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ESR STUDY OF COPPER(II) COMPLEXES OF α -AMINO ACIDS. COORDINATION MODES AND METAL-LIGAND BONDS IN FROZEN AQUEOUS SOLUTIONS

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ESR STUDY OF COPPER(II) COMPLEXES OF α -AMINO ACIDS. COORDINATION MODES AND METAL-LIGAND BONDS IN FROZEN AQUEOUS SOLUTIONS

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Various copper(II) complexes of potentially terdentate α -amino acids and, for comparison, those of ethylenediamine and histamine have been investigated. The ESR spectra at 1:1 and 1:4 metal-ligand concentration ratios over different pH regions have been recorded in frozen aqueous solutions. The parallel and perpendicular components of the g and A tensors, the nitrogen superhyperfine coupling constants in the different directions, and the numbers of equatorial nitrogen donor atoms have been determined by computer simulation of the spectra. The energies of the d-d electronic transitions have been determined by Gaussian analysis of the visible absorption bands. Molecular orbital coefficients characteristic of the metal-ligand bonds have been derived for an effective D_{4h} local symmetry. Near the freezing point, the equilibrium for the complexes involving bis(glycinato) coordination is shifted towards the *trans* isomer. The amino groups of *R,S*-2,3-diaminopropionic acid and *R,S*-2,4-diaminobutyric acid (Daba), which are protonated in acidic media, bind equatorially to copper(II) with increasing pH, except for the 1:2 complex of Daba above pH ~ 8 , where the fourth nitrogen is coordinated axially. In the 1:2 complexes of *S*-asparagine above pH ~ 9 , the first deprotonated amide nitrogen is bound axially, and the second one equatorially. In the 1:2 complexes of *S*-histidine, the imidazole nitrogens enter the equatorial plane when they lose the protons attached to them at low pH. A competition can be observed between the σ -bonds with different symmetries. The influence of the coordination modes on the covalent character of the metal-ligand bonds is discussed.

Keywords: Copper, esr, aminoacids, isomerization, speciation

INTRODUCTION

ESR spectroscopy has been widely used to study complexes formed in solutions between the copper(II) ion and various ligands, including α -amino acids.¹ ESR parameters obtained from the characteristic points of spectra² of frozen solutions and d-d electron excitation energies have been used to compute the molecular orbital coefficients which characterize the metal-ligand bonds.^{1,3,4} Goodman and coworkers^{5,6} utilized ESR spectroscopy to study the nature of the coordination of

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several α -amino acids to copper(II). The number of nitrogen donor atoms coordinated equatorially in the different isomers, and the concentration ratios of the isomers in aqueous solution, were determined by computer simulation of the nitrogen super-hyperfine structure of the spectra taken at room temperature. Isotropic spectra which provide no data on dipole-dipole interactions, afford less bonding information than anisotropic spectra of frozen solutions.

In the present work, copper(II) complexes of a series of potentially terdentate α -amino acids with oxygen or nitrogen donor atoms in their side-chains have been investigated. Computer simulation of the ESR spectra of frozen aqueous solutions has led to more accurate values of parameters than those obtainable with the Kneubühl approximation,² and has yielded additional ESR data. The number of equatorial nitrogen donor atoms in various species could also be determined. The ESR parameters have been used to compute molecular orbital coefficients in the knowledge of the energies of the d-d electronic transitions. The coordination modes and their influence on the covalent character of the metal-ligand bonds have been studied.

EXPERIMENTAL

Reagents of analytical grade from REANAL were used without further purification for preparation of the solutions. Optimal conditions for the formation of the different species were chosen by computing the pH-dependence of the concentration distribution of copper(II) among the different complexes. Equilibrium constants at 298 K were taken from the literature.⁷⁻¹³ The metal ion concentration was 2×10^{-3} mol dm⁻³ with glycine (Gly), *S*-threonine (Thr), *S*-serine (Ser), ethylenediamine (En), *R,S*-2,3-diaminopropionic acid (Dapa), *R,S*-2,4-diaminobutyric acid (Daba), *R,S*-ornithine (Orn), *S*-lysine (Lys), histamine (Hin) and *S*-histidine (His) as ligands, while with the less soluble ligand *S*-asparagine (Asn) the copper(II) concentration was 10^{-3} mol dm⁻³. The ligand to metal concentration ratios were 1:1 and 4:1. The solutions also contained 5 vol. % methanol to promote glass formation during freezing. The pH was adjusted with NaOH with an accuracy of 0.05 pH units, using a RADELKIS (Hungary) OP-208/1 digital pH-meter.

Electronic spectra were recorded between 450 and 900 nm on a Beckman DU spectrometer at 296 K, and in some cases at 273 K. The measured spectra were not corrected for those species the concentrations of which exceeded 97% of the total copper(II) concentration. In other cases the absorptions of the minor complexes were computed from their concentrations and spectra under different conditions, and were subtracted from the absorption of the solution to obtain the d-d spectrum of the predominant species. For the majority of the copper(II)-amino acid systems an iteration procedure was required to compute the d-d spectra of all species. The visible band was then resolved into Gaussian components using a FORTRAN IV program run on an IBM 360 compatible R-55 computer.

ESR spectra were recorded at 77 K on a JEOL JES-FE3X spectrometer with 100 kHz field modulation, using Mn(II)-doped MgO powder as standard. With the majority of the species predominating in acidic media, it was necessary to correct the pH of the solutions by about 0.2-0.3 pH unit (generally in the acidic direction) to counterbalance the changes in concentration distribution upon cooling. Simulation of the spectra was carried out on a PDP 11—equivalent EMU-11 (KFKI, Hungary) computer with a FORTRAN program. This program takes into account the *g* and *A* tensors of rhombic symmetry, axial quadrupole interactions, anisotropic superhyper-

fine structure, and orientation and magnetic quantum number-dependent linewidth.¹⁴

ESR results were evaluated by assuming an effective D_{4h} local symmetry of the complexes. In this case, the antibonding molecular orbitals of the copper(II) ions can be written¹⁵ as shown in (1) to (4).

$$\psi_{b_{1g}} = \alpha d_x^2 - y^2 - \alpha' \phi_L(x^2 - y^2) \quad (1)$$

$$\psi_{a_{1g}} = \alpha_1 d_z^2 - \alpha_1' \phi_L(z^2) \quad (2)$$

$$\psi_{b_{2g}} = \beta_1 d_{xy} - \beta_1' \phi_L(xy) \quad (3)$$

$$\psi_{e_g} = \beta d_{xz} - \beta' \phi_L(xz) \quad (4)$$

$$\psi_{e_g} = \beta d_{yz} - \beta' \phi_L(yz)$$

The x and y axes are directed towards the donor atoms of the ligands. The d and ϕ_L functions represent the copper(II) 3d orbitals and the ligand group orbitals of appropriate symmetry, respectively. In the case of elongated octahedral structures, the unpaired electron is placed in the $\psi_{b_{1g}}$ antibonding orbital. The MO coefficients α , β_1 and β characterizing the covalency of the in-plane σ , in-plane π and out-of-plane π -bonds, respectively, can then be related to the spin-Hamiltonian parameters as follows¹⁵⁻¹⁷

$$g_{\parallel} - g_e = -8\lambda_o/\Delta E_{xy}(\alpha^2\beta_1^2 - f_1) \quad (5)$$

$$g_{\perp} - g_e = -2\lambda_o/\Delta E_{xz,yz}(\alpha^2\beta^2 - f_2) \quad (6)$$

$$A_{\parallel} = -K + P[-4/7\alpha^2 + (g_{\parallel} - g_e)(1 + f_3) + 3/7(g_{\perp} - g_e)(1 + f_4)] \quad (7)$$

$$A_{\perp} = -K + P[2/7\alpha^2 + 11/14(g_{\perp} - g_e)(1 + f_4)] \quad (8)$$

where $g_e = 2.0023$ is the free electron g-factor, λ_o is the spin-orbit coupling constant (-828 cm^{-1}), and P is the dipole coefficient (0.036 cm^{-1}) of the free ion. ΔE_{xy} and $\Delta E_{xz,yz}$ are the energies of the $B_{2g} \leftarrow B_{1g}$ and $E_g \leftarrow B_{1g}$ electronic transitions, respectively, and f_1 , f_2 , f_3 and f_4 are small correction terms. K is the Fermi hyperfine contact term, which was calculated from equation (9)

$$K = -A_o + P(g_o - g_e) \quad (9)$$

where

$$A_o = 1/3(A_{\parallel} + 2A_{\perp}) \text{ and } g_o = 1/3(g_{\parallel} + 2g_{\perp}) \quad (10)$$

The parallel and perpendicular components of the g and A tensors obtained by spectrum simulation were used in equations (5)–(7) and (10), while ΔE_{xy} and $\Delta E_{xz,yz}$ were determined through Gaussian analysis of the visible spectra. The constants necessary for calculating α , f_1 , f_2 , f_3 and f_4 were those of Kivelson and Neiman.¹⁶ The whole calculation procedure has been described in detail in previous work.¹⁸ The corresponding FORTRAN program was run on an R-55 computer.

The σ -bonding orbital between the ligand and the metal 4s orbitals can be written¹⁹ as shown in (11).

$$\psi_{a_{1g}} = \epsilon'4s + \epsilon\phi_L(a_{1g}) \quad (11)$$

The MO coefficient ϵ' which characterizes the covalent character of the 4s σ -bond in the case of an effective D_{4h} symmetry, can be calculated from the Fermi hyperfine contact term according to equation (12)

$$K = \alpha^2(K_{\text{core}} + \epsilon'^2 K_{4s}) \quad (12)$$

where $K_{\text{core}} = 0.0185 \text{ cm}^{-1}$ and $K_{4s} = -0.015 \text{ cm}^{-1}$ are the core and outer s shell spin polarizations, respectively,¹⁹ while α^2 is obtained by the previous calculation method.

The isotropic nitrogen superhyperfine (shf) coupling constant, a_{N_0} , was also used to characterize the electronic structure of our complexes; a_{N_0} is the arithmetic average of the principal values of the nitrogen shf coupling tensor [$a_{\text{N}_\perp}(\text{N})$ and $a_{\text{N}_\parallel}(\text{N})$]. These principal values can be related to the shf coupling constants (\bar{a}_{N_\perp} and $\bar{a}_{\text{N}_\parallel}$) determined in the principal directions of the g-tensor as follows.

$$a_{\text{N}_\perp} = 1/\sqrt{2}\{[a_{\text{N}_\perp}(\text{N})]^2 + [a_{\text{N}_\parallel}(\text{N})]^2\}^{1/2} \quad (13)$$

$$a_{\text{N}_\parallel} = a_{\text{N}_\perp}(\text{N}) \quad (14)$$

From these

$$a_{\text{N}_0} = 1/3\{2a_{\text{N}_\parallel}^2 + [2a_{\text{N}_\perp}^2 - a_{\text{N}_\parallel}^2]^{1/2}\} \quad (15)$$

RESULTS AND DISCUSSION

The electronic spectral data for the different species in solution are listed in Table I. At temperatures close to the freezing points of the solutions, the spectra agreed with those at 296 K within experimental error. The only exception was the (120) complex of His, for which an increase in intensity was observed at lower temperatures (Table I).

The evaluation of the electronic spectral data was based upon the following facts and assumptions. In general, bis(*S*-amino acidato)copper(II) complexes have two or three CD bands below 22000 cm^{-1} ,²⁰ while there are three bands in the single-crystal polarized electronic spectra of bis(*S*-tyrosinato)copper(II)²¹ below 18000 cm^{-1} . If a fourth d-d band existed, covered by the charge transfer bands above 30000 cm^{-1} ,²²⁻²⁶ this would indicate a considerable splitting of the E_g level, accompanying a significant rhombic distortion, which in turn should yield a large rhombic splitting in the ESR spectrum. However, the spectrum displayed axial character in all cases (see below).

We therefore assumed that each of the d-d electronic transitions occurs in the visible or near infrared region, and that there is no significant splitting of the E_g level. Accordingly, the visible absorption spectra were resolved into three Gaussian components. The energies of the d-d transitions obtained by this procedure are given in Table I. The component bands were assigned according to the orbital energy sequence in bis(*S*-tyrosinato)copper(II)^{18,21} as follows:

$$A_{1g} \leftarrow B_{1g} < B_{2g} \leftarrow B_{1g} < E_g \leftarrow B_{1g}$$

The ESR spectra of species containing 1 possible nitrogen donor atom ((111) complexes of diaminocarboxylic acids and (110) complexes of the other amino acids),

TABLE I
Absorption spectral data for the complexes.

Complex $\text{Cu}_p\text{L}_q\text{H}_r$		Energy of Gaussian components ^{d,e}			
Ligand	pqr	$\nu_{\text{max}}^* (\epsilon_{\text{max}})^b$	1	2	3
Glycine	110	13.5 (35)			
	120	15.9 (46)	14304	15894	17798
S-Threonine	110	13.7 (35)			
	120	16.1 (54)	14667	16036	17803
	12-1	16.45(37)	14757	16333	18554
	12-2	16.75(37)	15039	16738	19618
S-Serine	110	13.7 (37)			
	120	16.1 (52)	14565	15992	17771
	12-1	16.25(42)	14662	16367	18550
	12-2	16.5 (38)	14909	16662	19129
S-Asparagine	110	13.9 (40)			
	120	16.15(57)	14539	15979	17843
	12-1	16.45(58)	14755	16421	18210
	12-2	17.05(55)	15173	17034	18758
Ethylenediamine	110	15.6 (27)	13466	15656	18386
	120	18.2 (65)	16951	18176	19167
R,S-2,3-Diamino-propionic acid	111	13.4 (32)			
	110	14.9 (34)			
	122	15.4 (47)			
	121	16.4 (61)			
	120	17.9 (63)	16266	17973	19493
R,S-2,4-Diamino-butyric acid	111	13.8 (38)			
	110	16.4 (40)	14317	16191	17713
	122	16.1 (57)	14233	15945	17609
	121	16.7 (66)	14622	16530	17932
	120	16.45(94)	14232	16439	18221
R,S-Ornithine	111	13.8 (38)			
	122	16.2 (58)	14437	16056	17959
S-Lysine	111	13.8 (39)			
	122	16.2 (58)	14504	16100	17992
Histamine	110	15.05(37)	12932	15050	16701
	120	16.4 (73)	14299	16231	17835
S-Histidine	111	13.8 (40)			
	110	14.4 (33)			
	121	16.3 (58)	14733	16180	17408
	120	15.6 (84)	13588	15460	16903
		15.6 (94) ^c	13410 ^c	15456 ^c	16944 ^c

^a In 10^3 cm^{-1} units. ^b In $\text{M}^{-1} \text{ cm}^{-1}$ units. ^c Aqueous solution, 273 K. ^d In cm^{-1} units. ^e Estimated error $\pm 70 \text{ cm}^{-1}$.

and of the (122) complex of Dapa cannot be evaluated, since a number of species are present. There are also a few other complexes for which the ESR spectra are difficult to analyse, as the hyperfine structure is unresolved due to the interaction between paramagnetic centres. It should be noted that the spectra did not depend on the rate of freezing, indicating that freezing was slow enough in all cases for chemical equilibria to adjust to the changes in temperature. Thus, the anisotropic spectra reflect the properties of the equilibrium systems at the freezing point. The (110)

complexes of Dapa and His and the (121) complex of Dapa contain carboxylate groups displaced from equatorial coordination by nitrogen donors from the side-chains. Near the freezing point, these carboxylate groups are possibly involved in intermolecular bonding, to copper(II) ions in other complex molecules, which smears the hyperfine structure. Similarly, the hyperfine splitting cannot be observed in the spectra of the (110) complexes of either *S*-aspartic acid or *S*-glutamic acid in frozen solution.²⁷ In the crystalline state, the carboxylate groups in the latter complex act as bidentate ligands to complete the coordination polyhedra connecting the copper(II) ions.²⁸ The carboxylate groups tend to form bridges between the copper centres in crystals of the bis(amino acidato) complexes as well.²⁹⁻³² There is probably a much lower degree of association of the molecules at room temperature, as the isotropic spectra exhibit a well-resolved hyperfine pattern.²⁷

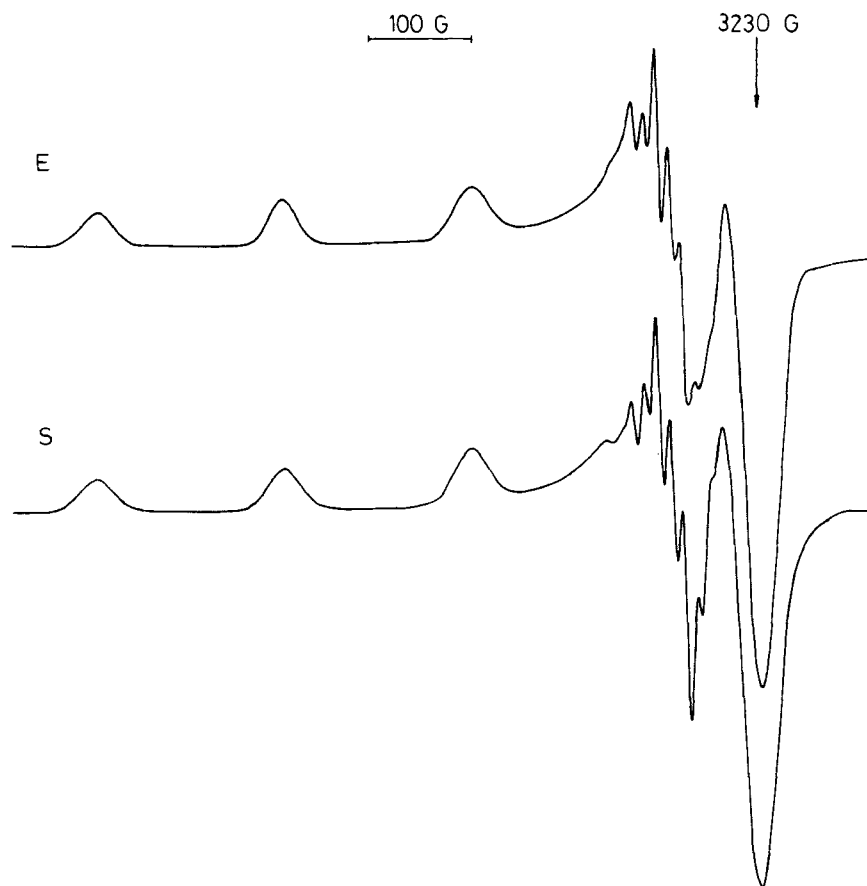


FIGURE 1 E.S.R. spectra of (120) complex of glycine at 77 K; E: experimental; S: simulated with the parameters in Table II, and with line widths (in $10^{-4}T$ units) of 9, 8, 9, 12 both in the parallel and the perpendicular region, in the sequence of increasing magnetic quantum number.

Good agreement between the experimental and simulated ESR spectra could be achieved for the other complexes if axial g and A tensors, anisotropic nitrogen superhyperfine coupling of equivalent nitrogen atoms, and a quadrupole coupling constant of 0.7 mT were assumed. The lines were Lorentzian in shape. In most cases, a weak strain effect³³ was indicated by the small increase in width of parallel lines with increasing magnetic quantum number. The slight inequality in spacing between the parallel lines caused an uncertainty of ~ 0.1 mT in the A_{\parallel} values. The line widths generally differed in the parallel and the perpendicular direction. Some examples are shown in Figs. 1-4. The ESR parameters are compiled in Table II, together with the number of equatorial nitrogen donor atoms ($n_{N_{eq}}$) in the various species.

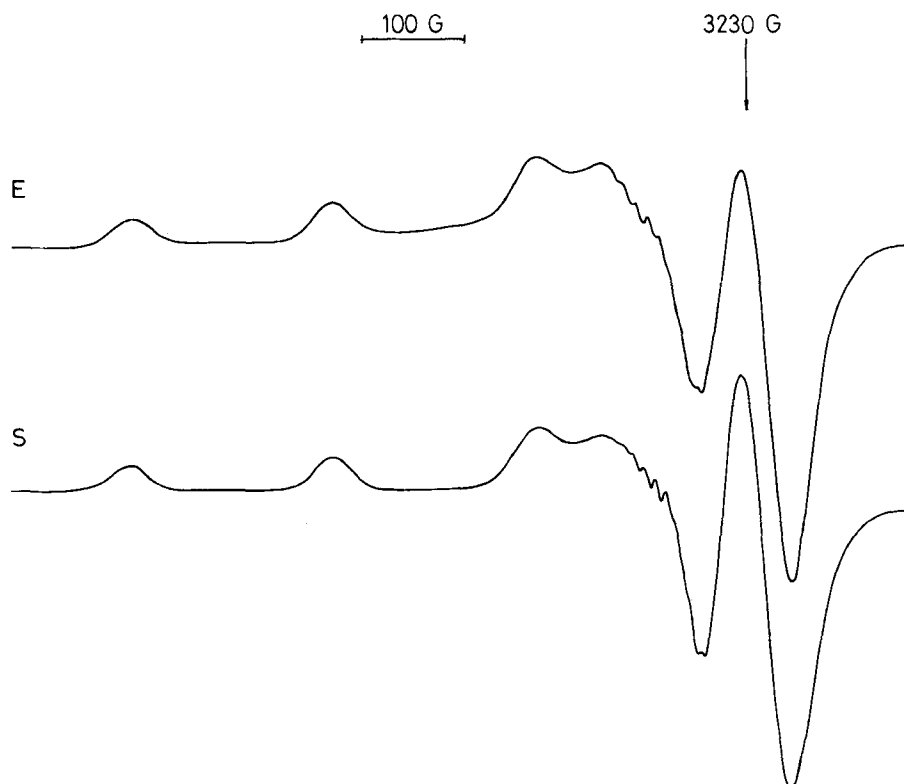


FIGURE 2 E.S.R. spectra of (120) complex of *R,S*-2,3-diaminopropionic acid at 77 K; E: experimental; S: simulated with the parameters in Table II, and with line widths (in 10^{-4} T units) of 9, 9, 12, 20 in the parallel and 11, 10, 12, 20 in the perpendicular region, in the sequence of increasing magnetic quantum number.

It has been found in pH-metric investigations¹⁵ that protonated amino groups of complexes of diaminocarboxylic acids lose their protons with increasing pH. All of these amino groups are presumed to bind to copper(II) equatorially, with the exception of the (120) complex of Daba, where the fourth N atom is likely to coordinate axially. These coordination modes have been proved by ^1H NMR relaxation and calorimetric studies,¹³ and are also supported by the blue shift in the absorption maxima of the species predominating at higher pH, and by the red shift

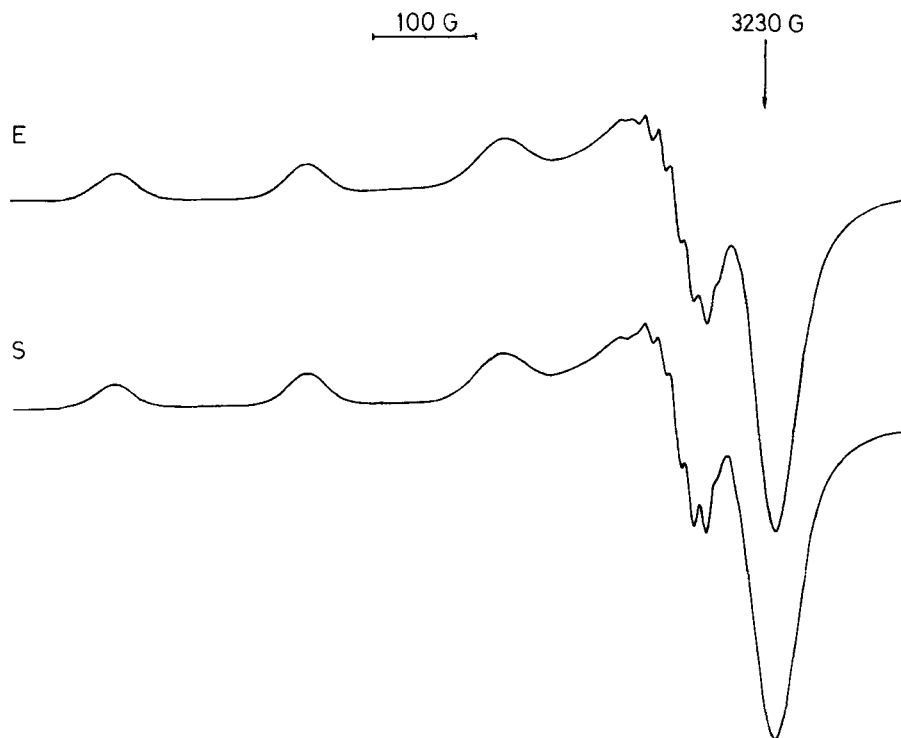


FIGURE 3 E.S.R. spectra of (121) complex of *S*-histidine at 77 K; E: experimental; S: simulated with the parameters in Table II, and with line widths (in 10^{-4} T units) of 14, 13, 13, 20 in the parallel and 14, 13, 12, 20 in the perpendicular region, in the sequence of increasing magnetic quantum number.

for the (120) complex of Daba¹³ (see Table I). Our spectral simulations confirm the above results, as the best fit of the spectra could be achieved with the same numbers of equatorial nitrogens (Table II). For the complexes of Gly, En, Hin, Ser and Thr, the number of equatorial N donors determined by our method is the same as that proposed on the basis of stability investigations.^{7,8,10-12} The ESR spectrum of the (120) complex of Asn is characteristic of bis(glycinato) coordination (carboxylate oxygens and amino nitrogens of both ligands as donors). The parameters of the (12-1) complex are rather different, though $n_{\text{N}_{\text{eq}}}$ remains 2, indicating axial coordination of the deprotonated amide nitrogen. The second deprotonated amide nitrogen in the (12-2) complex is probably in the equatorial plane, as the best fit of the spectra was achieved with three equatorial nitrogens. The main difference between the spectra simulated with $n_{\text{N}_{\text{eq}}} = 3$ and 4 appears in the low intensity bands indicated by an arrow in Fig. 5. A further evidence against $n_{\text{N}_{\text{eq}}} = 4$ is the value of the superhyperfine coupling constants (see below).

The coordination modes of the complexes of His have given rise to much controversy for a long time. Thermodynamic and spectral studies,³⁴ ESR investigations at room temperature,⁵ and CD and ultraviolet spectral evidence²² all suggest equatorial coordination of all three possible donor nitrogens in the (121) complex.

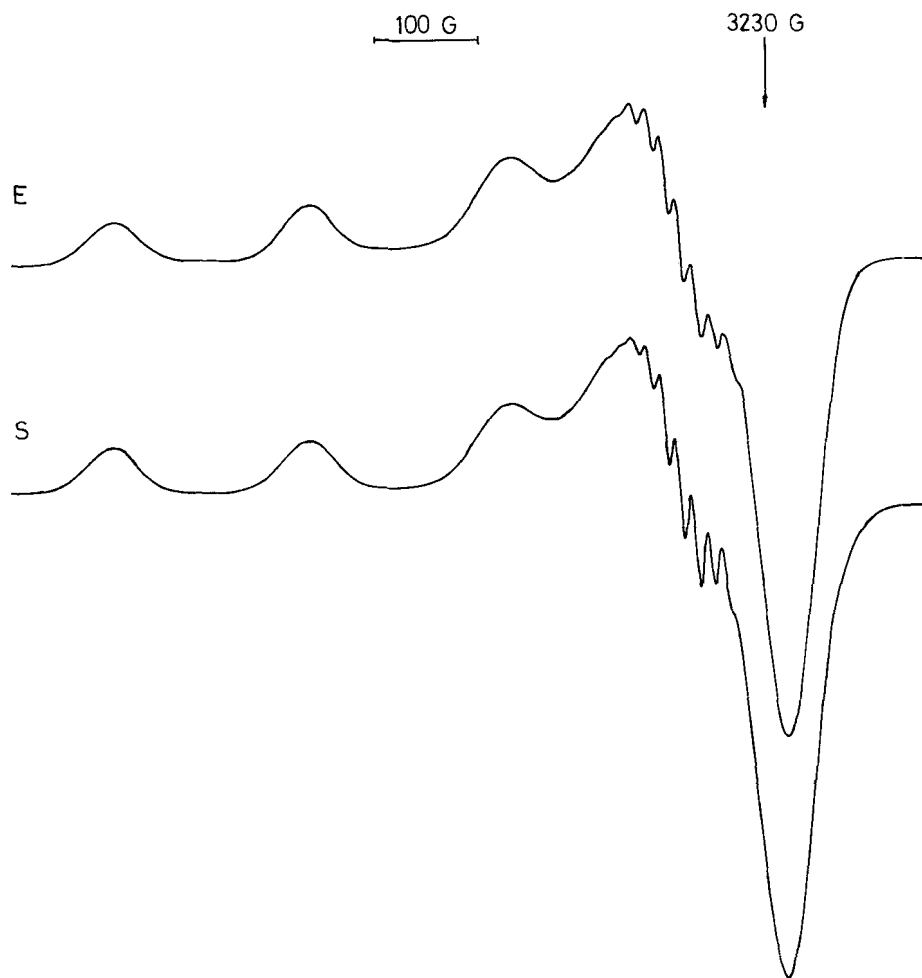


FIGURE 4 E.S.R. spectra of (120) complex of histamine at 77 K; E: experimental; S: simulated with the parameters in Table II, and with line widths (in 10^{-4} T units) of 9, 12, 16, 18 in the parallel and 12, 12, 13, 18 in the perpendicular region, in the sequence of increasing magnetic quantum number.

Simulation of its ESR spectrum in frozen solution (Fig. 3) confirms this coordination mode. The (120) complex has four nitrogen donor atoms, none of the imidazole nitrogens being protonated. The main question under debate is whether both His molecules coordinate in a histamine-like fashion (with the amino and the imidazole nitrogen in the equatorial positions), or one of them is bound to the copper in a glycine-like manner. The latter mode of coordination is proposed on the basis of NMR investigations³⁵ and the slight red shift in the absorption maximum as compared to that of the (121) complex. This red shift was considered analogous to that for the corresponding complexes of Daba, and was attributed to axial coordination of the fourth nitrogen atom.³⁶ On the other hand, bis(histamine)-like coordination was suggested by potentiometric, circular dichroism and electronic spectral results,^{34,37,38} a Raman scattering study,³⁹ and ^{13}C and ^1H NMR evidence

TABLE II
 ESR parameters^a for the complexes.

Complex $\text{Cu}_p\text{L}_q\text{H}_r$								
Ligand	pqr	g_{\perp}^b	g^b	$-A_{\perp}^c$	$-A_{\parallel}^c$	$n_{\text{N}_{\text{eq}}}$	$a_{\text{N}_{\perp}}^d$	$a_{\text{N}_{\parallel}}^d$
Glycine	120	2.048	2.257	25	180	2	11.5	9.5
<i>S</i> -Threonine	120	2.055	2.258	25	182	2	10.5	9
	12-1	2.055	2.274	19	162	2	10.5	9.5
	12-2	2.047	2.239	25	189	2	11.5	9
<i>S</i> -Serine	120	2.055	2.258	25	182	2	10.5	9
	12-1	2.053	2.269	19	168	2	10.5	9.5
	12-2	2.046	2.244	23	189	2	11.5	9
<i>S</i> -Asparagine	120 ^e	2.055	2.258	25	182	2	10.5	9
	12-1	2.055	2.271	20	164	2	11.5	8
	12-2	2.044	2.232	25	184	3	12	9.5
Ethylenediamine	110	2.062	2.292	22	168	2	10	6
	120	2.040	2.202	31	196	4	10	8
<i>R,S</i> -2,3-Diamino-propionic acid	120	2.046	2.216	32	196	4	10	9
<i>R,S</i> -2,4-Diamino-butyric acid	110	2.054	2.255	26	183	2	11	9
	122	2.054	2.257	26	182	2	11	9
	121	2.054	2.242	24	185	3	11	9.5
	120	2.053	2.238	24	184	3	11	10
<i>R,S</i> -Ornithine	122	2.055	2.257	25	182	2	10.5	9
<i>S</i> -Lysine	122 ^f	2.055	2.257	25	182	2	10.5	9
Histamine	110	2.060	2.308	15	163	2	13	9
	120	2.048	2.243	24	188	4	14	12.5
<i>S</i> -Histidine	121	2.054	2.246	24	184	3	11	9
	120	2.054	2.245	24	180	4	14	12

^a A non-SI unit, the gauss, is used; 1 G = 0.1 mT. ^b Estimated error ± 0.001 . ^c Estimated error ± 1 G. ^d Estimated error ± 0.5 G. ^e Isotropic hyperfine coupling constants (in G) are $A_0 = 77.3$ and $a_{\text{N}_0} = 10$ from the anisotropic values, while $A_0(^{63}\text{Cu}) = 71$ and $a_0(^{14}\text{N}) = 10.1$ for the *trans*, and $A_0(^{63}\text{Cu}) = 59$ and $a_0(^{14}\text{N}) = 9.1$ for the *cis* isomer from Ref. 6. ^f Isotropic hyperfine coupling constants (in G) are $A_0 = 77.3$ and $a_{\text{N}_0} = 10$ from the anisotropic values, while $A_0(^{63}\text{Cu}) = 70$ and $a_0(^{14}\text{N}) = 10.7$ for the *trans*, and $A_0(^{63}\text{Cu}) = 61$ and $a_0(^{14}\text{N}) = 8.9$ for the *cis* isomer from Ref. 6.

at 37°C in the presence of a large excess of His.⁴⁰ A detailed analysis of this species in frozen solution by multifrequency ESR⁴¹ has also led to the conclusion that the copper(II) is coordinated equatorially by four nitrogen atoms. Moreover, the effect of ¹⁵N substitution on the spectra has been explained in terms of four equatorial imidazole N atoms, assuming that His acts as a monodentate ligand in large excess at low temperature.⁴¹ At the same time, an equilibrium of isomers with three and four nitrogens in the equatorial plane has been shown at 298 K by analysis of isotropic ESR spectra.⁵ This finding was confirmed by CD and electronic spectral data,²² and by ¹H and ¹³C NMR studies at room temperature with a large excess of the ligand.⁴²

The anisotropic ESR spectrum of a slightly alkaline solution of His and copper(II) at a 4:1 ligand to metal concentration ratio is most probably that of the (120) complex. It is very similar to the spectrum of the (120) complex of Hin (Fig. 4), and its superhyperfine pattern (Fig. 6) is also reminiscent of that of the $\text{Cu}(\text{His})_n$ complex in

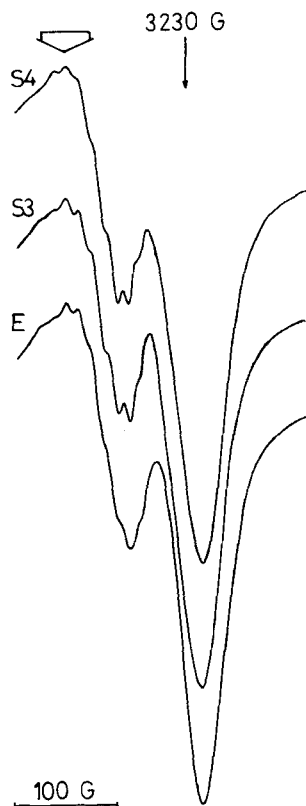


FIGURE 5 Perpendicular region of E.S.R. spectra of (12-2) complex of *S*-asparagine at 77 K; E: experimental; S3: simulated with the parameters in Table II, and with line widths (in 10^{-4} T) of 15, 14, 13, 20, in the sequence of increasing magnetic quantum number; S4: simulated with 4 equatorial N donors, $g_{\perp} = 2.046$, $g_{\parallel} = 2.232$, $A_{\perp} = 2.6$ mT, $A_{\parallel} = 18.4$ mT, $p = 0.7$ mT, $a_{N_{\perp}} = 1.13$ mT, while widths of perpendicular lines were 15, 13, 12, 20 (in 10^{-4} T units), in the sequence of increasing magnetic quantum number.

Ref. 41, which has likewise been shown to contain four nitrogens in the equatorial plane. The correct number and positions of lines in the perpendicular region can be obtained in the case of both 3 and 4 equatorial nitrogen donors and with two values of $a_{N_{\perp}}$ in the latter case (Fig. 6). The best fit is obtained when $n_{N_{\text{eq}}} = 4$ and the parameters are very similar to those of the (120) complex of Hin. It should be noted however, that superposition of a spectrum with similar parameters, but assuming only three equatorial nitrogens, did not affect the spectral fitting if its proportion was not larger than 25%. Thus, the presence of an isomer with three nitrogen donors cannot be excluded by our method, though bis(histamine)-like coordination certainly predominates. The change in the d-d absorption band upon cooling (Table I) may indicate a change in the concentration ratio of the isomers.

Additional information on the nature of the copper(II) coordination can be obtained from the nitrogen superhyperfine coupling constants. The isotropic nitrogen and copper hyperfine coupling constants calculated from the anisotropic values (Table II) agree well with those determined through analysis of the isotropic spectra

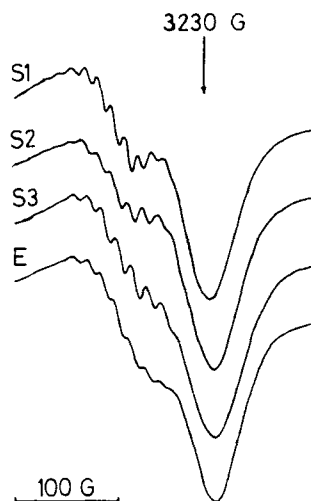


FIGURE 6 Perpendicular region of E.S.R. spectra of (120) complex of *S*-histidine at 77 K; E: experimental; S1: simulated with g , A , and p values in Table II, $n_{\text{N}_{\text{eq}}} = 4$, $a_{\text{N}_{\perp}} = 1.2$ mT, and line widths of 13, 11, 12, 18 (in 10^{-4} T units) in the sequence of increasing magnetic quantum number; S2: simulated with g , A , and p values in Table II, $n_{\text{N}_{\text{eq}}} = 3$, $a_{\text{N}_{\perp}} = 1.3$ mT, and line widths of 14, 13, 14, 18 (in 10^{-4} T units) in the sequence of increasing magnetic quantum number; S3: simulated with the parameters in Table II, and with line widths of 14, 12, 13, 18 (in 10^{-4} T units), in the sequence of increasing magnetic quantum number.

of the (120) complexes involving bis(glycinato) coordination⁵ and assigned to the trans isomers,⁶ while they differ significantly from the values for the cis isomers. Accordingly, the equilibrium seems to be shifted towards the trans isomer at lower temperatures. On the other hand, Iwaizumi and coworkers⁴³ have recently demonstrated a correlation between the superhyperfine coupling constants of the donor nitrogens in the g_{\parallel} parts of the spectra and the structure of the coordination sphere in an ^{14}N ENDOR study of a large number of copper(II) complexes. The ^{14}N shf coupling constants are grouped according to the hybridized state of the nitrogens and hence the nitrogens in a planar conformation (sp^2 hybridization, *e.g.*, aromatic aza nitrogens and deprotonated amide nitrogens) have larger coupling constants than those in a tetrahedral conformation (sp^3 hybridization, *e.g.*, amine nitrogens). Complexes with N_4 donor sets have larger hf coupling constants than those with N_2O_2 donor sets. Further, only minor changes are generally caused by axial ligation, and by distortion from planar geometry. Naturally, the a_{N} values determined by ENDOR spectroscopy are more accurate than those from the simulation of ESR spectra. However, the same structural features of the compounds certainly alter the parameters in the same way in both cases. For our complexes, the $a_{\text{N}_{\parallel}}$ values fall within a small range. The (110) complex of En exhibits the lowest $a_{\text{N}_{\parallel}}$ value. The change from the N_2O_2 donor set in the (110) complex to the N_4 donor set in the (120) complex of this ligand and also of the corresponding diaminocarboxylic acid, Dapa, causes an increase in $a_{\text{N}_{\parallel}}$ (Table II), similar to the corresponding complexes of Hin. The $a_{\text{N}_{\parallel}}$ values are significantly greater for the (120) complexes of Hin and His than those for the other complexes. This can be explained by the contribution from the two imidazole nitrogens, *i.e.*, by the equatorial N_4 coordination in the above-mentioned compounds. A marked increase in $a_{\text{N}_{\parallel}}$ would be expected for the (12-2)

complex of Asn as well, if both deprotonated amide nitrogens were bound to the copper(II) ion equatorially. The small value of the shf coupling constant, however, is in accordance with only three equatorial N donors, which assumption gave the best fit.

TABLE III
Molecular orbital coefficients for the complexes.

Complex $\text{Cu}_p\text{L}_q\text{H}_r$		Molecular orbital coefficients ^a			
Ligand	pqr	α^2	β_1^2	β^2	ϵ'^2
Glycine	120	0.775	0.864	0.727	0.259
S-Threonine	120	0.779	0.870	0.817	0.244
	12-1	0.753	0.962	0.876	0.281
	12-2	0.780	0.842	0.770	0.263
S-Serine	120	0.779	0.867	0.816	0.244
	12-1	0.767	0.932	0.833	0.291
	12-2	0.792	0.841	0.726	0.285
S-Asparagine	120	0.779	0.867	0.819	0.244
	12-1	0.752	0.958	0.863	0.272
	12-2	0.760	0.862	0.726	0.265
Ethylenediamine	110	0.780	0.946	0.929	0.249
	120	0.746	0.829	0.702	0.220
R,S-2,3-Diamino-propionic acid	120	0.757	0.858	0.793	0.201
R,S-2,4-Diamino-butyric acid	110	0.770	0.879	0.811	0.242
	122	0.775	0.866	0.801	0.237
	121	0.774	0.855	0.822	0.253
	120	0.768	0.846	0.827	0.254
R,S-Ornithine	122	0.778	0.869	0.825	0.243
S-Lysine	122	0.776	0.869	0.827	0.251
Histamine	110	0.804	0.930	0.808	0.319
	120	0.789	0.833	0.729	0.276
S-Histidine	121	0.777	0.848	0.799	0.256
	120	0.768	0.829	0.797	0.256

^a Estimated errors ± 0.01 .

Molecular orbital coefficients for the various complexes are listed in Table III. Their values show a fairly covalent character for each bond. There are no large differences in α^2 and ϵ'^2 , that is, the covalency of the in-plane σ and the 4s σ -bond does not vary strongly within the series. A linear relationship can be observed between them, however (Fig. 7). This correlation, which reflects a competition between σ -bonds of different symmetries, has been found for several types of copper(II) complexes.¹⁹ In our case, the deviation of most of the data points from the straight line is less than the experimental error. There are three species however, for which there is a significant upward deviation. This can be explained by the overestimation of ϵ'^2 due to 3d-4s orbital mixing which occurs in the event of rhombic distortion.¹⁹ Thus, the fact that one of the ligands is bidentate, while the other is terdentate in the (12-1) complexes of Thr, Ser and Asn, seems to lead to a slight rhombic distortion of the ligand field in these species. Their MO coefficients should therefore be regarded as less accurate. The slight rhombic distortion of these

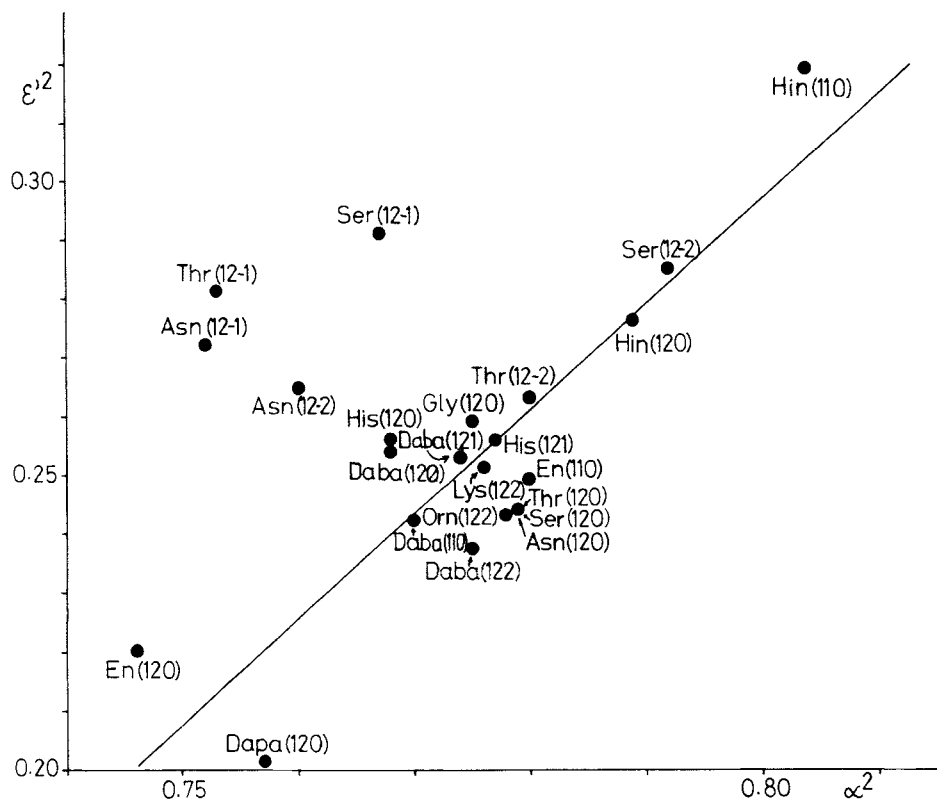


FIGURE 7 ϵ^2 vs α^2 plot for various copper(II) complexes of α -amino acids, ethylenediamine and histamine in frozen aqueous solutions. The solid line represents the best linear fit to data points for complexes with effective D_{4h} symmetry (regression coefficient: 1.50, intercept: -0.91 , standard error of regression coefficient: 0.28, standard error of estimate: 0.015, correlation coefficient: 0.784, F-value: 28.8, confidence level $> 99.5\%$).

compounds is also supported by smaller A_{aniso} ($A_{\text{N}} - A_{\text{O}}$) values (9.5–9.9 mT). The average A_{aniso} is 10.4 mT for the other complexes with N_2O_2 donor atom sets and sp^3 nitrogens. For the (12-1) complexes, a stronger s-character of the MO containing the unpaired electron is indicated, probably as a consequence of 3d-4s orbital mixing.

For the complexes with effective D_{4h} symmetry, A_{aniso} tends to increase with increasing number of equatorial (sp^3) nitrogen donor atoms; average A_{aniso} values are 10.4, 10.65, and 10.95 mT for $n_{\text{N}_{\text{eq}}} = 2, 3,$ and 4, respectively. Oxygen donor atoms seem to increase the s-character of the MO containing the unpaired electron to a larger extent than do sp^3 nitrogen donors. Simultaneously, a slight increase can also be observed in the covalency of the in-plane σ -bond; average α^2 values are 0.78, 0.77, and 0.75 for $n_{\text{N}_{\text{eq}}} = 2, 3,$ and 4, respectively.

The (110) complex of En has a significantly smaller A_{aniso} (9.7 mT) than the other complexes with effective D_{4h} symmetry and 2 sp^3 equatorial nitrogen atoms (10.4 mT). The unusually small a_{N_o} value (0.83 mT) indicates small unpaired spin densities at the nitrogen nuclei, suggesting a weak in-plane σ -bond between Cu(II) and the nitrogen atoms, while the overall covalency of this bond is average ($\alpha^2 = 0.78$). Therefore, the Cu–O σ -bond should be stronger, which is in accordance with

the decrease in A_{aniso} as the oxygen donors increase the s-character of the MO containing the unpaired electron (see above). Simultaneously, the π -bonds are found to be rather ionic (Table III). In (12-2) complexes of Thr and Ser, greater covalency of the Cu-N in-plane σ -bond is suggested by the increase in A_{aniso} (10.9 and 11.1 mT, respectively) and in a_{No} (1.04 mT, against the average value of 0.99 mT for complexes with glycinate coordination). With unchanged overall covalency of the in-plane σ -bond, the covalent character of the Cu-O σ -bond probably decreases, which is compensated by strongly covalent π -bonds (Table III).

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