Table VI. Non-Hydrogen Atomic Coordinates for **2c** with Esd's in Parentheses

	x	y	z	B_{iso}, Å^2
Pt	0.23633 (4)	0.81275 (3)	0.171561 (20)	1.955 (15)
P1	0.3093 (3)	0.64987 (20)	0.20193 (13)	2.22 (12)
P2	0.1980 (3)	0.76938 (19)	0.05211 (13)	1.93 (11)
Cl1	0.1430 (3)	0.98185 (20)	0.13735 (14)	3.74 (14)
Cl2	0.2677 (4)	0.85678 (23)	0.29793 (14)	4.52 (16)
C1	0.3006 (10)	0.5791 (7)	0.1137 (4)	1.9 (4)
C2	0.3570 (12)	0.4794 (8)	0.1127 (5)	2.9 (5)
C3	0.3593 (12)	0.4323 (8)	0.0485 (5)	3.3 (6)
C4	0.2986 (12)	0.4828 (8)	−0.0194 (5)	3.3 (5)
C5	0.2432 (11)	0.5819 (7)	−0.0200 (5)	2.7 (5)
C6	0.2462 (10)	0.6328 (7)	0.0479 (4)	1.9 (4)
C11	0.5006 (11)	0.6271 (7)	0.2583 (5)	2.7 (4)
C12	0.5253 (13)	0.6568 (9)	0.3406 (5)	4.1 (6)
C13	0.6126 (12)	0.6795 (10)	0.2239 (6)	4.7 (6)
C14	0.1866 (11)	0.5835 (8)	0.2495 (5)	2.8 (5)
C15	0.2235 (14)	0.4687 (9)	0.2670 (6)	4.7 (7)
C16	0.0279 (13)	0.5950 (10)	0.2082 (7)	5.5 (7)
C21	0.3156 (11)	0.8302 (7)	−0.0006 (5)	2.5 (5)
C22	0.2753 (13)	0.9441 (8)	−0.0215 (6)	4.3 (6)
C23	0.4767 (12)	0.8188 (9)	0.0415 (5)	4.1 (6)
C24	0.0070 (12)	0.7950 (8)	−0.0032 (5)	3.2 (5)
C25	−0.1047 (12)	0.7665 (9)	0.0390 (6)	4.7 (6)
C26	−0.0320 (13)	0.7488 (9)	−0.0824 (6)	4.5 (6)

done with a Bruker built-in PANIC program. The *J* values are according to the data in Table I, and LW = 1.6 Hz. All NMR data are summarized in Table I.

All of the reactions, manipulations, and purification steps involving phosphines were performed under a dry nitrogen or argon atmosphere. Other chemicals and solvents from commercial sources were used without further purification, except as noted.

Syntheses. *o*-**Phenylenebis(diisopropylphosphine)** (**1**)[2c] and **dichloro-[*o*-phenylenebis(diisopropylphosphine)]nickel(II)** (**2a**) were prepared according to the literature methods.[3d]

Dichloro[*o*-phenylenebis(diisopropylphosphine)]palladium(II) (**2b**). A mixture of DH (0.0723 mmol) and $(PhCN)_2PdCl_2$ (0.0723 mmol) in degassed dichloromethane (4 mL) was stirred at room temperature for

5 h, during which the solution became brown. Methanol (3 mL) was added to the reaction mixture, and the resulting solution was allowed to sit overnight. A colorless crystalline solid was collected (27.6 mg, 78%; mp 275 °C dec). Anal. Calcd for $C_{18}H_{32}P_2Cl_2Pd$: C, 44.33; H, 6.61. Found: C, 44.35; H, 7.00.

Dichloro[*o*-phenylenebis(diisopropylphosphine)]platinum(II) (**2c**). A flask was charged with DH (0.59 mmol) and K_2PtCl_4 (0.59 mmol), followed by a mixture of degassed water (5 mL) and ethanol (5 mL). The resulting suspension was stirred for 3 h, after which white precipitates were collected by filtration. The filtrate was extracted with CH_2Cl_2 to recover the remaining product, and the combined product was recrystallized from CH_2Cl_2/methanol. A colorless crystalline solid was obtained (195.2 mg, 57% dec). Anal. Calcd for $C_{18}H_{32}P_2Cl_2Pt$: C, 37.51; H, 5.60. Found: C, 38.03; H, 5.70.

Crystallography. Crystals of **2a–c** were obtained by recrystallization from cosolvents (vide supra). Cell parameters were determined on a CAD-4 diffractometer at 300 K and by a least-squares treatment. Atomic scattering factors are from ref 12. The computing program was the NRCC SDP VAX package.[13] The crystal data are listed in Table II, and the non-hydrogen atomic coordinates are listed in Tables IV–VI. The ORTEP diagram of complex **2a** is shown in Figure 4. Other crystallographic data are supplied as supplementary material.

Supplementary Material Available: Figures S2 and S3, showing ORTEP drawings of complexes **2b,c** respectively, and Tables S1–S13, listing atomic coordinates and thermal parameters, complete bond distances and bond angles, anisotropic thermal parameters, and detailed crystal data (15 pages); listings of structure factors for **2a–c** (36 pages). Ordering information is given on any current masthead page.

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Exchange Interactions in a Novel Copper(II) Linear-Chain Compound with Ladderlike Structure: $Cu_2(1,4\text{-diazacycloheptane})_2Cl_4$[1]

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The synthesis, crystal structure, and magnetic properties are reported for the novel compound $Cu_2(1,4\text{-diazacycloheptane})_2Cl_4$. The blue compound, $Cu_2C_{10}H_{24}N_4Cl_4$, crystallizes in the monoclinic space group $P2_1/c$. Cell dimensions are as follows: $a = 13.406$ (3), $b = 11.454$ (2), $c = 12.605$ (3) Å; $\beta = 115.01$ (2)°; $Z = 4$. The structure was solved at room temperature by Patterson and direct methods and refined to an R value of 0.037 ($R_w = 0.040$), for 2089 observed reflections and 183 parameters. The binuclear unit of the complex is roughly centrosymmetric, and the coordination environments around the two copper atoms are very similar. Each metal center shows distorted (4 + 1) square-pyramidal geometry. The four short bonds involve the two nitrogens of 1,4-diazacycloheptane, a terminal chlorine atom, and a bridging chlorine atom. The long, apical bond involves a basal chlorine atom of the other copper atom. The binuclear units are packed along the [101] direction. Each dimer is related to its two nearest neighbors along this axis by cristallographic inversion symmetry and is connected to each of them by two Cu–Cl···H–N–Cu hydrogen bonding interactions. As a result of this 1-D network of hydrogen bonds, the binuclear units are connected into infinite ladderlike chains. The X-ray analysis of the compound does not reveal any close contacts between chains that may be regarded as bonding interactions. The magnetic susceptibility vs temperature curve for the compound exhibits a maximum at about 8 K, strongly indicative of antiferromagnetic exchange. Comparisons between theory and experiment with use of approximate Heisenberg models have been made. The results indicate that, in order to account for the magnetic properties of the compound, both interactions between nearest neighbors and interactions between next nearest neighbors must be considered explicitly in the spin Hamiltonian, since they are of the same order of magnitude.

Introduction

Exchange-coupled magnetic systems that display large amounts of order in but one dimension, owing to their unique physical

properties, have occupied considerable experimental and theoretical work.[2]

In the realm of copper(II) crystal chemistry, there has recently

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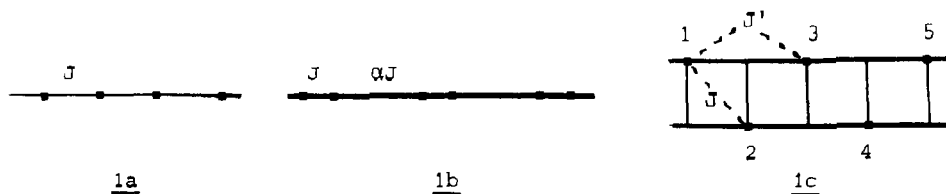
been a considerable amount of success in finding ligand-bridged uniform-chain systems (i.e. 1-D systems with a constant Cu···Cu separation, as in **1a**) and alternating-chain systems (**1b**), where pairs of spins are alternately coupled.[2]

Exchange interactions between copper(II) ions are largely an isotropic phenomenon, and their description, therefore, requires the use of Heisenberg exchange theory. Almost no analytical results are available for 1-D Heisenberg models; nevertheless, the magnetic behaviors of copper(II) chains of the **1a** or **1b** type have been characterized with considerable accuracy. This has been possible on account of extensive experimental data,[2d,e] reliable results of several approximate theoretical methods[2b] (of which the most successful has been the cluster approach as developed by Bonner and Fisher),[3] and the development of procedures for data analysis that are convenient to use.[4,5]

Bona fide examples of 1-D, exchange-coupled copper(II) compounds with the double-chain structure depicted in **1c** or structures derived from distortions of this model are instead very rare, and their magnetic properties and behavior remain poorly documented.[2c,d,4]

The distinctive feature of such double-chain compounds is that second neighbors interact with a strength which is comparable with that of the nearest neighbors; i.e., in the case of model **1c**, the Hamiltonian is

$$\hat{H} = -2\sum_{i=1}^{N}(J_n S_i \cdot S_{i+1} + J_{nn} S_i \cdot S_{i+2}) \tag{1}$$

where J_n is the coupling constant describing the nearest-neighbor interaction and J_{nn} pertains to the next-nearest-neighbor interaction. Part of the problem with these and related systems lies with the fact that, as discussed elsewhere,[6,7] the determination of the low-lying states for Hamiltonians such as (1), which is clearly a prerequisite for any meaningful comparison between theory and experiment, has not achieved the desired reliability. For example, exact numerical calculations on finite chains turn out to be often ambiguous in extrapolation to infinite chain lengths.[7] As a matter of fact, few attempts have been made to extract exchange-coupling constants from magnetic data for systems of **1c** type and they have been only partially successful,[2d,4] which may be understood in terms of the difficulty of the theo-

retical problem. Clearly, further experimental and theoretical studies are needed in order to attain an adequate understanding of the exchange problem in compounds with ladderlike structure. A variety of potential properties of these compounds provide the stimulation for such studies. For example, eq 1 is one of the simplest examples of a multiterm Hamiltonian where the interactions compete. For an antiferromagnetic system with both J_n and J_{nn} of negative sign, the nearest-neighbor interaction tends to align the next-nearest-neighbor spins, whereas the next-nearest-neighbor term tends to antialign them. As described in detail elsewhere, rich and varied magnetic[4] and phase[2b,8,10] behavior is to be expected from such Hamiltonians.

In a recent paper,[11] we have reported a novel structural ladderlike compound, Cu$_2$L$_2$(CH$_3$COO)$_2$·2H$_2$O (LH = N-methyl-N'-(5-methoxysalicylidene)-1,3-propanediamine), whose magnetic behavior is very close to that of an alternating chain. Here we describe the synthesis, X-ray structure, and magnetic properties of another new and interesting system, Cu$_2$(1,4-diazacycloheptane)$_2$Cl$_4$, that exhibits double-chain structure and attendant magnetic properties.

Experimental Section

Synthesis. A 0.40-g (4.00-mmol) quantity of 1,4-diazacycloheptane was dissolved in warm methanol (125 mL). The ligand solution was added to a solution of CuCl$_2$·2H$_2$O (0.70 g, 4.00 mmol) in the same solvent (125 mL). The resulting deep blue solution was heated at about 60 °C for 1 h, and then it was allowed to cool to room temperature. Deep blue, prismatic crystals separated. After the reaction mixture was allowed to stand for ca. 48 h, the crystals were decanted, washed twice with anhydrous ethanol, and dried under vacuum: yield 0.54 g (58%); mp 191–193 °C. Anal. Calcd for C$_{10}$H$_{24}$N$_4$Cl$_4$Cu$_2$: C, 25.60; H, 5.16; N, 11.94. Found: C, 25.84; H, 5.45; N, 11.76. The compound is slightly air sensitive and virtually insoluble in common organic solvents.

Magnetic Measurements. Variable-temperature magnetic susceptibility data were collected in the range 4.2–300 K, as previously described.[12] Susceptibilities were corrected[13] for the diamagnetism of the ligand system (−121 × 10^{-6} cgsu/Cu atom). Our analyses used a temperature-independent paramagnetic term, $N\alpha$, of 60 × 10^{-6} cgsu/Cu atom and did not include any zero-field splitting.

Crystallographic Data Collection and Structure Determination. A deep blue, prismatic crystal with dimensions 0.20 × 0.15 × 0.08 mm^3 was mounted on a computer-controlled Philips PW1100 single-crystal diffractometer equipped with a graphite-monochromatized Mo Kα radiation. Cell parameters were determined by a least-squares calculation based on the setting angles of 25 reflections with 2θ angles ranging between 14 and 26°. Cell dimensions and additional crystal data are listed in Table I. The intensities of hkl and $h\bar{k}l$ reflections were collected

Table I. Crystallographic Data for Cu$_2$(1,4-diazacycloheptane)$_2$Cl$_4$

Cu$_2$C$_{10}$H$_{24}$N$_4$Cl$_4$	fw = 469.3
cryst class: monoclinic	T = 20 °C
space group $P2_1/c$	λ = 0.71069 Å
a = 13.406 (3) Å	ρ = 1.775 g·cm^{-3}
b = 11.454 (2) Å	μ = 29.88 cm^{-1}
c = 12.605 (3) Å	transm coeff = 0.99–0.77
β = 115.01 (2)°	R = 0.037
V = 1754.04 Å^3	R_w = 0.040
Z = 4	

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Table II. Fractional Atomic Coordinates in $Cu_2(1,4$-diazacycloheptane$)_2Cl_4$

atom	x/a	y/b	z/c
Cu(1)	0.16545 (4)	-0.11721 (4)	0.19961 (4)
Cu(2)	0.34395 (4)	0.11374 (4)	0.28828 (4)
Cl(1)	0.2013 (1)	0.0765 (1)	0.1055 (1)
Cl(2)	0.3177 (1)	-0.0887 (1)	0.3737 (1)
Cl(3)	0.0427 (1)	-0.0460 (1)	0.2615 (1)
Cl(4)	0.4808 (1)	0.0676 (1)	0.2387 (1)
N(1)	0.2531 (3)	-0.2236 (4)	0.1456 (4)
N(2)	0.0509 (3)	-0.1875 (3)	0.0532 (3)
N(3)	0.2378 (3)	0.1967 (3)	0.3362 (3)
N(4)	0.4438 (3)	0.1913 (3)	0.4378 (3)
C(1)	0.2164 (5)	-0.2031 (6)	0.0200 (6)
C(2)	0.0917 (5)	-0.1826 (5)	-0.0377 (4)
C(3)	0.0289 (4)	-0.3075 (5)	0.0790 (5)
C(4)	0.1210 (5)	-0.3895 (4)	0.0956 (6)
C(5)	0.2339 (5)	-0.3459 (5)	0.1739 (5)
C(6)	0.2716 (4)	0.1749 (5)	0.4621 (4)
C(7)	0.3980 (4)	0.1722 (4)	0.5250 (4)
C(8)	0.4513 (4)	0.3171 (4)	0.4135 (5)
C(9)	0.3461 (5)	0.3820 (4)	0.3911 (5)
C(10)	0.2401 (4)	0.3225 (5)	0.3076 (5)
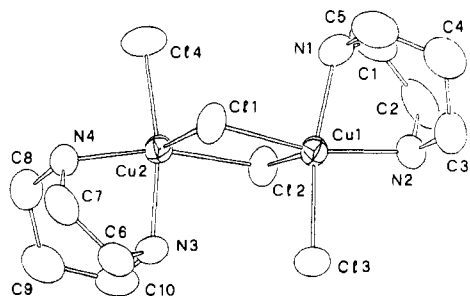
Figure 1. View of the molecular structure of the binuclear units in $Cu_2(1,4$-diazacycloheptane$)_2Cl_4$. Hydrogen atoms have been omitted for clarity.

up to $2\theta = 50°$; the $\omega-2\theta$ scan technique was employed, the scan range being 1.8° and the speed 0.06° s^{-1}. Three standard reflections that were measured periodically showed no apparent variation in intensity during the data collection. The data were corrected for Lorentz and polarization factors. A semiempirical absorption correction was applied on the basis of the variation in intensity during the azimuthal scans of some reflections, according to the method of North et al.[14] After the equivalent reflections were merged, a set of 2089 independent observed reflections ($I > 3\sigma(I)$) were retained for subsequent calculations.

The structure was solved by Patterson and direct methods and refined by the full-matrix least-squares method with use of the SHELX-76 package of programs.[15] Anisotropic thermal parameters were refined for all non-hydrogen atoms. The hydrogen atoms were included at the calculated positions and refined with an overall temperature factor ($U = 0.10$ Å^2). The refinement was carried out with use of 183 parameters and 2089 observed reflections ($R_w = (\sum(w(|F_o| - |F_c|)^2)^{1/2}/\sum(wF_o^2)^{1/2}$; $w = (\sigma^2(F_o) + 0.0019F_o^2)^{-1}$). The molecule is roughly centrosymmetric, with the pseudocenter at about $^1/_4$, 0, $^1/_4$. The atomic scattering factors were taken from ref 15 for the N, C, H, and Cl atoms and from ref 16 for the Cu atom; the correction for anomalous dispersion was included.

Results

Structural Information. Final positional parameters for Cu_2-$(1,4$-diazacycloheptane$)_2Cl_4$ are given in Table II. Figure 1 is a perspective view of the binuclear unit of the complex with the atomic numbering scheme indicated. Intradimer bond distances and angles are listed in Table III.

The halves of the binuclear unit are not related by crystallographic inversion symmetry; however, the coordination environments around the two copper atoms are very similar. The molecular symmetry is close to C_i. Each metal center shows distorted

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Table III. Bond Distances (Å) and Angles (deg) in $Cu_2(1,4$-diazacycloheptane$)_2Cl_4$

Cu(1)-Cl(1)	2.653 (1)	N(2)-C(3)	1.471 (6)
Cu(1)-Cl(2)	2.302 (1)	N(3)-C(6)	1.476 (6)
Cu(1)-Cl(3)	2.252 (1)	N(3)-C(10)	1.489 (7)
Cu(1)-N(1)	2.001 (3)	N(4)-C(7)	1.484 (5)
Cu(1)-N(2)	2.004 (3)	N(4)-C(8)	1.485 (6)
Cu(2)-Cl(1)	2.329 (1)	C(1)-C(2)	1.533 (6)
Cu(2)-Cl(2)	2.642 (1)	C(3)-C(4)	1.494 (6)
Cu(2)-Cl(4)	2.237 (1)	C(4)-C(5)	1.500 (7)
Cu(2)-N(3)	2.006 (3)	C(6)-C(7)	1.538 (5)
Cu(2)-N(4)	2.000 (3)	C(8)-C(9)	1.511 (5)
N(1)-C(1)	1.465 (8)	C(9)-C(10)	1.525 (7)
N(1)-C(5)	1.494 (7)	Cu(1)···Cu (2)	3.422 (0)
N(2)-C(2)	1.465 (5)		

Cl(1)-Cu(1)-Cl(2)	93.0 (0)	Cu(1)-N(1)-C(1)	107.0 (2)
Cl(1)-Cu(1)-Cl(3)	98.6 (0)	Cu(1)-N(1)-C(5)	107.7 (2)
Cl(1)-Cu(1)-N(1)	96.6 (1)	C(1)-N(1)-C(5)	113.3 (2)
Cl(1)-Cu(1)-N(2)	97.9 (1)	Cu(1)-N(2)-C(2)	108.1 (2)
Cl(2)-Cu(1)-Cl(3)	95.8 (0)	Cu(1)-N(2)-C(3)	108.6 (2)
Cl(2)-Cu(1)-N(1)	90.0 (1)	C(2)-N(2)-C(3)	112.6 (3)
Cl(2)-Cu(1)-N(2)	163.8 (1)	Cu(2)-N(3)-C(6)	108.0 (2)
Cl(3)-Cu(1)-N(1)	163.5 (1)	Cu(2)-N(3)-C(10)	107.2 (2)
Cl(3)-Cu(1)-N(2)	94.4 (1)	C(6)-N(3)-C(10)	113.3 (2)
N(1)-Cu(1)-N(2)	76.9 (1)	Cu(2)-N(4)-C(7)	108.1 (2)
Cl(1)-Cu(2)-Cl(2)	92.7 (0)	Cu(2)-N(4)-C(8)	108.3 (2)
Cl(1)-Cu(2)-Cl(4)	96.2 (0)	C(7)-N(4)-C(8)	112.4 (2)
Cl(1)-Cu(2)-N(3)	89.6 (1)	N(1)-C(1)-C(2)	109.8 (3)
Cl(1)-Cu(2)-N(4)	163.0 (1)	N(2)-C(2)-C(1)	108.4 (3)
Cl(2)-Cu(2)-Cl(4)	100.0 (0)	N(2)-C(3)-C(4)	112.8 (2)
Cl(2)-Cu(2)-N(3)	93.4 (1)	C(3)-C(4)-C(5)	115.3 (3)
Cl(2)-Cu(2)-N(4)	99.1 (1)	N(1)-C(5)-C(4)	112.5 (3)
Cl(4)-Cu(2)-N(3)	165.1 (1)	N(3)-C(6)-C(7)	109.2 (3)
Cl(4)-Cu(2)-N(4)	93.9 (1)	N(4)-C(7)-C(6)	109.0 (3)
N(3)-Cu(2)-N(4)	77.5 (1)	N(4)-C(8)-C(9)	112.1 (2)
Cu(1)-Cl(1)-Cl(2)	86.5 (0)	C(8)-C(9)-C(10)	115.6 (3)
Cu(1)-Cl(2)-Cu(2)	87.3 (0)	N(3)-C(10)-C(9)	112.0 (2)

(4 + 1) square-pyramidal coordination. The four short bonds are to the two nitrogens of 1,4-diazacycloheptane, a terminal chlorine atom, and a bridging chlorine atom. The long, apical bond involves a basal chlorine atom of the other copper atom. The copper–ligand bond lengths are in the range of Cu–N and Cu–Cl bond distances observed for structures of other parallel–planar bis(μ-chloro)-bridged copper(II) compounds.[2d,17]

Atoms N(1), N(2), Cl(2), and Cl(3) lie between 0.02 and 0.08 Å from the best plane calculated for those four atoms and Cu(1). Cu(1) sits 0.19 Å below that plane, toward the apical Cl(1) atom. The deviation of Cu(2) from its corresponding basal plane is also 0.19 Å, toward Cl(2). The four-membered Cu_2Cl_2 bridging unit is very nearly planar, the maximum deviation from planarity being 0.06 Å. The Cu(1)–Cl(1) and Cu(1)–Cl(2) bond distances of 2.653 (1) and 2.302 (1) Å, respectively, are longer and shorter than the corresponding Cu(2)–Cl(2) and Cu(2)–Cl(1) distances of 2.642 (1) and 2.329 (1) Å, respectively. A slight difference between the bridging angles at Cl(1), 86.5 (0)°, and Cl(2), 87.3 (0)°, parallels the difference between the bond lengths of the bridging unit. The intradimer Cu(1)···Cu(2) separation is 3.422 (0) Å.

The binuclear molecules are packed along the [101] direction of the monoclinic space group $P2_1/c$. Each dimer is related to its two nearest neighbors along this axis by crystallographic inversion symmetry and is connected to each of them by two Cu–Cl···H–N–Cu hydrogen-bonding interactions. The interdimer, hydrogen-bonding N···Cl contacts along [101] alternate between two values, one of 3.37 Å, between N(2) and Cl(1)' (and, of course, between the symmetry-related N(2)' and Cl(1) atoms), and the other of 3.29 Å, between N(4) and Cl(2)''. As a result of this 1-D network of hydrogen bonds, the binuclear units are connected into infinite ladderlike chains, as schematically shown in Figure 2. The separations between the copper atoms of nearest-neigh-

(17) Hatfield, W. E. *Comments Inorg. Chem.* **1981**, *1*, 105 and references therein.
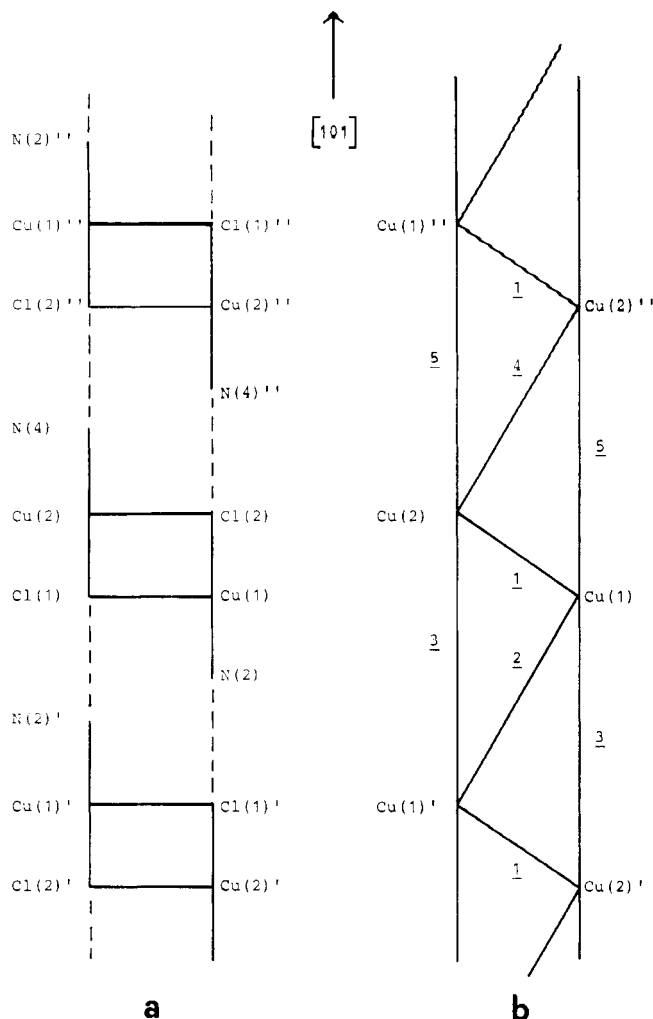
Figure 2. (a) Simplified scheme of a fragment of the ladderlike chain structure of Cu$_2$(1,4-diazacycloheptane)$_2$Cl$_4$. Symmetry code: (single prime) $\bar{x}$, $\bar{y}$, $\bar{z}$; (double prime) $1-x$, $\bar{y}$, $1-z$. Ligand atoms not involved in any bridging have been omitted for clarity. (b) Simplified scheme of the five pathways available for exchange.

boring binuclear units along the chains are as follows: Cu(1)·· ·Cu(1)$'$ = 5.774 (0) Å, Cu(1)···Cu(2)$'$ = 6.996 (0) Å, Cu(1)··· Cu(2)$''$ = 7.002 (0) Å, Cu(2)···Cu(2)$''$ = 5.822 (0) Å; Cu(1)·· ·Cu(1)$''$ = 9.359 (0) Å, and Cu(2)···Cu(2)$'$ = 9.380 (0) Å.

The X-ray analysis of the compound does not reveal any close contacts between chains that may be regarded as bonding interactions, suggesting that the individual chains in the structure are effectively isolated.

Magnetic Properties. Corrected magnetic susceptibility data for Cu$_2$(1,4-diazacycloheptane)$_2$Cl$_4$ are given in Figure 3. The presence of an antiferromagnetic interaction is clearly indicated by the maximum at about 8 K in the susceptibility vs temperature curve. The inverse susceptibility vs temperature plot obtained for data above ca. 20 K is linear with a slope of 2.353 (8) cgsu^{-1} K^{-1}, and hence there is a Curie constant, C, of 0.425 (1) cgsu·K and a calculated g value of 2.13 (0). This g value was held constant during all the fitting calculations described below.

Discussion

The most prominent structural feature of Cu$_2$(1,4-diazacyclohetane)$_2$Cl$_4$ is the presence of well-isolated ladderlike chains parallel to [101]. Inspection of Figure 2 shows that, basically, the double-chain structure of the compound deviates from the **1c** model in that the pathways connecting each copper atom to the two nearest-neighboring copper atoms are not equivalent. Figure 2 also shows that, owing to the low symmetry of the chain, five pathways corresponding to five different Cu···Cu separations are available for intrachain magnetic exchange between nearest neighbors or next-nearest neighbors. Strictly speaking, therefore,
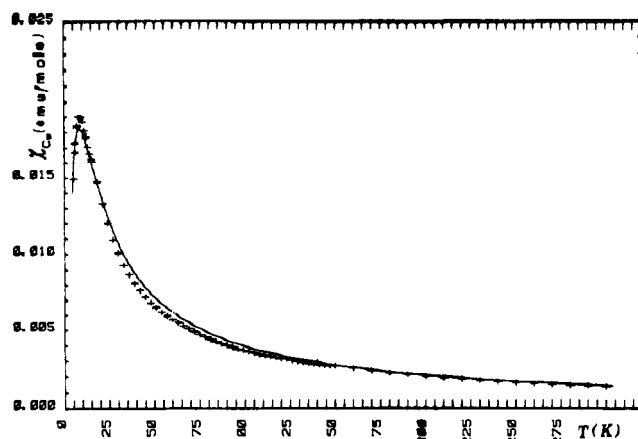

Figure 3. Magnetic susceptibility data for Cu$_2$(1,4-diazacyclohep-tane)$_2$Cl$_4$. The solid line through the data was generated by the expression given in the text for Heisenberg exchange in an alternatingly spaced chain with $J = -6.0$ cm^{-1}, $\alpha = 0.78$, and $g = 2.13$.

the spin problem for the compound involves five exchange-coupling constants and a Hamiltonian of the form

$$\hat{H} = -2J_1 \sum_{i=1}^{N/2} \hat{S}_{2i} \cdot \hat{S}_{2i-1} - 2J_2 \sum_{j=1}^{N/2} \hat{S}_{2j} \cdot \hat{S}_{2j+1} -$$
$$2J_3 \sum_{j=1}^{N/2} (\hat{S}_{2j+1} \cdot \hat{S}_{2j-1} + \hat{S}_{2j} \cdot \hat{S}_{2j+2}) - 2J_4 \sum_{k=2}^{N/2} \hat{S}_{2k} \cdot \hat{S}_{2k+1} -$$
$$2J_5 \sum_{k=2}^{N/2} (\hat{S}_{2k+1} \cdot \hat{S}_{2k-1} + \hat{S}_{2k} \cdot \hat{S}_{2k+2}) \quad (2)$$

where the J subscripts refer to the relative pathways in Figure 2, $i = 1,2,3,...,$ $j = 1,3,5,...,$ and $k = 2,4,6,....$ Such a complex Hamiltonian cannot presently be used for the analysis of magnetic data. We have, therefore, considered the question of whether the magnetic structure of the compound may approximately be described by some simpler, tractable model that is implicit in (2). This possibility clearly depends upon the relative magnitude of the coupling constants that characterize exchange along the chains. The A, B, and C models described below were tentatively selected.

Model A. We first note, with the aid of Figure 2 and eq 2, that if the intradimer exchange pathway **1** leads to an exchange interaction that is considerably stronger than those propagated by the interdimer **2–5** exchange pathways, then the model represented by eq 2 reduces to a model of weakly interacting spin pairs. The use of this model is suggested by the accepted[2e] notion that superexchange interactions are usually very short-ranged ($\sim r_{M-M}^{-10}$ dependence) and the fact that exchange pathway **1** corresponds to a Cu···Cu distance (3.422 (0) Å) which is much shorter than those (in the range 5.774 (0)–7.002 (0) Å) for the other pathways. In the molecular field approximation, the magnetic susceptibility for such a model is given[18,19] according to eq 3, where χ_M, the

$$\chi'_M \text{ (per Cu)} = \chi_M/[1 - (4zJ'/Ng^2\beta^2)\chi_M] \quad (3)$$

$$\chi_M \text{ (per Cu)} = Ng\beta \sinh(g\beta H/kT)/H[\exp(-2J/kT) +$$
$$2 \cosh(g\beta H/kT) + 1] + N\alpha \quad (4)$$

susceptibility of the isolated pair system, is given by expression 4, z is the number of nearest-neighboring dimers (in this case $z = 2$), and J' accounts for the presence of weak magnetic interactions between neighboring dimers. The best fit of eq 3 to our data yielded $J = -4.6$ (3) cm^{-1} and $zJ' = -4.7$ (2) cm^{-1}. The agreement factor, defined as $F = \sum_i (\chi_i^{obs})^{-1} (\chi_i^{obs} - \chi_i^{calcd})^2$, was 9.42 × 10^{-4} for 77 observations. The use of eq 4 (to which eq 3 reduces for $zJ' = 0$) yielded $J = -5.9$ (3) cm^{-1} but only a marginal fit to this model was obtained, with $F = 1.09 \times 10^{-2}$. Although the model represented by eq 3 provides a rather precise fit to the experimental data, it is not an acceptable physical picture

(18) Myers, B. E.; Berger, L.; Friedberg, S. A. *J. Appl. Phys.* **1968**, *40*, 1149.
(19) Smart, J. S. *Effective Field Theories of Magnetism*; Saunders: Philadelphia, PA, 1966.

of the material, since the correction term is virtually equal to the primary interaction parameter. Clearly, the intermolecular interactions cannot be considered as a weak perturbation on the isolated pair system. They must be considered explicitly in the spin Hamiltonian.

Model B. The second model that was attempted in data fitting was the simplest extended-system model suggested by the structure of the compound. This is the alternating-chain model that obtains from eq 2 if $|J_1|$ and $|J_2|$ (the nearest-neighbor interactions) are considerably larger than $|J_3|$ (the next-nearest-neighbor interaction) and, in addition, $J_2 \sim J_4$ and $J_3 \sim J_5$. This latter condition is suggested by the fact that pathways **2** and **4** on one hand and pathways **3** and **5** on the other involve closely similar Cu···Cu separations and bridging moieties that are of the same chemical nature and symmetry. The magnetic susceptibility of alternating chains of isotropically coupled $s = {}^1/_2$ ions may be written as in (5), where $X = -J/kT$ and constants A–F are power series in terms

$$\chi_M \text{ (per Cu)} = (Ng^2\beta^2/kT)(A + BX + CX^2) \times$$
$$(1 + DX + EX^2 + FX^3)^{-1} + N\alpha \quad (5)$$

of the alternating parameter $\alpha = J'/J$.[4,20] The two J values obtained from the best fit of eq 5 to our data were −6.0 (2) and −4.7 (2) cm^{-1}. F was 1.45×10^{-3}. The theoretical susceptibility curve is drawn in Figure 3 and represents again a rather precise fit to the experimental data. It should however be noted that although the J values of −6.0 and −4.7 cm^{-1} are in the range (from −8.0 to +3.2 cm^{-1}) so far observed[2d] for chloride-bridged copper(II) dimers and chains, neither of these values conform to the dependence of J upon the ratio ϕ/R_0 (ϕ = angle at the bridging chlorine, R_0 = long, out-of-plane Cu–Cl bond distance) established for such compounds.[2d,17,21,22] On the basis of this correlation, for the ϕ/R_0 values of 32.6 and 33.0°/Å found for the compound, an either nearly zero or small positive value would be expected for J_1, as actually observed, for example, for Cu(dmg)Cl$_2$ that exhibits $\phi/R_0 = 32.6°/$Å and $J = +3.2$ cm^{-1}.[23–25] Another difficulty with the alternating-chain model lies with the fact that the condition $|J_2| \gg |J_3|$ is difficult to justify. In fact, although the Cu···Cu separation pertaining to pathway **3** (6.996 (0) Å) is considerably longer and less favorable than that (5.774 (0) Å) for pathway **2**, the superexchange pathway distance between the copper(II) ions is actually longer for **2** (8.027 Å) than for **3** (7.703 Å). In addition, both **1** and **2** pathways have a less favorable symmetry than **3** (vide infra) for propagating magnetic exchange.

Model C. Finally, we take into account the electronic structure of the copper(II) ions and tentatively assume that the two virtually equivalent exchange interactions by the **3** and **5** pathways (which

involve in-plane electron density of square-pyramidal copper(II), with a $d_{x^2-y^2}$ ground state) are much stronger than those which involve out-of-plane unpaired electron density, i.e. the interactions mediated by **1, 2** and **4**. The resultant picture is one of two weakly interacting uniform chains of copper atoms. The magnetic susceptibility for such a model system may be written[26] as in (6),

$$\chi'_M \text{ (per Cu)} = \chi_M(1 - 2zJ'\chi_M/Ng^2\beta^2)^{-1} \quad (6)$$

$$\chi_M = (Ng^2\beta^2/kT)(0.25 + 0.14995X + 0.30094X^2) \times$$
$$(1.0 + 1.9862X + 0.68854X^2 + 6.0626X^3)^{-1} + N\alpha \quad (7)$$

where χ_M, the susceptibility of an isolated Heisenberg chain, is given[5] by eq 7 (where $X = J/kT$) and the zJ' correction term makes allowance for a weak interaction between the two chains. The best fit of eq 6 to the data yielded $J = -4.5$ (3) cm^{-1}, $zJ' = -2.4$ (3) cm^{-1}, and $F = 1.3 \times 10^{-3}$. Once again, the model provides a rather precise fit to the experimental data, but this fit is meaningless for the correction term and the primary interaction parameters are of similar magnitude.

The main conclusion that can be drawn from the results of the A, B, and C model calculations, especially when they are considered collectively, is that models that neglect J_1, J_2, or J_3 (i.e. exchange interactions between nearest neighbors or next-nearest neighbors in the chain structure depicted in Figure 2) with respect to one another are not realistic. This relevant feature, which, by itself, is fully consistent with the X-ray structural results for the compound, clearly implies that in order to achieve an adequate description of its magnetic structure, a Hamiltonian must be used that simultaneously contains at least J_1, J_2, and J_3, i.e. a Hamiltonian of the form

$$\hat{H} = 2J_1 \sum_{i=1}^{N/2} \hat{S}_{2i}\cdot\hat{S}_{2i-1} - 2J_2 \sum_{i=1}^{N/2} \hat{S}_{2i}\cdot\hat{S}_{2i+1} - 2J_3 \sum_{i=1}^{N} \hat{S}_i\cdot\hat{S}_{i+2} \quad (8)$$

Adequate results for the low-lying states for (8) have to be obtained before the J values that characterize exchange in the present and similar compounds can be reliably deduced from magnetic data.

Conclusion

The congruent structural and magnetic properties of Cu$_2$-(1,4-diazacycloheptane)$_2$Cl$_4$ suggest its use for further experimental and theoretical studies as a bonafide example of next-nearest neighbor chain systems. It does not appear possible to attain a deeper insight into the interesting potential properties of condensed systems of this type without further synthetic efforts aimed at obtaining additional examples of such compounds and without concurrent theoretical efforts aimed at obtaining convenient procedures for the analysis of their magnetic properties.

Supplementary Material Available: Tables SI and SII, listing thermal parameters and derived hydrogen positions (2 pages); a table of calculated and observed structure factors (12 pages). Ordering information is given on any current masthead page.

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