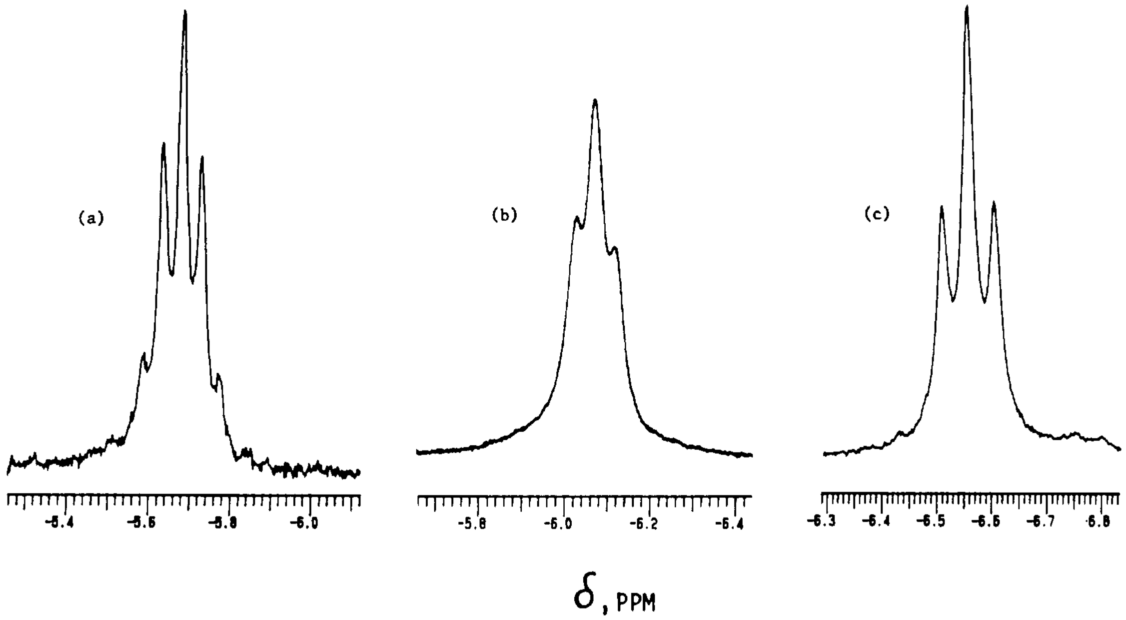

Figure 1. 200-MHz ^1H NMR spectra (recorded in C_6D_6) of $Re_2H_8(PMe_2Ph)_2(EPh_3)_2$ showing Re–*H* resonances: (a) E = P; (b) E = As; (c) E = Sb.

relative intensities of the P–CH_3 and Re–*H* resonances were in excellent agreement with the expected stoichiometric ratio of 3:2.

In the ^1H NMR spectra of $Re_2H_8(PMePh_2)_3(EPh_3)$ (E = As, Sb), the P–CH_3 resonances were observed as two sets of doublets in an intensity ratio of 2:1. This accords with a structure in which two $PMePh_2$ ligands are bound to one metal and one PMe_2Ph and one EPh_3 ligand are bound to the other metal; i.e., the disposition of phosphine ligands as present in $Re_2Cl_5(PMePh_2)_3$ is preserved. The spectrum of $Re_2H_8(PMePh_2)_3(AsPh_3)$ was recorded (in CD_2Cl_2) over the temperature range +25 to −100 °C; little change was observed upon varying the temperature. These results imply that while the hydride ligands are fluxional, the phosphine (and arsine and stibine) ligands are not undergoing exchange. In support of this, we note that the $^{31}P\{^1H\}$ NMR spectrum of $Re_2H_8(PMePh_2)_3(AsPh_3)$ shows two singlets (δ +15.6 and δ +10.2) in an intensity ratio of 2:1. A similar measurement of the $^{31}P\{^1H\}$ NMR spectrum of $Re_2H_8(PMe_2Ph)_2(PPh_3)_2$ shows two singlets of equal intensity at δ +43.2 and δ −7.6 (Table I); the former is due to the PPh_3 ligand while the latter is due to PMe_2Ph.[36] Note that the $^{31}P\{^1H\}$ NMR spectrum of $Re_2H_8(PMe_2Ph)_4$ has a singlet at δ −8.1.[24] For $Re_2H_8(PMe_2Ph)_2(PPh_3)_2$ and other complexes of the type $Re_2H_8(PR_2Ph)_2(EPh_3)_2$, it is likely that each Re atom is coordinated by one PR_2Ph and one EPh_3 ligand; however, since several isomeric forms are possible, we do not know which one has been isolated in each case.[37]

(c) Concluding Remarks. We have demonstrated that the strategy outlined in Scheme I works well for the synthesis of $Re_2H_8(PR_2Ph)_2(EPh_3)_2$ (R = Me, Et; E = P, As, Sb) and $Re_2H_8(PRPh_2)_3(EPh_3)$ (R = Me, Et; E = As, Sb). This procedure should work for other mixed-ligand systems; it requires that the appropriate $Re_2Cl_6(PR_3)_2$ and $Re_2Cl_5(PR_3)_3$ precursors be available and that the phosphine ligands which are already bound to the dirhenium core (in the aforementioned chloride complexes) not be labile. While these complexes probably have the structures $(Ph_3E)(PhR_2P)H_2Re(\mu\text{-}H)_4ReH_2(PR_2Ph)(EPh_3)$ and $(Ph_2RP)_2H_2Re(\mu\text{-}H)_4ReH_2(PRPh_2)(EPh_3)$ in the solid-state, the fluxional nature of the hydride ligands in solution prevents us from drawing any further structural conclusions at this time.

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(35) As an example, consider $Re_2H_8(PPh_3)_4$ and $Re_2H_8(PMe_2Ph)_4$, for which δ = −6.22 and δ = −5.01, respectively. Thus, the calculated value for $Re_2H_8(PMe_2Ph)_2(PPh_3)_2$ is δ −5.62, which is in excellent agreement with the experimental value of δ −5.66. Similarly, with δ −5.8 and δ −6.88 for $Re_2H_8(PMePh_2)_4$ and $Re_2H_8(SbPh_3)_4$, respectively, we calculate δ −6.07 for $Re_2H_8(PMePh_2)_3(SbPh_3)$; the experimental value is δ −6.10.

(36) We see no resolvable P–P′ coupling in any of these $^{31}P\{^1H\}$ NMR spectra. Since structure determinations on complexes of the type $Re_2H_8(PR_3)_4$ (PR_3 represents a monodentate phosphine) have shown that the P–Re–P angles are close to 105°, we are obviously dealing with a "cis" disposition of phosphine ligands for which *J*(P,P′) can be expected to be small. We find little evidence for measurable P–P′ coupling being transmitted via the Re–Re "bond".

(37) The individual $[Re(PR_2Ph)(EPh_3)]$ units can be eclipsed or staggered with respect to one another;[2] in the former case, the "planar" $(Ph_3E)(PhR_2P)Re\text{–}Re(PR_2Ph)(EPh_3)$ unit can exist with the PR_2Ph ligands in cis or trans dispositions to one another.

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Superexchange Coupling Mediated by Carboxylate and Hydrogen Bridges in Copper Amino Acid Complexes

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The study of the exchange interaction between metal centers occupies a crossing point between the search for magnetic materials and the elucidation of the role of polymetallic sites in proteins. In the first subject, many efforts have been made studying the orbital mechanisms of the exchange interactions in order to design polymetallic systems with predictable magnetic properties.[1,2] Several successes have been achieved in this direction.[3] On the other subject, the relation between the matrix elements for electron transfer and the magnetic exchange splitting (*J*) has been pointed out[4] and can be obtained from Anderson's model for superexchange[5] or with the simpler expression of Hay et al.[1] for exchange-coupled dimers. In this work we analyze magnetostructural correlations in copper amino acid complexes ($Cu(aa)_2$), in order to learn about the effectiveness and possible interferences

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of carboxylate bridges and hydrogen bonds as pathways for superexchange.

We have studied by ESR spectroscopy at ν = 9 and 35 GHz single crystals of bis(L-phenylalaninato)copper(II), Cu(L-Phe)$_2$,[6] bis(L-methioninato)copper(II), Cu(L-Met)$_2$,[7] and bis(L-leucinato)copper(II), Cu(L-Leu)$_2$.[8] These systems crystallize in the $P2_1$ space group, with similar parameters, as shown in Table I.[9] The copper ions are arranged in layers, with intralayer distances of about 5 Å and interlayer distances of about 15 Å. There are two chemically equivalent, but magnetically inequivalent, species A and B of Cu(II) ions per unit cell, related by a 180° rotation around the $\hat{b}$ axis. The individual resonances corresponding to these species are collapsed to one due to the isotropic (Heisenberg) exchange interaction $\mathcal{H}_{\mathrm{ex(A,B)}} = -\sum_{i,j} J\vec{S}^i{}_{\mathrm{A}}\cdot\vec{S}^j{}_{\mathrm{B}}$ between the i and j nearest neighbor Cu(II) ions of different species. However, the difference between the orientations of their gyromagnetic tensors introduces a contribution to the ESR line width of the single resonance, which decreases as the magnitude of J increases. This provides a method to obtain the value of the exchange parameter J using Kubo and Tomita's theory for exchange-coupled systems.[10] The frequency and angular dependences of this contribution to the line width are given by

$$\Delta B(\theta,\phi) = \frac{\sqrt{2\pi/3}\,h^2\nu^2[g_{\mathrm{A}}(\theta,\phi) - g_{\mathrm{B}}(\theta,\phi)]^2}{8\mu_{\mathrm{B}}|J|g^3(\theta,\phi)} \qquad (1)$$

where g_{A} and g_{B} are the gyromagnetic factors for sites A and B, $g = (g_{\mathrm{A}} + g_{\mathrm{B}})/2$, μ_{B} is the Bohr magneton, and h is the Planck constant. With use of eq 1, ESR is a powerful technique for detecting changes in the magnitude of the exchange interactions, which can be correlated with small structural variations. Recently, Gennaro[6b] obtained the value $|J|$ = 0.37 K between neighboring coppers of different species in Cu(L-Phe)$_2$ by using the same method. This value is analyzed here, together with the values $|J|$ = 0.10 K for Cu(L-Met)$_2$[7] and $|J|$ = 0.23 K for Cu(L-Leu)$_2$,[8] in terms of the chemical paths between Cu(II) ions of different species. It is important to mention that in all these systems the single exchange-collapsed ESR line has a characteristic Lorentzian shape as was observed and shown in single crystals of similar copper amino acid complexes.[11] This fact was used to derive eq 1.[7] The values obtained for $|J|$ are complemented by magnetic susceptibility measurements which indicate that Cu(L-Met)$_2$,[9a] Cu(L-Leu)$_2$,[12a] and Cu(L-Phe)$_2$,[12a] like other carboxylate-bridged Cu(aa)$_2$ species as bis(L-alaninato)copper(II), Cu(L-Ala)$_2$,[12b] and bis(2-aminoisobutyrato)copper(II), Cu(AIB)$_2$,[11b] are antiferromagnetic. In the systems analyzed here, the distances between copper ions are sufficiently large to preclude direct magnetic exchange interactions, and there is no correlation between the exchange coupling and the Cu$_{\mathrm{A}}$–Cu$_{\mathrm{B}}$ distances given in Table I. Thus, the mechanism for magnetic coupling is superexchange via the bridging carboxylate linkages or the N–H···O hydrogen bonds connecting different species of Cu(II) ions. According to well-known criteria,[13] the N–H···O angles and H···O distances involved in H-bridges correspond to very weak bonds. Besides, we have not found correlations between these bond parameters and the J values. In contrast, a systematic trend has been observed for carboxylate bridges, which involve apical and equatorial oxygens from Cu(II) nearest neighbors (see Figure 1). The only structural parameters of the carboxylate bridges that vary significantly from Cu(L-Phe)$_2$ to Cu(L-Leu)$_2$ and to Cu(L-Met)$_2$ are the lengths of the apical oxygen–copper bonds. Since the ground orbital state for the unpaired electron of Cu^{2+} in the three systems studied is a $d_{x^2-y^2}$, as can be inferred from their gyromagnetic tensors,[6-8] this electron density is zero in the $\hat{z}$ direction normal to the orbital. However, the Cu–O$_{\mathrm{ap}}$ bonds are deviated from the right angle with the N$_2$O$_2$ equatorial plane of ligands outlined in Figure 1 by the angle α given in Table I. This indicates that the apical oxygen shares some of the unpaired electron density mainly localized at the $d_{x^2-y^2}$ orbital.

We display in Figure 2 the values of $|J|$ as a function of the Cu–O$_{\mathrm{ap}}$ distance $l_{\mathrm{Cu-O}}$ to the nearest apical oxygen. The strong correlation observed led us to conclude that carboxylate bridges are the main superexchange paths between A and B Cu(II) ions in these systems. On the other side, we have observed that in bis(L-isoleucinato)copper(II), where there are no carboxylate bridges and weak hydrogen bonds are the only pathways for superexchange, the exchange coupling results in ferromagnetism.[14]

The observations on the sign of J can be interpreted in the light of the theories of Anderson[5] and Hay et al.[1] for the exchange interaction in infinite solid lattices and in molecular bridged dimers, respectively. Within these theories, the exchange-coupling constant is a sum of ferromagnetic (J_{F}) and antiferromagnetic (J_{AF}) contributions. Usually, J_{AF} is the more important and more sensitive to changes in the system because it results as being proportional to the square of the effective hopping matrix element $\tilde{V}$ between nearest-neighbor paramagnetic ions. In the carboxylate-bridged Cu(L-aa)$_2$, $\tilde{V}$ is large enough to stabilize the low-spin state, leading to antiferromagnetic exchange. In contrast, in Cu(L-Ile)$_2$, the hydrogen bridges produce a small through-bond coupling, unable to "counterbalance" the ferromagnetic contribution to J, less dependent on changes in the system. Our interpretation is supported by the very weak exchange interaction $|J| \simeq 0.006$ K, observed by Hoffmann et al. in *cis*-bis(glycinato)copper(II) monohydrate, *cis*-Cu(Gly)$_2$·H$_2$O,[15] a Cu(aa)$_2$ having an apical water oxygen at 2.40 Å from Cu and a carboxylate bridge with a long Cu–O$_{\mathrm{ap}}$ distance of 2.74 Å. However, the sign of J is not known in this system, and it would be interesting to determine it.

The correlation displayed by the experimental points in Figure 2 can be understood qualitatively with the equation

$$J_{\mathrm{AF}} = \frac{-2|\tilde{V}|^2}{U} \qquad (2)$$

obtained by Anderson[5] for the superexchange constant. Here, U is the Hubbard repulsion for two electrons in the same copper

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Table I. Crystallographic and Molecular Data for Bis(L-methioninato)copper(II),[9b] Bis(L-leucinato)copper(II),[9a] and Bis(L-phenylalaninato)copper(II)[9c][a]

	Cu(L-Met)$_2$	Cu(L-Leu)$_2$	Cu(L-Phe)$_2$
a, Å	9.487 (5)	9.725 (4)	16.710 (14)
b, Å	5.061 (3)	5.127 (1)	5.217 (9)
c, Å	15.563 (8)	14.689 (6)	9.509 (7)
β, deg	92.46 (3)	105.79 (3)	98.40 (6)
intralayer Cu$_A$–Cu$_B$ dists, Å	5.34	5.49	5.39
	5.42	5.51	5.48
Cu–O$_{ap}$ bond lengths, Å	2.75	2.75	2.69
	2.68	2.63	2.58
α, deg	7.27	7.17	6.00
	5.55	3.98	5.26

[a] In Cu(L-Met)$_2$ and Cu(L-Leu)$_2$, the layers of coppers are parallel to the *ab* plane, while, in Cu(L-Phe)$_2$, they are parallel to the *bc* plane. The angle α between the normal to the square of ligands to copper and the Cu–O$_{ap}$ bonds is also given.

ion and $\tilde{V}$ is the effective nearest-neighbor hopping parameter, which considers contributions to J_{AF} from all superexchange paths.[16] These contributions may interfere in constructive or destructive forms,[16–18] depending on the topology of the system and on the hopping parameters and site energies involved in these paths. Then, the good correlation observed in Figure 2 between J and the relevant parameter of the carboxylate bridges tells us that the contributions of the H-bridges to the superexchange are too weak to interfere with the stronger contributions to $\tilde{V}$ arising on the carboxylate bridges. As a consequence, we neglect contributions to $\tilde{V}$ arising from the hydrogen bonds in the carboxylate-bridged Cu(aa)$_2$. Then, $\tilde{V}$ results as being proportional to the overlap, $S_{Cu-O} \simeq \exp(-R/\lambda)$, between the copper $d_{x^2-y^2}$ and the apical-oxygen sp^2 orbitals.[16] Here, R is the length of the Cu–O$_{ap}$ bond and λ is an overlap attenuation constant. Under the usual criteria,[1] J_F does not depend on R. Hence, a variation ΔR produces a variation of J due only to the antiferromagnetic contribution of the carboxylate bridge, which is given by

$$\Delta J \simeq \frac{-2J\Delta R}{\lambda} \qquad (3)$$

A value $\lambda = 0.18$ Å is obtained for the overlap attenuation parameter, using the data given in Figure 2.

We included in Figure 2 only experimental points corresponding to Cu(aa)$_2$ with large distances between copper layers. It is important to keep constant the magnetic dimensionality, in order to make reliable use of eq 1. Also, the three compounds considered in this figure maintain constant all the other structural parameters. Note that the value $|J| \simeq 0.006$ K obtained for *cis*-Cu(Gly)$_2$·H$_2$O,[15] a Cu(aa)$_2$ with $l_{Cu-O} = 2.74$ Å, follows well the trend of Figure 2. However, we do not include this point because in *cis*-Cu(Gly)$_2$·H$_2$O several structural parameters vary with respect to the other three systems, and we cannot be sure that it has the same magnetic dimensionality. In particular, it belongs to another space group, one apical position in each copper is occupied by a water oxygen, and the coppers are not arranged in layers.

It is interesting to note that the values of $|J|$ obtained for Cu(L-Leu)$_2$, Cu(L-Met)$_2$, and Cu(L-Phe)$_2$ are about 3 orders of magnitude smaller than the ones in systems linked by Cu–O–C–O–Cu carboxylate bridges in which both Cu–O bonds involve equatorial oxygens. In these cases, the interactions between the $d_{x^2-y^2}$ orbitals of the Cu(II) ions are much stronger.[19] In the case of the Cu(aa)$_2$ analyzed here, the through-space Cu–O$_{ap}$ section of the superexchange path heavily reduces the magnitude of J. However, our results indicate that although the overlap for the Cu–O$_{ap}$ bond is small, the carboxylate group is more effective in allowing for electron spin delocalization than the pathways between equatorial ligands and Cu(II) ions involving hydrogen bonds. This result is important in view that these chemical pathways are present in most metalloproteins.

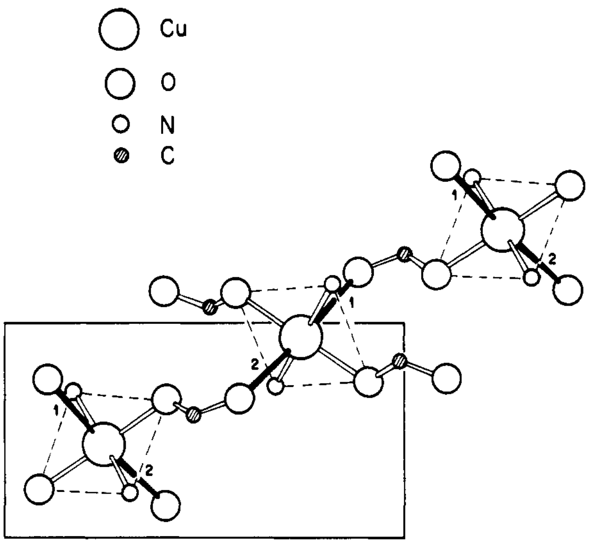

Figure 1. Projection of a typical portion of the crystal lattices of Cu(L-Met)$_2$, Cu(L-Leu)$_2$, and Cu(L-Phe)$_2$, showing the carboxylate-bridged structure. The Cu–O$_{ap}$ bonds are marked with heavy lines. The lengths of the two Cu–O$_{ap}$ bonds of each copper labeled by 1 and 2 are different, as indicated in Table I.

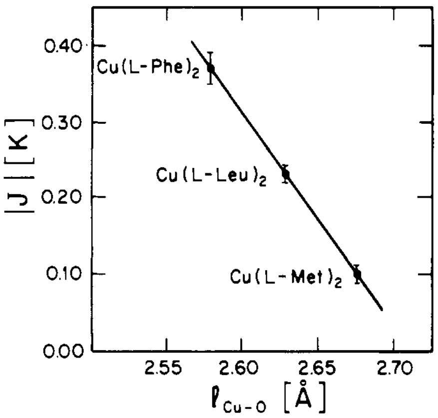

Figure 2. Value of the superexchange parameter $|J|$ between inequivalent copper ions, as a function of the length of the shortest copper–apical oxygen bond l_{Cu-O}. The uncertainties of the values of $|J|$ were obtained from the least-squares analyses used to extract the contribution of eq 1 to the line-width data. The included copper amino acid crystals have the other structural parameters essentially constant.[20]

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(20) The correlation displayed in Figure 2 indicates that the $|J|$ value corresponding to the longest copper–apical oxygen bond of each complex given in Table I gives a contribution to the exchange frequency which is negligible compared to the $|J|$ value corresponding to the shortest one. Thus, each copper ion should be considered as effectively connected to two inequivalent copper neighbors instead of four, as assumed in ref 7 in the derivation of eq 1. This would imply that all the $|J|$ values in Figure 2 must be multiplied by a factor $\sqrt{2}$.