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they may be sensitive to the relative π-bonding ability of the ligands, since the pyridyl- and imidazole-type ligands tend to form complexes which have higher peak potentials than the ammine complexes. Obviously additional data are needed to firmly establish such a trend.

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Registry No. Co(TEP)$^{2+}$, 64740-13-2; Co(4-IMDIEN)$^{2+}$, 71302-39-1; Co(EPYDEN)$^{2+}$, 64740-09-6; Co(PYDIEN)$^{2+}$, 64740-01-8; Co(PYDPT)$^{2+}$, 64740-05-2; Co(4-IMDPT)$^{2+}$, 71302-40-4; Co(2-IMDPT)$^{2+}$, 71302-41-5; Co(trien)(OH$_2$)$_2^{3+}$, 33865-40-6; Co(EDDA)(OH$_2$)$_2^{+}$, 55177-51-0; Co(DTMA)(OH$_2$)$_2^{2+}$, 71302-42-6; Co(dien)(OH$_2$)$_3^{3+}$, 25426-87-3; Co(en)$_2$(OH$_2$)$_2^{3+}$, 21247-59-6; Co(gly-his)(OH$_2$)$_2^{+}$, 71302-43-7; Co$_2$(TEP)$_2$O$_2^{4+}$, 71302-44-8; Co$_2$(4-IMPIEN)$_2$O$_2^{4+}$, 71302-45-9; Co$_2$(EPYDEN)$_2$O$_2^{4+}$, 71359-28-9; Co$_2$(PYDIEN)$_2$O$_2^{4+}$, 71328-32-0; Co$_2$(PYDPT)$_2$O$_2^{4+}$, 71328-33-1; Co$_2$(4-IMDPT)$_2$O$_2^{4+}$, 71302-46-0; Co$_2$(2-IMDPT)$_2$O$_2^{4+}$, 71302-47-1; Co$_2$(trpy)$_2$(phen)$_2$O$_2^{4+}$, 71302-48-2; Co$_2$(DGENTA)$_2$O$_2^{8-}$, 36002-59-2; Co$_2$(NH$_3$)$_{10}$O$_2^{4+}$, 16483-06-0; Co$_2$(trien)$_2$(OH)O$_2^{3+}$, 36431-46-6; Co$_2$(DTMA)$_2$(OH)O$_2^{+}$, 55701-24-1; Co$_2$(EDDA)$_2$(OH)O$_2^{-}$, 55177-53-2; Co$_2$(dien)$_2$(OH)O$_2$(OH$_2$)$_2^{3+}$, 36885-27-5; Co$_2$(gly-his)$_2$(OH)O$_2^{-}$, 71307-86-3; Co$_2$(trien)$_2$(NH$_2$)O$_2^{3+}$, 71302-49-3.

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Preparation and Magnetic Characterization of the Linear-Chain Series M^{II}L$_2$Cl$_2$ with M = Mn^{2+}, Cu^{2+}, and Ni^{2+} and L = 4-Phenylpyridine

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Magnetic susceptibilities have been determined on powdered samples of the title compounds M^{II}L$_2$Cl$_2$. The data for the copper(II) compound may be fit by the Heisenberg linear-chain results of Bonner and Fisher with $\langle g \rangle = 2.06$ and $J/k = -12.2$ K. The data for the manganese(II) compound may be fit by the scaled form of the infinite-spin linear-chain results modified by a molecular field correction term with the parameters $g = 1.98$, $J/k = -0.39$ K, and zJ'/k (the molecular field term) $= -0.133$ K. Magnetic susceptibility data for the nickel(II) compound were field dependent with a maximum occurring at about 9 cm^{-1}. Magnetization data are consistent with a metamagnetic transition. At 50 kOe the material was not fully saturated ($\mu = 1.62\ \mu_B$). The magnetic data may be fit with the parameters $D/k = -52$ K, $J/k = 8.5$ K, and $g = 2.3$, where D is the zero-field splitting parameter of the ^{3}A state. Thus Ni(4-Ph-Py)$_2$Cl$_2$ exhibits ferromagnetic intrachain exchange, very large single-ion anisotropy, and antiferromagnetic interchain interactions which lead to metamagnetism.

Introduction

The magnetic and thermal properties of low-dimensional transition-metal ion complexes have been studied extensively over the last few years.[1] Theoretical studies of these interesting polymers have been primarily aimed toward providing an analysis of the properties of completely isolated one- or two-dimensional lattices. Even with this simplication, the problem is so intractable that only a few such models can be solved exactly, those being the one-dimensional Ising chain,[2] the 2-D Ising layer,[3] the 1-D XY,[4] and the 1-D Heisenberg model with infinite spin.[5] Several other models, especially those of isotropically interacting Heisenberg spins, are known to a high degree of accuracy through various degrees of approximation. Bonner and Fisher[6] have performed exact calculations on small systems of $S = {}^1/_2$ Heisenberg spins and have been able to extrapolate to the infinite 1-D limit. Also, Weng has utilized a similar procedure to calculate the properties of linear Heisenberg chains $S \geq 1$.[7] Furthermore, Wagner and Friedberg[8] have shown that the infinite-spin linear model of Fisher can be scaled to the "exact" results of the high-temperature series expansions[9] for the limiting case of large spins (i.e., $S = {}^5/_2$).

Unfortunately, from an experimental viewpoint, real magnetic systems rarely, if ever, obey the full spirit of the available theories for low-dimensional cooperative phenomena.[1] Generally one must also take into account additional interactions such as (a) *intrachain* exchange between next nearest neighbors, (b) *interchain* exchange, (c) anisotropy in the near-neighbor exchange,[10] (d) single-ion crystal field anisotropy (in magnetic ions with $S \geq 1$), and (e) antisymmetric exchange interactions between neighboring magnetic ions within a chain or between ions in different chains.[10] The above interactions are often strong enough to induce long-range three-dimensional (3-D) spin ordering at low temperatures.[1] Since the 3-D ordering process of an assembly of 1-D magnetic chains involves a "crossover" of either spin and/or lattice dimensionality, valuable information into the nature of cooperative phenomena can be gained by studying simple magnetic model systems.[1,11] Furthermore, it is of primary importance in such studies to eliminate or control as many of the complicating terms as possible.

A large number of transition-metal complexes of the general stoichiometry M^{II}L$_2$X$_2$ (where M = divalent first-row transition-metal ion, L = heterocyclic nitrogen-containing organic base, and X = Cl$^-$ or Br$^-$) can be readily synthesized.[12] Crystallographic data have been obtained for several members of the above class of complexes including Cu(py)$_2$X$_2$ (X = Cl$^-$, Br$^-$),[13] Mn(py)$_2$Cl$_2$,[14] and Mn(pz)$_2$Cl$_2$[15] (pz = pyrazole). In all of the above structures, the metal ions are situated on

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distorted "4 + 2" octahedral sites. Two nitrogen atoms from the organic bases and two closely bound halide ions form a plane, with the remaining positions in the octahedron being occupied by two weakly bound halide ions from neighboring complexes above and below the reference complex. In $Cu(py)_2Cl_2$, for example, a one-dimensional dichloride-bridged chain is formed parallel to the crystal *c* axis. Within a given chain, the metal–metal separations are about 4.0 Å and the M–X–M angles are approximately 90°. The *interchain* separation of neighboring metal ions is determined by the orientation of the pyridine rings which yields the shortest *interchain* distances (along the *b* axis) of about 8.5 Å. Although these *interchain* distances are rather large, recent heat capacity experiments[16,17] have shown that *interchain* exchange interactions are present, although they are small, and these additional exchange interactions give rise to long-range 3-D ordering in several of the above compounds.

It should be possible to synthesize a linear polymeric species whose "chainlike" character is largely unchanged (i.e., bond distances and angles comparable to those in $M(py)_2Cl_2$) but whose environment relative to other chains is changed dramatically. By employing a pyridine-type organic base with a large bulky substituent in the position trans to the coordinated nitrogen (the 4-position), one would expect the unit cell of $Cu(py)_2Cl_2$ to be elongated along the *b* axis and along the diagonal to the site at $(0, {}^1/_2, {}^1/_2)$. The use of 4-phenylpyridine should force an approximately 4 Å greater interchain separation. Consequently, we have prepared the $(4\text{-Ph-py})_2MCl_2$ complexes of copper(II), manganese(II), and nickel(II) and wish to report the results of our studies in this paper.

Experimental Section

4-Phenylpyridine (99% purity) was obtained from Aldrich Chemical Co. (Atlanta, GA) and was used without further purification. Hydrated metal chloride salts (ACS Reagent grade) were obtained from J. T. Baker Chemical Co. and were used directly.

$Cu(4\text{-Ph-py})_2Cl_2$. To a warm solution of 1.70 g (0.01 mol) of $CuCl_2{\cdot}2H_2O$ in 100 mL of reagent grade methanol plus 25 mL of triethyl orthoformate was added 3.10 g (0.02 mol) of 4-phenylpyridine in 35 mL of CH_3OH. An immediate turquoise blue precipitate resulted. The mixture was stirred for 10 min, filtered, washed liberally with ether, and allowed to air-dry under suction. Although repeated attempts were made to recrystallize this complex, none proved successful. The compound was insoluble in all common strongly coordinating solvents such as dimethylformamide (DMF) as well as a variety of alcohols, and the complex is soluble with decomposition in concentrated aqueous ammonia. Attempts to obtain small crystals via slow diffusion across a fine-glass frit were also unsuccessful. This solubility property observation is quite different from the solubilities of other Cu(substituted pyridine)$_2X_2$ species studied previously in our laboratories.[12] Anal. Calcd for $Cu(C_{11}H_9N)_2Cl_2$: C, 59.39; H, 4.08. Found: C, 59.77; H, 4.19.

$Ni(4\text{-Ph-py})_2Cl_2$ and $Mn(4\text{-Ph-py})_2Cl_2$ were prepared as above. However, these complexes were reasonably soluble in methanol and were recrystallized from saturated solutions of that solvent to yield yellow-green hairlike needles (nickel(II) complex) and pale cream-colored needles (manganese(II) complex). Anal. Calcd for $Ni(C_{11}H_9N)_2Cl_2$: C, 60.05; H, 4.12. Found: C, 59.73; H, 4.14. Calcd for $Mn(C_{11}H_9N)_2Cl_2$: C, 60.56; H, 4.96; N, 6.42. Found: C, 60.28; H, 4.39; N, 6.23.

All microanalyses were performed by Integral Microanalytical Laboratories, Raleigh, NC.

Near-zero-field dc magnetic susceptibilities were obtained on an ultrasensitive SQUID magnetometer (Model A-401 SQUID sensor and Model A-201 magnetometer control circuit) made by Superconducting Technology, Inc. (SCT), Mountain View, CA. The magnetic field was supplied by a superconducting solenoid, and the field strength was calculated from the known coil geometry of the solenoid by measuring the current supplied by a precision constant-current source (Keithley, Model 227; output current resolution better than 5 μA). The magnetic field depends on the current trapped in the solenoid; the range of field available is 0–20 kOe. Temperatures at the sample zone were regulated by a gas flow/heater arrangement that was controlled by a Lakeshore Cryotronics Model DTC-500 temperature controller. Sample temperature were measured with a calibrated Si diode (Lakeshore Cryotronics Model DT-500) using a 10-μA excitation current and a Dana Model 4700 4.5-digit digital voltmeter; details of the diode calibration and temperature–voltage function have been discussed elsewhere.[18] Polycrystalline samples were contained in ultrapure synthetic quartz (Supracil) tubes of ~4-m i.d.; typical sample weights can be as low as a few micrograms on the SQUID system, but we used weights of about 10 mg for increased accuracy. The SQUID system was calibrated by the manufacturer by measuring the moment induced by a known current in a tiny precision-wound coil and was also calibrated by us using manganese Tutton salt; the two methods agreed to within 1.5%.

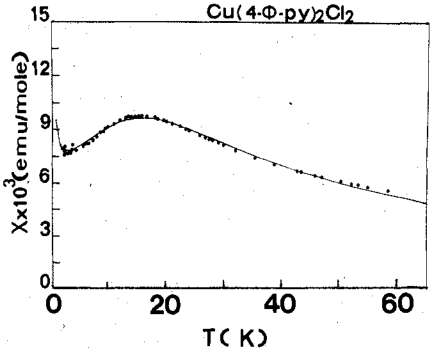

Figure 1. Temperature dependence of the susceptibility of $Cu(4\text{-Ph-py})_2Cl_2$. The solid curve is best fit to the one-dimensional Heisenberg model (see text for parameters).

Additional susceptibility measurements were made by using a PAR Model 155 vibrating-sample magnetometer. High-resolution magnetization data were also obtained on the PAR Model 155 magnetometer (0.1–15 kOe) and a PAR Model 150-A magnetometer (6–50 kOe). Details of the procedure and calibration of the PAR systems have been described elsewhere.[19] EPR spectra were obtained on a Varian E-3 spectrometer operating at X band (~9.5 GHz). The magnetic field of the E-3 was calibrated by NMR techniques using a Magnion G-502 gaussmeter and a Hewlett-Packard 5340 A frequency counter. The free radical DPPH ($g = 2.0036$) was used as a frequency marker in all cases. Spectra were obtained at room temperature and at 77 K. The 77 K data were obtained through the use of a liquid-nitrogen insertion Dewar made by Varian. Commercially available quartz sample tubes were used throughout.

All data-manipulation and curve-fitting procedures were carried out on the Raytheon 706 computer in the UNC Chemistry Department. A modified version[20] of a Simplex function-minimization subroutine was used to obtain fits to the various theoretical models. In all cases involving the theoretical fits, the function minimized was $F = (1/n)\sum[(\chi_{\text{calcd}} - \chi_{\text{obsd}})^2/\chi_{\text{obsd}}^2]$ and individual points were assigned unit weight.

Results

As we noted in the Introduction, most of the theoretical results available for linear-chain systems have been centered around the use of the spin–spin Hamiltonian[1] (1) where J is

$$\mathcal{H} = -2J\sum_{i<j}[a\hat{S}_{iz}\hat{S}_{jz} + b(\hat{S}_{ix}\hat{S}_{jx} + \hat{S}_{iy}\hat{S}_{jy})] \qquad (1)$$

the nearest-neighbor exchange parameter, $S_{i(x,\,y,\,z)}$ is the *x*,

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y, or z component of the spin angular momentum of atom i, and a and b are anisotropy parameters. The Ising model ($a = 1$, $b = 0$)[2] and the XY or transverse-coupled model ($a = 0$, $b = 1$)[4] are special subsets of the Hamiltonian. The isotropic or Heisenberg limit is obtained for the general case $a = b = 1$.[5-7] Since copper(II), nickel(II), and manganese(II) ions in octahedral crystal fields possess orbitally nondegenerate A ground states, one may expect that the Heisenberg model would be applicable.[1] However, as it will be shown below, this approach does not work in the case of the nickel(II) complex.

(a) $Cu(4\text{-}Ph\text{-}py)_2Cl_2$. The magnetic susceptibility (1.6–60 K) data for $Cu(4\text{-}Ph\text{-}py)_2Cl_2$ are shown in Figure 1. The data follow the Curie–Weiss law above 30 K yielding $\langle g \rangle = 2.15 \pm 0.03$ and $\Theta = -25.8$ K. Below 30 K there is a marked deviation from Curie–Weiss behavior, and a broad maximum in the susceptibility occurs near 14 K. From the broad shape of the curve, and the fact that the susceptibility does not appear to tend to zero as the temperature approaches zero,[6] it is probable that the infinite-linear-chain model should be able to account for the observed susceptibility.

EPR spectra of powdered $Cu(4\text{-}Ph\text{-}py)_2Cl_2$ were recorded at room temperature and 77 K. Full rhombic **g**-tensor anisotropy was observed with $g_x = 2.274$, $g_y = 2.093$, $g_z = 2.049$, and $g_{av} = {}^1/_3(g_x + g_y + g_z) = 2.138$. Note that the observed average g value from the EPR measurements agrees nicely with that estimated from the high-temperature susceptibility data. Also, the work of Richards and co-workers[16,24] on $Cu(py)_2Cl_2$ suggests that the observation of full anisotropy in the g factors may be indicative of a very small *interchain* interaction, J'. This is reasonable because the exchange between chains, J', will tend to average the lines along a given crystal direction into one line despite the fact that the copper sites are known to be of rhombic symmetry. In $Cu(py)_2Cl_2$, for example, an *interchain* ($|J'/J| \simeq 1.2 \times 10^{-2}$) is strong enough to average the two lines into one line along any crystal direction even at rather high microwave frequencies (35 GHz).[24] Presumably such an interaction would have an even more drastic averaging effect on polycrystalline samples at low microwave frequencies (~9 GHz).

Since single-ion crystal field anisotropy is not possible for $S = {}^1/_2$ copper(II) ions,[1] one expects the Heisenberg model (eq 1, $a = b = 1$) for isotropically interacting spins to be appropriate. Bonner and Fisher[6] have accurately estimated the limiting behavior of this model for $S = {}^1/_2$. We have fit the observed data to Bonner and Fisher's results. Excellent agreement between theory and experiment result for $J/k = -12.2$ K and $g = 2.06$. Since inspection of the data in Figure 1 reveals a small Curie-like tail at the lowest temperatures, the experimental data were corrected for the presence of monomeric $S = {}^1/_2$ impurities by using the relation $\chi_{obsd} = \chi_{chain} + \chi_{imprty}$. Under the assumption that the impurity obeys the Curie law, the expression for the total susceptibility may be written

$$\chi_{obsd} = \frac{P}{100}\left(\frac{Ng^2\beta^2S(S+1)}{3kT}\right) + \frac{100-P}{100}\chi_{chain} \quad (2)$$

where $S = {}^1/_2$, g is the average g value, and P is the percent impurity present. By use of this approach, the best fit obtained is $J/k = -12.2$ K, $g = 2.06$, and $P = 0.5\%$. There is a discrepancy of about 4% between the "best-fit" g value and the experimentally observed average g value. Effects of a similar magnitude have often been observed for related systems.[12] Thus, it appears that the linear chains in $Cu(4\text{-}Ph\text{-}py)_2Cl_2$ are isolated and adequately described by the Bonner–Fisher model over the whole temperature range used in this study.

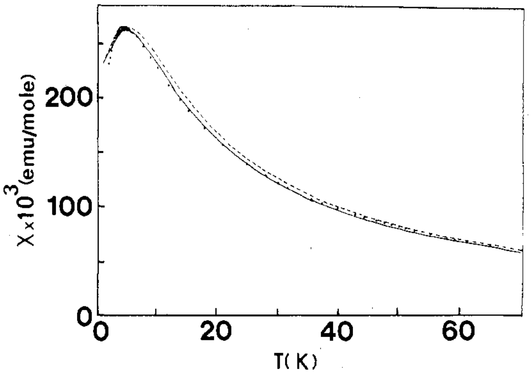

Figure 2. Temperature dependence of the susceptibility of $Mn(4\text{-}Ph\text{-}py)_2Cl_2$. The solid and dashed curves are the best fits to the scaling model with and without molecular field corrections, respectively.

(b) $Mn(4\text{-}Ph\text{-}py)_2Cl_2$. The experimental susceptibility data for $Mn(4\text{-}Ph\text{-}py)_2Cl_2$ (1.6–70 K) are shown in Figure 2. The field dependence of the measured susceptibility was checked at 4.2 K and found to be independent of applied field up to 10 kOe. The data above 17 were fitted to the Curie–Weiss law from which we obtained $g = 2.03$ and $\Theta = -11.1$ K. The data below 17 K show increasing deviations from Curie–Weiss behavior, and a broad maximum in the susceptibility–temperature curve occurs near 4.2 K.

Manganese(II) ions in weak octahedral crystal fields give rise to a ^6A ground state. Thus, one generally finds the magnetic properties to be isotropic, and the **g** tensor is almost invariably close to the free-electron g value.[26] The isotropic Heisenberg model (eq 1, $a = b = 1$) for $S = {}^5/_2$ is then expected to be applicable for a manganese(II) linear chain.[8,9,27] Although a rigorous theoretical interpretation is lacking for a linear array of $S = {}^5/_2$ ions, Friedberg and his co-workers[8,27] have shown that Fisher's[5] infinite-spin linear model may be scaled to the leading terms of the "exact" high-temperature-series expansion model for $S = {}^5/_2$. The resulting equation is

$$\chi_c = [N_g{}^2\beta^2S(S+1)/3kT][(1+u)/(1-u)] \quad (3)$$

where $u = \coth\,[2JS(S+1)/kT] - 1/[2JS(S+1)]$ and the other symbols have their usual meaning. The maximum in the susceptibility (χ_{max}) and the temperature corresponding to χ_{max} are related by the expressions

$$|J|\chi_{max}/Ng^2\beta^2 = 0.1004 \qquad kT_{max}/|J| = 8.2 \quad (4)$$

We have used the "scaled model" to obtain estimates of the isotropic exchange coupling constant. Since manganese(II) ions usually have isotropic g values very near 2.0, our initial fits to eq 3 were performed by fixing the value of g at 2.00 and allowing J to vary freely. This resulted in $J/k = -0.62$ K, and a calculated susceptibility shown as the dashed line in Figure 2, but inspection of this best-fit value and the experimental data revealed that the calculated curve was systematically higher than the observed data even for $T \approx 6T_{max}$. As a test of the sensitivity of the model, a second fit to eq 3 was performed by allowing g and J to vary freely. This yielded $g = 1.93$ and $J/k = -0.59$ K. Although the quality of the second fit improved rather dramatically, the resulting g value seemed unrealistically low for manganese(II) ions especially in view of the fact that the Curie–Weiss fits yield an estimate of g of about 2.03 ± 0.01. In an attempt to improve the

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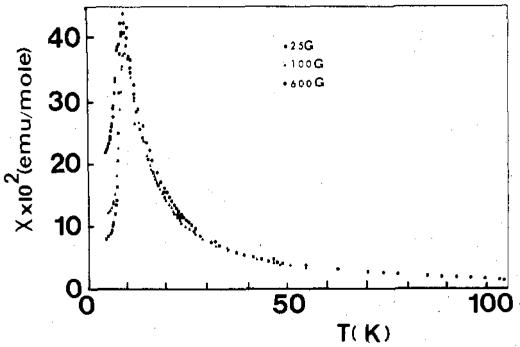

Figure 3. Field dependence of the susceptibility of Ni(4-Ph-py)$_2$Cl$_2$. The data at 25 and 100 G were collected on the SQUID magnetometer while the other set was collected on the VSM system.

agreement between theory and experiment, a third fit was performed by assuming the susceptibility given by eq 2 should be modified by a molecular field correction[28] such that

$$\chi_{MF} = \chi_c/[1 - (zJ'/Ng^2\beta^2)\chi_c] \qquad (5)$$

where J' is the exchange between chains and z is the number of nearest neighbors. This fit resulted in $g = 1.98$, $J/k = -0.39$ K, and $zJ'/k = -0.133$ K, and substantially better agreement between the calculated and observed susceptibilities was obtained especially for higher temperatures, i.e., $T \geq 6T_{max}$ (see the solid curve in Figure 2). Although it is very difficult to definitely assign the zJ' term to only exchange between neighboring chains, this explanation is probably quite reasonable since one could hardly expect single-ion anisotropy (zero-field splittigs) to be so noticeable in the higher temperature susceptibility data. In this regard, we note that the experimental data below T_{max} begin to show fairly large deviations from all of the calculated curves. This could be a consequence of single-ion effects such as those observed by Klaaijsen et al.[17] for similar complexes, *interchain* exchange, or an inadequacy of the theory. Clearly, susceptibility measurements on powders will probably never allow a clear choice to be made. Further theoretical work on the susceptibility of linear chains with $S \geq 1$ and anisotropic interactions or single-ion anisotropy is clearly of interest to augment the theoretical specific heat calculations of Blöte.[29]

The magnetic parameters suggest that the complex [Mn(4-Ph-py)$_2$Cl$_2$] may have a structure (Mn–Mn distances and Mn–Cl–Mn angle) similar to those of MnCl$_2$·2H$_2$O[14,28] and other pyridine-like complexes of manganese.[30,31] In arriving at these results, we have assumed that the zJ' molecular field corrections arise solely from *interchain* exchange and that the number of next nearest neighbors is four ($z = 4$). It is certainly true that one cannot distinguish *interchain* effects from single-ion anisotropy solely from susceptibility data, but Smith et al.[27] have shown that the effect of a D term on eq 3 will be averaged to zero in the powder limit. Finally note that the estimate of the *interchain* exchange ($|J'/J|$) is very close to that for Mn(py)$_2$Cl$_2$, which is known to be a well-isolated chain from the work of Klaaijsen et al.[17] ($T_N < 1.3$ K). Further experiments to lower temperatures would be highly desirable as would heat capacity measurements. Also, dilute EPR studies of Mn^{2+} doped into an isomorphous diamagnetic host (if one can be found) should permit the measurement of the single-ion crystal field terms quite accurately.

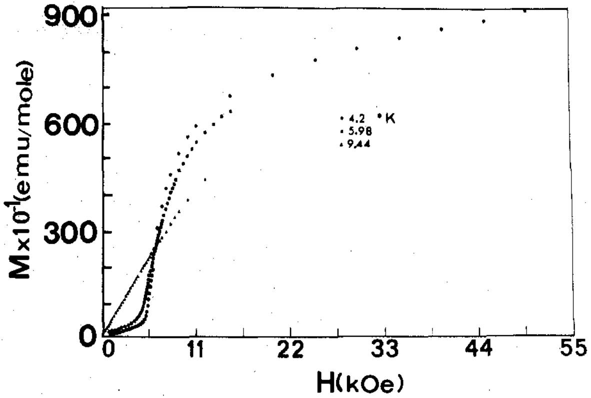

Figure 4. Magnetization isotherms at selected temperatures for Ni(4-Ph-py)$_2$Cl$_2$. The data observed at 4.2 K were not saturated at 50 kOe.

(c) Ni(4-Ph-py)$_2$Cl$_2$. The highly unusual low-field susceptibility data for Ni(4-Ph-py)$_2$Cl$_2$ are shown in Figure 3. Inspection of the data in Figure 3 shows a very strong dependence on external field down to about 100 G, and below 100 G the data were found to be essentially independent of applied field. The data collected at 25 and 100 G were taken from our SQUID magnetometer while those at 600 G were collected on a PAR Model 155 VSM. When the data were collected in fields stronger than 600 G, the sharpness of the maximum began to broaden and the temperature associated with this maximum, T_{max}, shifted to lower values. The value of T_{max} for the data collected in Figure 3 was 9.15 ± 0.40 K. Behaviors such as those observed in Figure 3 are characteristic of the powder susceptibilities of metamagnetic or canted spin systems.[32-39] Since metamagnetic species have frequently been shown to exhibit sharp jumps in the isothermal magnetization,[40] we have measured the magnetization in applied fields ranging from 250 Oe to 55 kOe. These results are shown in Figure 4. In addition, inspection of the magnetization reveals that as T approaches 0 K, the metamagnetic transition field, H_c, increases with decreasing T. This is just the expected behavior for a metamagnetic transition[38,40] whereas a "spin-flow" transition field (H_{sf}) increases with increasing temperature.[41] It is of interest to note that similar behavior has been observed for other di-μ-chloro nickel species,[37,38] and, furthermore, in Ni(py)$_2$Cl$_2$ two such critical fields were observed as well as two anomalies in the specific heat.[42] Since the magnetization data were collected point by point, the values of critical fields were extracted from calculations of the ratio of small differences, $(\Delta M/\Delta H)_T$, which is essentially equal to the derivative $(\partial M/\partial H)_T$.[40] Even at the highest field attained (50 kOe) the complex was not fully saturated ($\mu = 1.62\ \mu_B$). This atypical behavior suggests unusually large single-ion anisotropy.[38]

As noted in the Introduction, to a first approximation, one normally expects the $^3A_2$ ground state in octahedral nickel(II) complexes[43] to give rise to fairly isotropic magnetic properties.

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However, since the nickel(II) has a "non-Kramers" electronic ground state, the combined influence of spin–orbit coupling and lower symmetry ligand fields often gives rise to a zero-field splitting (D) of the ^{3}A ground state. Usually this splitting amounts to less than 10 cm^{-1}, but recent specific heat[42] and susceptibility data[37] for analogous nickel(II) chain compounds reveal that $D/k \approx 30$ cm^{-1} for several members of the series. Furthermore, these investigations revealed that the sign of D/k was negative; i.e., the magnetic doublets $|1,1\rangle$ and $|1,-1\rangle$ lie lowest. Griffith has shown[44] that for non-Kramers ions (even-electron systems such as nickel(II)) in which only a lowest lying doublet is populated at very low temperatures, $g_\perp \rightarrow 0$ and $g_\| \rightarrow 2g_\|$. Thus, at temperatures $T << D/k$, only the S_z components of the total spin have any appreciable expectation value, and the spin system should be characterized by a ficticious $S_f = {}^1/_2$ ground state and a very strong anisotropy in the exchange interaction. Furthermore, if the spins are coupled along the chains by an *interchain* J such that $|J| < |D|$, then for temperatures ($T < |D|/k$) the exchange interaction should be Ising-like[2] whereas at higher temperatures ($T >> D/k$) the Heisenberg model may apply. This unfortunate set of circumstances makes it very difficult to extract accurate values for the *intrachain* exchange from susceptibility data, and to our knowledge, no theoretical work exists for such a situation other than the specific heat calculations of Blöte.[29] Within the limitations of a molecular field approach, Watanabe[45] has treated the problem of $S = 1$ ions with single-ion crystal field anisotropy coupled by Heisenberg exchange. On the assumption of a crystal field of tetragonal symmetry and an isotropic **g** tensor, the spin Hamiltonian for such a system can be approximated by

$$\mathcal{H} = D\hat{S}_z{}^2 + g\beta(H_x\hat{S}_x + H_y\hat{S}_y + H_z\hat{S}_z) + A\hat{S}\cdot\langle\hat{S}\rangle \quad (6)$$

where D is the zero-field splittings, S_x, S_y, and S_z are the components of the true spin ($S = 1$), and the term $A\hat{S}\cdot\langle\hat{S}\rangle$ is a thermal equilibrium approximation of $2\sum_{i<j}J_{ij}\hat{S}_i\cdot\hat{S}_j$. In this model the molecular field coefficient A is related to the isotropic exchange by $-2\sum J_{ij}\hat{S}_i\cdot\hat{S}_j \approx -2ZJ\hat{S}\cdot\langle\hat{S}\rangle = A\hat{S}\cdot\langle\hat{S}\rangle$ from which it follows that $A = 2zJ$ where z is the number of nearest-neighbor spins ($z = 2$ for a linear array). For the limiting high-temperature susceptibility, i.e., $T >> (A,D)/k$, Watanabe obtained

$$\chi_\perp = (2Ng^2\beta^2/3kT)[1 - (D + 4A)/6kT] \quad (7)$$

$$\chi_\| = (2Ng^2\beta^2/3kT)[1 + (D - 2A)/3kT] \quad (8)$$

For our purposes, we must calculate the powder average of the above equations which is given by $\chi_p = (2\chi_\perp + \chi_\|)/3$.

High-temperature data were fitted to the Curie–Weiss law to obtain estimates of $g_{av} = 2.3$ and $\Theta = 19$ K. Not surprisingly,[44] the values obtained depended on the temperature range chosen, and the values ranged from $g_{av} = 2.4$ to 2.25 and from $\Theta = 11.0$ to 19.0 K. The values quoted above were obtained by fitting the data collected from 75 to 120 K (the highest temperatures used in this study).

In initial attempts to fit the observed data, the experimental data were truncated below 25 K and g_{av} was kept as a fixed parameter while A and D were allowed to vary freely. Unfortunately, this approach revealed that there was a rather serious "uniqueness of parameters" problem since fairly large changes in the best-fit parameters made little difference in the quality of the fit as judged by the criterion of least-squares deviations. As a reluctant compromise, the value of g_{av} was then allowed to vary freely to see if the correlation of parameters persisted with an additional variable. This approach appeared to alleviate the problem somewhat, and, to check its validity, we then limited the data set to those data above 50 K and allowed all three variables to vary freely. A difference of less than 10% in the values of D and A resulted while g_{av} converged to essentially the Curie–Weiss estimate. Thus the values from fitting the data in range 30–120 K were judged acceptable with the results being $D/k = -52$ K, $J/k = 8.5$ K, and $g = 2.3$.

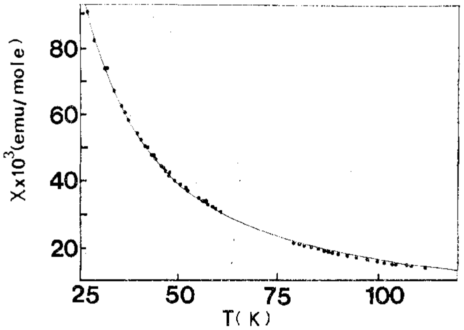

Figure 5. High-temperature susceptibility of Ni(4-Ph-py)$_2$Cl$_2$. The solid curve is the best fit to eq 7 and 8. See text for parameters.

These parameters are compared with the experimental data in Figure 5, where the quality of the fit appears excellent (minimum deviation of a point from calculated curve is approximately 2.5% only at the highest temperatures), but this may be somewhat fortuitous and the true uncertainty in parameters may be quite high. More reliable estimates could be obtained from specific heat experiments.[29,42]

The existence of ferromagnetic *intrachain* exchange, very large single-ion anisotropy, and antiferromagnetic long-range order leads to interesting behavior of Ni(4-Ph-py)$_2$Cl$_2$ in applied magnetic fields. Since the single-ion anisotropy is much larger than the *intrachain* exchange,[1,46] the ordered state should then be characterized as an assembly of ferromagnetic chains coupled together by a weak antiferromagnetic *interchain* exchange, J'. In such situations, a metamagnetic transition is expected when the applied field is strong enough to overcome the *interchain* exchange ($H_c > J'$). Thus, the spins in the ordered state, $T < T_N$, will be uncoupled by the applied field and will "flop" directly to the saturated paramagnetic (ferromagnetic) state.[47] With use of molecular field theory, an estimate of the *interchain* exchange can be obtained from the following considerations: With the assumption of complete antiferromagnetic alignment of the spins in two sublattices, the energy of the spin system at 0 K is given by[37,39] $E_1 = -NS^2z_1J - NS^2z_2J'$. Above the critical field, the spins are aligned parallel and the energy is $E_2 = -NS^2z_1J + NS^2z_2J' - Ng\beta SH$, where $H > H_c$. In linear chains $z_1 = 2$ and the number of nearest neighbors coupled by J' is $z_2 = 4$. Equating E_1 and E_2, we obtain the molecular field, H_{2E}, corresponding to the *interchain* exchange J': $H_2E = 8|J|S/g\beta = H_c$. We obtained a value of 5.6 kOe for H_c. The *intrachain* exchange field, H_{1E}, can be estimated by $H_{1E} = 2z_1|J|S/g\beta$, where $z_1 = 2$, to be 201 kOe. Thus, by calculation of the ratio $H_{2E}/2H_{1E}$, the ratio of the *inter-* to *intrachain* exchange can be obtained. This was found to be 1.38×10^{-2}. It is of interest to note that Ni(4-Ph-py)$_2$Cl$_2$ apparently shows somewhat stronger *intrachain* exchange than the other similar complexes and somewhat stronger *interchain* exchange interactions, as judged by the magnitude of $|J'/J|$ and higher ordering temperature, T_N of 7.9 K. The choice of the two-sublattice model for the ordered state appears to be appropriate since at no

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temperature below T_N could we observe more than one peak in $(\partial M/\partial H)_T$. This is in contrast to $Ni(py)_2Cl_2$ where as many as three peaks in $\partial M/\partial H$ and two anomalies in the specific heat were observed.[37,42] Presumably such behavior implies an ordered state with more than two and perhaps as many as six sublattices.[34,39]

Discussion

From susceptibility and electron paramagnetic resonance data, we suggest that $Cu(4\text{-}Ph\text{-}py)_2Cl_2$ is a well-isolated antiferromagnetic linear chain whose *intrachain* exchange character is largely unchanged relative to other analogous complexes but whose *interchain* coupling is much smaller. Thus, the speculations advanced in the Introduction are at least partially fulfilled in this case. Also, this complex may lend itself to a more easily interpreted analysis of EPR line width and angular-variation studies such as Richards and co-workers have done for $Cu(py)_2Cl_2$.[16,24] A possible shortcoming of this suggestion may be due to the insolubility of $Cu(4\text{-}Ph\text{-}py)_2Cl_2$, but we note that McGregor and Soos[48] have recently been able to obtain reasonable results on powder samples of $Cu(ox)\cdot{}^1/_3H_2O$, another highly insoluble copper(II) compound.

We find that $Mn(4\text{-}Ph\text{-}py)_2Cl_2$ has *intrachain* exchange comparable to those of other manganese(II) complexes of simple pyridines, and *interchain* interactions (even at these suspected greater distances) or perhaps single-ion effects are noticeable. It should be of considerable interest to obtain low-temperature heat capacity experiments on this compound since Klaaijsen et al.[17,42] have shown that this experiment is particularly sensitive to both of these types of interactions while powder susceptibility data are not. Furthermore, a choice between single-ion and *interchain* effects may be made by performing EPR experiments on crystals of a magnetically dilute isomorphous compound containing manganese ions as guests. Such resonance methods are very sensitive to a single-ion anisotropy, and these parameters can be measured with very high precision.[50]

The observation that $Ni(4\text{-}Ph\text{-}py)_2Cl_2$ has a substantially larger *interchain* exchange and also larger single-ion anisotropy than its previously reported analogues is a surprising result. The fact that the ordering temperature, T_N, is nearly 1.5 K higher than that of the closest unsubstituted analogue[37,42] was unexpected. If one adheres to the accepted notion[1] that superexchange interactions are usually very short-ranged ($\sim r_{m-m}^{-10}$ dependence), then it is very difficult to propose a mechanism for enhanced *interchain* exchange unless a rather dramatic structural change occurs. Of course, it is possible that the very large anisotropy plays an intimate role in the above process or that long-range dipole–dipole effects are in some way implicated. At best, these effects are not well understood, and more examples of systems showing this type of behavior need to be studied.

Many of the above ideas are quite speculative in the absence of full crystallographic information on these substances, and such data are highly desirable. If these results were available, then additional experiments on single crystals would likely provide additional insight into the unusual properties of these complexes.

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Registry No. $Cu(4\text{-}Ph\text{-}py)_2Cl_2$, 71500-56-6; $Ni(4\text{-}Ph\text{-}py)_2Cl_2$, 71500-54-4; $Mn(4\text{-}Ph\text{-}py)_2Cl_2$, 71500-52-2.

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Lower Valence Fluorides of Vanadium. 4. The Rutile-like Compounds VF_2, $MgVF_4$, $Li_{0.50}VF_3$, and Opaque $VF_{2+\delta}$

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The rutile-like compounds VF_2, $MgVF_4$, $Li_{0.50}VF_3$, and opaque $VF_{2+\delta}$ were studied. A solid solution $MgVF_4$ was prepared from equimolar amounts of VF_2 and MgF_2, and its lattice dimensions obey Vegard's rule. Lattice constants for trirutile $Li_{0.50}VF_3$ are $a = 4.699$ Å and $c = 9.288$ Å. The opaque rutile phase $VF_{2+\delta}$ is very close to VF_2 in composition with lattice dimensions $a = 4.801$ Å and $c = 3.234$ Å vs. those of VF_2 $a = 4.804$ Å and $c = 3.236$ Å. All four compounds order magnetically above 4.2 K. In these materials, all important magnetic interactions are antiferromagnetic except in trirutile $Li_{0.50}VF_3$ which appears to have ferromagnetic interactions as well. A small remnant moment ~ 0.01 μ_B was observed for the solid solution $MgVF_4$. Magnetic constants for VF_2, $MgVF_4$, $Li_{0.50}VF_3$, and $VF_{2+\delta}$ are T_N = 8, 25, 26, and 20 K, C_M = 1.82, 1.82, 1.24, and 1.76, and Θ = −88, −57, −3, and −80 K, respectively.

Introduction

Vanadium difluoride was first synthesized by Stout and Boo[1] and was verified by them to be isostructural with MnF_2, FeF_2, CoF_2, NiF_2, and ZnF_2. All of these compounds have the rutile structure, space group $P4_2/mnm\text{-}D_{4h}^{14}$. A significant difference was found in the low-temperature magnetic properties of VF_2 vs. those of the other divalent fluorides of the first transition series. Antiferromagnetic ordering of the A–B sublattice type was reported for MnF_2, FeF_2, CoF_2, and NiF_2 to occur at 67.30,[2] 78.25,[3] 37.70,[3] and 73.22 K,[4] respectively. VF_2, however, displays long-range order below 7 K and its ordered structure is reported to consist of spiraled chains directed along its *c* axis.[1,5] The reason for the difference is in the relative strengths of magnetic-exchange interactions

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