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The Magnetism of Methyl-Substituted Pyrazine Complexes of Copper(II)

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The magnetic susceptibilities of powdered samples of six substituted pyrazine complexes of copper(II) halides have been measured, and the data have been compared with the Ising model for linear chains and the dimer model. Structural assignments which have been proposed for the complexes are supported by far-infrared spectral data.

Introduction

The steric effects of substituted pyrazines (pz) and related ligands such as quinoxaline, pyridine, and other diazines have been the subject of numerous studies. Lever, Lewis, and Nyholm have investigated the substituted pyrazine complexes of cobalt(II),[1] nickel(II),[2] and copper(I).[3] Reimann and Gordon[4] have prepared copper(II) complexes of various unsubstituted diazines and Hyde, *et al.*,[5] have measured the susceptibilities at 110 and 369°K for (pz)$CuCl_2$ and (2-Me(pz))$CuCl_2$. Room-temperature moments, reflectance spectra, and infrared spectra have been obtained for (pz)$CuCl_2$ and (pz)$CuBr_2$ by Ferraro, *et al.*[6]

As a part of the continuing study in this laboratory of ligand and halogen bridged copper complexes, the magnetic and spectral properties have been investigated for a series of methyl-substituted pyrazine complexes of copper(II). Pyrazine, like quinoxaline, possesses two nitrogen donor atoms, each capable of coordination to copper, thereby resulting in the formation of ligand-bridged polymeric species. Copper chloride and copper bromide complexes have been prepared with 2-methyl-, 2,5-dimethyl-, and 2,6-dimethylpyrazine. The magnetic susceptibilities have been determined for these complexes over the temperature range 4.2–300°K and the far-infrared spectra have been obtained from 410 to 150 cm^{-1}.

Experimental Section

The following complexes were prepared by adding an ethanol solution containing excess $CuCl_2 \cdot 2H_2O$ or $CuBr_2$ (0.015 mol) to an ethanol solution (~20 ml) containing 0.01 mol of the ligand. In some instances it was necessary to add more ethanol in order to facilitate stirring. The resulting precipitates were filtered, washed with ethanol and ether, and dried at 25° at ~25 mm. The resulting stoichiometries for all complexes except (2,6-DiMe(pz))$_2CuCl_2$ were $CuLX_2$.

Anal. Calcd for (2-Me(pz))$CuCl_2$ (blue-green powder): C, 26.3; H, 2.65; N, 12.3; Cl, 31.0. Found: C, 26.0; H, 2.74; N, 12.2; Cl, 30.7. Calcd for (2-Me(pz))$CuBr_2$ (green powder): C, 18.9; H, 1.90; N, 8.82; Br, 50.3. Found: C, 18.6; H, 2.03; N, 8.73; Br, 49.5. Calcd for (2,5-DiMe(pz))$CuCl_2$ (green powder): C, 29.7; H, 3.32; N, 11.5; Cl, 29.2. Found: C, 29.3; H, 3.51; N, 11.3; Cl, 29.0. Calcd for (2,5-DiMe(pz))$CuBr_2$ (dark brown powder): C, 21.7; H, 2.43; N, 8.45; Br, 48.2. Found: C, 22.1; H, 2.53; N, 8.42; Br, 47.7. Calcd for (2,6-DiMe(pz))$_2CuCl_2$ (light blue fibrous precipitate): C, 41.1; H, 4.60; N, 16.0; Cl, 20.2. Found: C, 41.3; H, 4.58; N, 15.9; Cl, 20.3. Calcd for (2,6-DiMe(pz))$CuBr_2$ (dark brown powder): C, 21.7; H, 2.43; N, 8.45; Br, 48.2. Found: C, 21.7; H, 2.52; N, 8.31; Br, 48.1.

Magnetic susceptibilities below 77°K were measured with a Princeton Applied Research Model-155 vibrating sample magnetometer of the Foner[7] type. Susceptibilities above 77°K were measured with a Faraday apparatus.[8] Mercury tetrathiocyanatocobaltate(II) was used as a standard[9] for both methods, and diamagnetic corrections were estimated from Pascal's constants.[10] The temperature-independent paramagnetism was taken to be 60×10^{-6} cgsu.

The far-infrared spectra were obtained on a Hitachi-Perkin-Elmer far-infrared spectrophotometer at North Carolina State University. Samples were run as Nujol mulls between polyethylene plates.

Results

Plots of magnetic susceptibility *vs.* temperature are shown in Figures 1-5 and Table I. The solid and broken-line curves are the best fits calculated from Ising and dimer models, respectively. All complexes showed maxima in their susceptibility curves indicative of antiferromagnetic interactions. The temperatures at which the maxima occurred ranged from 18 to 160°K. Using a least-squares method, the data were fitted to the magnetic susceptibility eq 1 for an infinite linear chain of spins $S = {}^1/_2$, where $K = J/kT$. These equa-

TABLE I

MAGNETIC DATA FOR DICHLORO(2,5-DIMETHYLPYRAZINE)COPPER(II)

T, °K	$10^{-2}\chi_m^{cor}$, cgs	μ_{eff}, BM	T, °K	$10^{-2}\chi_m^{cor}$, cgs	μ_{eff}, BM
4.4	0.2835	0.31	13.2	0.3922	0.64
4.7	0.2950	0.33	13.3	0.3820	0.63
5.3	0.3132	0.36	14.2	0.3969	0.67
5.9	0.4195	0.44	16.0	0.3955	0.71
6.6	0.4266	0.47	18.0	0.3834	0.74
7.1	0.4063	0.48	23.0	0.3908	0.84
8.4	0.4111	0.52	29.5	0.3935	0.96
10.8	0.4246	0.60	32.4	0.3881	1.00
11.1	0.4225	0.61	42.0	0.3618	1.10
11.5	0.4171	0.61	56.0	0.3470	1.24
12.0	0.4077	0.62	76.0	0.3099	1.37
12.5	0.4117	0.64			

$$\langle\chi\rangle = {}^1/_3\chi_{\parallel} + {}^2/_3\chi_{\perp}$$

$$\chi_{\parallel} = \frac{Ng^2\beta^2}{4|J|} Ke^{2K}$$

$$\chi_{\perp} = \frac{Ng^2\beta^2}{8|J|}(\tanh |K| + |K| \operatorname{sech}^2 K) \qquad (1)$$

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[1] A. B P. Lever, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 1235 (1962).

[2] A. B. P. Lever, J. Lewis, and R. S. Nyholm, *ibid.*, 5042 (1963).

[3] A. B. P. Lever, J. Lewis, and R. S. Nyholm, *ibid.*, 3156 (1963).

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[6] J. R. Ferraro, J. Zipper, and W. Wozniak, *Appl. Spectrosc.*, **23** (2), 160 (1969).

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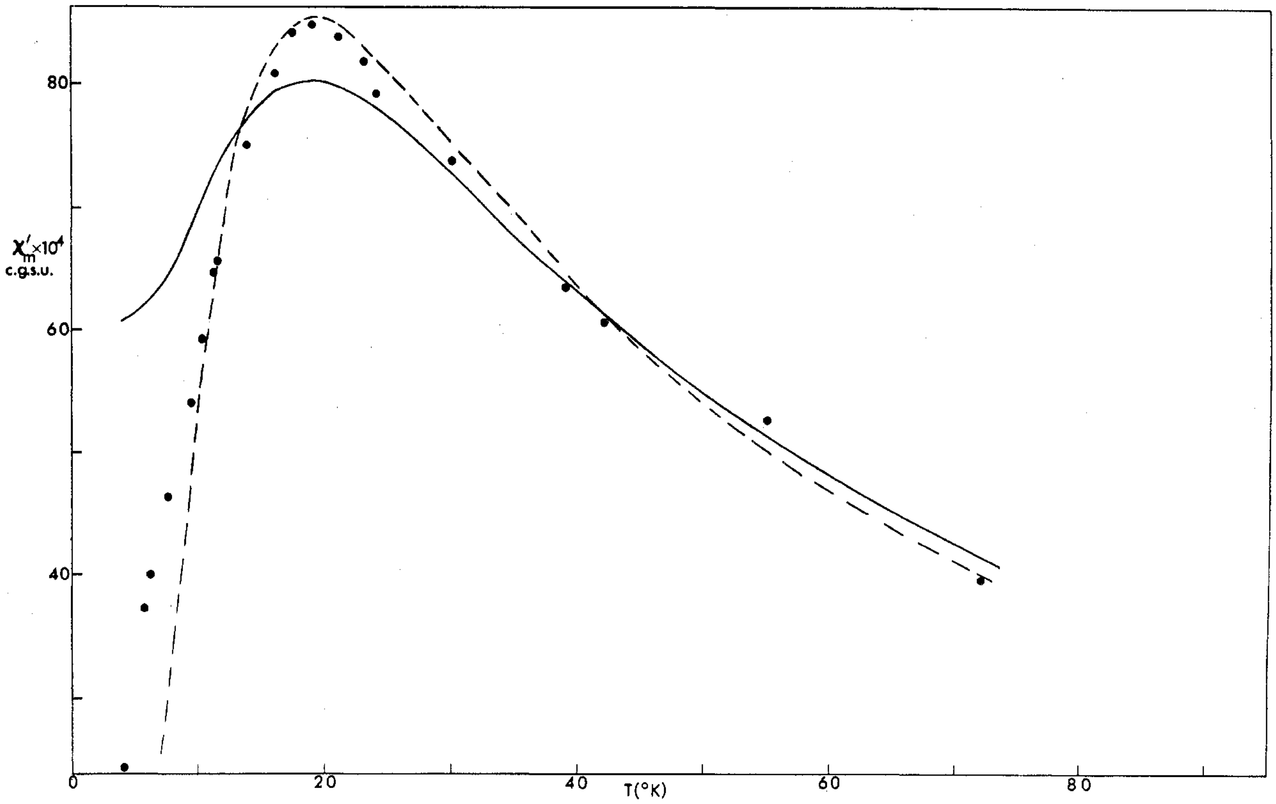

Figure 1.—Magnetic susceptibility *vs.* temperature for (2-Me(pz))$CuCl_2$. Experimental points and calculated curves: solid line, Ising model; broken line, dimer model.

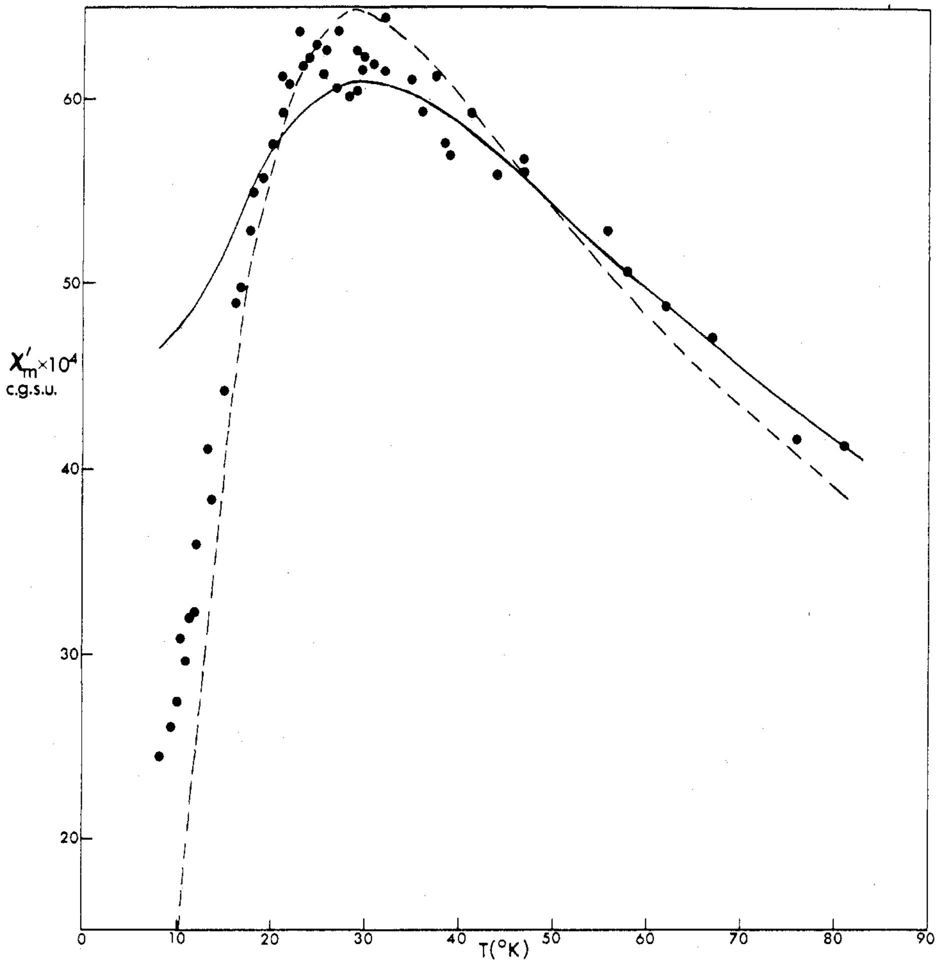

Figure 2.—Magnetic susceptibility *vs.* temperature for (2-Me(pz))$CuBr_2$. Experimental points and calculated curves: solid line, Ising model; broken line, dimer model.

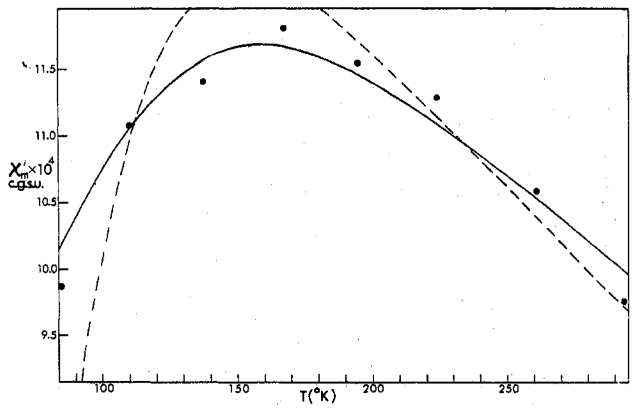

Figure 3.—Magnetic susceptibility *vs.* temperature for (2,5-DiMe(pz))CuBr$_2$. Experimental points and calculated curves: solid line, Ising model; broken line, dimer model.

TABLE II

DATA FITTING RESULTS FOR METHYL-SUBSTITUTED PYRAZINE COMPLEXES OF COPPER(II)

Compound	T_{max}, °K	Model	g	Exchange energy, cm^{-1}	$\Sigma_i^N(\delta_i)^2$
(2-Me(pz))CuCl$_2$	19	Ising	1.95	$J = -14$	0.0020
		Dimer	1.85	$2J = -21$	0.0011
(2-Me(pz))CuBr$_2$	28	Ising	2.16	$J = -22$	0.0046
		Dimer	1.99	$2J = -32$	0.0043
(2,5-DiMe(pz))CuCl$_2$	~25	Ising			
		Dimer			
(2,5-DiMe(pz))CuBr$_2$	160	Ising	2.12	$J = -116$	0.00010
		Dimer	1.95	$2J = -172$	0.00031
(2,6-DiMe(pz))$_2$CuCl$_2$	18	Ising	2.11	$J = -14$	0.00075
		Dimer	1.97	$2J = -20$	0.0058
(2,6-DiMe(pz))CuBr$_2$	47	Ising	1.89	$J = -33$	0.0023
		Dimer	1.61	$2J = -40$	0.0082

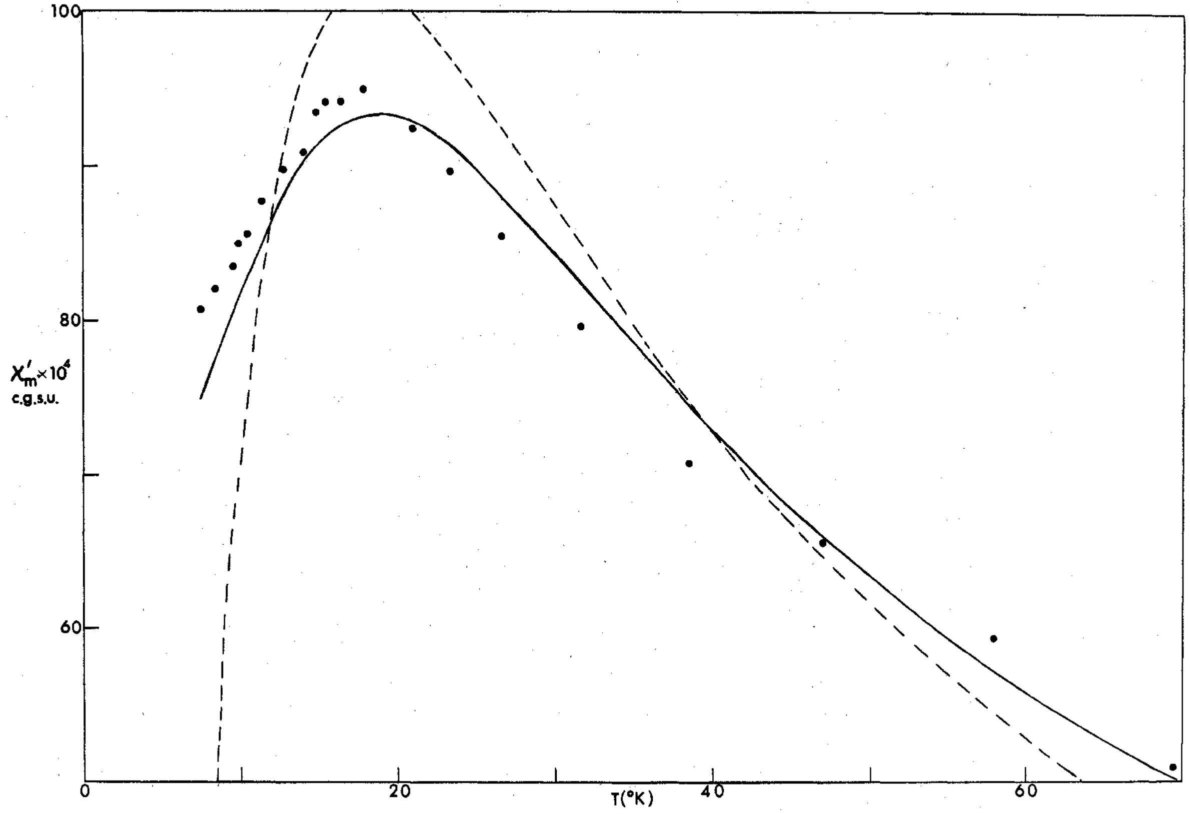

Figure 4.—Magnetic susceptibility *vs.* temperature for (2,6-DiMe(pz))$_2$CuCl$_2$. Experimental points and calculated curves: solid line, Ising model; broken line, dimer model.

tions are based on the Ising model and were derived by Fisher[11] using the Hamiltonian

$$\mathcal{H} = -J\sum\nolimits_{ij}\sigma_i^z\sigma_j^z - mH_z\sum\nolimits_i\sigma_i^z - mH_x\sum\nolimits_i\sigma_i^x$$

where σ_i^x and σ_i^z are Pauli spin operators and $m = g\beta/2$. The data were also fitted to the Van Vleck–Bleaney–Bowers equation[12] for exchange coupled pairs of spins with $S = \frac{1}{2}$

$$\langle\chi\rangle = \frac{Ng^2\beta^2}{3kT}[1 + \tfrac{1}{3}e^{-2J/kT}]^{-1} \qquad (2)$$

where $2J$ is the singlet–triplet separation. This equation was derived using the Hamiltonian, $\mathcal{H} = -2JS_1 \cdot S_2$. The data fitting in both cases was accomplished by parameterization of J and g; and by minimizing the least squares function $\Sigma_i^N(\delta_i)^2$, where $\delta_i = \Delta\chi_iT_i$. Results of these fitting procedures are summarized in Table II.

Since there are no X-ray crystal structure data available for the complexes studied here, the far-infrared spectra were obtained to complement magnetic susceptibility data. This was done with a view toward determining the nature of the Cu–X bond. The most important features of the spectra for our purposes are the halide-sensitive bands that range from 308 to 345 cm^{-1} for the chlorides and 251 to 264 cm^{-1} for the bromides. These Cu–X stretching frequencies are tabulated in Table III along with frequencies of other related compounds, some of which are known to contain bridging Cu–X bonds.

Discussion

The magnetic properties of some of the complexes

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[11] M. E. Fisher, *J. Math. Phys.* (*N. Y.*), **4**, 124 (1963).

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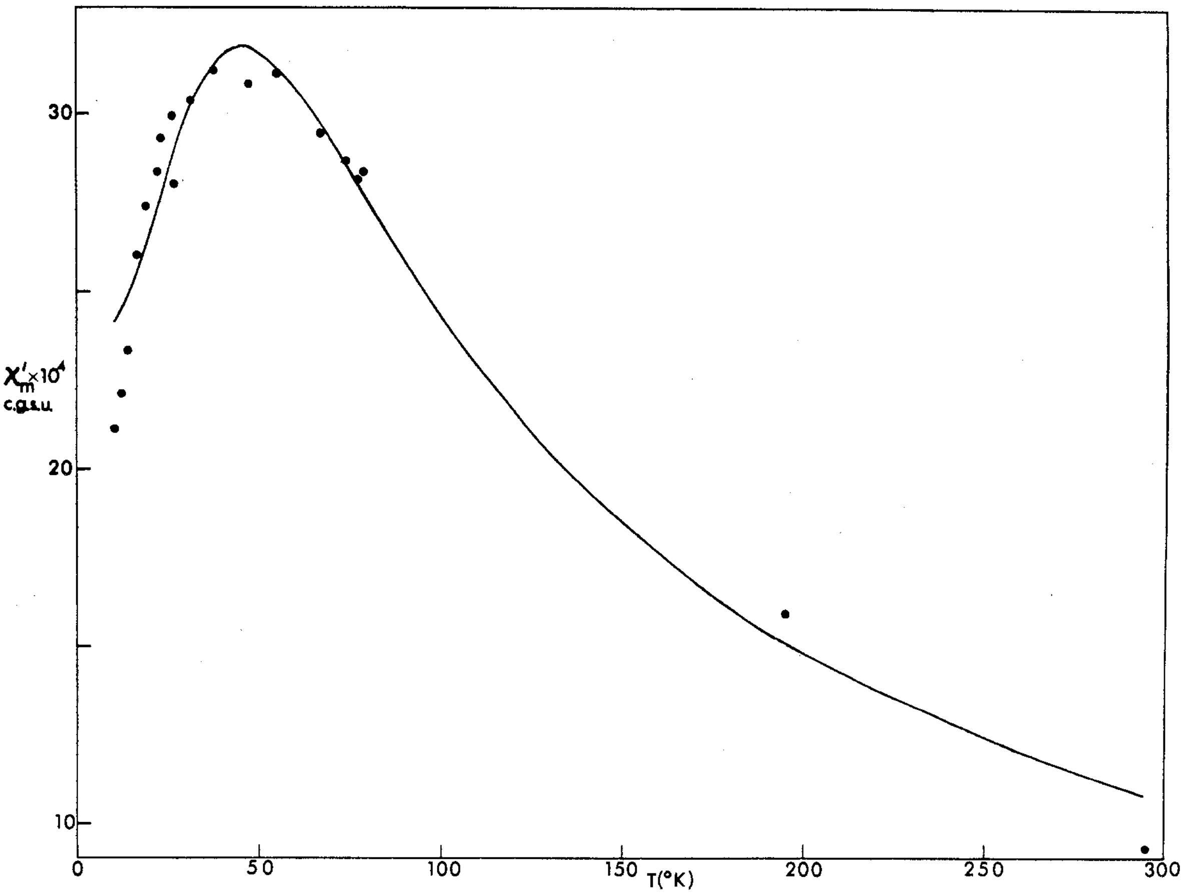

Figure 5.—Magnetic susceptibility *vs.* temperature for (2,6-DiMe(pz))CuBr$_2$. Experimental points and curve calculated from the Ising model.

TABLE III

Cu–X STRETCHING FREQUENCIES (CM^{-1})[a]

Compound	ν(Cu–Cl)	ν(Cu–Br)	Cu–X bond type	Ref
CuX$_2$	329, 277	255, 225	Bridging[b]	*c*
(py)$_2$CuX$_2$	287, 229	256, 204	Bridging[b]	*d*
(2-Me(py))$_2$CuX$_2$	308	233	Bridging[b]	*d*
(quin)CuX$_2$	324	255	Weakly bridging	*e*
(2-Me(quin))$_2$CuX$_2$	320	252	Bridging	*e*
(2,3-DiMe(quin))CuX$_2$	368	278	Terminal	*e*
(2,3-Diphenyl(quin))$_2$CuX$_2$	337	269	Weakly bridging or terminal	*e*
(pz)CuX$_2$	306	248	Bridging	6
(2,5-DiMe(pz))CuX$_2$	345	265	Weakly bridging or terminal	This work
(2-Me(pz))CuX$_2$	316	251	Weakly bridging	This work
(2,6-DiMe(pz))$_2$CuCl$_2$	308, 228		Bridging	This work
(2,6-DiMe(pz))CuBr$_2$		262	Weakly bridging	This work

[a] py = pyridine, quin = quinoxaline, pz = pyrazine, and X = Cl or Br. [b] Bridging character known from X-ray structural data. [c] D. M. Adams, M. Goldstein, and E. F. Mooney, *Trans. Faraday Soc.*, **59,** 2228 (1963). [d] M. Goldstein, E. F. Mooney, A. Anderson, and H. A. Gebbie, *Spectrochim. Acta*, **21,** 105 (1965). [e] D. E. Billing, A. E. Underhill, D. A. Adams, and D. M. Morris, *J. Chem. Soc. A*, 902 (1966).

studied here can best be described by the Ising model for linear chains of spins which are interacting antiferromagnetically. This behavior would tend to support a structural proposal that these complexes consist of infinite chains for which there is little or no interchain spin–spin coupling. The magnetic data for the complexes of 2-methylpyrazine are equally consistent with a dimer model. However, it is unlikely that these complexes possess strict dimeric structures and more probable that this behavior is due either to dimer-like units within the polymeric lattice or interchain effects. The nature of the magnetic data is discussed below for each complex.

(2-Me(pz))CuX$_2$.—The susceptibility curve for the chloro complex is shown in Figure 1 and exhibits a maximum at 19°K indicative of an antiferromagnetic interaction. Fitting the magnetic data with eq 1 for an Ising model gives $g = 1.95$ and an exchange energy, $J = -14$ cm^{-1}. The calculated susceptibilities from the dimer eq 2 fit the experimental curve better and predict a $g = 1.85$ and a singlet–triplet separation, $2J = -21$ cm^{-1}. The far-infrared spectrum exhibits a halide-sensitive band at 316 cm^{-1} which has been assigned to a (Cu–Cl) stretching frequency. The position of this band is indicative of a weakly bridged Cu–Cl bond. The lack of a band due to a terminal Cu–Cl stretching mode does not require the absence of a terminal Cu–Cl bond. The complex, (2-Me(py))$_2$CuCl$_2$, known to be a dimer,[13] gives a single far-infrared band at 308 cm^{-1} due to a Cu–Cl stretch. Although the magnetic data for (2-Me(pz))CuCl$_2$ are more consistent with a dimeric interaction, it is unlikely that the complex exists as a strict dimer. Stoichiometry would require the copper atoms in the dimer to be four-coordinate with a tetrahedral or square-planar geometry.

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(13) V. F. Duckworth and N. C. Stephenson, *Acta. Crystallogr.*, **25**, 1795 (1969).

Such a situation is highly improbable; especially since the potential for further coordination is considerable. Given the tendency of copper(II) to form distorted octahedral complexes and the ability of pyrazine to coordinate at both donor atoms,[1-3,14] a polymeric lattice structure shown in Figure 6 is more likely. Although the overall structure may be an extended polymer, the methyl groups may tend to force some of the chlorides (labeled X′ in the figure) away from a neighboring copper atom, thus creating isolated dimer-like units. There is another possibility that the lower susceptibilities observed below $T_{\max}$ are caused by increased antiferromagnetic exchange between chains at these lower temperatures. The magnitude of J (-14 cm^{-1}) calculated from the Ising model for (2-Me(pz))-$CuCl_2$ is comparable to the $J = -14$ cm^{-1} [15] calculated for $(py)_2CuCl_2$, known[16] to be a chain consisting of chloride bridges.

The bromo complex exhibits magnetic behavior similar to that of the chloro complex (see Figure 2) with a maximum in the susceptibility curve at 28°K. A $g = 2.16$ and $J = -22$ cm^{-1} are calculated from the Ising model while the dimer model gives a $g = 1.99$ and $2J = -32$ cm^{-1}. The far-infrared spectrum contains a halide-sensitive band at 251 cm^{-1} indicative of a bridging Cu–Br bond. Again the $J = -22$ cm^{-1} is comparable to the $J = -29$ cm^{-1} calculated[15] for $(py)_2CuBr_2$ known[17] to be a bromide-bridged chain. In any case the structures of both the chloro and bromo complexes are probably similar to that shown in Figure 6, wherein each copper is fully coordinated and there is extensive but probably weak bonding between chains.

(2,5-DiMe(pz))CuX$_2$.—The magnetic data for the chloro complex are tabulated in Table I and show a low broad maximum in susceptibility at ~26°K characteristic of an antiferromagnetic interaction. However, the magnetic behavior at low temperatures is anomalous and the susceptibility data cannot be fitted by the Ising model.

The susceptibility curve for the bromo complex exhibits a maximum at ~160°K and can be fitted by the Ising model, yielding a $g = -2.12$ and $J = -116$ cm^{-1}, and by the dimer model with $g = 1.95$ and $2J = -172$ cm^{-1}. The far-infrared spectrum shows a band at 265 cm^{-1}, a position associated with a terminal or weakly bridging Cu–Br bond. It is unlikely that the halide bridge in this complex could transmit enough unpaired spin to produce an exchange energy equal to -116 cm^{-1}. The spin–spin interaction probably occurs primarily along the Cu–Pz–Cu bridge and is enhanced by the presence of the electron-donating methyl groups on the pyrazine ring. The proposed structure for both the bromo and chloro complexes is shown in Figure 7. The copper atoms are pictured as being six-coordinate with weak bonds from copper to halides from neighboring units.

(2,6-DiMe(pz))$_2$CuCl$_2$.—The susceptibility curve for this complex is plotted in Figure 4 and shows a maximum at 18°K. The curve can be fitted by the Ising equation with $g = 2.11$ and $J = -14$ cm^{-1}. The

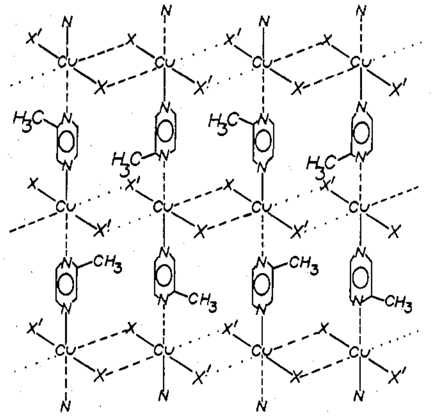

Figure 6.—Proposed structure for (2-Me(pz))CuX$_2$.

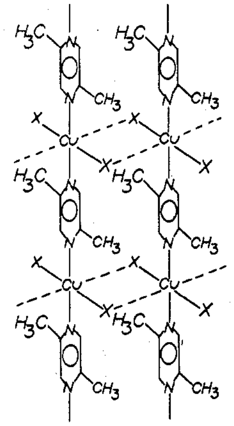

Figure 7.—Proposed structure for (2,5-DiMe(pz))CuX$_2$.

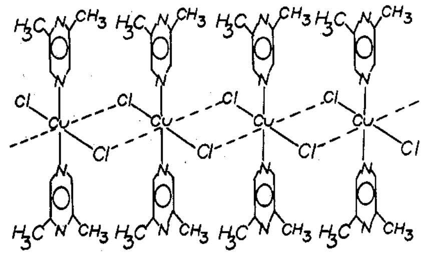

Figure 8.—Proposed structure for (2,6-DiMe(pz))$_2$CuCl$_2$.

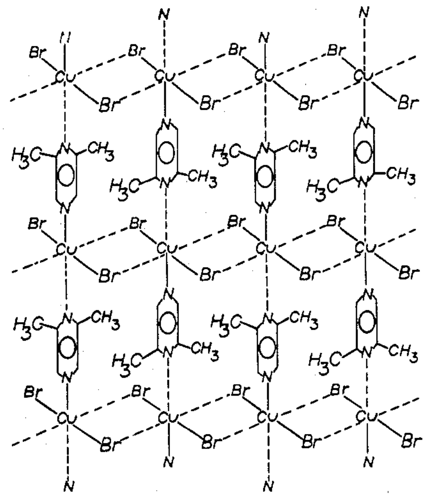

Figure 9.—Proposed structure for (2,6-DiMe(pz))CuBr$_2$.

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[14] A. Santoro, A. D. Mighell, and C. W. Reimann, *Acta Crystallogr., Sect. B*, **26**, 979 (1970).

[15] D. Y. Jeter and W. E. Hatfield, *J. Inorg. Nucl. Chem.*, **34**, 3055 (1972).

[16] J. D. Dunitz, *Acta Crystallogr.*, **10**, 307 (1957).

[17] V. Kupcik and S. Durovic, *Czech. J. Phys.*, **10**, 182 (1960).

structure of this complex is probably similar to that of $(py)_2CuCl_2$ since both have identical J values and similar far-infrared spectra. The spectrum of the 2,6-dimethylpyrazine complex has bands at 308 and 228 cm^{-1}, which are analogous to the bands observed[18] for $(Py)_2CuCl_2$ at 287 and 229 cm^{-1}. These bands have been assigned[18] to Cu–Cl stretching frequencies and in both cases are indicative of a large amount of bridging character. On the basis of the above spectral and magnetic data, the structure shown in Figure 8 is proposed for this complex wherein each $(2,6\text{-DiMe(pz)})_2CuCl_2$ unit is linked together solely by chloride bridges.

$(2,6\text{-DiMe(pz)})CuBr_2$.—The magnetic properties of the complex are consistent with an Ising model from which $g = 1.89$ and $J = -33$ cm^{-1} may be calculated. A plot of experimental susceptibility *vs.* temperature is given in Figure 5 along with the best-fit curve. The fit which is obtained when the dimer equation is applied yields a $g = 1.61$, a value too small to be realistic. The halide-sensitive band in the far-infrared spectrum appears at 262 cm^{-1}, a position associated with a weakly bridging Cu–Br bond. The calculated J of -33 cm^{-1} is close to the $J = -29$ cm^{-1} for the complex $(py)_2CuBr_2$,[15] which is known[17] to possess a bromide-bridged chain structure. The principal pathway for exchange is also probably a bromide bridge in $(2,6\text{-DiMe(pz)})CuBr_2$; however, the stoichiometry of this complex will not allow the same structure. A probable configuration would be one in which the nitrogen donor atom in the four position is weakly bonded to a neighboring copper atom forming links between the halide bridged chains (see Figure 9).

Conclusions

The results of this study support past proposals[1-4] that these complexes are generally polymeric with considerable interaction between chains. The magnetic interactions in all of these complexes are antiferromagnetic in nature and the magnitude of the exchange energy, J, generally reflects the nature of the chain linkages. These chain linkages are highly dependent on the type and number of substituents on the pyrazine ring. Pyrazines such as 2,5-dimethylpyrazine, symmetrically substituted with respect to the nitrogen donor atoms, tend to form copper(II) halide complexes in which pyrazine forms the bridging unit in the primary chain. Steric hindrance from the methyl groups reduces the amount of halide bridging in the secondary chain. Similar behavior is observed with the stoichiometrically similar copper(II) halide complexes of 2,3-dimethylquinoxaline. Both chloride[19] and bromide[20] complexes exhibit exchange coupling which appears to be too large to be transmitted through weakly bridging terminal Cu–X bonds. The nature of the polymeric linkages in complexes of 2-methylpyrazine is not clear, but probably both halides and pyrazines participate in the bridging with halide bridges transmitting much of the spin–spin interaction. The complexes of asymmetrically substituted 2,6-dimethylpyrazine probably consist primarily of halide bridged chains. The magnitudes of their J values are consistent with those of similar complexes for which structural data are available. Final conclusions regarding the relationship between type of chain linkage and exchange energy await precise structural data.

Acknowledgments.—We wish to thank Dr. G. G. Long and Dr. Dennis Wertz at North Carolina State University for the use of their far-infrared spectrophotometer. This research was supported by the National Science Foundation through Grant GP-22887, and by the Materials Research Center of the University of North Carolina through Contract DAHC 15 67 C 0223 with the Advanced Research Projects Agency.

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Bonding Studies from Charge-Transfer Absorption and Magnetic Circular Dichroism Spectra. I. D_{4h} Complexes of Iridium(IV)

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We have measured the absorption and MCD spectra of a series of complexes $IrCl_4L_2$ where L = PR_3, AsR_3, SEt_2, and pyridine and have identified transitions arising from charge-transfer transitions from chlorine and L to the metal. We find AsR_3 and $PR_3 \rightarrow$ metal to be at exceptionally low energy, $SEt_2 \rightarrow$ metal somewhat higher, and py → metal at still higher energy. These transition energies give a good approximation to the energies of the bonding orbitals of L with respect to the metal and these energies are used to draw correlations between the energy of the ligand σ orbital and the stability of the metal–ligand bond.

Introduction

There is considerable interest in determining the sequence of the filled bonding orbitals in metal complexes since this gives insight into the nature of the bonding processes and the distribution of the electrons in bonds. This information may be obtained in two ways, first from photoelectron spectroscopy and second from a study of electronic transitions. Using this latter method researchers in inorganic chemistry have mainly concentrated on the intra-d-shell transitions