at $g \approx 4$).[4-6] A soft ligand core (S_6 and S_3O_3 vs. O_6) appears to favor an effectively more symmetrical electronic environment around manganese(IV).

Experimental Section

Starting Materials. Thiohydroxamic acids (HMePh, HMeAn, HMeBz) were prepared[20] from appropriate dithiocarboxy methyl esters[21] and *N*-methylhydroxylamine. Tris(acetylacetonato)manganese(III) was made as reported.[22] Electrochemically pure acetonitrile and tetraethylammonium perchlorate were obtained as before.[23] All other solvents and chemicals used were of analytical grade available commercially.

Physical Measurements. Solution electrical conductivity and electronic and infrared spectra were recorded with a Philips PR9500 bridge and Hitachi 330 and Perkin-Elmer 783 spectrophotometers, respectively. Magnetic susceptibility was measured in a Princeton Applied Research (PAR) Model 155 vibrating-sample magnetometer. Electrochemical measurements were made with the help of a PAR Model 370-4 electrochemistry system incorporating the following components: 174A, polarographic analyzer; 175, universal programmer; RE0074, X-Y recorder; 173, potentiostat; 179, digital coulometer; 377A, cell system. Measurements were carried out under a dry and purified dinitrogen atmosphere. A planar Beckman Model 39273 platinum-inlay working electrode, platinum-wire auxiliary electrode, and a saturated calomel reference electrode (SCE) were used in the three-electrode measurements. A platinum wire-gauge working electrode was used in coulometric experiments. All electrochemical data were obtained at 298 K and are uncorrected for junction potentials. X-band EPR spectra were recorded with a Varian E-109C spectrometer fitted with a quartz Dewar for measurements at 77 K (liquid nitrogen). The spectra were calibrated with the help of DPPH ($g = 2.0037$). The microwave power level was maintained at around 0.2 mW.

Preparation of Complexes. The utility of reaction 1 is illustrated below with a specific example.

Tris(*N*-methyl-*p*-methoxybenzothiohydroxamato)manganese(III), $Mn(MeAn)_3$. To an ethanolic solution (20 mL) of HMeAn (0.6 g, 0.003 mol) was added an ethanolic solution (20 mL) of tris(acetylacetonato)manganese(III) (0.36 g, 0.001 mol), and the mixture was stirred at room temperature for $^1/_2$ h. The green solution was then evaporated, and a residue obtained was dissolved in benzene followed by slow addition of petroleum spirit (60–80 °C) with stirring. The green precipitate formed was collected by filtration. The process of dissolution in benzene and precipitation by petroleum spirit was repeated for another three times to obtain pure compound: yield 0.59 g (90%). Anal. Calcd for $MnC_{27}H_{30}N_3O_6S_3$: Mn, 8.55; C, 50.39; H, 4.67; N, 6.53. Found: Mn, 8.61; C, 50.60; H, 4.90; N, 6.20.

Tris(*N*-methyl-*p*-methoxybenzothiohydroxamato)manganese(IV) Hexafluorophosphate, $[Mn(MeAn)_3]PF_6$. Through an acetonitrile solution (25 mL) of $Mn(MeAn)_3$ (0.2 g, 0.31 mmol) was passed pure dry, Cl_2 gas until the green color changed to red-brown. To this solution was added excess NH_4PF_6, and the solution was allowed to evaporate at room temperature. The dark precipitated complex was collected by filtration, washed thoroughly with water, and dried under vacuum over P_4O_{10}. It was recrystallized from acetonitrile: yield 0.19 g (80%). Anal. Calcd for $MnC_{27}H_{30}N_3O_6S_3PF_6$: Mn, 6.97; C, 41.12; H, 3.81; N, 5.33. Found: Mn, 7.02; C, 41.33; H, 3.93; N, 5.54. The complexes $[Mn(MePh)_3]PF_6$ (yield 83%) and $[Mn(MeBz)_3]PF_6$ (yield 72%) were prepared by the same procedure as described above with use of the ligands HMePh and HMeBz, respectively, in place of HMeAn. Anal. Calcd for $[Mn(MePh)_3]PF_6$, $MnC_{24}H_{24}N_3O_3S_3PF_6$: Mn, 7.87; C, 41.27; H, 3.44; N, 6.02. Found: Mn, 7.83; C, 41.40; H, 3.50; N, 5.84. Anal. Calcd for $[Mn(MeBz)_3]PF_6$, $MnC_{27}H_{30}N_3O_3S_3PF_6$: Mn, 7.43; C, 43.79; H, 4.06; N, 5.68. Found: Mn, 7.48; C, 43.44; H, 4.17; N, 5.80.

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Registry No. $Mn(MeAn)_3$, 97825-97-3; $[Mn(MeAn)_3]PF_6$, 97825-99-5; $[Mn(MePh)_3]PF_6$, 97826-01-2; $[Mn(MeBz)_3]PF_6$, 97826-03-4; $Mn(MePh)_3$, 97826-04-5; $Mn(MeBz)_3$, 97826-05-6; $Mn(acac)_3$, 14284-89-0.

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Magnetic Properties of (2,3-Pyrazinedicarboxylato)copper(II) Hydrochloride: Another Look, at Lower Temperatures

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The *prediction* by O'Connor et al.[1] that CuL·HCl, where H_2L = 2,3-pyrazinedicarboxylic acid, is a ferromagnetic linear chain was based on the observation that the Curie–Weiss fit of magnetic susceptibility data (6–300 K) gave a positive Weiss constant ($\Theta = +1.4$ K) and that an X-ray crystal structure determination showed the molecule to crystallize in linear chains. A fit of the data to the Bonner–Fisher model was diagnostically inconclusive since the lack of data in the important low-temperature range precluded a definitive assignment of magnetic dimensionality.

In order to determine with greater precision the magnetic model that best describes the behavior of this complex, the magnetic susceptibility has now been measured to lower temperatures. We find no evidence for linear-chain behavior but, contrarily, that the substance undergoes three-dimensional magnetic ordering.

Experimental Section

The polycrystalline sample used was prepared as earlier.[1] It appeared clear, without decomposition. Measurements in the ^{4}He region were made in a glass cryostat in which each data point was calibrated against CMN. Measurements at lower temperatures were made in a dilution refrigerator. Our procedures have been described previously.[2,3]

Results and Discussion

The data above 3 K may be fit by the Curie–Weiss law for $S = {}^1/_2$ with $\langle g \rangle = 2.17 \pm 0.02$ and $\Theta = 1.17 \pm 0.02$ K, but this may be an unreliable analysis because the temperatures of measurement are of the same order as Θ.

The data (1.1–4.2 K) are displayed together with the later low-temperature measurements in Figure 1 along with several calculated fits. It has been found to be impossible to fit the data to a Heisenberg linear-chain model, $S = {}^1/_2$, with ferromagnetic interaction. Beyond the calculation illustrated in the figure, one knows[4] that χT must diverge as $T^{-2/3}$ for such a magnetic model; the measured values have a much stronger divergence at low temperature.

Several other linear-chain models were examined, such as with the introduction of some spin anisotropy as well as a lattice anisotropy. Even in the limit of the completely anisotropic linear chain (the Ising case), with an exponential divergence at low temperatures, values smaller than the experimental ones are found. Furthermore, copper(II) is well-known to exhibit very small spin anisotropy. None of these calculations were found to improve the fit. We were surprised however by the result that the data can be fitted perfectly in the limit of Heisenberg linear-chain calculation with a molecular field correction of the same magnitude. In other words, contrary to the earlier suggestion,[1] the data may be fit with the three-dimensional, $S = {}^1/_2$ Heisenberg magnetic model.

In view of the above results, measurements were then carried out to lower temperatures. Two rather sharp peaks are observed at temperatures below 1 K, as shown in Figure 2. The first is at 0.770 ± 0.015 K, and the second is at 0.470 ± 0.005 K. Large values of the susceptibility are found at each maximum, 21.9 and 23.3 emu/mol, respectively. These peaks correspond to long-range ordering and occur at what will be referred to, respectively, as

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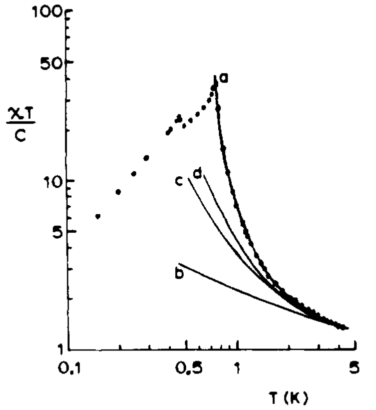

Figure 1. Zero-field *ac* susceptibility of polycrystalline CuL·HCl. The points are experimental and plotted as $\chi T/C$ vs. T, where C is the Curie constant, taking $\langle g \rangle = 2.21$. Curve a represents the Heisenberg simple cubic model, $S = {}^1/_2$, described in the text, with $J/k_B = 0.465$ K. Curve b is drawn for the Heisenberg linear chain with $J/k_B = 1.9$ K. Curve c is estimated for an Ising linear chain with $J/k_B = 1.5$ K; this curve is included only to show the trend in the calculation as spin anisotropy is increased. Curve d is drawn for the Heisenberg diamond lattice with $J/k_B = 0.74$ K. All the theoretical curves have been corrected for demagnetization effects.

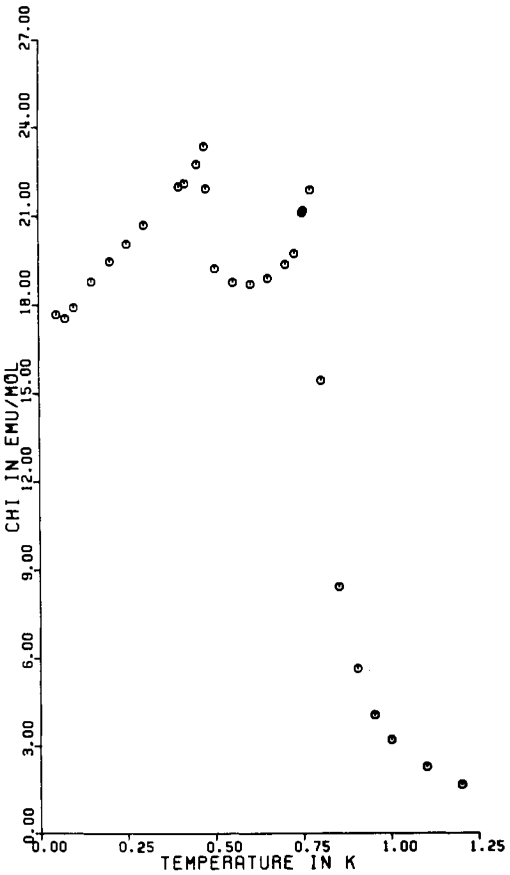

Figure 2. Susceptibility of CuL·HCl at low temperatures.

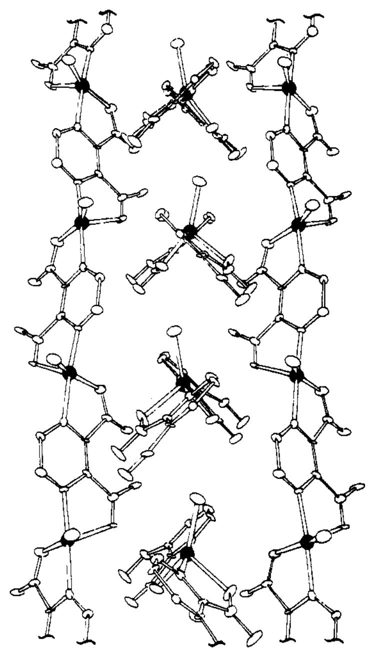

Figure 3. ORTEP view of the packing of CuL·HCl molecules forming structural chains in the crystal. The view is down the [011] axis with the chains propagated along [0$\bar{1}$1] tilted slightly out of the plane of the figure.

Table I. Closest Interchain Contacts (Å) in CuL·HCl, Where H_2L = 2,3-Pyrazinedicarboxylic Acid

Cu–O4	3.695 (10)	O1–O4	3.178 (13)
Cl–O1	3.797 (9)	O3–O4	3.779 (17)
Cl–O2	3.405 (11)	O4–O2	3.250 (14)
Cl–O3	3.510 (10)		

T_{c_1} and T_{c_2}. The behavior illustrated (the sharp peak) is like that of a powdered sample of a ferromagnetic material in which demagnetization effects become important. An earlier example is provided by the data on $[Cr(H_2O)(NH_3)_5][Cr(CN)_6]$.[5] The existence of two peaks suggests that first ferromagnetic ordering occurs at T_{c_1} and then a spin reorientation may take place (to a ferromagnetic state with a different spin arrangement, for example) at T_{c_2}, but field-dependent studies are required in order to elucidate this phenomenon. These results remind one of an earlier caveat[6] that magnetic susceptibility measurements need to be made in a temperature region where magnetic exchange makes a significant contribution to the measured quantity if inferences regarding the character of the magnetic exchange are to be made.

There is nothing remarkable in the behavior of the absorptive (out-of-phase) component of the signal, there being no anomaly at T_{c_1} and only a small increase in χ'' at the lower temperature peak.

In light of this new information, a reexamination of the crystal structure is in order. Figure 3 shows an ORTEP diagram of the crystal packing of CuL·HCl in the *Pna*2$_1$ lattice. The copper ions are distributed in a rhombic arrangement in the *yz* planes with four neighbors at 6.678 Å and two more at 7.719 Å. Stacked in parallel planes are two more nearest neighbors at a closer distance of 4.812 Å, though there seems to be no structural connection between them. The most striking structural feature remains the one-dimensional linear chain of (CuL·HCl) molecules. The symmetry of the space group requires the chains to be propagated in the [011] direction at $x = {}^1/_4$ and in the [0$\bar{1}$1] direction at $x = {}^3/_4$. Although the interchain copper(II) binuclear distance (4.812 Å) is less than the intrachain distance (6.678 Å), there is no apparent pathway that involves atom contacts suitable for the propagation of magnetic exchange via weak bonding or hydrogen bonding. The same lack of pathways holds for parallel chains in the same *yz* plane. The closest intrachain contacts are

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listed in Table I; all of these distances are over 3 Å.

Every attempt to fit the data with a low-dimensional model was unsuccessful. In order to look for other possible superexchange interactions, we considered the possibility of pathways through the two neighbors at 4.812 Å, with strengths comparable to that in the linear chain. Even in this case, treating the problem as a diamond lattice, with four nearest neighbors and three-dimensional ordering, a satisfactory fit could not be obtained.

Only in the case of a three-dimensional (simple cubic) $S = {}^1/_2$ Heisenberg model, with six magnetic neighbors, was a fit obtained. Using the Pade approximants to the high temperature series expansion for which 10 terms are known,[7] we obtained a remarkable fit to the experimental values with $\langle g \rangle = 2.21$ and $J/k_B = 0.465$ K. Demagnetization effects have been corrected in the calculated values with the expression

$$\chi_{cor} = \chi/(1 + D\chi)$$

estimating D from the maximum experimental value of the susceptibility at the peak. Moreover, the value obtained for J coincides with that predicted from the experimental value of the transition temperature and the known critical value for this model of $J/k_BT_c = 0.597$.

One factor that may contribute to the three-dimensional magnetic interactions is that the crisscrossing of the chains in the lattice may cause an enhancement of the dipolar interactions between the chains. This would then lead to a three-dimensional coupling model. The ordering occurs at low enough temperatures for dipole–dipole interaction to be a contributing factor.[8]

Specific heat measurements below 1 K would be particularly valuable in order to further elucidate the nature of the magnetic properties of this material.

We are therefore faced with the paradoxical result that the data require a three-dimensional magnetic interaction while only a one-dimensional superexchange path is apparent in the crystal structure. Nevertheless, our result is a real one and illustrates the primitive nature of our understanding of magnetic interactions and superexchange paths.

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Registry No. CuL·HCl, 79329-64-9.

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Matrix-Isolation Studies of the Iron/Cyclopentadiene System: Infrared Detection of Cyclopentadienyliron Hydride

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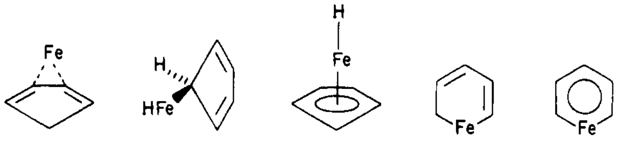
There has been much work done in the area of matrix-isolated metal atom chemistry, not only in the study of the metal atoms themselves[1-3] but also in studying reactions of metal atoms with other matrix-isolated species.[4-6] One specific area of recent investigation has been the study of metal atom insertion into the bonds of small molecules. For example, earlier work from this laboratory has shown that iron atoms will, upon photolysis, insert into the carbon–hydrogen bonds of methane[5] and the oxygen–hydrogen bonds of water.[7,8] Many other metals are found to react similarly.[9] Klabunde has found[10] that Al atoms will spontaneously insert into the C–H bonds of methane. Even more recently, it was found that iron atoms will photoinsert into the carbon–carbon bonds of cyclopropane, forming a four-membered metallacyclic ring.[11]

With these results in mind, it was decided to investigate the reactions of iron atoms with cyclopentadiene (C_5H_6) in an argon matrix at 14 K. It is possible that a reaction might lead simply to the very stable and well-known compound, ferrocene ($FeCp_2$); this compound was found by Timms in 60% yield via direct condensation of Fe vapors and cyclopentadiene at liquid nitrogen temperatures.[12] However, in the case of a 1:1 reaction, one might envision several possible products, such as **1**–**4**.



1 **2** **3** **4a** **4b**

1 is a simple π-bonded adduct. Product **2** is the result of iron atom insertion into a carbon–hydrogen bond to form a σ-bonded product. Product **3** is also a product of C–H bond insertion, but in this case a η^5 complex is formed. Products **4a** and **4b** are the result of an iron atom inserting into a carbon–carbon bond of cyclopentadiene. **4a** is a simple insertion product with the conjugated double bond system intact. **4b**, on the other hand, represents an interesting possibility: Would the iron atom insert into one of the C–C bonds of cyclopentadiene and donate an electron to the π-electron system and by hence satisfying Hückel's rule make an aromatic ring? If found, this would be the first metal-substituted benzene ring detected.

Experimental Section

A complete description of the matrix-isolation device is forthcoming.[13] Typical matrix concentrations for iron were 0–10 parts per thousand and for cyclopentadiene were <1–20 parts per thousand. Concentrations were measured by utilizing a quartz crystal microbalance with a frequency of approximately 6 MHz. The iron was deposited from an alumina crucible wrapped with tantalum foil, which was resistively heated to the temperature range 1150–1350 °C. Temperatures were measured by viewing the tantalum furnace with a microoptical pyrometer from the Pyrometer Instrument Co. The iron was obtained from Aesar, and had a purity of 99.98%. The cyclopentadiene was freshly cracked from dicyclopentadiene obtained from the Enjay Chemical Co. When not in use, the cyclopentadiene was stored over molecular sieves and in a freezer. During deposition the cyclopentadiene vapor flow was regulated by a high-precision needle valve. In order to decrease the formation of dicyclopentadiene in the vapor, heating tape was wrapped around the stainless-steel delivery tube, which was kept at a temperature of approximately 70 °C. Comparison of spectra obtained with and without heating the delivery tube showed heating to be an efficient method for reducing peaks attributed to the cyclopentadiene dimer. Argon (Matheson, 99.9998%) was used without further purification.

Iron and cyclopentadiene were codeposited with excess argon onto a polished rhodium-plated copper surface cooled to 14 K with a closed-cycle helium refrigerator. Each deposition listed 30 min. After deposition, the surface was rotated 180° and the infrared spectrum was mea-

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