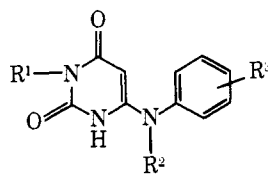


Table IV. 6-(*N*-Alkylanilino)uracils

Compd no.	R ¹	R ²	R ³	Mp, ^a °C	Yield, %	Formula	Analyses
IIa	H	CH ₃	H	304	95	C ₁₁ H ₁₁ N ₃ O ₂	C, H, N
IIb	H	C ₂ H ₅	H	299	94	C ₁₂ H ₁₃ N ₃ O ₂	C, H, N
IIc	H	<i>n</i> -C ₃ H ₇	H	242	88	C ₁₃ H ₁₅ N ₃ O ₂	C, H, N
IId	H	<i>n</i> -C ₄ H ₉	H	229	85	C ₁₄ H ₁₇ N ₃ O ₂	C, H, N
IIe	CH ₃	CH ₃	H	210	96	C ₁₂ H ₁₃ N ₃ O ₂	C, H, N
IIf	CH ₃	C ₂ H ₅	H	218	92	C ₁₃ H ₁₅ N ₃ O ₂	C, H, N
IIg	CH ₃	<i>n</i> -C ₃ H ₇	H	166	93	C ₁₄ H ₁₇ N ₃ O ₂	C, H, N
IIh	CH ₃	<i>n</i> -C ₄ H ₉	H	138	88	C ₁₅ H ₁₉ N ₃ O ₂	C, H, N
IIi	H	CH ₃	7,8-(CH ₃) ₂	281	88	C ₁₃ H ₁₅ N ₃ O ₂	C, H, N
IIj	CH ₃	CH ₃	7,8-(CH ₃) ₂	232	93	C ₁₄ H ₁₇ N ₃ O ₂	C, H, N
IIk	H	D-Ribityl	7,8-(CH ₃) ₂	185	80	C ₁₇ H ₂₃ N ₃ O ₆	C, H, N

^a All the products were recrystallized from ethanol.

tals thus separated were collected by filtration, washed with water, dried, and recrystallized from ethanol.

By this method, IVe, IVf, and 8-chloro-3,10-dimethylisoalloxazine (IVI) were prepared. IVI did not melt below 330°. Anal. (C₁₂H₉N₄O₂Cl) C, H, N.

10-Acetoxyethyl-7,8-dimethylisoalloxazine 5-Oxide (VI). A suspension of riboflavin (0.5 g, 0.0013 mol) and *m*-chloroperbenzoic acid (3 g, 0.017 mol) in acetic acid (100 ml) was heated at 90° for 5 hr, whereby the reaction mixture became clear. After cooling, the reaction solution was concentrated to one-third volume and diluted with ether (100 ml) and allowed to stand overnight at room temperature to cause the separation of orange crystals, which were collected by filtration and washed with ether. Recrystallization from a mixture of acetic acid and ether gave 0.23 g (52%) of orange prisms, mp 270°. Anal. (C₁₅H₁₄N₄O₅) C, H, N.

Decomposition of VI to Lumichrome (VII). Stirring of VI (0.2 g, 0.0006 mol) in aqueous solution (5 ml) including sodium dithionite (0.4 g) for 1 hr at room temperature. The precipitates were collect-

ed by filtration, washed with water, and dried. Recrystallization from ethanol gave 0.09 g (61%) of pale yellow needles.

References and Notes

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On the Superexchange Mechanism in Polymeric, Pyrazine-Bridged Copper(II) Complexes

H. Wayne Richardson and William E. Hatfield*

Contribution from the Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514. Received June 16, 1975

Abstract: Magnetic susceptibilities (1.9–250 K) and electron paramagnetic resonance and electronic spectra have been obtained on a variety of systems related to [Cu(pyr)(NO₃)₂]_n (pyr = pyrazine) in order to determine the mode of superexchange; a novel π mechanism has been formulated on the basis of the results. All the systems can be described by the isotropic Heisenberg model for antiferromagnetically coupled linear chains of $S = \frac{1}{2}$ ions.

There has been considerable interest in polymeric transition metal complexes in which the metal ions are bridged by heterocyclic aromatic diamines, especially pyrazine (pyr).¹⁻⁷ Magnetic susceptibility measurements made at low temperatures on powdered³ and single-crystal⁴ samples of the pyrazine-bridged linear polymer⁸ [Cu(pyr)(NO₃)₂]_n revealed antiferromagnetic chainlike behavior which could be described by the Heisenberg linear-chain model⁹ and not the Ising model.¹⁰

In addition to the pyrazine bridges in [Cu(pyr)(NO₃)₂]_n, there are also rather weakly bound nitrate bridges between the copper(II) ions of the chains. Since it is known^{11,12} that nitrate bridges between copper(II) ions support antiferromagnetic superexchange interactions in Cu(NO₃)₂·2.5H₂O,¹³ it was deemed necessary to investigate the nature of the superexchange interactions in related polymeric chain complexes of copper(II) nitrate in order to determine the exchange pathway. Spectroscopic and magnetic investi-

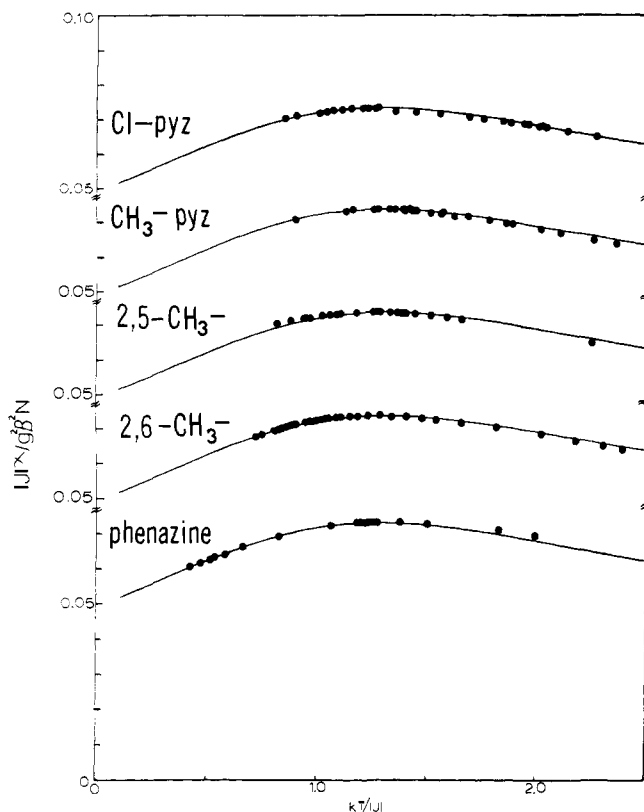


Figure 1. Proportionate susceptibility vs. temperature, illustrating the Heisenberg model approximation for (from top to bottom) [Cu(Cl-pyr)(NO₃)₂]_n (a), [Cu(CH₃-pyr)(NO₃)₂]_n (b), [Cu(2,5-(CH₃)₂-pyr)(NO₃)₂]_n (c), [Cu(2,6-(CH₃)₂-pyr)(NO₃)₂]_n (d), and [Cu(phenazine)(NO₃)₂]_n (e).

gations on substituted pyrazine complexes which confirm the superexchange pathway are reported herein. The ligands used in this report include phenazine, quinoxaline, pyrazine, methylpyrazine, 2,5-dimethylpyrazine, 2,6-dimethylpyrazine, and chloropyrazine.

Experimental Section

Preparation of the Complexes. An ethanol solution of copper(II) nitrate trihydrate was treated with 2,2-dimethoxypropane for the removal of the waters of hydration, and the resulting solution was added to an ethanol solution of the appropriate ligand. The blue precipitates which came out of the solution were collected immediately, washed with ethanol and ether, and then dried in air. All compounds were submitted to Galbraith Laboratories, Inc., Knoxville, Tenn. for C, H, N analysis, and all samples utilized in the measurements described below had satisfactory analysis; i.e., in no case was $|\% R_{\text{calcd}} - \% R_{\text{found}}| > 0.3$ ($R = \text{C, H, N}$), and in most cases the agreement between the calculated value and the experimental value was much less than 0.3.

Physical Measurements. Magnetic susceptibilities were measured in the temperature range 1.9 to 250 K using a Foner-type¹⁴ vibrating sample magnetometer which was calibrated with Hg[Co(NCS)₄].^{15,16} Details of the procedures have been given elsewhere.¹⁷ The data were corrected for temperature-independent paramagnetism (taken to be 60×10^{-6} cgs units) and for the diamagnetism of the constituent atoms using Pascal's constants.¹⁸

Electronic spectra were recorded on a Cary 14 recording spectrophotometer using the filter paper/mull technique which has been described by Lee et al.,¹⁹ and EPR spectra were recorded on a Varian E-3 X-band spectrometer.

Results

As can be seen in Figure 1, a maximum in susceptibility, which is indicative of antiferromagnetic interactions, was

observed for each of the five new compounds [Cu(Cl-C₄H₃N₂)(NO₃)₂]_n, [Cu(CH₃-C₄H₃N₂)(NO₃)₂]_n, [Cu(phenazine)(NO₃)₂]_n, and [Cu(2,5(2,6)-(CH₃)₂-C₄H₂N₂)(NO₃)₂]_n.²⁰ The magnetic data were analyzed using the Hamiltonian

$$\mathcal{H} = -2J \sum_{i=1}^N [S_{iz}S_{(i+1)z} +$$

$$\gamma(S_{ix}S_{(i+1)x} + S_{iy}S_{(i+1)y})] - g\beta \sum_{i=1}^N \mathbf{H} \cdot \mathbf{S}_i$$

where a negative value of J is indicative of an antiferromagnetic interaction. If γ is set equal to zero, the anisotropic Ising model results, while for γ equal to 1, the isotropic Heisenberg model obtains. Since we have shown conclusively by single crystal measurements⁴ on [Cu(pyr)(NO₃)₂]_n that the Ising model fails to account for the observed magnetic behavior, and that the Heisenberg model gives a satisfactory description of the magnetic properties, we have used the latter to obtain the magnetic parameters. From machine calculations and subsequent extrapolations by Bonner and Fisher,⁹ the following expressions for the magnetic parameters are available:

$$kT_{\text{max}}/|J| \approx 1.282$$

$$|J|\chi_{\text{max}}/g^2\beta^2N \approx 0.07346$$

The best least-squares fits, using the minimum value of the parameter

$$P = \sum_{i=1}^N [(\chi_i^{\text{obsd}} - \chi_i^{\text{calcd}})T_i]^2$$

as the criterion of the best fit, yielded the magnetic parameters listed in Table I. It was necessary to correct the data for the presence of small amounts of presumed paramagnetic impurities which are also listed in Table I. The details of this correction have been described elsewhere.²¹ While this impurity correction has little effect on the value of $|2J|$, it does permit a better description of the observed behavior at the very low-temperature limit of the experiment.

The electronic spectra of the chloropyrazine, methylpyrazine, dimethylpyrazines, and phenazine complexes of copper(II) nitrate are very similar to the spectrum of [Cu(pyr)(NO₃)₂]_n as well as that of [Cu(quinoxaline)(NO₃)₂]_n, a compound which is also thought to contain heterocyclic aromatic diamine bridges.²² The electronic spectra, EPR g values, and magnetic parameters for all of the compounds are given in Table I.

There is a small variance in the g values obtained by EPR and magnetic susceptibility. This difference has been noted previously⁴ in similar systems and has been attributed to the possible temperature dependence of the g value. The Heisenberg model of Bonner and Fisher derives the g value strictly from the temperature at the maximum in susceptibility (less than 12 K in all the substituted pyrazines studied), whereas the EPR g value is taken from room-temperature results.

Discussion

The molecular and crystal structure of [Cu(pyr)(NO₃)₂]_n, as determined by Santoro, Mighell, and Reimann,⁸ is illustrated in Figures 2 and 3. The environment about a particular copper(II) ion includes two nitrogen atoms from pyrazines and two oxygen atoms from nitrate ions which are tightly bonded. The average Cu-N bond distance is 1.98 Å, and the average Cu-O in-plane bond distance is 2.01 Å. The nitrate ions lie in a plane which is perpendicular to the -Cu-pyrazine-Cu- chain, and a second oxygen from each nitrate is semicoordinated giving the cop-

Table I. Spectral and Magnetic Properties of $[\text{Cu}(\text{R-pyrazine})(\text{NO}_3)_2]_n$

Ligand	$2J$, cm^{-1}	$\langle g \rangle$ Heisenberg	EPR $\langle g \rangle$	d-d transition, (complex), kK	$\pi-\pi^*$ (complex), kK	Ligand band, kK	pK_a , (ref 32)	% Impurity correction
Phenazine	-12.6 ± 0.4	2.14 ± 0.04	2.137		27.6	27.4	1.23	0.75
Quinoxaline	-9.0 ± 0.3	2.14 ± 0.04	2.15	18.5	29.0	31.0 ^a	0.56	0.20
2,6-Dimethylpyrazine	-8.0 ± 0.2	2.10 ± 0.04	2.14	18.2	35.1		1.90	0
Pyrazine	-7.4 ± 0.1	2.08 ± 0.01	2.133	17.86	34.6	38.46 ^{a-e}	0.65	0
2,5-Dimethylpyrazine	-7.0 ± 0.2	2.10 ± 0.04	2.14	18.3	33.7	36.6 ^{b,e}	1.85	0
Methylpyrazine	-6.2 ± 0.1	2.06 ± 0.04	2.145	17.9	34.2	37.90 ^b	1.45	0
Chloropyrazine	-2.8 ± 0.2	2.09 ± 0.04	2.153	17.8	36.4	37.0 ^e		1.80

^aReference 29. ^bReference 27. ^cReference 28. ^dReference 30. ^eReference 31.

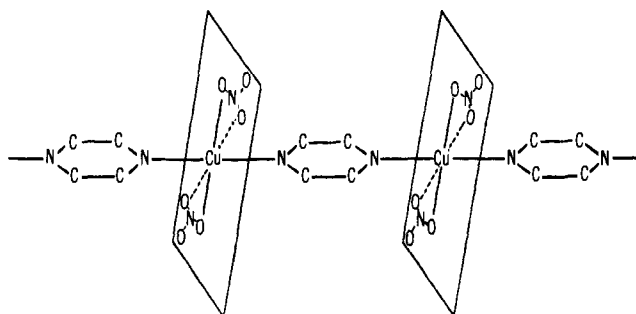


Figure 2. The molecular structure of $[\text{Cu}(\text{pyr})(\text{NO}_3)_2]_n$.

per ion a very distorted "4 + 2" coordination. While a precise description of the orbital containing the unpaired electron is not available, it is very likely that the unpaired electron is in the σ^* orbital, which for our purposes will be labeled $d_{x^2-y^2}$, and which is directed along the four short copper-ligand bonds. This description is consistent with the conclusions drawn by Kokoszka and Reimann²³ based on their EPR study of a polycrystalline sample.

The plane of the pyrazine ring is tilted out of the xy plane described by CuO_2N_2 by approximately 48° , and pyrazine separates the magnetic ions by 6.7 \AA in the crystallographic a direction. Copper(II) ions in adjacent chains are separated in the b direction by 5.14 \AA , and as shown in Figure 3, there is the possibility of a superexchange pathway by way of the weak nitrate bridge which exists between these ions. The purpose of this work is to determine which of these bridging pathways supports the superexchange mechanism. A working hypothesis was constructed. First, it was conjectured that changes in the electronic nature of the pyrazine, as surely occurs in substituted pyrazines, should be reflected by the exchange coupling constants of structurally similar complexes prepared by substituted pyrazines if the mechanism occurred by way of the aromatic heterocyclic ring. However, if the nitrate ion orbitals carry the antiferromagnetic interactions, then the substituent effect should be steric, not electronic, in nature. This assertion is borne out by examination of Figure 3 which clearly shows that the separation between the chains will be markedly increased by substituents on the pyrazine ring and by numerous observations^{24,26} that exchange coupling is attenuated upon an increase in the separation between interacting magnetic centers.

Before we can use the data in Table I to establish the superexchange pathway, it is necessary to establish the structures of the compounds. The similarities in the EPR $\langle g \rangle$ values and in the energies of the d-d transitions for all seven compounds are very strong evidence that all members of the series have the same structure. The conclusion that this is an isostructural series is further supported by the linear chain behavior of the magnetic data. We have not succeeded in preparing crystals suitable for x-ray diffraction stud-

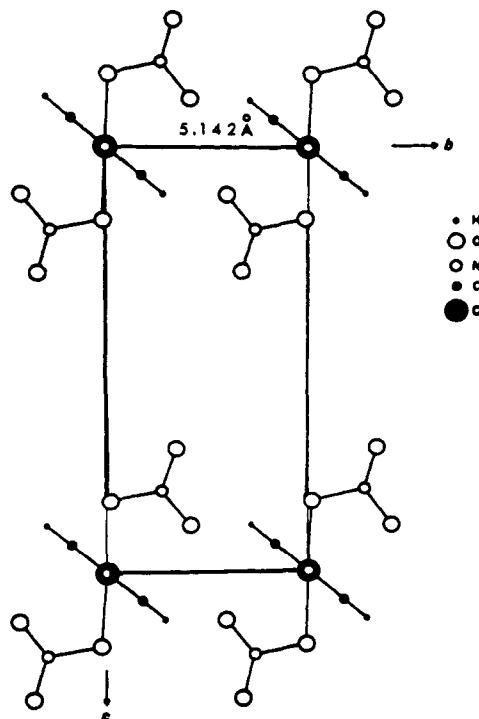


Figure 3. The crystal structure of $[\text{Cu}(\text{pyr})(\text{NO}_3)_2]_n$ in the bc plane. The heterocyclic chain runs along the a axis.

ies; this remains an important goal since structural data are required in order to answer some of the detailed questions concerning the superexchange mechanism. However, precise details of the structures are not required for the following discussion.

In addition to the d-d transition envelope near 18000 cm^{-1} , there is an additional band in the near-uv for each complex. These are listed in Table I under the heading " $\pi \rightarrow \pi^*$ (complex)". Our assignment of the band was guided by the chemical nature of the compounds. One possibility for the assignment would be charge transfer, and since chloropyrazine is harder to oxidize than pyrazine, it follows that if this assignment is correct, then the transition should be ligand-to-metal in nature since the band in the chloropyrazine complex is at higher energy. However, $\text{Zn}(\text{pyr})(\text{NO}_3)_2$ exhibits a similar band at 39000 cm^{-1} , and comparable bands for $[\text{Zn}(\text{bpy})_3](\text{NO}_3)_2$ and $[\text{Zn}(\text{phen})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$ ³³ (bpy = bipyridine; phen = 1,10-phenanthroline) have been shown to be internal ligand transitions. A ligand-to-metal band would not be of such low energy for the Zn^{2+} complexes. Thus, we favor a ligand $\pi-\pi^*$ assignment. Also, these bands showed the generally characteristic bathochromatic (to lower energy) shift of the $\pi-\pi^*$ transitions when complexed as expected from the Stark effect.^{34,35}

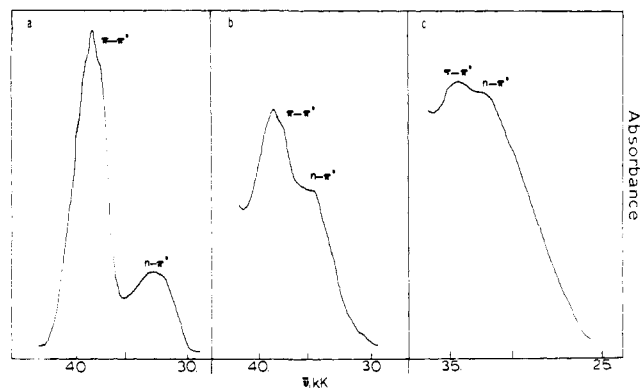


Figure 4. The ultraviolet spectra of pyrazine (a), $[\text{Zn}(\text{pyr})(\text{NO}_3)_2]$ (b), and $[\text{Cu}(\text{pyr})(\text{NO}_3)_2]_n$ (c).

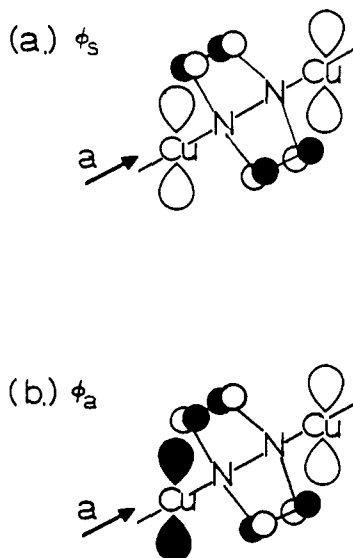


Figure 5. The two bonding molecular orbitals: (a) $\phi_s = (1/\sqrt{2})(d_s + \pi_s)$ and (b) $\phi_a = (1/\sqrt{2})(d_a + \pi_a)$, are shown for the copper-pyrazine-copper magnetic couple. The antibonding MO's (ϕ_s^* and ϕ_a^*) can be visualized if the sign of both copper orbitals in a couple is reversed relative to the carbon π orbitals.

The effect of complexation on the positions of the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions in the complexes $[\text{Zn}(\text{pyr})(\text{NO}_3)_2]$ and $[\text{Cu}(\text{pyr})(\text{NO}_3)_2]$ are shown in Figure 4. These bands overlap in the copper complexes, and some ambiguities exist in the determination of the energies of the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions owing to overlap of the two bands. The value of λ_{max} was arbitrarily chosen as the ligand $\pi \rightarrow \pi^*$ transition in each case.

Electronic transitions of the ligands²⁷⁻³¹ have been well documented in most cases. The transition moment for pyrazine (D_{2h} symmetry) does not vanish for transitions to states of B_{1u} , B_{2u} , or B_{3u} symmetry. The lowest symmetry allowed transition to a $\pi\pi^*$ state involves the $b_{1g}b_{3u}$ orbital configurations. If the substituent effects are considered to be minor perturbations on the energies of the lowest lying



Figure 6. Simplified molecular orbital diagram depicting a spin coupled pair of copper ions interacting with the spin transmitting orbitals of the ligand.

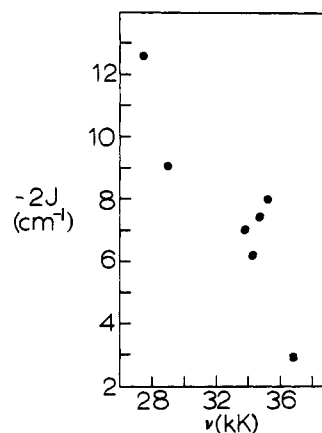


Figure 7. A display of the relationship between the exchange energy, $|2J|$, and the ligand $\pi-\pi^*$ separation of the complexes. (The data are given in Table I.)

and $a_u(\pi_a^*)$ ligand orbitals, with the symmetric and antisymmetric combinations of the metal orbitals, $d_s = (1/\sqrt{2})(d^1_{x^2-y^2} + d^2_{x^2-y^2})$ and $d_a = (1/\sqrt{2})(d^1_{x^2-y^2} - d^2_{x^2-y^2})$, respectively. The two bonding molecular orbitals are shown in Figure 5, where the lowest partly filled metal orbital combinations (d_s and d_a) are combined with the highest filled ligand orbital (π_s) and its antisymmetric analogue (π_a), respectively. An MO scheme for a Cu-pyrazine-Cu fragment is illustrated in Figure 6; the ground-state configuration is indicated. The singlet-triplet splitting is related to the difference in energy of the symmetric states with configuration $\phi_s^2\phi_a^2$, and the triplet state which arises from the configuration $\phi_s^2\phi_a^1\phi_s^*1$.³⁶ This overlap is shown in Figure 5 where the highest filled ligand orbitals are shown along with the lowest partly filled metal orbitals.

As remarked earlier, if spin exchange occurs along the nitrate-bridged chain, steric perturbations should be of a major consequence in determining the magnitude of J . As shown in Table I, no correlation was found between steric properties of the heterocycle and J . Also, the extended heterocyclic bridged copper chain, $[\text{Cu}(4,4'\text{-bpy})](\text{NO}_3)_2$, which probably should be analogous to the $[\text{Cu}(\text{pyr})](\text{NO}_3)_2$ structure along the nitrate chain, shows no magnetic spin coupling down to 1.90 K.³⁷ Also, there is little possibility that a σ -bonded mechanism through the heterocycle is significantly operative in view of the fact that

$\pi\pi^*$ state, a general π mechanism for spin exchange can be formulated. In this mechanism, superexchange occurs through the π network and involves overlap of the $b_{1g}(\pi_s)$

the exchange coupling constants do not correlate with the pK_a 's, which, of course, should reflect the σ electron density.

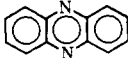
The π - π^* transitions of the complexes also support the π -heterocyclic mechanism. From the results in Table I, it can be seen that in general the antiferromagnetic exchange increases as the π - π^* separation decreases. The EPR results²³ indicate that the unpaired electrons of the copper ions lie in orbitals which are energetically fixed between the π and π^* orbitals, and since there will be a greater mixing of the metal orbitals with the π and π^* orbitals of the ligands as the energy differences between them decrease, then magnetic interactions should increase as the π - π^* separation decreases. The trend which is suggested by the data in Table I is emphasized by the display in Figure 7, where it may be seen that the correlation is not exact. We attribute the deviations to electronic effects brought about by structural changes in the polymer chain, with the most important features being the tilt of the heterocyclic ring with respect to the copper xy plane and variances in the copper-nitrogen bond distances as a result of the steric requirements of the substituents on the pyrazine ring.

In conclusion, since steric perturbations and σ -electron density of the heterocycle offer no correlations with the magnetic data, we suggest that spin coupling occurs by way of a π -heterocyclic mechanism. This conclusion is supported by recent broad-line ¹H NMR studies.³⁸

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