Notes

Electron Spin Resonance Parameters for some Copper(II)–Bis(amino-acid) Complexes†

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The presence of two components, presumably *cis* and *trans* isomers, was previously indicated by the ^{14}N superhyperfine structure pattern in the e.s.r. spectra of a number of copper(II)–bis(amino-acid) complexes in aqueous solution. In the present work the *g* and hyperfine values of the individual species have been obtained from spectra of the ^{63}Cu and ^{65}Cu isotopes. Significantly different values have been observed for the two components and these differences are discussed in terms of possible deviations from the ideal square-planar structure in the *cis* and *trans* isomers.

In a recent paper[1] we showed that, by use of the ^{63}Cu isotope and D_2O solvent, ^{14}N superhyperfine structure could be resolved on the high-field copper peak of the e.s.r. spectra of some copper(II)–bis(amino-acid) complexes. In cases where the only nitrogens co-ordinated to the copper arose from amide groups, it was possible to resolve this structure into two quintets (intensity ratios 1:2:3:2:1), which were interpreted as arising from the presence in equilibrium of isomers with nitrogens co-ordinated in *cis* and *trans* arrangements. However, it was not possible to resolve any superhyperfine structure on the other copper hyperfine peaks so that, although values for the nitrogen superhyperfine splitting could be measured for both components, the *g* and copper hyperfine values could not be individually resolved and only average values were reported.

The conventional approach to resolving these parameters is to obtain spectra at different frequencies, when the superhyperfine envelopes from the separate species are shifted relative to one another if their *g* values are different. However, no suitable spectrometer was available to us and we describe here how these measurements can be accomplished by using the individual magnetic isotopes of copper (^{63}Cu and ^{65}Cu).

Since the magnitude of the copper hyperfine structure is directly proportional to the magnetic moment of the isotope [both ^{63}Cu and ^{65}Cu have nuclear spin $I = \frac{3}{2}$ and their magnetic moments (μ) are 2.2206 and 2.3789 nuclear magnetons, respectively[2]] the superhyperfine structures of the two components on the high-field copper peak will shift relative to one another if the two species have different copper hyperfine values. From the magnitudes of such shifts, the copper hyperfine and *g* values of the two components can be evaluated.

An example of such a measurement is shown in Figure (*i*) and (*ii*) for the bis(glutamic acid) complex. It should be noted that because of the high degree of accuracy required for these measurements, a solution of Fremy's salt $\{K_2[NO(SO_3)_2]$: g = 2.0054, A = 1.30 mT (ref. 3)$\}$, in a capillary tube attached to the sample cell, was used as an internal calibration standard. The positions, *H*, of the centres of the resonances of the superhyperfine envelopes of the two components are given by (1) and (2) for the ^{63}Cu isotope and by (3) and (4) for the ^{65}Cu isotope,

$$H_0(a) + 1.5A(^{63}Cu_a) - 0.75A^2(^{63}Cu_a)/H \quad (1)$$

$$H_0(b) + 1.5A(^{63}Cu_b) - 0.75A^2(^{63}Cu_b)/H \quad (2)$$

$$H_0(a) + 1.5A(^{65}Cu_a) - 0.75A^2(^{65}Cu_a)/H \quad (3)$$

$$H_0(b) + 1.5A(^{65}Cu_b) - 0.75A^2(^{65}Cu_b)/H \quad (4)$$

where $H_0(a)$ and $H_0(b)$ are the fields at the centres of the resonances and A the isotropic hyperfine coupling constant. Therefore, since $A(^{63}Cu)/A(^{65}Cu) = \mu(^{63}Cu)/\mu(^{65}Cu)$, we have four equations with four unknowns and the values for *g* (calculated from $h\nu = g\beta H_0$) and $A(^{63}Cu)$ obtained for the components of each of the amino-acid complexes previously studied[1] are given in the Table.

With the exception of the aspartic acid complex, illustrated in Figure (*iii*), the *g* values for the two components are very similar for all of the complexes, their differences being less than the errors in the measurements, whereas there are significant differences between the copper hyperfine values. It should also be noted that the components with the larger copper hyperfine values also had the larger nitrogen superhyperfine splittings, suggesting that the different A(Cu) values do not result from different degrees of delocalization of the unpaired electron density onto the amide groups of the amino-acid ligands. In this respect a comparison of the anisotropic values would have been more informative, because the unpaired electron is located primarily in the copper $d_{x^2-y^2}$ orbital, but as yet it has not been possible to resolve any peaks that could be assigned to the individual components in the solid state. This lack of resolution of the two different $A_\parallel$ envelopes indicates that the magnitudes of the $A_\parallel$ values differ by a smaller factor than the 14—20% differences in the isotropic values, which further supports the suggestion that the magnitudes of the isotropic A values are not directly proportional to the electron density on the copper. It would appear, therefore, that there is some involvement of copper 4*s* orbitals in the molecular orbital that contains the unpaired electron, since the 4*s* electron density produces a contribution to the isotropic A value of opposite sign to that from the polarization of core *s* electrons by the electron density in 3*d* orbitals.[4] The complex with the smaller isotropic A value has the greater unpaired electron density in the 4*s* orbital, if, as expected, the core polarization makes the major contributions to the isotropic A values. By using the calculations of Goodman and Raynor[5] for the hyperfine coupling expected for a free copper atom with an outer shell electron configuration of $3d^{10}4s^1$, the A values for the two components from the amino-acid complexes correspond to differences in 4*s* electron density of about 0.6%. The different involvements of the 4*s* orbitals in the molecular orbitals containing the unpaired electron

† *Non-S.I. unit employed:* Nuclear magneton = 5.051×10^{-27} J T^{-1}.

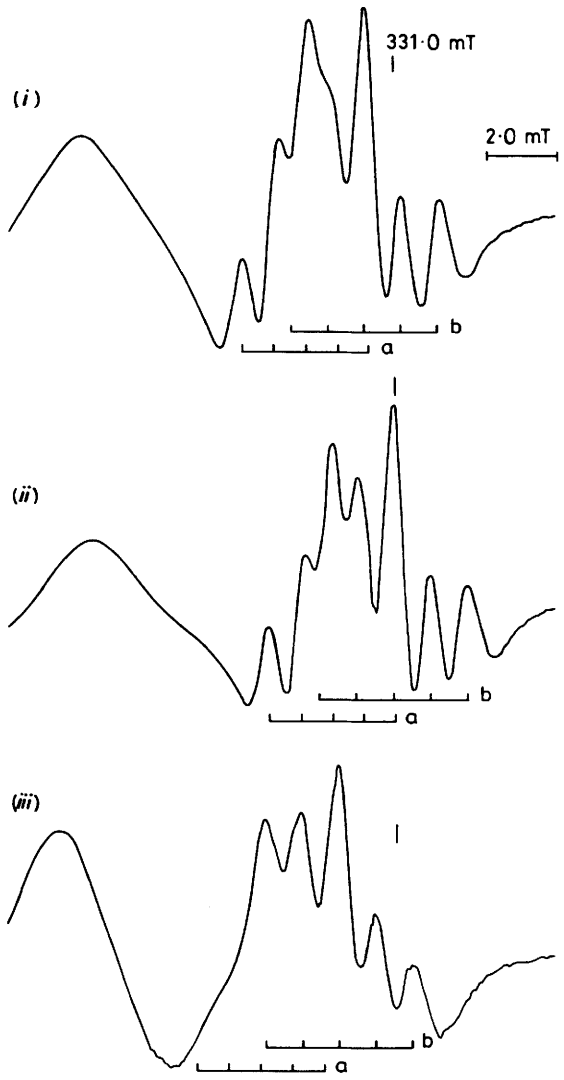

Figure. The high-field portion of the second-derivative e.s.r. spectra of (*i*) ^{63}Cu–bis(glutamic acid), (*ii*) ^{65}Cu–bis(glutamic acid), and (*iii*) ^{63}Cu–bis(aspartic acid) in D_2O solution at ambient temperature

probably result from the different symmetries of the copper ions in the two components. If, as previously suggested, those two components correspond to the *cis* and *trans* isomers, the lower symmetry in the *cis* isomer would be expected to facilitate the mixing of the 4*s* orbital into the molecular orbital, so that the component with the smaller isotropic copper *A* value can be assigned to the *cis* isomer. Since this component also has the smaller ^{14}N hyperfine splitting, this assignment is different from that which was made in our original paper,[1] where the component with the smaller ^{14}N *A* value was tentatively assigned to the *trans* isomer.

Table. E.s.r. parameters[a] for some ^{63}Cu–bis(amino-acid) complexes

Amino acid	Component[b]	$A(^{63}Cu)$/mT	$A(^{14}N)$/mT	*g*
Lysine	(a)	6.1	0.89	2.121
	(b)	7.0	1.07	2.119
Glutamic acid	(a)	6.1	0.90	2.120
	(b)	7.2	1.06	2.121
Alanine	(a)	6.0	0.90	2.122
	(b)	6.9	1.04	2.119
Valine	(a)	6.2	0.91	2.120
	(b)	7.1	1.05	2.118
Glutamine	(a)	6.0	0.88	2.120
	(b)	6.9	1.00	2.119
Asparagine	(a)	5.9	0.91	2.121
	(b)	7.1	1.01	2.123
Proline	(a)	6.0	0.95	2.118
	(b)	7.0	1.08	2.118
Aspartic acid	(a)	6.9	0.90	2.138
	(b)	7.0	1.05	2.125

[a] All parameters were obtained by computer simulation. Approximate errors are ±0.2 T for *A*(Cu), ±0.03 T for *A*(N), and ±0.003 for *g*. [b] Components (a) probably correspond to *cis* and components (b) to *trans* isomers, which is the opposite assignment to that used in ref. 1.

The reasons for the different nitrogen *A* values are not altogether clear since they arise from the direct overlap of the copper $3d_{x^2-y^2}$ and nitrogen 2*s* orbitals and the above arguments suggest that both components have similar electron densities in their $d_{x^2-y^2}$ orbitals. It would appear, therefore, that there are different degrees of overlap between the copper $d_{x^2-y^2}$ and nitrogen 2*s* orbitals for the two isomers. Since there is little variation in the copper–nitrogen bond lengths in amino-acid complexes,[6] the most obvious source of the different nitrogen *s*-electron densities is a deviation of the nitrogen atoms from the *x*- and *y*-axes of the copper ion. This could arise either because of deviations of O–Cu–N angles from 90°, typical values being in the region 83—84° for α-amino acids,[6] or because of tetrahedral distortions,[6] which correspond to a movement out of the equatorial plane of the nitrogen and oxygen atoms bound to the copper.

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