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Article

$[Cu(H_4C_3N_2S)Cl_2]_n$, an Unprecedented Diazole-Bridged One-Dimensional Copper Halide: Synthesis, Structure, and Magnetic Properties

Jun-Ling Song,[†] Zhen-Chao Dong,*[,†,‡] Hui-Yi Zeng,[†] Wen-Bo Zhou,[†] Takashi Naka,[‡] Qiang Wei,[†] Jiang-Gao Mao,[†] Guo-Cong Guo,[†] and Jin-Shun Huang[†]

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China, and National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

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The simultaneous desulfurization of 2-mercapto-5-methyl-1,3,4-thiadiazole with $CuCl_2{\cdot}2H_2O$ via mutual diffusion in solvents results in the isolation of air-stable dark-green crystals of $[Cu(H_4C_3N_2S)Cl_2]_n$ (~65% yield). The structure is characterized by a unique one-dimensional copper chain bridged by diazine N–N single bonds rather than halogens, in sharp contrast with the halide bridging mode in conventional copper halide coordination polymers. Each Cu(II) ion shows a square planar coordination geometry featuring a strong Jahn–Teller distortion, as also supported by EPR data. The phase follows a Curie–Weiss paramagnetic behavior over 6–300 K. However, the intrachain antiferromagnetic interaction is evident ($-2J = 21.1$ cm^{-1}). Such magnetic coupling is related to the interplay between the Cu(II)-$d_{x^2-y^2}$ and diazine N–N p-orbitals.

Introduction

Low dimensional metal−organic halide networks have received increasing attention in recent years for their potential applications as electronic and catalytic materials.[1,2] Copper is a very attractive framework former because of its readiness to coordinating with unsaturated bidendate nitrogen ligands as a result of the soft−soft bonding preference.[3] Of particular interest is the superexchange interaction between paramagnetic Cu(II) ions that is tunable through the control of the aromatic nature of bridging ligands and their coordination modes. Numerous dinuclear coordination compounds with such spin exchange coupling between metal centers have been known for decades.[4]

In quest of low-dimensional copper(II) complexes with novel magnetic properties, we use 2-mercapto-5-methyl-1,3,4-thiadiazole (mmtz, structure **I**), a heterocyclic aromatic ligand containing single N−N bonds, to produce N_2-diazine-bridged d^9−d^9 systems for magneto−structural correlation studies. The 1,3,4-thiadiazole and its derivatives are versatile ligands that can bridge over a variety of metal centers,[5,6] but the coordination to copper through the N−N azine is limited mainly to diuclear complexes.[2,7,8] One-dimensional polymeric structures were found only in $[Cu(BPMTD)Cl_2]_n$[2] but without the involvement of the thiadiazole nitrogens in bonding to copper. To our knowledge, the present structure is the first example of a polymeric chain with Cu(II) centers bridged by diazine N−N bonds. More strikingly, the chain condensation occurs via the diazine bridges alone even under

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* To whom correspondence should be addressed. E-mail: Dong.Zhen-Chao@nims.go.jp.

[†] Chinese Academy of Sciences.

[‡] National Institute for Materials Science.

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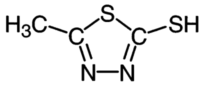
the presence of halide ions. Such feature is unique since the polymerization of copper halide complexes is usually through halide bridging, presumably due to steric effects.[9,10] In contrast with the antiferromagntic or ferromagnetic ordering commonly observed in related dinuclear compounds,[2,7,8] the present one-dimensional structure shows a Curie−Weiss paramagnetic behavior down to 6 K. However, the antiferromagnetic interaction is evident. In this sense, the present compound provides a unique one-dimensional example for the magneto−structural study involving N−N bonds. In this article, we report the synthesis, structure, spectroscopy, and magnetic properties of this one-dimensional polymeric compound, $[Cu(H_4C_3N_2S)Cl_2]_n$.



I

Experimental Section

Physical Measurements. The elemental analysis was performed using a German Elementary Vario EL III instrument. The FT-IR spectra were recorded on a Nicolet Magna 750 FT-IR spectrometer using KBr pellets (4000−400 cm^{-1}). The UV−visible spectra were obtained on a Shimadzu UV-2450PC spectrophotometer and emission spectra on a Shimadzu RF-5300 fluorescence spectrophotometer in the CH_3CN solution at 298 K. Optical diffuse reflectance spectra were also measured using an integrating sphere attachment on a solid sample with $BaSO_4$ as reference. The absorption spectrum was calculated from reflection spectra by the Kubelka−Munk function: $\alpha/S = (1 - R)^2/2R$, in which α is the absorption coefficient, *S* is the scattering coefficient, and *R* is the reflectance. EPR spectra of the complex were recorded at X-band frequencies with a Bruker ER-420 spectrometer at 293 K for the solution in CH_3CN and at 293 and 78 K for the polycrystalline sample mixed with MgO. Magnetic susceptibility measurements on polycrystalline $[Cu(H_4C_3N_2S)Cl_2]_n$ (30 mg) were performed with a Quantum Design SQUID magnetometer at a field of 1 T over the range of 6−300 K. The raw data were corrected for the diamagnetic contribution of the cores (-113.9×10^{-6} cm^3/mol) from Pascal's constants[11] and for the magnetization of the sample holder. Nevertheless, the temperature-independent paramagnetism of 60×10^{-6} cm^3/mol per Cu(II) is not applied to the correction.

Materials. The 2-mercapto-5-methyl-1,3,4-thiadiazole ligand was purchased from ACROS, and $CuCl_2{\cdot}2H_2O$, from the Fourth Factory of Shanghai Reagent. All chemicals and solvents were of reagent grade and used as received.

Synthesis of $[Cu(H_4C_3N_2S)Cl_2]_n$. A U-shape tube with the middle filled with CH_2Cl_2 was used for the reaction and crystal growth of the title compound. $CuCl_2{\cdot}2H_2O$ (0.17 g, 1 mmol) was dissolved in CH_3CN (10 mL), and the resultant solution was added slowly drop by drop into one end of the tube, while a solution of the mmtz (0.06 g, 0.5 mmol) in THF (10 mL) was added dropwise to the other end. The reaction occurs through the mutual diffusion of the reactants. The concentration gradient built up from this slow diffusion process results in the formation of high-quality single crystals appropriate for single-crystal X-ray diffraction studies. Air-stable dark-green crystals of the title compound were isolated from deposit after 20 days with a yield of ∼65%. The deposit also contains blue crystals of $CuSO_4{\cdot}4H_2O$, which was also confirmed by the single-crystal X-ray diffraction. An effort designed to synthesize the Zn analogue was not successful. Anal. Calcd for $Cu(H_4C_3N_2S)Cl_2$: C, 15.35; H, 1.637; N, 11.76; S, 13.48. Found: C, 15.35; H, 1.705; N, 11.94; S, 13.64. IR (KBr, cm^{-1}): 3122 s, 3003 m, 2972 m, 2926 m, 1483 s, 1460 s, 1439 m, 1423 vs, 1381 s, 1248 m, 1221 vs, 1045 m, 1120 s, 1007 m, 930 vs, 841 s, 818 m, 717 s, 704 s, 592 m. UV/vis (CH_3CN, nm): 255 (sh), 310 s, 461 s, 550−800 (br). UV/vis (solid, nm): 303 w, 357 (br), 530−850 (br). The broad band from 530 to 850 nm is associated with d−d transitions and accounts for the deep-green color observed. No luminescence was detected up to 900 nm from either the solid or solution sample in CH_3CN at room temperature.

Table 1. Crystal and Structure Determination Data for $[Cu(H_4C_3N_2S){\cdot}Cl_2]_n$

formula	$Cu(H_4C_3N2_S)Cl_2$
fw	234.58
T, K	293
cryst color	dark green
cryst size, mm	$0.20 \times 0.20 \times 0.10$
a, Å	8.1546(5)
b, Å	11.9203(8)
c, Å	7.1098(4)
β, deg	99.737(2)
V, $Å^3$	681.15(7)
space group	$P2_1/c$
Z	4
D_x, g/cm^3	2.287
μ(Mo Kα), cm^{-1}	41.95
R^a	0.0353
$wR2^b$	0.1062
GOF	0.893
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$, e/$Å^3$	+0.574, −0.626

^{a} $R = \sum||F_0| - |F_c||/\sum|F_0|$. ^{b} $wR2 = [\sum w(F_0^2 - F_c^2)^2/\sum w(F_0^2)^2]^{1/2}$.

Single-Crystal Structure Determination. A tetragonal prismatic dark-green single crystal for the title compound was selected and mounted on a Siemens Smart CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). Intensity data were collected in the $\omega\angle 2\theta$ scan mode with $5 < 2\theta < 51°$ at 293 K and corrected for Lorentz−polarization as well as for absorption by the SADABS program.[12] The assignment of the space group $P2_1/c$ was made on the basis of systematic absences, statistical analyses of intensity distribution, and subsequent successful refinements. A total of 1196 independent reflections were collected, in which 995 reflections were viewed as observed ($I > 2\sigma(I)$) and used in subsequent structural determination and refinements. The structure was solved by the direct methods and refined by full-matrix least-squares fitting on F^2 by SHELX-97.[13] All non-hydrogen atoms were located by a series of least-squares cycles and difference Fourier syntheses and refined anisotropically. Hydrogen atoms were located at geometrically calculated positions. Crystallographic data and refinement residuals are summarized in Table 1. Important bond distances and angles are listed in Table 2. Positional coordinates and isotropic and anisotropic thermal displacement parameters as well as other crystallographic details are available from a CIF file in Tables S1−S4 as the Supporting Information for $[Cu(H_4C_3N_2S)Cl_2]_n$.

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Table 2. Important Bond Lengths (Å) and Angles (deg) in $[Cu(H_4C_3N_2S)Cl_2]_n$[a]

Cu(1)−N(1)^{i}	2.058(3)	N(1)^{i}−Cu(1)−N(2)	171.1(1)
Cu(1)−N(2)	2.058(4)	N(1)^{i}−Cu(1)−Cl(1)	93.2(1)
Cu(1)−Cl(1)	2.266(1)	N(2)−Cu(1)−Cl(1)	87.3(1)
Cu(1)−Cl(2)	2.271(1)	N(1)^{i}−Cu(1)−Cl(2)	87.1(1)
S(1)−C(2)	1.697(5)	N(2)−Cu(1)−Cl(2)	91.7(1)
S(1)−C(3)	1.709(4)	Cl(1)−Cu(1)−Cl(2)	175.18(5)
N(2)−C(2)	1.298(6)	C(2)−S(1)−C(3)	87.8(2)
N(2)−N(1)	1.382(5)	C(2)−N(2)−N(1)	112.7(4)
N(1)−C(3)	1.311(5)	C(2)−N(2)−Cu(1)	122.0(3)
N(1)−Cu(1)^{ii}	2.058(3)	N(1)−N(2)−Cu(1)	125.1(3)
C(3)−C(1)	1.487(6)	C(3)−N(1)−N(2)	111.3(3)
N(1)−C(3)−S(1)	113.9(3)	C(3)−N(1)−Cu(1)^{ii}	129.9(3)
C(1)−C(3)−S(1)	121.1(4)	N(2)−N(1)−Cu(1)^{ii}	117.9(2)
N(2)−C(2)−S(1)	114.1(3)	N(1)−C(3)−C(1)	125.0(4)

[a] Symmetry transformations used to generate equivalent atoms: i, $x, -y - 1/2, z + 1/2$; ii, $x, -y - 1/2, z - 1/2$.

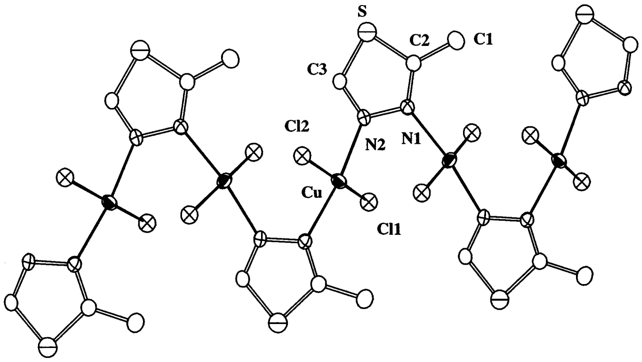
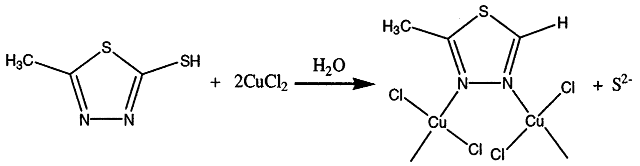


Figure 1. One-dimensional chain of the square-coordinated Cu complex $[Cu(H_4C_3N_2S)Cl_2]_n$.

Results and Discussion

Structure. The unique structural feature of the title compound is the formation of one-dimensional copper chains through the bridging of dinitrogen N−N units rather than halide ions, as shown in Figure 1. Similar bridging modes were previously reported but limited to only dicopper units.[2,7,8] In a copper halide system with both organic bridging ligands and halide ions, the polymerization into one-dimensional, two-dimensional, or three-dimensional structures is usually via the halogen bridging.[9,10] The formation of the present structure is presumably related to the simultaneous downsizing of the mmtz ligand to 5-methyl-1,3,4-thiadiazole (mtz) through desulfurization. Such desulfurization is known to occur for thiols in the aqueous solution, particularly in the presence of metals (e.g., Ni, Fe, Cu) or metal complexes.[14] The additional blue precipitate of $CuSO_4 \cdot 4H_2O$ in the products leads us to speculate the following process of desulfurization followed by the slow oxidation of S^{2-} to S^{6+} in air:



$$Cu^{2+} + S^{2-} + 2O_2 + 4H_2O \rightarrow CuSO_4 \cdot 4H_2O$$

The downsizing of mmtz to mtz ligands results in a smaller steric effect for the desulfurized ligand, which, together with the soft−soft bonding preference of Cu to N atoms, leaves halide ions in merely terminal coordinating modes. The CuN_2Cl_2 moiety has nominal Cu−N (2.058(3) Å) and Cu−Cl (2.266(1)−2.271(1) Å) distances comparable to those in related dicopper chlorides[7,8] and Cl-bridged chains.[9] For example, Cu−N = 1.984(3)−2.027(3) Å and Cu−Cl = 2.233(1)−2.265(2) Å in dinuclear $[Cu_2(PAHAP)_2Cl_4$;[8a] Cu−N = 2.030(7)−2.037(8) Å and Cu−Cl = 2.259(3)−2.291(3) Å in chainlike $Cu(bipy)Cl_2$.[9] However, the local symmetry of approximate D_{2h} for the present CuN_2Cl_2 moiety is in sharp distinction from the rough C_{2v} symmetry of the CuN_2Cl_2 unit in the dinuclear $Cu_2(PAHAP)_2Cl_4$ complex[8a] and $Cu(bipy)Cl_2$ chain,[9] the latter two having Cl−Cu−Cl and N−Cu−N angles close to 90° rather than the 180° in the present structure. Each copper atom is in a nearly planar square coordination geometry, typical of a Cu(II) ion with a strong Jahn−Teller distortion. Alternatively, the coordination can be described as a 4 + 2 octahedral geometry, if two additional weak axial contacts with Cl^- (2.800(1) and 3.099(1) Å, respectively) are included. The copper chain is not exactly linear but slightly zigzag running along the (001) direction. The intrachain Cu−Cu separation is 3.5689(2) Å, shorter than the corresponding distance in the $Cu_2(PAHAP)_2Cl_4$ complex (3.845(1) Å)[8a] and $Cu(bipy)Cl_2$ chain compound (4.010(3) Å).[9] Nevertheless, the observed distance is well above the single-bond distance of 2.34 Å and thus suggests no direct metal−metal bonding interactions. Figure 2 shows how isolated parallel chains are held together by the weak hydrogen-bonding network of C−H···Cl (3.474(1) Å) and van der Waals interactions. The observed hydrogen-bond distance is comparable to those in the $Cu(bipy)Cl_2$ chain (3.215(9)−3.616(9) Å).[9] It is worth reiterating that the present reaction has the effect of desulfurization; the side-sulfur atom of the mmtz ligand is stripped off and then oxidized to yield the blue byproduct of $CuSO_4$.

The N−N distance in the thiadiazole of the title compound is 1.382(5) Å, the same as the distance in the free mmtz ligand[15] but only slightly smaller than the N−N distance of 1.411(4) Å in $[Cu_2(PAHAP)_2Cl_4$[8a] and the single-bond distance of 1.40 Å. As a result, the copper ions are connected by essentially N−N single bonds. The C−N bond distances range from 1.298(6) to 1.311(5) Å, sufficiently short to suggest double-bond character. The C−S bond distances are in the range of 1.697(5)−1.709(4) Å, slightly shorter than the value of 1.77 Å for a C(sp^2)−S single bond. Consequently, the desulfurized mtz ligand, though almost planar (root-mean-square deviation = 0.023 Å), remains as a nonconjugate system or with minor conjugation, if any. The dihedral angle between the ligand plane and the Cu coordination plane (rms deviation = 0.058 Å) is 60.80(7)°. The dihedral angle between neighboring Cu planes is 43.73(6)°

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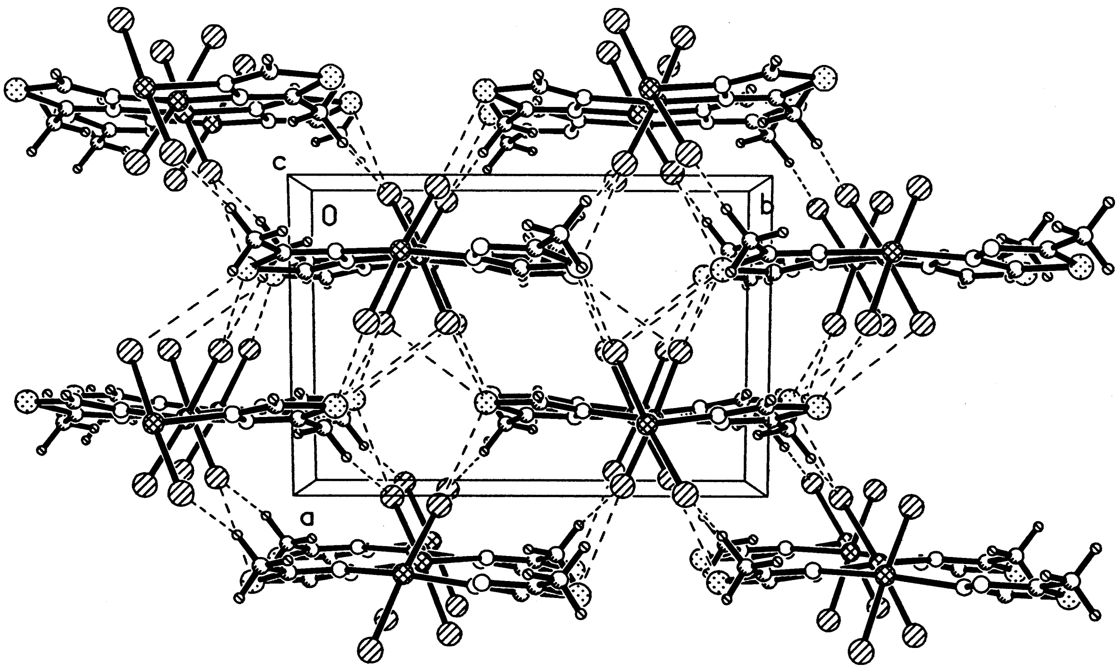

Figure 2. Packing of parallel one-dimensional chains along the (001) direction with weak C−H···Cl hydrogen bonds illustrated.

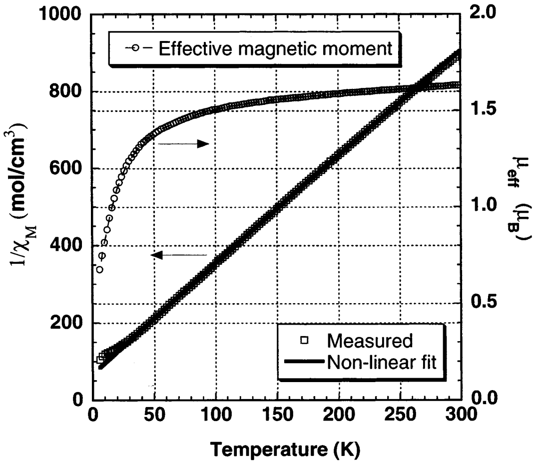

Figure 3. Plot of $1/\chi_M$ versus T over 6−300 K showing a Curie−Weiss paramagnetic behavior. The gradual but significant decrease of μ_{eff} upon cooling indicates the presence of an antiferromagnetic interaction.

with a Cu−N−N−Cu torsion angle of 17.5(4)°. These coordination modes together with the nature of the heterocyclic ligand and the N−N bonding character play important roles in the spin exchange interaction between the Cu(II) centers of the title compound.

Magnetic Properties. The neutrality requirement for $[Cu(H_4C_3N_2S)Cl_2]_n$ and the square-planar coordination around copper strongly suggest a formal oxidation state of +2 for copper ions. Such a single-spin picture for Cu(II) is confirmed by the temperature-dependent magnetic susceptibility measurement. A $1/\chi_{M}$–T plot in Figure 3 shows that the phase is paramagnetic over 6−300 K. A nonlinear fit via $\chi_M = C/(T - \Theta) + \chi_0$ to the data above 60 K reveals a Curie−Weiss behavior with the Curie constant $C = 0.342(1)$ cm^3 mol^{-1} K and Weiss constant $\Theta = -22.9(2)°$, leading to an effective magnetic moment of 1.65(1) μ_B for each Cu center. (The background susceptibility $\chi_0 = 4.5 \times 10^{-4}$ cm^3/mol.) The observed effective magnetic moment is close to the 1.73 μ_B predicted for a single spin, indicating the presence of one localized unpaired electron associated with each Cu(II) (d^9) ion. The existence of Cu(II) centers is also supported by the EPR signal of a nearly isotropic g-factor of 2.116 in the CH_3CN solution, which falls in the range of 2.0−2.3 expected for Cu(II) due to its large spin−orbital coupling.[16] Although Cu(II) ions have no zero-field splitting effects due to its electronic spin of only 1/2, the g-factors are often slightly anisotropic. This is again verified for the present compound. The EPR data from the solid sample diluted with MgO gave the following anisotropic g-factors: $g_{\parallel}/g_{\perp} = 2.2375/2.0990$ at 295 K and 2.2339/2.0927 at 77 K, respectively. The observed trend of $g_{\parallel} > g_{\perp}$ is characteristic of a tetragonal Cu(II) complex with a $d_{x^2-y^2}$ ground state, indicating the occupation of the unpaired d electron in the $d_{x^2-y^2}$ orbital. The measured EPR data are in good agreement with the observed square planar geometry around Cu(II) with its $d_{x^2-y^2}$ orbital directed toward two in-plane chlorine donors and two nitrogen donors.

The present compound does not show any antiferromagntic or ferromagnetic ordering down to 6 K that was commonly observed in dinuclear compounds.[2,7,8] Nevertheless, the presence of antiferromagnetic interactions between the Cu(II) centers is evident in terms of both the smaller μ_{eff} value relative to the theoretical single spin and the relatively large negative Weiss constant. Such antiferromagntic interaction is clearly reflected in the μ_{eff}–T plot of Figure 3 with the effective magnetic moment decreased significantly upon cooling (μ_{eff} is defined as $2.828(\chi_M T)^{1/2}$ μ_B).

A good approximation to the antiferromagnetic coupling of an N-member chain is that only the intrachain interaction of the adjacent pairs contributes to the short-range order. The present structure can be treated as a uniformly spaced

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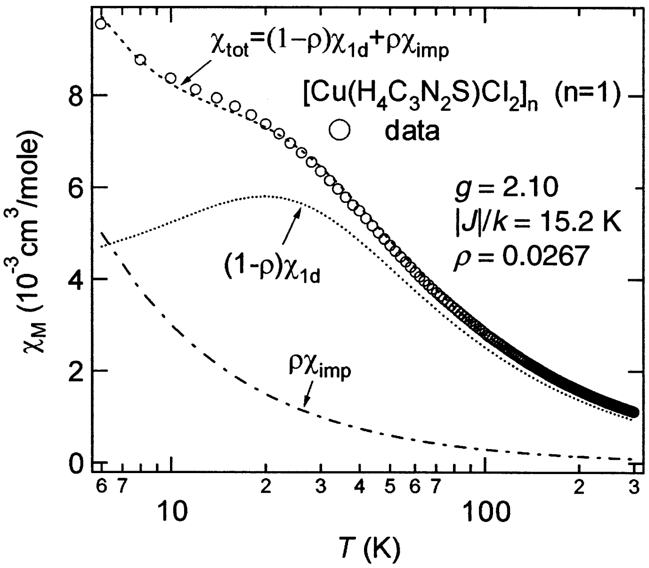

Figure 4. Molar magnetic susceptibility plotted as a function of temperature. The curves are the best fit to the data via the Bonner−Fisher model (eq 1). The broad maximum around 20 K for the one-dimensional chain model is evident, which is characteristic of one-dimensional intrachain antiferromagnetic interactions.

regular linear chain of spin = 1/2, with the magnetic coupling between Cu(II) ions mediated by the diazine bridges. To figure out how strong the intrachain interaction is, the data of the total molar magnetic susceptibility were fitted as follows with the inclusion of a small fraction (ρ) of a magnetically dilute impurity:

$$\chi_{tot} = (1 - \rho)x_{1d} + \rho\chi_{imp}$$

Here the impurity contribution $\chi_{imp} = [Ng_e^2\mu_B^2S_e(S_e + 1)]/3kT$, with $g_e = 2$ and $S_e = 1/2$, while the important one-dimensional intrachain antiferroamgnetic interaction is simulated by the Bonner−Fisher model[17] using the following polynomial expression:[18]

$$\chi_{1d} = \frac{Ng^2\beta^2}{kT}\,\frac{0.25 + 0.14995x + 0.30094x^2}{1 + 1.9862x + 0.68854x^2 + 6.0626x^3} \quad (1)$$

In this expression, $x = |J|/kT$ ($2J$ is the singlet−triplet splitting energy or the exchange integral in the spin Hamiltonian $H = -2Js_1s_2$) and other symbols have their usual meaning. The results of the best fit are shown in Figure 4 for $g = 2.10$, $|J|/k = 15.2$K ($-2J = 21.1$ cm^{-1}), and $\rho = 0.0267$. The small coupling constant of -21.1 cm^{-1} indicates a weak intrachain antiferromagnetic interaction. This value is smaller than that in the related dinuclear $Cu_2(PMK)Cl_4$ ($-2J = 52$ cm^{-1})[7a] and anhydrous $Cu_2(PAHAP)_2Cl_4$ ($-2J = 44$ cm^{-1})[8a] but larger than that in the Cl-bridged Cu(bipy)-Cl_2 chain compound ($-2J = 2.3$ cm^{-1}).[9]

It is known that the intrachain interaction will not lead to long-range ordering for one-dimensional Heisenberg systems.[17,19] The lack of long-range order down to 6 K signifies a weak *interchain* interaction, which is probably mediated through the C−H···Cl hydrogen-bonding network. Nevertheless, such interchain interaction, no matter how small it is, will become important at certain lower temperature as one-dimensional systems (e.g., $Cu(NH_3)_4SO_4{\cdot}4H_2O$[20]) will ultimately interact and undergo a three-dimensional phase transition, leading to long-range magnetic ordering. As expected for a paramagnetic material, the field dependence of magnetization at 6 K shows no hysteresis effects.

Given the long separation between neighboring Cu(II) ions (3.57 Å), the spin exchange is unlikely to originate from direct (through-space) orbital coupling between Cu(II) ions but rather mediated via the N−N diazine bridges. Since the exchange integral between two *localized* molecular orbitals is always ferromagnetic in character and is negligible in the present compound for Cu-$d_{x^2-y^2}$, the net spin coupling depends on the extent of antiferromagnetic interactions mediated through the diazine bridges.[8] Magnetic exchange in the dinuclear complexes has been found to correlate with the angle between the copper magnetic planes and the extent of p-orbital overlap along the N−N single bond and is dominated by σ-interactions.[8a] Despite the small Cu−N−N−Cu torsion angle of 17.5(4)°, the twist angle between the magnetic planes with the $d_{x^2-y^2}$ ground state is 43.73-(6)°, which leads to the misalignment with the adjacent p-orbitals in the diazine bridge. Such poor overlap and alignment between the Cu-$d_{x^2-y^2}$ and N-p orbitals is probably responsible for the weak intrachain antiferromagnetic interaction observed. Sophisticated theoretical calculations will help to gain insights into the magnetic exchange interaction. On the other hand, further tuning of the size and bonding character of ligands may modify the twist between magnetic planes and produce low-dimensional structures with interesting magnetic ordering.[21]

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Supporting Information Available: Tables S1−S4, listing crystal data and geometrical dimensions, Figure S1, showing absorption spectra of $[Cu(H_4C_3N_2S)Cl_2]_n$ in CH_3CN solution and from diffuse reflectance measurements of a solid, Figure S2, showing field-dependent magnetization data, and a crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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