in the presence of excess histidine is similar to the simulated spectrum composed of 80% by concentration, of cupric ion bound to four nitrogen donor atoms, Cu-4^{14}N, and 20% of a cupric complex bound to three nitrogen donor atoms, Cu-3^{14}N (Figure 4A-B).
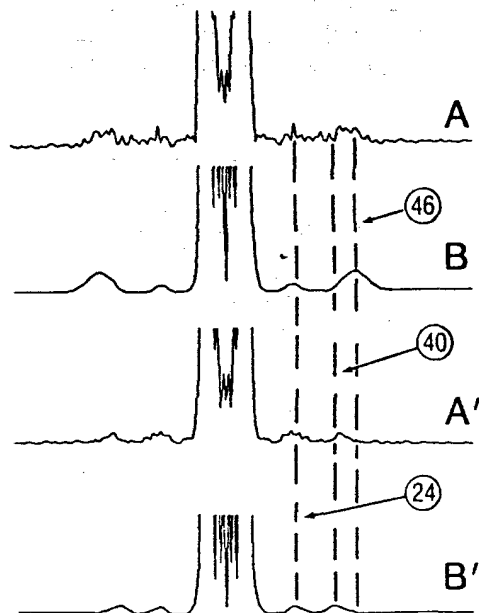
Fig.4 - Fourier Transform for experimental data for ^{63}Cu in the presence of excess histidine, Cu-^{14}N-exp (A); Transform for simulated data assuming 80% relative concentration of a cupric complex with four ^{14}N nitrogen donor atoms, Cu-4^{14}N, and 20% with three ^{14}N nitrogen donor atoms, Cu-3^{14}N; transform for experimental data for ^{63}Cu in the presence of excess histidine 1,3 $^{15}N_2$, (A'); and Transform, for simulated data assuming 80% concentration of a cupric complex with two ^{14}N and two ^{15}N nitrogen donor atoms, Cu-2^{14}N 2^{15}N, and 20% Cu-2^{14}N1^{15}N, (B').

The ESR spectrum for ^{63}Cu in the presence of excess histidine with ^{15}N in the imidazole ring, Cu-^{14}N, ^{15}N is similar to the spectrum composed of 80% cupric ion bound to two ^{15}N donor atoms plus two ^{14}N donor atoms, Cu-2^{14}N2^{15}N, and 20% of cupric ion bound to one ^{15}N plus two ^{14}N donor atoms, Cu-2^{14}N1^{15}N (Fig.4 A'-B'). It is not surprising that the spectral fits in Figs.1 and 2 complement the fits for the Fourier Transform domain in Fig.4.

In conclusion Fourier Transform can become an useful tool in interpreting hyperfine coupling constants for spectra which are well resolved but complicated due to overlap of many lines.

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