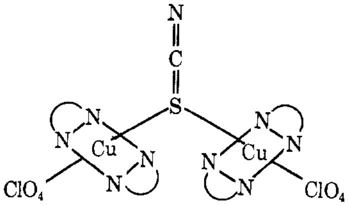
many reports[6] that the C–N stretching vibration of a bridging thiocyanate group occurs above 2100 cm^{-1}, structure I is postulated. Recently this type of bonding has been confirmed by X-ray analysis in [Pd(SCN)$_4$]$^{2-}$.



I

Electron Spin Resonance Spectra.—Electron spin resonance spectra of polycrystalline samples of some copper(II) complexes are presented in Figure 4. The esr spectrum of [Cu(DBen)$_2$Br]ClO$_4$ is isotropic, with a *g* value of 2.16, consistent with a square-pyramidal structure undergoing free rotation, such as that observed[23] in Cu(NH$_3$)$_5$(BF$_4$)$_2$ ($g = 2.126$).

The esr spectrum of [Cu(DBen)$_2$Br]Br is anisotropic, with *g* values of 2.034, 2.074, and 2.203, consistent with a distorted trigonal-bipyramidal structure with a d$_{z^2}$ ground state. From the nature of the spectrum, the distortion in this complex seems opposite to that[33] in [Cu(bipy)$_2$I]I, which may reflect the rigidity of bipyridine as opposed to the flexibility of DBen.

The esr spectrum of [Cu(DBen)$_2$(NCS)(NO$_3$)] is highly anisotropic. The average *g* value in an anisotropic system can be calculated using the relation[34]

$$g_{\text{av}} = \sqrt{g_{\parallel}^{2/3} + 2g_{\perp}^{2/3}} \qquad (1)$$

where $g_{\parallel} = g_z$ and $g_{\perp} = g_x = g_y$. Using the values $g_{\parallel} = 2.036$ and $g_{\perp} = (g_x + g_y)/2 = 1.981$ in the present case, the value $g_{\text{av}} = 2.000$ can be obtained.

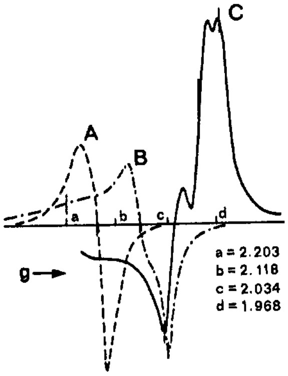


Figure 4.—The powder esr spectra (first derivative) of [Cu(DBen)$_2$Br]ClO$_4$ (A), [Cu(DBen)$_2$Br]Br (B), and [Cu(DBen)$_2$(NCS)(NO$_3$)] (C).

Acknowledgment.—We are indebted to Professor Juan McMillan of Argonne National Laboratory for helpful discussions on the esr spectra and to Dr. L. F. Larkworthy of the University of Surrey, Surrey, England, for helpful discussions.

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The Magnetism of Substituted Quinoxaline Complexes of Copper(II)

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The magnetic susceptibilities of dichloro(2,3-dimethylquinoxalinato)copper(II) and dichlorobis(2-methylquinoxalinato)copper(II) have been measured over the temperature range 4.2–77°K and show maxima indicating an antiferromagnetic alignment of spins. The experimental data can best be fitted by the Ising model for an infinite linear chain, supporting past structure proposals that these compounds have polymeric structures. The values of the coupling constants are also consistent with chloride bridges in the 2-methyl complex and quinoxaline bridges in the 2,3-dimethyl complex. The magnetic data for dichlorobis(2,3-diphenylquinoxalinato)copper(II) show Curie–Weiss behavior down to very low temperatures where a small deviation indicative of a weak ferromagnetic interaction is observed.

Quinoxaline complexes of copper(II) halides were first prepared by Underhill.[1] On the basis of infrared and magnetic properties he proposed a polymeric structure for these compounds involving an infinite chain of CuX$_2$ units with quinoxaline molecules as bridges between copper atoms in different chains. Later work by Billing, *et al.*,[2] showed that the nature of the polymeric linkages was dependent on the degree and type of substitution on the quinoxaline ring. Their structural proposals were based on room-temperature moments, molecular models, and reflectance and infrared spectra. Campbell, *et al.*,[3] measured the magnetic susceptibility of dichloro(2,3-dimethylquinoxalinato)copper(II) over the temperature range 80–300°K and were able to fit their data to the Ising model for antiferromagnetic chains, although they did not observe a maximum in the susceptibility *vs.* temperature curves. To provide additional information bearing on the structures and properties of these compounds, we have measured the susceptibilities of dichloro(2,3-dimethylquinoxalinato)copper(II), dichlorobis(2,3-diphenylquinoxalinato)copper(II), and dichlorobis(2-methylquin-

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[2] D. E. Billing, A. E. Underhill, D. M. Adams, and D. M. Morris *ibid.*, *A*, 902 (1966).

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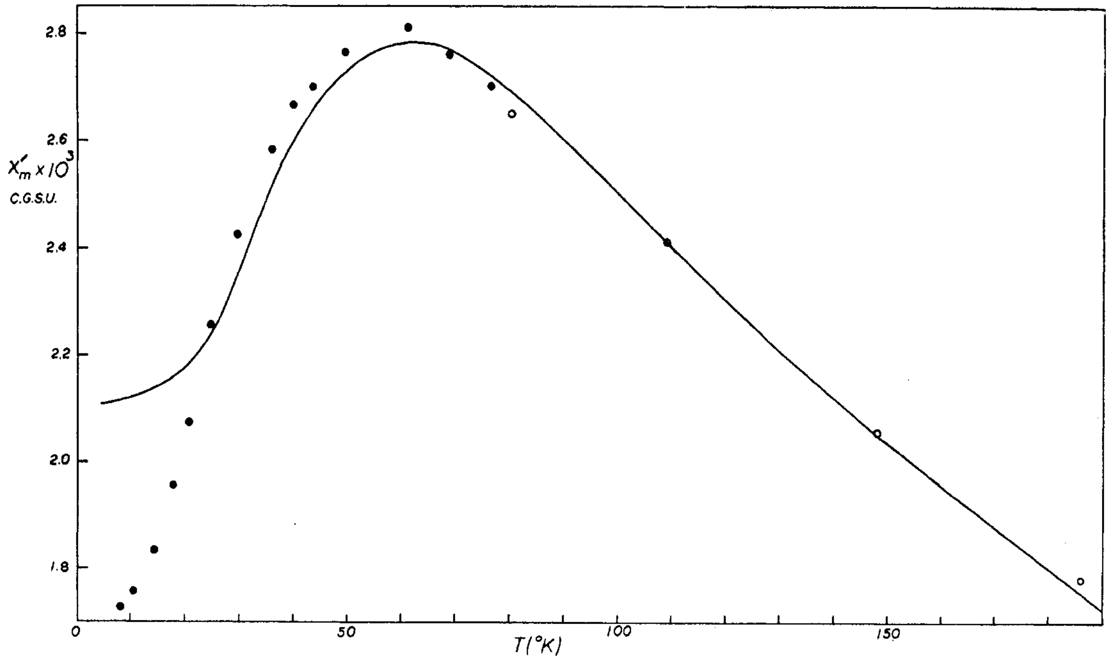

Figure 1.—Magnetic susceptibility *vs.* temperature for dichloro(2,3-dimethylquinoxalinato)copper(II). Experimental points are compared to the best fit theoretical curve calculated from the Ising model; points above 77°K were from Campbell, *et al.*[3]

oxalinato)copper(II) over the temperature range 4.2–77°K. The results of these measurements are reported in this article.

Experimental Section

The complexes were prepared by the method of Biling, *et al.*,[2] and the analytical data are given in Table I. Magnetic susceptibilities were determined by a Foner-type vibrating-sample magnetometer[4] operating at a field strength of 10,000 G. Field dependence of susceptibility for the 2,3-diphenyl complex was determined at 10,000 and 15,000 G. Diamagnetic corrections for all compounds were estimated from Pascal's constants[5] and the susceptibilities were corrected for a temperature-independent paramagnetism of 60 × 10^{-6} cgsu. The magnetometer was calibrated with a sample of $Hg[Co(SCN)_4]$[6] and temperatures were measured with a calibrated, precision germanium resistance therometer.

TABLE I

ANALYTICAL DATA

% C		% H		% N		% Cl	
Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
Dichlorobis(2-methylquinoxalinato)copper(II)							
41.0	41.0	3.40	3.49	9.60	9.63	24.2	24.4
Dichloro(2,3-dimethylquinoxalinato)copper(II)							
51.1	50.9	3.80	3.88	13.3	13.3	16.8	17.0
Dichloro(2,3-diphenylquinoxalinato)copper(II)							
68.7	68.7	4.1	4.1	8.1	7.8	10.1	10.3

Results

The susceptibility *vs.* temperature data for the 2,3-dimethyl compex are given in Figure 1, where a maximum in the susceptibility at ~62°K may be seen. Using a least-squares method, the data were fitted to the magnetic susceptibility equations for an infinite linear chain of Ising spins

$$\langle \chi \rangle = \frac{1}{3}\chi_{\parallel} + \frac{2}{3}\chi_{\perp}$$

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

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

where $K = J/kT$. These equations were derived by Fisher[7] using the Hamiltonian

$$\mathcal{H} = -J\sum_{ij}\sigma_i^z\sigma_j^z - mH_z\sum_i\sigma_i^z - mH_x\sum_i\sigma_i^x$$

where σ_i^x and σ_i^z are Pauli spin operators. The values for the exchange parameters were $J = -45$ cm^{-1} and $g = 2.08$. An attempt to fit the data to the Van Vleck equation[8] for a pairwise magnetic interaction gave the values of $J = -65$ cm^{-1} and $g = 1.91$. The susceptibilities calculated from the dimer equation decrease much more rapidly, in the region below the maximum point, than the observed susceptibilities.

The magnetic data (see Figure 2) for the 2-methyl complex show a maximum at 27°K and can be fitted to Fisher's Ising model with $J = -19$ cm^{-1} and $g = 2.02$. The best fit, using the dimer equation, gave $J = -29$ cm^{-1} and $g = 1.87$. The calculated low-temperature points were considerably lower than our observed points; *i.e.*, at 10°K the observed susceptibility is twice that calculated from the dimer equation. The results of the fitting processes are summarized in Table II.

The magnetic data for the 2,3-diphenyl-substituted complex (see Figure 3) show no maximum indicative of a large interaction among neighboring copper atoms. This supports past structural proposals[2] that the complex is monomeric. There is a deviation from Curie–Weiss behavior below 12°K and the susceptibility at low temperatures decreases with increasing field strength.

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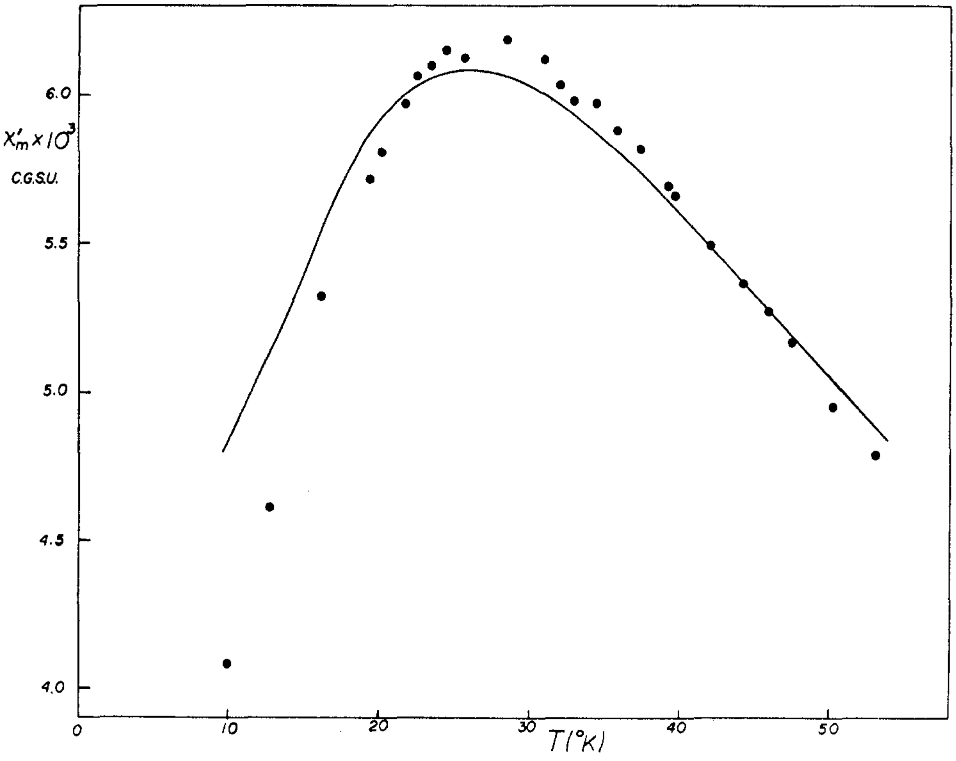

Figure 2.—Magnetic susceptibility *vs.* temperature for dichlorobis(2-methylquinoxalinato)copper(II). Experimental points are compared to the best fit theoretical curve calculated from the Ising model.

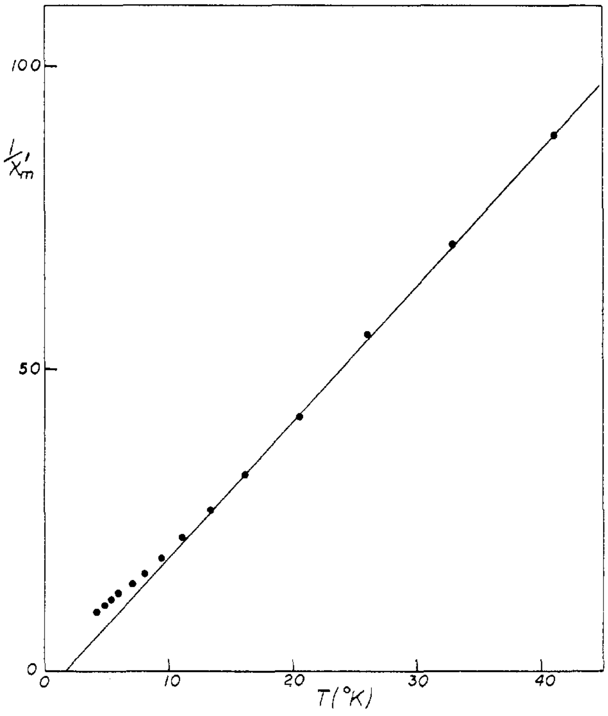

Figure 3.—Inverse molar susceptibility *vs.* temperature for dichlorobis(2,3-diphenylquinoxalinato)copper(II).

Discussion

The results of these studies appear to support past proposals[2,3] that structures of the 2,3-dimethyl- and the 2-methylquinoxaline complexes consist of chains and that the magnetic interactions are predominantly short range and antiferromagnetic in nature. Since the data for both complexes are more consistent with Fisher's Ising model than the dimer equation, the interactions among neighboring spins probably occur along an infinite chain rather than between atoms in a strict dimer. This is evident on close examination of the data fitting results for both of the above complexes (see Table II). Fitting the dimer equation to data obtained from the 2,3-dimethyl complex yields a sum of the squares of deviations which is larger by a factor of 40 than those obtained from the other equations. Also a g value of 1.91 is probably too low to be realistic. The data for the 2-methyl complex can be fitted to the dimer equation reasonably well, but again, the low g value of 1.87 is unrealistic.

TABLE II
RESULTS OF DATA FITTING

Equation	$2J$, cm^{-1}	g	$\sum_i^N (\delta_i)^2$
Dichloro(2,3-dimethylquinoxalinato)copper(II) (T_{max} = ~62°K)			
Fisher–Ising (polymeric)	−45	2.08	1.4×10^{-4}
Dimer	−65	1.91	5.2×10^{-3}
Dichlorobis(2-methylquinoxalinato)copper(II) (T_{max} = ~27°K)			
Fisher–Ising (polymeric)	−19	2.02	2.6×10^{-4}
Dimer	−29	1.87	8.5×10^{-4}

Although the Ising model appears to give the best fits to our data, calculated susceptibilities below the maxima are still higher than those observed from experiment (see Figures 1 and 2). The one-dimensional model used in our data fitting does not account for interactions between atoms in neighboring chains. These kinds of interactions could occur through chloride atoms in the 2,3-dimethyl complex but are rather unlikely in the 2-methyl complex in which the copper atoms should be fully coordinated.

The isotropic Heisenberg coupling scheme is generally considered to be more realistic for most systems. Bonner and Fisher[9] have performed exact calculations for linear chains of spin $S = {}^1/_2$ with the Hamiltonian

$$\mathcal{H} = -2J\sum_{i=1}^{N}\{S_i^zS_{i+1}^z + \gamma(S_i^xS_{i+1}^x + S_i^yS_{i+1}^y)\} - g\beta\sum_{i=1}^{N}\vec{H}\cdot\vec{S_i}$$

where $\gamma = 1$ for the isotropic Heisenberg case and $\gamma = 0$ for the anisotropic Ising model. Their calculations also included cases of intermediate anisotropy wherein $0 < \gamma < 1$. Their plot of susceptibility *vs.* temperature for an infinite linear Heisenberg chain shows a susceptibility which passes through a broad maximum and then converges to a finite value at 0°K. For finite chains the susceptibility either diverges (for odd values of N) or converges (for even values of N) to a value smaller than that for the infinite chain. The parallel susceptibility for an Ising chain ($\gamma = 0$) passes through a narrower maximum and converges to zero, plots for $N = 8$ and $N = \infty$ being almost indistinguishable. The perpendicular susceptibility approaches a finite value at 0°K.[7] As γ is increased to 1, this finite value becomes much smaller and the maximum in the parallel susceptibility becomes broader. The effect on the total susceptibility curve in going from the Ising to the Heisenberg case is a lowering of the susceptibility near 0°K and a broadening of the maximum. Using the relationships derived by Bonner and Fisher[9] for pure Heisenberg coupling, $\chi_{\max}|J|/Ng^2\beta^2 \cong 0.0735$ and $kT_{\max}/|J| \cong 1.28$, a g value of 2.2 and a J parameter of -33 cm^{-1} were calculated for the 2,3-dimethyl complex. Using these values and the plots of $\chi|J|/Ng^2\beta^2$ *vs.* $kT/|J|$ given by Bonner and Fisher,[9] susceptibilities were calculated for pure Heisenberg coupling. Although the Heisenberg susceptibility at 10°K (2.0×10^{-3} cgsu) is smaller than that calculated from the Ising model (2.1×10^{-3} cgsu), the improvement is hardly significant. This is especially true in light of the possibility for interchain effects.

Our results would probably best be described by a model closer to the pure Ising than to the Heisenberg model. The Ising model gives good fits to our data in the area of the maxima and deviates only at lower temperatures.

(2-Methylquinoxaline)$_2$CuCl$_2$.—The proposed structure[2,3] for this complex is a chain involving chloride bridges with 2-methylquinoxaline functioning as a unidentate ligand (see Figure 4). The calculated value of $J = -19$ cm^{-1} is smaller than that found for the 2,3-dimethyl complex and is consistent with an interaction transmitted through chloride bridges. Another polymeric chloride-bridged copper(II) complex, $(DMSO)_2CuCl_2$,[10] has an antiferromagnetic interaction with $J = -9.6$ cm^{-1}. The chloride-bridged dimer,[11,12] $[Cu_2Cl_8]^{4-}$, has $2J = -17$ cm^{-1} and Cu(2-methylpyridine)$_2$Cl$_2$[13] $2J = -7.4$ cm^{-1}. The only other chloride-bridged copper(II) complex with a relatively large value of J is $CuCl_2$[14] for which $T_c = 70$°K and $J = -49$ cm^{-1} (assuming $T_c = -2J/k$); however, both Cu–Cl distances in $CuCl_2$ are small (2.3 Å). In $(DMSO)_2CuCl_2$[15] and $[Cu_2Cl_8]^{4-}$ the intraunit Cu–Cl distances are about 2.3 Å, and the bridging Cu–Cl lengths are about 2.7 Å.

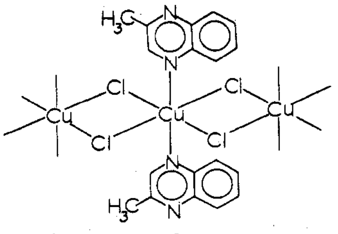

Figure 4.—Proposed structure for dichlorobis(2-methylquinoxalinato)copper(II).

(2,3-Dimethylquinoxaline)CuCl$_2$.—Billing, *et al.*,[2] and Campbell, *et al.*,[3] have proposed a linear-chain structure for this complex in which the quinoxaline ring acts as a bridging ligand between copper atoms (see Figure 5). Our experimental measurements verify

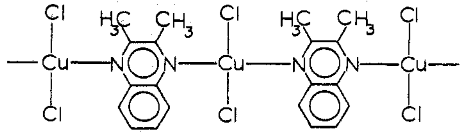

Figure 5.—Proposed structure for dichloro(2,3-dimethylquinoxalinato)copper(II).

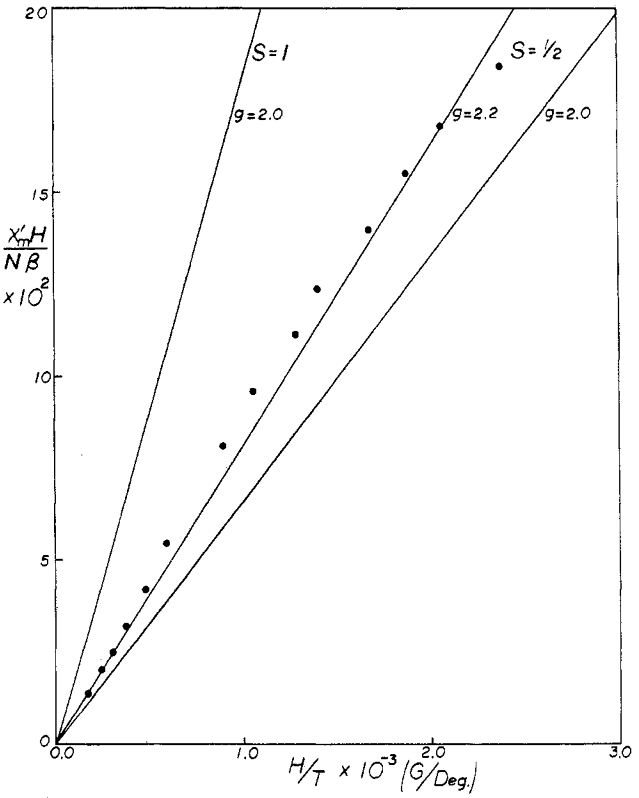

Figure 6.—Magnetization plot for dichlorobis(2,3-diphenylquinoxalinato)copper(II). Solid lines are calculated Brillouin functions.

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the predicted maximum in the susceptibility *vs.* temperature curve. Using data taken above 80°K and fitting it with the Ising model, Campbell, *et al.*, have calculated values of $J = -47$ cm^{-1} and $g = 2.09$. These parameters agree well with our values of -45 cm^{-1} and 2.07. This large value of J for these methyl-substituted quinoxaline complexes may be indicative of a magnetic interaction taking place through bridging quinoxaline ligands rather than through chloride ions. Antiferromagnetic J values for chloride-bridged complexes of known structures appear to be small (less than -20 cm^{-1}) for most cases and are larger ($\simeq 45$ cm^{-1}) only when both bond distances are small as in $CuCl_2$.[14] The magnetism of the complex (pyrazine)$Cu(NO_3)_2$, known to consist of linear chains in which a pyrazine molecule acts as a bridging ligand,[16] has been studied in this laboratory. Experimental results[17] show a maximum in the susceptibility at $\simeq 9$°K, indicating a weak antiferromagnetic interaction. This weaker interaction may mean that a fused-ring compound such as quinoxaline has available more electron density for the transmission of the spin–spin coupling across the bridging ligand. The interaction would be further enhanced by the electron-donating methyl groups. Hyde, *et al.*,[18] have calculated $J \simeq -20$ cm^{-1} for the unsubstituted quinoxaline complex which is also thought to contain bridging quinoxaline ligands. Since their calculations were based on a small number of data points taken above 77°K, a more careful study of the magnetism is necessary.

(2,3-Diphenylquinoxaline)$_2$CuCl$_2$.—The deviation from Curie–Weiss behavior for this complex probably represents a very weak ferromagnetic coupling of spins on neighboring copper atoms. The ferromagnetic nature of the coupling is evident from the field dependence of susceptibility, from a positive intercept at $\sim$2°K in the $1/\chi_{m'}$ plot, and from the magnetization which is plotted as a function of H/T in Figure 6. The calculated curves for spins, $S = 1$ and $^1/_2$, were generated by Brillouin functions.[19] A comparison of the experimental and calculated curves shows the complex to be more easily magnetized at certain fields and temperatures than a complex with a pure doublet ground state.

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Electronic Structure and Bonding in Methyl- and Perfluoromethyl(pentacarbonyl)manganese

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Using approximate molecular orbital calculations, we have investigated the electronic structure and bonding of $CH_3Mn(CO)_5$ and $CF_3Mn(CO)_5$. The appearance of an unexpected additional band in the photoelectron spectra can explain both the apparent reversal in the b_2 and e bands of the methyl compound and the increased intensity of the first band in the perfluoromethyl compound. Other experimental evidence, such as the carbon–fluorine force constant of the CF_3 group, for which $d\pi$(metal)–$\sigma^*(CF_3)$ back-bonding has been proposed as an explanation, can be understood in terms of σ donation from an antibonding CF_3 orbital and energy stabilization due to the effect of charges on neighboring atoms. The influence of the CX_3 ligands on the metal ionization potentials and on the carbonyl force constants can also be interpreted in terms of these two effects.

Introduction

Recently there has been considerable interest in the bonding of the methyl and perfluoromethyl groups to transition metals. Evans, *et al.*, have reported the photoelectron (pe) spectra of methyl and perfluoromethylmanganese pentacarbonyl compounds.[1] These workers interpreted the spectra in terms of the changes one would expect relative to the octahedral complex $Mn(CO)_6^+$. If one assumes that methyl and perfluoromethyl act essentially as σ donors and that the idealized symmetry, C_{4v}, is applicable, the loss of the π-acceptor ability in the sixth position in going from $Mn(CO)_6^+$ to $Mn(CO)_5L$ should split the upper t_{2g}^6 level into b^2e^4 with the e level at higher energy, *i.e.*, lower ionization potential, than the b_2 level. On the basis of intensity arguments Evans, *et al.*, suggested that the expected order is correct for $CF_3Mn(CO)_5$ but that the order is reversed for $CH_3Mn(CO)_5$.

A controversial aspect of the bonding by the perfluoromethyl ligand involves the ability of this ligand to accept π-electron density by the interaction of its empty σ^* orbitals with the filled $d\pi$ metal orbitals. Thus, from an approximate force constant analysis of the perfluoromethyl infrared spectra, Cotton and Wing concluded that the perfluoromethyl group is a good π-electron acceptor.[2] In addition, the greater stability and shorter metal–carbon bond lengths observed for fluoroalkyl complexes relative to alkyl complexes are also cited as evidence favoring the strong π-electron accepting ability of fluoroalkyl groups.[3-5]

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