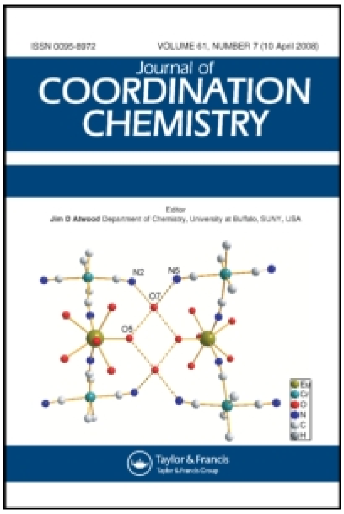

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EPR STUDIES OF COPPER(II) COMPLEXES OF α-AMINO ACIDS IN HOST CRYSTALS OF THE CORRESPONDING POLYCRYSTALLINE ZINC(II) COMPLEXES: METAL-LIGAND BONDS AND MOLECULAR STRUCTURE

Terézia Szabó-Plánka[a]; László I. Horváth[b]
[a] Institute of General and Physical Chemistry, Attila József University, Szeged, Hungary [b] Institute of Biophysics, Biological Research Center of the Hungarian Academy of Science, Szeged, Hungary

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EPR STUDIES OF COPPER(II) COMPLEXES OF α-AMINO ACIDS IN HOST CRYSTALS OF THE CORRESPONDING POLYCRYSTALLINE ZINC(II) COMPLEXES: METAL-LIGAND BONDS AND MOLECULAR STRUCTURE

TERÉZIA SZABÓ-PLÁNKA
Institute of General and Physical Chemistry, Attila József University, P.O.B. 105, 6701 Szeged, Hungary

and

LÁSZLÓ I. HORVÁTH
Institute of Biophysics, Biological Research Center of the Hungarian Academy of Science, Szeged, Hungary

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The coordinative bonds in the copper(II) complexes of twelve α-amino acids have been studied. Molecular orbital coefficients have been calculated according to D_{4h} symmetry, using the EPR spectral data on the corresponding polycrystalline copper(II)-doped zinc(II) complexes in conjunction with the electronic transition energies obtained by Gaussian analysis of the reflectance spectra of the pure copper (II) compounds. Multiple linear regression analysis has been carried out between the MO coefficients and various structural data. It has been established that (*a*) with increasing covalency of the in-plane σ bond, the covalency of the in-plane π bond decreases, and (*b*) the greater the deviation from elongated octahedral towards square-pyramidal geometry, the more covalent the out-of-plane π bond becomes.

INTRODUCTION

The copper(II) chelates of α-amino acids encountered in proteins are generally of square-planar, square-pyrimidal or elongated octahedral geometry. Besides the equatorial amino nitrogen and carboxylate oxygen atoms, one or two water, carboxylate or amido oxygen atoms may be coordinated as axial ligands to the copper(II) ion. The axial Cu-O distance varies between 0.23 and 0.29 nm.[1-11] EPR spectral parameters for computation of the molecular orbital coefficients characterizing the metal-ligand bonds can be obtained by eliminating the interactions between copper(II) ions in such a manner that the structure of the complex molecule should be altered as little as possible. Doping of the corresponding zinc(II) complex with the copper(II) compound seems to be appropriate for this purpose, because these zinc and copper compounds are nearly isomorphous,[8,9,11-13,15] or, at least, their crystal structures are very similar to each other.[10,14]

In the present work we report an investigation of eleven copper(II) complexes of known (and one of unknown) crystal structure in host crystals of the corresponding polycrystalline zinc(II) complexes. The aim of our studies is to seek correlations between the covalency of the different metal-ligand bonds and molecular structure.

EXPERIMENTAL

Preparation of Complexes

Copper(II) complexes of glycine, *l*-alanine, *l*-proline, *l*-serine and *l*-glutamic acid (Gly, *l*-Ala, *l*-Pro, *l*-Ser, *l*-Glu) were prepared by the method of Jung and coworkers,[23] while those of *l*-phenylalanine, *l*-isoleucine, *dl*-proline, *l*-asparagine, *l*-tyrosine, *l*-methionine and *dl*-methionine (*l*-Phe, *l*-Ileu, *dl*-Pro, *l*-Asn, *l*-Tyr, *l*-Met, *dl*-Met) were prepared according to Neuberg and coworkers.[16]

The copper(II)-doped zinc(II) complexes were prepared by the method of Ou *et al.*[9] All the reagents were of analytical grade from REANAL.

Besides the analysis of the usual elements (C, H, N, Cu, Zn), the water contents of the copper(II) compounds were also determined from their thermogravimetric curves. The derivatograms were recorded with a MOM G-425 derivatograph in air at atmospheric pressure. All the compounds gave satisfactory analyses.

EPR Spectra

EPR spectra were recorded on a JEOL JES-PE-1X X-band spectrometer, using the diphenylpicrylhydrazyl free radical and Mn(II)-doped MgO as standards. The spectra of the copper(II)-doped zinc(II) complexes were recorded at room temperature. Isotropic spectra of the copper(II) complexes were recorded in water at room temperature, at a concentration of ~1 mole m^{-3}.

Reflectance Spectra

Diffuse reflectance spectra of the finely-powdered copper(II) complexes were measured at room temperature with a Beckman DU spectrometer equipped with a reflectance attachment, using MgO as standard.

Calculation method

EPR results were evaluated on the basis of the well-known molecular orbital scheme,[17] where the antibonding molecular orbitals of the copper(II) ions under D_{4h} symmetry are given by (*1*)-(*4*).

$$\psi_{b_{1g}} = \alpha d_{x^2-y^2} - \alpha' \varphi_L(x^2 - y^2) \tag{1}$$

$$\psi_{a_{1g}} = \alpha_1 d_{z^2} - \alpha_1' \varphi_L(z^2) \tag{2}$$

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

$$\left.\begin{aligned} \psi_{e_g} &= \beta d_{xz} - \beta' \varphi_L(xz) \\ \psi_{e_g} &= \beta d_{yz} - \beta' \varphi_L(yz) \end{aligned}\right. \tag{4}$$

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 occupies the $\psi_{b_{1g}}$ antibonding orbital. The MO coefficients α, β_1, and β characterizing the covalency of the σ-in-plane, π-in-plane and π-out-of-plane bonds, respectively, can be calculated from the expressions[17-19] (*5*)-(*8*) where

$$g_{\parallel} - g_e = -8\lambda_0/\Delta E_{xy}\,(\alpha^2\beta_1^2 - f_1) \tag{5}$$

$$g_{\perp} - g_e = -2\lambda_0/\Delta E_{xz,yz}\,(\alpha^2\beta^2 - t_2) \tag{6}$$

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

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

$g_e = 2.0023$ is the free electron g-factor and λ_0 is the spin-orbit coupling constant of the free copper (II) ion ($-828\ \text{cm}^{-1}$). K is the Fermi hyperfine contact term. $P = 0.036\ \text{cm}^{-1}$ is the dipole coefficient 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 given by (*9*)-(*12*) for which

$$f_1 = \alpha\beta_1\,[\alpha'\beta_1 S + \alpha'\beta_1'\,T(n)/2] \tag{9}$$

$$f_2 = \alpha\beta[\alpha'\beta S + \alpha'\beta' T(n)/\sqrt{2}] \tag{10}$$

$$f_3 = f_1/(\alpha^2\beta_1^2 - f_1) \tag{11}$$

$$f_4 = f_2/(\alpha^2\beta^2 - f_2), \tag{12}$$

α', β_1', and β' can be obtained from equations (*13*) and (*14*).

$$\alpha^2 + \alpha'^2 - \alpha\alpha' S - 1 = 0 \tag{13}$$

$$\beta_1' = (1 - \beta_1^2)^{1/2},\ \beta' = (1 - \beta^2)^{1/2}. \tag{14}$$

The constants calculated by Kivelson and Neiman[19] were applied; the value of the overlap integral (S) is 0.076 and $T(n) = 0.22$ for oxygen, whereas for nitrogen donor atoms $S = 0.093$, $T(n) = 0.33$ at a metal-donor atom distance of ~0.19 nm. The MO coefficients were calculated by an iteration procedure, analogous to that described by Misra and Sharma,[26] using a FORTRAN IV program written by us. Eq. (*7*) can be rearranged to give (*15*)

$$\alpha^2 = 1/8[-14(A_{\parallel} + K)/P + 11(g_{\parallel} - g_e) + 9(g_o - g_e)] + F, \tag{15}$$

where F contains the correction terms. First approximate values of MO coefficients can be obtained from Eqs. (*5, 6, 15*) by neglecting the correction terms. If we compute F, using approximate values of α, β_1, β, and α' obtained from Eq. (*13*), we get a refined value of α^2, which can be used in turn for calculating refined values of α', β_1, and β.

The Fermi hyperfine contact term (K) was determined from isotropic EPR spectra according to (*16*)

$$K = -A_0 + P(g_o - g_e), \tag{16}$$

where the equations (*17*) apply.

$$A_0 = 1/3(A_{\parallel} + 2A_{\perp}) \text{ and } g_o = 1/3(g_{\parallel} + 2g_{\perp}). \tag{17}$$

A_0, obtained in aqueous solution, refers to a different species as compared to a molecule in the solid complex. In solution an equilibrium exists between *cis* and *trans* isomers[30] and, in addition, axial positions are occupied by water molecules instead of carboxylate or amido oxygen atoms. However, for lack of single crystal data, we think this approximate K value to be rather acceptable, considering the work of Rockenbauer,[20] who made a thorough examination of why the assumption regarding the proportinality of K to α^2 is frequently in contradiction with the experimental results.

RESULTS AND DISCUSSION

The EPR spectra of the Cu(II) complexes in the polycrystalline Zn(II) host can be interpreted as of axial type. The most likely axial symmetry is D_{4h}, since significant tetrahedral distortion can be found in neither copper(II) chelates nor zinc(II) compounds.[1–15] The experimental data, including A_0 values obtained from the isotropic spectra, are shown in Table I. For comparison, we note that the Cu(II) ion doped in the *l*-alanine single crystals has a strongly distorted square-planar coordination geometry with axial *g* and *A* tensors ($g_\parallel = 2.2543, g_\perp = 2.0513, A_\parallel = 0.01804$ cm^{-1}),[33] while in the aqua*tris*(*l*-glutamato) cadmium monohydrate single crystals the coordination polyhedron around the copper(II) ion is a strongly distorted octahedron with rhombic *g* and *A* tensors ($g_z = 2.3545, g_y = 2.0920, g_x = 2.0678, A_z = 0.0135$ cm^{-1}).[31]

The electronic excitation energies necessary to compute the MO coefficients were determined from the diffuse reflectance spectra. The single, broad band between 1.55 and 1.70 μm^{-1} was resolved into Gaussian components using a program written in FORTRAN IV.[28] Brown and coworkers found three bands in the single-crystal polarized electronic

TABLE I

EPR Spectral Data for the Copper(II) Complexes of α-Amino Acids.

Compound	$-A_\parallel \cdot 10^{6}$ [a] μm^{-1}	$g_\parallel$ [a]	$g_\perp$ [a]	g_0 [a]	$-A_0 \cdot 10^{5}$ [b] μm^{-1}
Cu(Gly)$_2$•H$_2$O	1.521	2.270	2.060	2.130	0.643
Cu(*l*-Ala)$_2$	1.546	2.300	2.060	2.140	0.658
Cu(*l*-Phe)$_2$	1.679	2.273	2.054	2.127	d
Cu(*l*-Ileu)$_2$•H$_2$O	1.767	2.278	2.053	2.128	0.667
Cu(*l*-Pro)$_2$•2H$_2$O	1.722	2.276	2.065	2.135	0.687
Cu(*dl*-Pro)$_2$•2H$_2$O	1.704	2.274	2.066	2.135	0.688
Cu(*l*-Ser)$_2$	1.709	2.271	2.053	2.126	0.663
Cu(*l*-Asn)$_2$	1.719	2.276	2.062	2.133	0.697
Cu(*l*-Tyr)$_2$	1.504	2.275	2.056	2.129	0.695
Cu(*l*-Glu)•2H$_2$O	1.604	2.277	2.054	2.128	0.566
Cu(*l*-Met)$_2$	1.608[c]	2.273[c]	2.059[c]	2.130	d
Cu(*dl*-Met)$_2$	1.533[c]	2.277[c]	2.062[c]	2.134	d

[a] From EPR spectra of copper(II)-doped zinc(II) complexes.
[b] From isotropic EPR spectra of Cu(II) complexes.
[c] Data from Ref. 9.
[d] These compounds are insoluble in water. Average of A_0 values of the other nine complexes was used for the computation of K.

spectra of the Cu(*l*-Tyr)$_2$ complex,[22] at about the following energies: 1.46, 1.61 and 1.73 μm^{-1}. They stated that the band at 1.61 μm^{-1} arises from a transition between molecular orbitals in the basal plane of the molecule. Consequently, it can be assigned to the $d_{xy} \leftarrow d_{x^2-y^2}$ transition. Since the molecule is approximately of square-pyramidal geometry, the band of the $d_{xz,yz} \leftarrow d_{x^2-y^2}$ transition can be expected to lie at higher energy than that of the former[21] (at 1.73 μm^{-1} in this case). Thus, the band at 1.46 μm^{-1} corresponds to the $d_{z^2} \leftarrow d_{x^2-y^2}$ transition. Allen and coworkers[24] used a $\Delta E_{xz,yz}$ value of ~2.75 μm^{-1} in their calculations regarding three complexes of the type discussed. However, such a great difference for complexes of such similar composition and structure is unlikely, while, on the other hand, a splitting of ~1.0 μm^{-1} in the E_g level occurs in the case of great rhombic distortion, which would be manifested in a rhombic EPR spectrum. Accordingly, we assumed that the energy of each d-d transition is below 2.0 μm^{-1} and that the splitting of the E_g level is not significant for any of the compounds discussed. The visible absorption band was analysed into three component bands, which were assigned according to the sequence of energy levels of the Cu(*l*-Tyr)$_2$ chelate (Table II). The $\Delta E_{xz,yz}$ energy of the latter compound, obtained by Gaussian analysis, well agrees with the single crystal value, while the two values for ΔE_{xy} differ from each other by ~0.07 μm^{-1} (Table II).

The MO coefficients and some structural data characteristic of the coordination sphere of crystalline Cu(II) complexes are listed in Table III. The in-plane σ bonds are rather covalent. Covalency of the in-plane π bonds varies from a rather small value of β_1^2 (0.78 for Cu(*l*-Glu)•2H$_2$O) to the ionic limiting case ($\beta_1^2 = 1.0$ for Cu(*l*-Tyr)$_2$ and Cu(*dl*-Met)$_2$). The result of linear regression analysis carried out on α^2 and β_1^2 data sets (Table IV) is in good accordance with observations on copper(II) complexes of tridentate Schiff-base complexes[27] in different solvents. The structural effects which make the in-plane σ bond more ionic, simultaneously increase the covalency of the in-plane π bond, which stabilizes the molecule (Figure 1). Crystal packing forces must play an important role, since the covalency of the bonds characterized by the MO coefficients is different for the molecules under study only if the measurements are carried out on crystalline samples, while for frozen solutions almost identical parameters are obtained.[25]

TABLE II
Absorption Spectral Data for the Copper(II) Complexes of α-Amino Acids.

Compound	Maximum energy[a]	Energy of Gaussian components[a] 1	2	3
cis-Cu(Gly)$_2$•H$_2$O	1.545	1.399	1.557	1.652
trans-Cu(*l*-Ala)$_2$	1.63	1.540	1.678	1.808
trans-Cu(*l*-Phe)$_2$	1.575	1.357	1.554	1.703
cis-Cu(*l*-Ileu)$_2$•H$_2$O	1.64	1.543	1.655	1.780
Cu(*l*-Pro)$_2$•2H$_2$O	1.64	1.546	1.670	1.918
trans-Cu(*dl*-Pro)$_2$•2H$_2$O	1.62	1.333	1.596	1.723
cis-Cu(*l*-Ser)$_2$	1.64	1.424	1.635	1.771
trans-Cu(*l*-Asn)$_2$	1.68	1.553	1.654	1.783
trans-Cu(*l*-Tyr)$_2$	1.685	1.524	1.682	1.726
		1.46[b]	1.61[b]	1.73[b]
Cu(*l*-Glu)•2H$_2$O	1.37	1.234	1.357	1.509
trans-Cu(*l*-Met)$_2$	1.61	1.503	1.623	1.783
trans-Cu(*dl*-Met)$_2$	1.66	1.487	1.665	1.787

[a] Units of μm^{-1}.
[b] From single-crystal polarized electronic spectra.[22]

TABLE III

The Molecular Orbital Coefficients and Various Structural Data for the Copper(II) Complexes of α-Amino Acids.

Compound[a]	MO coefficients			Structural data		
					Axial bonds[e]	
	α^2	β^2	β_1^2	δ_{Cu}[b]	s[c]	l[d]
$Cu(Gly)_2 \cdot H_2O$[1]	0.76	0.85	0.90	0.005	0.240W	0.274C
Cu(*l*-Ala)$_2$[2]	0.82	0.85	0.98	0.004	0.270C	0.290C
Cu(*l*-Phe)$_2$[4]	0.81	0.74	0.85	0.006	0.258C	0.269C
Cu(*l*-Ileu)$_2 \cdot H_2O$[3]	0.88	0.69	0.84	0.017	0.248W	0.384C
Cu(*l*-Pro)$_2 \cdot 2H_2O$	0.85	0.92	0.88			
Cu(*dl*-Pro)$_2 \cdot 2H_2O$[5]	0.85	0.85	0.84	0	0.254C	0.254C
Cu(*l*-Ser)$_2$[8]	0.84	0.73	0.85	0.014	0.236C	0.363C
Cu(*l*-Asn)$_2$[10]	0.82	0.87	0.90	0.006	0.253A	0.277A
Cu(*l*-Met)$_2$[9]	0.77	0.88	0.93	0.0035	0.268C	0.275C
Cu(*dl*-Met)$_2$[6]	0.73	0.96	1.00	0	0.271C	0.271C
Cu(*l*-Tyr)$_2$[7]	0.72	0.87	1.00	0.011	0.234C	0.307P
Cu(*l*-Glu)$\cdot 2H_2O$[11]	0.79	0.68	0.78	0.015	0.230C	0.259C

[a] Upper index refers to the crystal structure reference.

[b] Deviation of the copper(II) in nm from the best plane of the equatorial donor atoms.

[c] The shorter bond length in nm.

[d] The longer bond length in nm.

[e] W denotes a water, C a carboxylate, and A an amide oxygen atom as the axial donor, while P stands for carbon atoms of the phenolic ring.

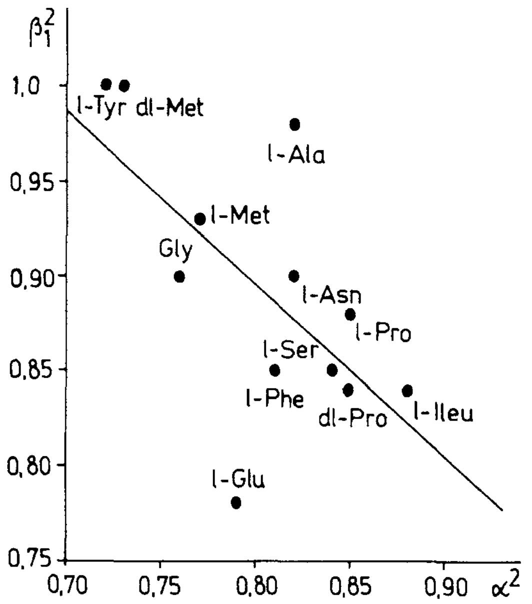

FIGURE 1 The β_1^2 *vs* α^2 plot for Cu(II)-doped Zn(II) complexes of α-amino acids. The solid line represents the best linear fit to data points.

TABLE IV
Results of Multiple Linear Regression Analysis.

Dependent variable	Independent variable	Regression coefficient	Intercept	Sterc[e]	Stees[f]	Partial correlation coefficient	Multiple correlation coefficient	F	CI[b]	N[c]
β_1^2 [a]	α^2	− 0.876	1.599	0.345	0.0573	−0.626	0.626	6.46	95.0%	12
δ_{Cu} [d]	shorter axial Cu-O distance	− 0.229	0.0429	0.0678	0.0031	−0.723	0.888	14.94	99.5%	11
	longer axial Cu-O distance	0.075		0.0236		0.699				
β^2 [a]	δ_{Cu}	−12.34	0.907	2.97	0.0558	−0.811	0.811	17.26	99.5%	11

[a] Polynomial regression analysis gave only a negligible improvement.
[b] Confidence level.
[c] Number of points in set.
[d] Deviation of the Cu(II) from the best plane of the equatorial donor atoms.
[e] Standard error of regression coefficient.
[f] Standard error of estimate.

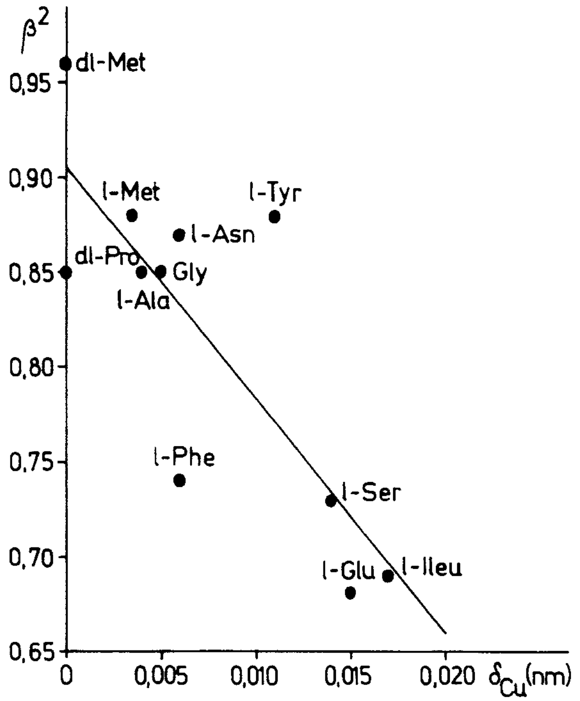

FIGURE 2 The β^2 vs δ_{Cu} plot for Cu(II) complexes of α-amino acids. δ_{Cu} denotes the deviation of copper(II) from the best plane of equatorial donor atoms in the pure Cu(II) compound. The solid line represents the best linear fit to data points.

Previous workers found the out-of-plane π bond to be purely ionic,[24] in contrast to our data (Table III), which suggest a fairly covalent character for this bond. The main cause of this deviation should be the high value of $\Delta E_{xz,yz}$ (2.75 μm^{-1}) applied by Allen and coworkers[24] (see above). The value of β^2 decreases as the deviation (δ_{Cu}) of the copper(II) ion from the best plane of the equatorial donor atoms increases (Table IV, Figure 2). Since the increase of δ_{Cu} indicates the distortion of inversion symmetry, the observed correlation may be explained by 3d-4p mixing. Such a mixing observed with tetrahedral distortion is manifested in the decrease of $A_{\|}$.[29] However, no correlation between δ_{Cu} and $A_{\|}$ can be observed for the complexes discussed. The deviation of the Cu(II) ion from the equatorial plane is proportional to the longer axial Cu-O distance, and inversely proportional to the shorter one (Table IV). The above facts can be summarized as follows. The greater the deviation from elongated octahedral towards square-pyramidal geometry in the pure copper(II) complex, the more covalent the out-of-plane π bond of the Cu(II) chelate in the host crystals.

There are several approximations and assumptions in the calculation method[17-19] used to derive the MO coefficients. Therefore the question may arise as to whether the above correlations are of significance or not. Smith has discussed the relationship between the g-values and the MO coefficients in tetragonal copper(II) systems in detail.[32] He assessed the relative importance of all the factors contributing to the anisotropic g-values, and stressed the importance of matrix elements involving charge transfer states and of the taking into proper account of ligand-ligand and metal-ligand overlap integrals. The metal-ligand π-overlap integrals are neglected in the method of Maki and McGarvey.[17] According to the calculations of Smith,[32] the neglect of π-interactions increases $g_{\|}$ and $g_{\perp}$ by 0.020 and 0.001, respectively, in a tetragonal CuO_4 system with a Cu–O distance of 0.200 nm. If $g_\perp$ and $g_\parallel$ are varied by these quantities, the changes of MO coefficients, calculated by the method of Maki and McGarvey[17] are smaller than 0.03 for the compounds discussed. The equatorial Cu-O distance varies between 0.193 and 0.203 nm in the series,[1-11] while the π-overlap integral decreases by about 25% (from 0.051 to 0.040).[32] Thus, the greatest differences in α^2, β_1^2, and β^2 between the members of the series caused by the neglect of this contribution must be less than 0.01. The effect of the nitrogen ligands is even smaller, since the Cu-N distance varies within a smaller range than the Cu-O bond length.[1-11] The axial ligands make very little direct contribution to the g-values.[32] There are other terms, too, neglected by Maki and McGarvey,[17] contributing to the g-values, which partly cancel each other in a fortuitous way, and of which, for example, the charge transfer states have slightly greater effect on $g_\perp$ and $g_\parallel$ than the above-discussed π interactions.[32] In fact, the inaccuracies caused by the different approximations involved in the calculation method[17-19] restrict the comparability of Cu(II) complexes of different type, and especially those with different donor atom sets. However, these approximations are most unlikely to give the correlations recognized with complexes of such similar structure.

Unfortunately, the crystal structures of the zinc(II) complexes of *l*-Tyr and *l*-Phe are unknown. Thus, the possibility cannot be excluded that the relatively large deviations of the complexes of these amino acids from the β^2 *vs* δ_{Cu} curve (Figure 2) are mainly caused by structural changes in the host, these being greater than in other cases. In addition, MO coefficients highly depend on the $g_\perp$ values and the excitation energies, the latter of which could particularly be subject to rather large uncertainties, since they were determined by Gaussian analysis. If we vary $g_\perp$ by 0.001, β^2 varies by about 0.01-0.02, and a difference of 0.07 μm^{-1} in ΔE_{xy} (see Cu(*l*-Tyr)$_2$, Table II) causes the β_1^2 values to deviate from each other by about 0.04. However, it is noteworthy that in the Cu(*l*-Tyr)$_2$ complex there can be a direct interaction between the copper(II) and the π electrons of the axial phenolic ring parallel to the equatorial plane, the distance between them being only about 0.3 nm.[7] Such an interaction could inhibit back-donation from the copper $d_{xz,\ yz}$ orbitals to the π^* orbitals of the ligands. In Cu(*l*-Phe)$_2$ the aromatic rings are separated from the copper(II) spatially,[4] and accordingly an interaction of the former type is unlikely. The presence of the phenyl ring, however, may change the ligand MOs. An increase in delocalisation of the d_{xy}, and particularly of the $d_{xz,yz}$ electrons, is observed.

Copper(II) and zinc(II) complexes of *l*-Glu are closely isostructural.[11,15] The increase in the number of carboxylate oxygen atoms in the coordination sphere at the expense of the number of amino nitrogen atoms leads to the altered covalency of the π bonds. Back-donation, especially from d_{xy} orbitals of the Cu(II) to the ligand orbitals, is increased as compared with the 1:2 complexes (Figure 1).

The above-discussed correlations support our assignment of the electron excitation energies. Moreover, the correlation between δ_{Cu} and β^2, characteristic of the copper(II) complexes in the pure crystalline state and in the host crystals, respectively, indicates the applicability of bonding information drawn from doping studies for the pure Cu(II) compounds. The equatorial metal-donor atom distances in the zinc(II) complexes are 0.004-0.016 nm longer, while the axial metal-oxygen distances are about 0.03 nm shorter, than those in the copper(II) chelates,[6,9,11,13,15] Since the square-planar units are connected by carboxylate (or amido) bridges which form the axial bonds, and hydrogen bonds also exist in the coordination sphere, changes are expected in the metal-donor atom distances and bond angles and hence in the MO coefficients, when the copper(II) complex is doped into crystals of the isostructural zinc(II) complex. However, the existence of a β^2 *vs* δ_{Cu} correlation suggests that the changes are similar in character and magnitude for the majority of the compounds discussed. Thus, it seems reasonable to assume that the α^2 *vs* β_1^2 and δ_{Cu} *vs* β^2 correlations reflect the main features of the coordinative bonds in the series, both in the pure crystalline state and in the doped crystals of the corresponding zinc(II) complex.

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