

Magnetic interactions in homometallic chains $M(4\text{-cyanopyridine})_2\text{Cl}_2$, $M=\text{Cu}, \text{Ni}, \text{Co}$

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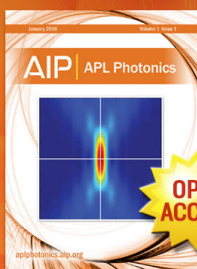
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Magnetic interactions in homometallic chains $M(4\text{-cyanopyridine})_2\text{Cl}_2$, $M=\text{Cu}, \text{Ni}, \text{Co}$

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The title compounds have been synthesized for the first time. The crystal structure of the copper compound has been determined to consist of chloride bridged chains of copper ions with the 4-cyanopyridine (4-CNPy) ligands coordinated to the metal ions through the pyridine nitrogens in the axial sites. Chemical and powder x-ray analysis indicate that the compounds form an isostructural series. The powder susceptibilities have been measured between 2 and 300 K. Effects of either antiferromagnetic exchange (Cu) or ferromagnetic exchange (Ni, Co) within the chains have been seen. The copper data has been fit to the model of a $S=\frac{1}{2}$ Heisenberg antiferromagnetic linear chain with exchange constant $J/k = -13.7(2)$ K. The nickel data has been fit to the model of a $S=1$ ferromagnetic Heisenberg linear chain with exchange constant $J/k = +4.8(2)$ K. The cobalt data has been fit to the model of a $S=\frac{1}{2}$ ferromagnetic Ising linear chain with exchange constant $J/k = +6.6(2)$ K. The Ni and Co compounds order antiferromagnetically at 7.2(2) and 2.1(2) K, respectively. Magnetic-field-induced phase transitions have been observed in the Ni and Co compounds. The critical fields extrapolated to $T=0$ are $H_c=4.2(2)$ kOe and $H_c=1.4(2)$ kOe for the Ni and Co compounds, respectively.

I. INTRODUCTION

As a result of our long-term interest in the preparation of lattices of magnetic ions with specific dimensionality requirements, we have been investigating a number of ligands with the potential to bridge metal ions in a selective fashion. A search of the literature suggested that the ligand 4-cyanopyridine (4-CNPy) could satisfy this requirement. It is known to bond to metals through either the ring nitrogen^{1(a)} or the nitrile nitrogen^{1(b)} and has been shown to bridge metal ions.^{1(c)} We have recently prepared the compound $\text{Cu}(4\text{-CNPy})_4(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ which contains planar CuL_4 units with the ligands bonded to the copper ions through the ring nitrogens.² These units are weakly linked into chains through semicoordinate bonds between the nitrile nitrogens and an adjacent copper ion via the axial sites. We attempted to exploit this nitrile bridging ability to make a homometallic alternating site chain by linking the cationic $[\text{CuL}_4]^{2+}$ groups with anionic $(\text{CuCl}_4)^{2-}$ groups, as has been done previously.³ However, the CuL_4 units were found to be unstable in the presence of halide ions and a series of linear chains, of formula $[\text{ML}_2\text{Cl}_2]_n$, were formed instead. We report here on the crystal structure of the copper member of this new series and the magnetic properties of the series for $M=\text{Cu}, \text{Ni}$, and Co .

II. EXPERIMENT

A. Synthesis: $\text{Cu}(4\text{-CNPy})_2\text{Cl}_2$

Copper (II) chloride dihydrate (1.705 g, 10 mmol) was dissolved in 30 ml of ethanol(abs) and 4-cyanopyridine (2.08 g, 20 mmol) was dissolved in 70 ml of ethanol. The metal solution was added to the 4-CNPy solution and allowed to stir. A light blue precipitate formed immediately upon addition. After the addition was complete, the mixture was stirred for an additional one hour and then filtered, and the precipitate was washed with 3×15 ml of ethanol. The precipitate was then air dried to give 3.34 g (97.4%). The product was recrystallized from water. Small blue needlelike crystals of $\text{Cu}(4\text{-CNPy})_2\text{Cl}_2$ were harvested after a few weeks.

$\text{Ni}(4\text{-CNPy})_2\text{Cl}_2$ and $\text{Co}(4\text{-CNPy})_2\text{Cl}_2$ were synthesized following the method described above.

B. X-ray studies

The crystal structure of the copper analog was determined by single-crystal x-ray diffraction. X-ray powder patterns of the other members of the series, including the Mn and Fe analogs, showed all the compounds to be iso-morphous.

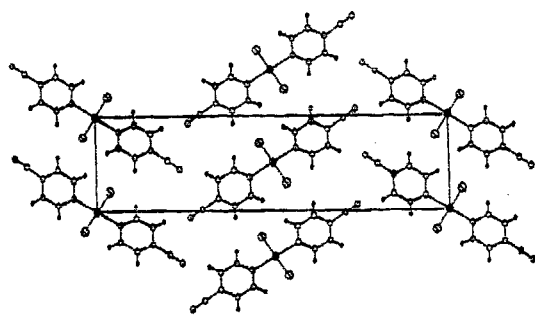


FIG. 1. The crystal structure of $\text{Cu}(\text{4-CNPy})_2\text{Cl}_2$ as viewed down the chains.

C. Magnetic measurements

Powder magnetic susceptibilities were determined as a function of temperature between 1.8 and 300 K using a commercial vibrating sample magnetometer equipped with a continuous-flow cryostat.⁴ Magnetic fields up to 1 T were applied. The data were corrected for diamagnetism and temperature independent paramagnetism. Measurement of the magnetic moment M as a function of applied field H and temperature T were made for powder samples of the nickel and cobalt complexes below their ordering temperatures.

III. RESULTS AND DISCUSSION

A. Crystal structure of $[\text{Cu}(\text{4-CNPy})_2\text{Cl}_2]_n$

The crystal structure of the copper complex consists of chloride bridged chains of copper ions with the 4-CNPy ligands coordinated to the copper ions through the pyridine nitrogens in the axial sites (Fig. 1). The compound is isostructural with the well-known series of one-dimensional compounds $M(\text{py})_2\text{X}_2$, where py=pyridine and $\text{X}=\text{Cl}, \text{Br}$.⁵ However, the additional bulk of the 4-CNPy ligands provides even better isolation between the chains.

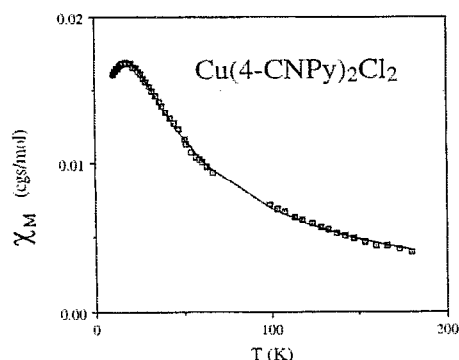


FIG. 2. The powder magnetic susceptibility vs temperature for $\text{Cu}(\text{4-CNPy})_2\text{Cl}_2$. The solid line is the prediction for the $S=\frac{1}{2}$ antiferromagnetic Heisenberg linear chain with $J/k_B = -13.7(2)$ and $g=2.06(1)$.

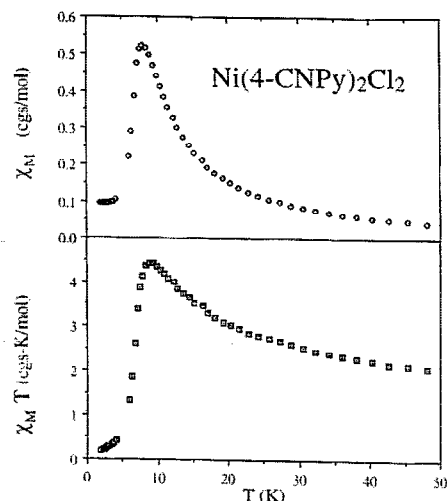


FIG. 3. The upper portion is a plot of the powder magnetic susceptibility of $\text{Ni}(\text{4-CNPy})_2\text{Cl}_2$ vs temperature. The lower portion is a plot of the product $\chi_M T$ vs temperature for the same compound.

B. Magnetic behavior: $\text{Cu}(\text{4-CNPy})_2\text{Cl}_2$

The powder susceptibility as a function of temperature of the copper analog is shown in Fig. 2. The rounded maximum in the susceptibility, located near 18 K, is characteristic of low-dimensional antiferromagnetic interactions in the compound. Given the one-dimensional structure of the compound and the low anisotropy typical for the copper(II) ion, interpretation of the data in terms of a $S=\frac{1}{2}$ Heisenberg antiferromagnetic linear chain model is suggested. The data have been fit to the results of Bonner and Fisher⁶ for this model with the exchange constant J and the splitting parameter g as free parameters. An excellent agreement was found for $J/k_B = -13.7(2)$ and $g=2.06(1)$. The results of the best fit appears as a solid curve in Fig. 2.

The value of the exchange constant found for the 4-CNPy copper chloride chain is the same as found previously⁵ for $\text{Cu}(\text{py})_2\text{Cl}_2$. This confirms the result of the structural determination which found essentially identical chloride bridged copper chains in the two compounds. The additional separation between chains due to the substituted pyridine in the present compound indicates that the 3D ordering temperature should be even lower than the $T_c=1.13$ K found⁵ for $\text{Cu}(\text{py})_2\text{Cl}_2$.

C. $\text{Ni}(\text{4-CNPy})_2\text{Cl}_2$

The magnetic susceptibility χ_M of a polycrystalline sample of the nickel analog (Fig. 3) indicates significantly different behavior than that found in the copper compound. The rapid growth in the product $\chi_M T$ with decreasing temperature signifies net ferromagnetic interactions J . This product reaches a maximum value of 4.5 cgs K/mol at 8.5 K before decreasing rapidly to zero at lower temperatures. The susceptibility itself reaches a maximum at temperature $T_{\text{max}}=7.8(2)$ K, decreasing rapidly to a finite value of 0.1 cgs/mol. This decrease is interpreted

as arising from the influence of antiferromagnetic interactions J' between the chains. The transition temperature T_N is taken to be the temperature at which the product $\chi_M T$ has the maximum slope, $T_N = 7.2(2)$ K.

The high temperature (25–300 K) susceptibility data were fit to the theoretical prediction⁷ for a linear chain of $S=1$ Heisenberg ions with zero single-ion anisotropy in order to extract a value for the ferromagnetic intrachain exchange interaction strength J . The best fit was obtained for the values $J/k_B = 4.8(2)$ K and $g = 2.30(1)$. No information can be obtained about J' from this model.

The magnetization as a function of external field H is nonlinear below T_N . Definite inflection points are observable in the powder data between 2 and 5 K. Critical fields $H_c(T)$, defined as the field for which $\partial M/\partial H$ is a maximum, have been obtained from the M vs H data as a function of temperature. The resulting phase diagram indicates the limiting critical field $H_c(T=0) \approx 4.2(2)$ kOe.

The exchange constant and Néel temperature for $\text{Ni}(4\text{-CNPy})_2\text{Cl}_2$ are similar to those found⁸ for $\text{Ni}(\text{py})_2\text{Cl}_2$ which are $J/k_B = 5.4$ K and $T_N = 6.75$ K, respectively. Detailed comparison must be made carefully, however, since the analysis⁸ of the specific heat of $\text{Ni}(\text{py})_2\text{Cl}_2$ included the effect of the large single-ion anisotropy, $D/k = -27$ K. The field induced transition found in the present compound is suggestive of a metamagnetic transition, since the magnetization of the polycrystalline sample shows nearly a discontinuous jump at H_c and then approaches saturation rapidly. Confirmation of this hypothesis must await the availability of single crystals.

D. $\text{Co}(4\text{-CNPy})_2\text{Cl}_2$

Both the susceptibility and the low-temperature magnetization of the cobalt analog behave in a manner similar to that of the nickel compound. The susceptibility product $\chi_M T$ initially increases rapidly, reaches a maximum of 5.6

cgs K/mol near 2.6 K, and then decreases towards zero. The maximum of the magnetic susceptibility is found at temperature $T = 2.4(1)$ K. The data have been fit to the predictions of the susceptibility of a $S = \frac{1}{2}$ ferromagnetic Ising chain, similar to the treatment given to $\text{Co}(\text{py})_2\text{Cl}_2$.⁵ The best-fit parameters were $J/k_B = 6.6(2)$ and $g = 5.30(2)$. The antiferromagnetic ordering temperature, taken as the temperature at which $\chi_M T$ has the maximum slope, was found to be $T_N = 2.1(2)$ K. The isothermal magnetization curves show inflection points below T_N , similar to those seen in the nickel complex. The critical field, extrapolated to $T = 0$, has been determined to be $H_c = 1.4(2)$ kOe.

A full report on the structure and properties of $M(4\text{-CNPy})_2\text{Cl}_2$ ($M = \text{Mn, Fe, Co, Ni, Cu}$) and $\text{Cu}(4\text{-CNPy})_4(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ will appear elsewhere.

ACKNOWLEDGMENT

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