

layer structure as the phenylphosphonates and therefore have octahedrally coordinated Zn atoms rather than the tetrahedra as described for the ethyl phosphate derivative reported here. It is interesting to note that the layered zinc ethyl phosphonate has a *b* axis which is almost half as large (10.14 Å)¹⁹ as the *b* axis of the zinc ethyl phosphate reported here. The interlamellar space is fully packed in both the zinc ethylphosphonate and ethyl phosphate. The distance between adjacent methyl groups in the latter compound is 4.02–4.10 Å, which is close to the required van der Waals distance. However, in the ethyl phosphate O2 and phosphorus have very similar *b* parameters, while the OC₂H₅ groups tilt in the *c* direction. Both of these conditions shorten the total extension in the *b* direction (perpendicular to the layers) of the ethyl phosphate groups to a value of 4.37 Å. If we add half the distance of the layer thickness (0.77 Å) to this value, we obtain the requisite distance of 5.14 Å. The comparable extension of the pendant groups in the ethylphosphonate, including the van der Waals distance between the ethyl groups in adjacent layers,

is very similar, being half the *b*-axis distance or 5.07 Å.

It is of interest now to see if organic phosphates of group II metals can form layered compounds similar to the layered phosphonates. Such work is in progress.

Acknowledgment. This work was supported by the Army Research Office (Grant No. DAAG29-85-K-0124) and the Robert A. Welch Foundation (Grant No. A673), for which grateful acknowledgment is made. The diffractometer facility was made possible by DOD Grant No. 00014-86-G-0194.

Registry No. Zn(O₃POCH₂CH₃)·H₂O (coordination compound entry), 120313-05-5; Zn(O₃POCH₂CH₂NH₃)(O₂CCH₃), 120313-06-6; BaO₃POCH₂CH₂NH₂, 63441-18-9; Zn(O₃POCH₂CH₃)·H₂O (salt entry), 120313-04-4; ethyl phosphate, 1623-14-9; zinc acetate, 557-34-6.

Supplementary Material Available: Tables SI and SIII, listing thermal parameters for zinc ethyl phosphate hydrate and zinc 2-aminoethyl phosphate acetate (2 pages); Tables SII and SIV, listing calculated and observed structure factors (10 pages). Ordering information is given on any current masthead page.

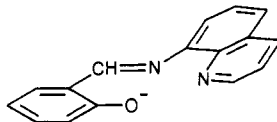
Contribution from the Dipartimento di Chimica and Dipartimento di Scienza della Terra, Sezione Cristallografia, Università di Perugia, 06100 Perugia, Italy

Exchange Coupling in Cu₂L₂Cl₂·2CH₃OH (LH = 8-(Salicylideneamino)quinoline), a New Compound with a Temperature-Dependent Structure¹

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The synthesis, room-temperature crystal and molecular structure, and magnetic properties are reported for the new compound Cu₂L₂Cl₂·2CH₃OH, where L⁻ is the anion of 8-(salicylideneamino)quinoline:



The compound, Cu₂C₃₄H₃₀N₄O₄Cl₂, crystallizes in the triclinic space group *P* $\bar{1}$. Cell dimensions are as follows: *a* = 11.951 (3) Å, *b* = 8.943 (2) Å, *c* = 8.111 (2) Å, α = 112.02 (2)°, β = 107.45 (2)°, γ = 79.20 (2)°, *Z* = 1. The structure was solved at room temperature by direct methods and refined to an *R* value of 0.038 (*R*_w = 0.039), for 213 parameters and 1914 observed reflections. The structure consists of binuclear molecules and uncoordinated methanol molecules of solvation. The binuclear molecule exhibits a centrosymmetric, parallel-planar structure in which each copper atom shows distorted (4 + 1) square-pyramidal coordination. The long, apical bond is to the basal chlorine atom of the other copper atom. Therefore, each bridging chlorine simultaneously occupies an in-plane coordination site on one copper(II) ion and an apical site on the other copper(II) ion. The dimeric units in the structure are well separated from one another. In particular, the oxygen atom of the solvent molecule is not involved in any bridging between dimers. Surprisingly, in light of the dimeric structure of the compound at room temperature, the variable-temperature magnetic susceptibility data between 4.2 and 50 K cannot be reproduced by the dimer exchange model. A precise description of the experimental data can instead be achieved with use of the Heisenberg model for isotropic antiferromagnetic exchange in linear chains, with *J* = -9.30 cm⁻¹ and *g* = 2.08. The noncongruent structural and magnetic properties of the compound are briefly discussed.

Introduction

The study of magnetic exchange in solids is mainly aimed toward relating the observed magnetic properties of a material to the nature of its chemical constituents and the way in which these are bound together to form the crystal lattice.²

A common experimental approach for such a study is to correlate low-temperature magnetic susceptibility data (from which the sign and magnitude of the exchange coupling constant, *J*, are generally deduced) with X-ray results obtained at room temperature.

This approach obviously relies on the dual expectation that the prominent structural features of a given substance dictate its magnetic properties in the whole temperature region which is of interest and that variations in structure with temperature can be

neglected. As an example, compounds having zero-dimensional (clusters) or one-dimensional (chains) structures at room temperature are expected to obey theoretical models whose statistics treats only spins interacting in the individual structural cluster or chain.

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Table I. Crystallographic Data for $\text{Cu}_2\text{L}_2\text{Cl}_2 \cdot 2\text{CH}_3\text{OH}$

$\text{Cu}_2\text{C}_{32}\text{H}_{22}\text{N}_4\text{O}_2\text{Cl}_2$	fw: 692.6
$a = 11.951(3) \text{ \AA}$	space group: $P\bar{1}$
$b = 8.943(2) \text{ \AA}$	$T = 20 \text{ }^\circ\text{C}$
$c = 8.111(2) \text{ \AA}$	$\lambda = 0.71069 \text{ \AA}$
$\alpha = 112.02(2)^\circ$	$\rho = 1.643 \text{ g}\cdot\text{cm}^{-3}$
$\beta = 107.45(2)^\circ$	$\mu = 15.80 \text{ cm}^{-1}$
$\gamma = 79.40(2)^\circ$	transmissn coeff = 0.99–0.86
$V = 763.9 \text{ \AA}^3$	$R = 0.038$
$Z = 1$	$R_w = 0.039$

Actually, a magnetic system can potentially disappoint such expectations through several processes: magnetic lattice dimensionality "crossovers" or long-range order,³ spin–Peierls transitions,⁴ exchange elasticity,⁵ exchange striction,⁶ lattice-driven phase transitions,⁷ to name a few examples. These processes involve temperature-induced transformations of the crystal and/or spin structure and can lead to seeming discrepancies between structure and magnetism. Such mechanisms are, therefore, of fundamental importance for an adequate understanding of relationships between structure and magnetism.

From a chemical point of view, however, the factors that bring about the effects mentioned above are extremely difficult to control during the synthesis process. As far as structural transformations are concerned, very useful results have been obtained^{8–18} with copper(II) compounds with halide bridges. In several of these compounds, in fact, apparently because of the versatility of the halides to act as bridging ligands between copper(II) ions and the relative flatness of the potential surface defining the copper coordination geometry, dissociation of ligand bridges and/or geometrical distortions can occur rather easily upon changes in either temperature or pressure.

With this in mind we here report the synthesis of the new bis(μ -chloro)-bridged compound $\text{Cu}_2\text{L}_2\text{Cl}_2 \cdot 2\text{CH}_3\text{OH}$ (LH = 8-(salicylideneamino)quinoline) along with its interesting structural and magnetic properties.

Experimental Section

Synthesis. LH. 8-Aminoquinoline (2.88 g, 0.02 mol) was dissolved in anhydrous methanol (40 mL), at about 60 °C, in a dry nitrogen atmosphere. To the resultant solution was added a 2.44-g (0.02-mol) quantity of salicylaldehyde. The addition was made over a period of 15

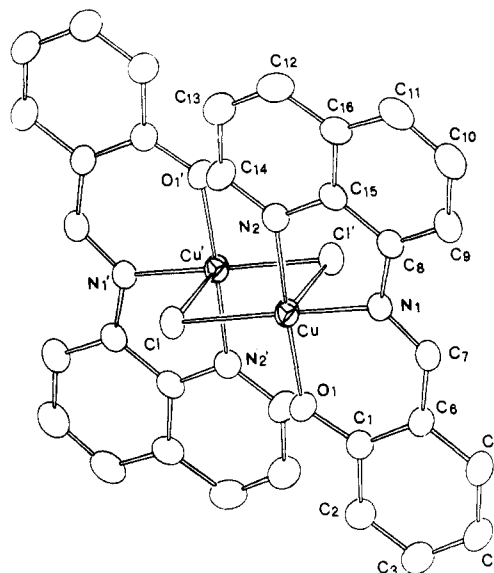


Figure 1. View of the molecular structure of the binuclear units in $\text{Cu}_2\text{L}_2\text{Cl}_2 \cdot 2\text{CH}_3\text{OH}$. Hydrogen atoms have been omitted for clarity. Unlabeled atoms are related to labeled atoms by the inversion center.

Table II. Fractional Atomic Coordinates in $\text{Cu}_2\text{L}_2\text{Cl}_2 \cdot 2\text{CH}_3\text{OH}$

atom	z/a	y/b	z/c
Cu	0.54148 (5)	0.17636 (6)	0.18572 (8)
Cl	0.5712 (1)	-0.0802 (1)	0.1981 (2)
O(1)	0.6898 (3)	0.1460 (4)	0.1301 (5)
O(2)	0.8407 (4)	0.8567 (5)	0.1157 (5)
N(1)	0.5225 (3)	0.4106 (4)	0.2251 (5)
N(2)	0.3909 (3)	0.2303 (4)	0.2644 (5)
C(1)	0.7440 (4)	0.2537 (6)	0.1164 (6)
C(2)	0.8531 (4)	0.2024 (6)	0.0676 (7)
C(3)	0.9165 (5)	0.3089 (7)	0.0549 (7)
C(4)	0.8736 (5)	0.4703 (6)	0.0845 (8)
C(5)	0.7687 (5)	0.5231 (6)	0.1285 (7)
C(6)	0.7008 (4)	0.4167 (5)	0.1445 (6)
C(7)	0.5951 (4)	0.4866 (5)	0.1982 (6)
C(8)	0.4220 (4)	0.4914 (5)	0.2859 (6)
C(9)	0.3879 (5)	0.6542 (6)	0.3300 (7)
C(10)	0.2866 (5)	0.7188 (6)	0.3932 (7)
C(11)	0.2166 (5)	0.6212 (7)	0.4085 (7)
C(12)	0.1857 (5)	0.3440 (7)	0.3837 (7)
C(13)	0.2251 (5)	0.1865 (6)	0.3424 (8)
C(14)	0.3289 (5)	0.1317 (7)	0.2825 (7)
C(15)	0.3525 (4)	0.3898 (6)	0.3036 (6)
C(16)	0.2485 (4)	0.4548 (6)	0.3660 (6)
C(17)	0.9070 (6)	0.9078 (9)	0.2986 (9)

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min, at about 60 °C and with constant stirring. The yellow reaction mixture was refluxed for 2 h in a dry atmosphere and then evaporated under vacuum. A yellow, oily residue (4.9 g) of the new LH ligand was obtained, which was used without any further purification.

$\text{Cu}_2\text{L}_2\text{Cl}_2 \cdot 2\text{CH}_3\text{OH}$. A solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.68 g, 4 mmol) in hot absolute methanol (150 mL) was added to a hot solution of the LH ligand (1.00 g, 4 mmol) in the same solvent (150 mL). The addition was made over a period of 10 min, with constant stirring. The reaction mixture was heated at 60 °C for 1 h, and it was then allowed to stand at room temperature for 12 h. Bright green crystals separated, which were collected by filtration and dried under vacuum; yield 1.2 g (79%); mp ca. 310 °C dec. Anal. Calcd for $\text{C}_{34}\text{H}_{30}\text{N}_4\text{O}_2\text{Cl}_2\text{Cu}_2$: C, 53.99; H, 3.99; N, 7.40; Cu, 16.80. Found: C, 53.85; H, 3.85; N, 7.35; Cu, 16.92. The compound is air stable and sparingly soluble in dichloromethane or chloroform.

Magnetic Measurements. Variable-temperature magnetic susceptibility data were collected in the range 4.2–300 K, as previously described.¹⁹ Susceptibilities were corrected²⁰ for the diamagnetism of the ligand system (-177.1×10^{-6} cgsu/Cm atom). The results were evalu-

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Table III. Bond Distances (Å) and Angles (deg) in $\text{Cu}_2\text{L}_2\text{Cl}_2 \cdot 2\text{CH}_3\text{OH}$

Cu-Cl	2.291 (1)	C(8)-C(15)	1.410 (5)
Cu-O(1)	1.904 (3)	C(8)-N(1)	1.404 (5)
Cu-N(1)	1.976 (2)	C(14)-(2)	1.325 (6)
Cu-N(2)	2.003 (3)	C(15)-N(2)	1.360 (4)
Cu-Cl'	2.856 (2)	O(2)-C(17)	1.400 (8)
O(1)-C(1)	1.310 (5)	Cu...Cu'	3.502 (1)
C(6)-C(7)	1.416 (6)		
C(7)-N(1)	1.307 (5)		
Cl-Cu-O(1)	89.4 (1)	C(6)-C(7)-N(1)	125.7 (4)
Cl-Cu-N(1)	169.4 (1)	C(9)-C(8)-C(15)	119.0 (4)
Cl-Cu-N(2)	94.5 (1)	C(9)-C(8)-N(1)	126.9 (4)
Cl-Cu-Cl'	95.0 (0)	C(15)-C(8)-N(1)	114.1 (4)
O(1)-Cu-N(1)	93.4 (1)	C(8)-C(15)-N(2)	117.4 (1)
O(1)-Cu-N(2)	174.0 (1)	C(16)-C(15)-N(2)	122.0 (4)
O(1)-Cu-Cl'	89.5 (1)	Cu-N(1)-C(7)	124.4 (3)
N(1)-Cu-N(2)	82.0 (1)	Cu-N(1)-C(8)	113.7 (2)
N(1)-Cu-Cl'	95.3 (1)	C(7)-N(1)-C(8)	121.8 (3)
N(2)-Cu-Cl'	94.6 (1)	Cu-N(2)-C(14)	128.1 (3)
Cu-O(1)-C(1)	127.6 (3)	Cu-N(2)-C(15)	112.8 (3)
O(1)-C(1)-C(2)	117.9 (4)	C(14)-N(2)-C(15)	119.1 (4)
C(5)-C(6)-C(7)	116.4 (4)		

ated by using standard least-squares minimization computer programs. Our analyses used a temperature-independent paramagnetic term, $N\alpha$, of zero and did not include any zero-field splitting.

X-ray Data and Structure Solution. A green, prismatic crystal with dimensions $0.15 \times 0.10 \times 0.10 \text{ mm}^3$ was mounted on a computer-controlled Philips PW1100 single-crystal diffractometer equipped with a molybdenum tube and graphite monochromator. The crystals are triclinic. Cell parameters were determined by a least-squares calculation based on the setting angles of 25 reflections with 2θ angles ranging from 12 to 16° . Cell dimensions and additional crystal data are listed in Table I. The intensities of the reflections were collected up to $2\theta = 50^\circ$; the ω - 2θ scan technique was employed, the scan range being 1.6° and the speed 0.05 s^{-1} . A total of 2697 reflections were measured, 783 of which, having $I < 3\sigma(I)$ were considered as "unobserved" and excluded from the refinement. Three standard reflections, which were measured periodically, showed no apparent variation in intensity during the data collection. The data were corrected for Lorentz and polarization factors. A semi-empirical 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.²¹

The structure was solved by direct methods, with the SIR program,²² and refined by the full-matrix least-squares method, with use of the SHELX-76 package of programs.²³ Anisotropic thermal parameters were refined for all non-hydrogen atoms. The hydrogen atoms were included at the calculated positions ($\text{C-H} = 1.08 \text{ \AA}$) and refined with an overall temperature factor, $U = 0.06 \text{ \AA}^2$. The methyl group was refined as a rigid group, starting from the staggered position. The H atom of the OH group of methanol was not located. The refinement was carried out with use of 213 parameters and 1914 observed reflections ($R_w = (\sum w(|F_o| - F_c)^2)^{1/2} / (\sum wF_o^2)^{1/2}$, $w = (a^2(F_o + 0.0039F_c)^{-1})$). The atomic scattering factors were taken from ref 23 for the O, N, C, H, and Cl atoms and from ref 24 for the Cu atom; the correction for anomalous dispersion was included.

Results

Description of the Structure. Structural information about $\text{Cu}_2\text{L}_2\text{Cl}_2 \cdot 2\text{CH}_3\text{OH}$ is reported on Figure 1 and Tables II and III. The unit cell comprises one dichloro-bridged $\text{Cu}_2\text{L}_2\text{Cl}_2$ binuclear molecule and two uncoordinated CH_3OH molecules of solvation. The bridging Cu_2Cl_2 unit is constrained to be planar by the presence of the crystallographic inversion center in the middle of the dimer. The geometry at the copper(II) centers is close to tetragonal pyramidal, with the base plane formed by the cis nitrogen atoms and the phenolic oxygen atom of the tridentate L-

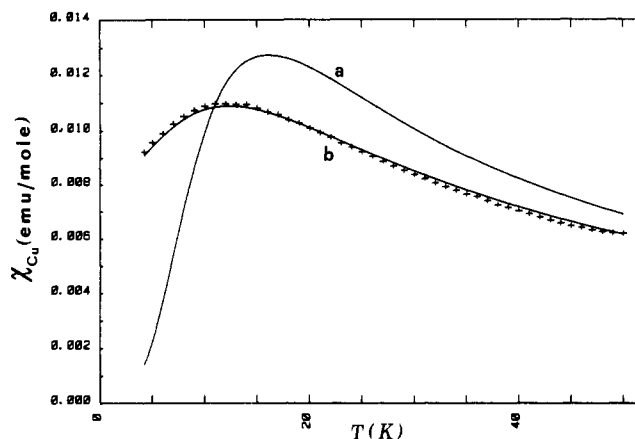


Figure 2. Magnetic susceptibility data for $\text{Cu}_2\text{L}_2\text{Cl}_2 \cdot 2\text{CH}_3\text{OH}$. The data are least-squares fit to the Van Vleck equation for a pair of exchange coupled $s = 1/2$ ions (curve a) and to an equation for a uniform-chain model (curve b); see text for an explanation.

ligand and one chloride ion; the fifth, apical site is occupied by a chloride ligand which is in the base plane of the other copper center in the dimer. The Cu-Cl (2.291 (1) Å), Cu-N (1.976 (2) and 2.003 (3) Å) and Cu-O (1.904 (3) Å) bond distances in the basal plane are comparable with corresponding values reported in a number of other structurally related copper(II) complexes.^{2b,25} The out-of-plane Cu-Cl' distance of 2.856 (2) Å is in the range (2.70–3.37 Å) so far reported²⁵ for similarly bridged copper(II) dimers, but the bridging CuCl'Cu' angle of 85.0 (0)° is smaller than that found in any other tetragonal-pyramidal dichloro-bridged copper(II) dimer.

The X-ray analysis of the compound does not reveal any close contacts between binuclear units that may be regarded as bonding interactions. In particular, the solvent molecules are not involved in any discernible interdimer exchange pathway. The methanol oxygen atom, O(2), is involved in two rather loose contacts ($\text{O}(2) \cdots \text{Cl} = 3.386 \text{ \AA}$, $\text{O}(2) \cdots \text{O}(1) = 2.848 \text{ \AA}$) that may be indicative of some hydrogen-bonding interaction, but such contacts concern ligand atoms belonging to only one dimeric unit.

In view of the noncongruent magnetic behavior (vide infra) of the compound, care was taken to make sure that the crystal used for the structural determination is representative of the bulk sample used for the magnetic measurements. This was accomplished by performing X-ray measurements on several crystals of the compound. Such measurements yielded identical results.

Magnetic Properties. Variable-temperature magnetic susceptibility data for the title compound have been collected between 4.2 and 300 K. The data between 4.2 and 50 K are shown in Figure 2. A maximum around 12 K provides strong evidence for the presence of antiferromagnetic exchange interaction.

The inverse susceptibility vs temperature plot obtained for data above 30 K is linear with a slope of $2.46 \text{ cgsu}^{-1}\cdot\text{K}^{-1}$, from which a g value of 2.08 is calculated. This g value was held constant during the fitting calculations described below. Also, in these calculations, only the data between 4.2 and 50 K were considered, owing to the small magnitude of χ_M above $\sim 50 \text{ K}$ and the coincidences of the χ_M values calculated by different models.

As noted above, the X-ray analysis of the compound does not reveal any discernible exchange pathway between dimers. The compound would therefore be expected to act magnetically as an assemblage of essentially noninteracting dimers and to obey the Van Vleck equation²⁶ for a pair of exchange coupled $s = 1/2$ ions, namely eq 1, where the exchange Hamiltonian is given by $\hat{H} =$

$$\chi_M(\text{per Cu}) = [Ng^2\beta^2/3kT][1 + \frac{1}{3} \exp(-2J/kT)]^{-1} \quad (1)$$

$-2J(\hat{S}_A \cdot \hat{S}_B)$. The "best fit" curve a (corresponding to a J value

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of -9.00 cm^{-1}) in Figure 2 shows the inability of the dimer model to describe the susceptibility data.

Inspection of the data in Figure 2 reveals that the maximum in the experimental susceptibility vs temperature curve, relative to that in the curve calculated from the dimer model, occurs at a lower temperature and has a broader shape and a reduced height. These features indicate²⁷⁻²⁹ higher magnetic dimensionality. In addition, the experimental susceptibility does not appear to tend to zero as the temperature approaches zero. This behavior is expected for a uniform chain, in which there is no gap between the ground state and the first excited state, in contradistinction to a dimeric or alternating-chain system, which, at low enough temperature, will always become nonmagnetic owing to the presence of a gap between the singlet ground state and the nearest excited level.^{4,28,31,32} An appropriate Hamiltonian for a uniform chain, in the Heisenberg model, may be written as $\hat{H} = -2J\sum_r \hat{S}_r \hat{S}_{r+1}$. Hall,³⁰ with use of the results obtained by Bonner and Fisher²⁸ for this model Hamiltonian, has shown that the temperature dependence of the magnetic susceptibility for a uniform chain of $s = 1/2$ ions may be described by the polynomial given in (2), where $X = |J|/kT$. Equation 2 was used to fit the

$$\chi_M(\text{per Cu}) = \frac{Ng^2\beta^2}{kT} \frac{0.250 + 0.14995X + 0.3394X^2}{1 + 1.9862X + 0.68854X^2 + 6.0626X^3} \quad (2)$$

experimental data for $\text{Cu}_2\text{L}_2\text{Cl}_2 \cdot 2\text{CH}_3\text{OH}$, with the criterion of best fit being the minimum value of the function $F = \sum_i (\chi_i^{\text{obsd}})^{-1} (\chi_i^{\text{obsd}} - \chi_i^{\text{calcd}})^2$. The best fit yielded $J = -9.30 \text{ cm}^{-1}$ and $F = 6.9 \times 10^{-5}$, for 46 observations. The theoretical susceptibility curve is drawn in Figure 2 (line b) and represents a precise fit to the experimental data. The value of the exchange coupling constant is in the range (from $+2.5$ to -10 cm^{-1})^{2a,b} so far observed for chloride-bridged copper(II) chain compounds.

Discussion

The magnetic susceptibility data for $\text{Cu}_2\text{L}_2\text{Cl}_2 \cdot 2\text{CH}_3\text{OH}$ below 50 K can be explained only in terms of a uniform-chain Heisenberg model with an exchange parameter of -9.30 cm^{-1} . The quality of the fit to this model (which has been characterized to a high degree of accuracy from both an experimental and theoretical point of view)^{2b,4,28} is so good as to leave little doubt that, below 50 K, there is a dominant and relatively effective 1-D exchange pathway in the compound.

This 1-D uniform feature is not apparent in the room-temperature crystal structure of $\text{Cu}_2\text{L}_2\text{Cl}_2 \cdot 2\text{CH}_3\text{OH}$, which consists of distinct binuclear units held together by van der Waals forces only. Although a J value of -9.30 cm^{-1} may be not unreasonable^{2b,25} for the interaction of the copper atoms within the individual dimers, an exchange interaction of such a magnitude cannot be propagated by simple van der Waals contacts.

The most plausible explanation that can be offered for the dichotomy in the structural and magnetic results for the compound is the occurrence of a temperature-induced structural transformation, presumably to a uniformly spaced chain, as suggested by the low-temperature magnetic data.

As mentioned in the Introduction, a variety of related, halide-bridged compounds of copper(II) are known in which seeming discrepancies between structure and magnetism stem from temperature-induced phase transitions. For example, $\text{Cu}(\text{4-methylpyridine})_2\text{Cl}_2$ ⁸⁻¹¹ and $\text{Cu}(\text{N-methylimidazole})_2\text{Br}_2$ ^{8,12,13} have uniform-chain structures at room-temperature but exhibit alternating-chain magnetism below 50 and 100 K, respectively.

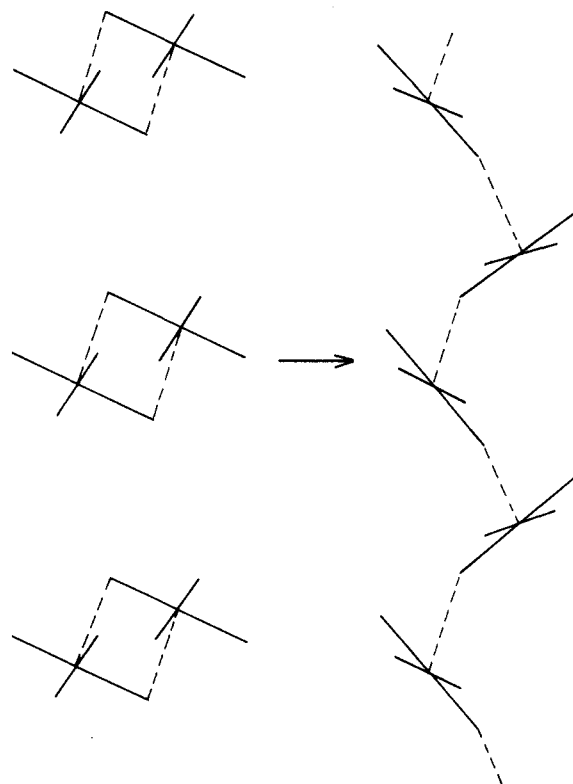


Figure 3. Hypothetical dimer \rightarrow uniform-chain transformation in $\text{Cu}_2\text{L}_2\text{Cl}_2 \cdot 2\text{CH}_3\text{OH}$. Full and dashed lines represent in-plane and long, out-of-plane bonds, respectively.

First-order phase transitions were observed in both compounds by means of variable-temperature capacitance experiments⁸ and were tentatively ascribed^{8,32} to a "freezing-in" of the expected free rotation of the *N*-methyl groups. Another interesting example is $(\text{CH}_3)_2\text{CHNH}_3\text{CuCl}_3$.¹⁴ This compound undergoes, upon decreasing the temperature, a phase transition from a structure containing ferromagnetically coupled, tribridged uniform chains of $(\text{CuCl}_3)_n^{n-}$ stoichiometry to a structure containing antiferromagnetically coupled, bibrridged alternating chains of $\text{Cu}_2\text{Cl}_6^{2-}$ dimers. One alternating-chain compound that appears to display enhanced superexchange along the chain (i.e. a structural transformation toward a uniform chain) has also been recently reported.¹⁵ The compound is $\text{Cu}(\text{2,5-dithiahexane})\text{Cl}_2$.

No abrupt change in temperature dependence of magnetic susceptibility signals the transition temperature in $\text{Cu}_2\text{L}_2\text{Cl}_2 \cdot 2\text{CH}_3\text{OH}$. We note that a similar difficulty was met, for example, with both $\text{Cu}(\text{4-methylpyridine})_2\text{Cl}_2$ and $\text{Cu}(\text{N-methylimidazole})_2\text{Br}_2$ and that, as mentioned above, it was overcome⁸ with use of variable-temperature capacitance experiments. These measurements will be undertaken when the necessary equipment becomes available to us.

Experimental and theoretical results concerning spin-Peierls transitions (which are driven by the spin subsystem and involve a progressive dimerization of an antiferromagnetically coupled uniform chain of spins below a transition temperature) have provided convincing evidence in support of the concept that the ground magnetic energy of a uniform chain decreases when the chain dimerizes.^{4,32-34} This leads us to conclude that the transformation in $\text{Cu}_2\text{L}_2\text{Cl}_2 \cdot 2\text{CH}_3\text{OH}$, which occurs in the opposite direction, is driven by a lattice structure instability in which the spin subsystem plays no important role.

Since the postulated dimer \rightarrow uniform-chain transformation in the present compound is without precedent, it is difficult to argue what structural changes are involved in the polymerization process. In speculation of this point it may be noted that, as

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schematically shown in Figure 3, a simple reorientation of the copper square-pyramidal moieties might suffice, in principle, to bring about the dimer \rightarrow uniform-chain transformation without any dramatic change in the geometry of the first coordination sphere around the metal centers or in the occupancy of space. An arrangement of dimers similar to that depicted in Figure 3 exists along the c axis of the title compound, and we also note that competition between neighboring copper atoms for bonding to apical chlorine atoms has been shown to be a relevant factor in determining the crystal chemistry of chloride-bridged chain compounds of copper(II).¹⁶⁻¹⁸ In any event, the precise nature of the low-temperature phase of the present compound and the mechanism or reason for the postulated transition are interesting problems that remain open to further studies, particularly low-temperature X-ray studies.

In conclusion, the results presented in this paper confirm the utility of synthesizing new halide-bridged copper(II) compounds with heterocyclic ligands as appropriate candidates for studying

the impact of structural phase transitions on the magnetic interactions.³⁵ As more of these types of systems are prepared and studied, it will hopefully be possible to provide some insight into the mechanisms that underlie the structural changes in them. This problem, of course, is also relevant to the family of distortion models typified by the spin-Peierls instability, i.e., those in which changes in lattice energy and changes in exchange energy are of comparable magnitude.

Registry No. $\text{Cu}_2\text{L}_2\text{Cl}_2 \cdot 2\text{CH}_3\text{OH}$, 120232-12-4; 8-aminoquinoline, 578-66-5; salicylaldehyde, 90-02-8.

Supplementary Material Available: Tables SI-SIII, listing angles and distances associated with the aromatic rings, thermal parameters, and the derived hydrogen positions (3 pages); a table of calculated and observed structure factors (11 pages). Ordering information is given on any current masthead page.

(35) See paper by L. J. de Jongh in ref 2a.

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Luminescence and Metal-Metal Interactions in Binuclear Gold(I) Compounds

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$[\text{Au}(\text{dppm})]_2(\text{BF}_4)_2$ is phosphorescent in solution ($\lambda_{\text{max}} = 593 \text{ nm}$, $\tau = 21 \mu\text{s}$, $\Phi = 0.31$). An SCF-X α -SW molecular orbital calculation carried out on the model compound $[\text{Au}(\text{H}_2\text{PCH}_2\text{PH}_2)]_2^{2+}$ found the Au-Au σ^* HOMO to have 78% Au character. Of this, 41% is from the 6s orbital and 41% is from the 5d $_z$ orbital. The metal-metal interactions are discussed. The 293-nm ($\epsilon = 21\,000 \text{ M}^{-1} \text{ cm}^{-1}$) absorption band is attributed to a $\sigma(p_z) \leftarrow \sigma^*(s, d_z)$ transition. The Au^I emissive state appears to be $^3A_u(\sigma^*)(\sigma)$ (C_{2h} symmetry). The binuclear Au^I compounds $[\text{Au}(\text{dppm})]_2\text{Cl}_2$, $[\text{Au}(\text{CH}_2)_2\text{PPh}_2]_2$, $[n\text{-Bu}_4\text{N}]_2[\text{Au}(\text{S}_2\text{C}=\text{C}(\text{CN})_2)]_2$, $[\text{Au}(\text{CH}_2\text{P}(\text{S})\text{Ph}_2)]_2$, and $[\text{Au}(\text{S}_2\text{CNEt}_2)]_2$ are luminescent in the solid state at room temperature with λ_{max} ranging from 465 to 593 nm and excited-state lifetimes ranging from 1 to 24 μs . $(\text{Ph}_3\text{PAu})_2(\text{S}_2\text{C}=\text{C}(\text{CN})_2)$ is luminescent at 77 K but not at room temperature. Mononuclear Ph_3PAuCl luminesces in the solid state ($\lambda_{\text{max}} = 491 \text{ nm}$, $\tau = 3 \mu\text{s}$).

Introduction

Absorption of light in what has been assigned as a metal-centered $p \leftarrow d$ transition leads to phosphorescence from the d¹⁰ compounds $\text{Pt}^0(\text{PPh}_3)_3$, $\text{Pd}^0(\text{PEt}_3)_3$, and $\text{Ni}^0(\text{P}(\text{O}-o\text{-tol})_3)_3$.^{1,2} Luminescence has also been observed from mononuclear d¹⁰ Cu^I, Ag^I, and Au^I arylphosphine compounds.³ For the gold compound the same $p \leftarrow d$ transition may be involved, since $\text{Au}(\text{PEt}_3)_2^+$ and $\text{Au}[\text{P}(\text{OCH}_2)_3\text{CEt}]_2^{+,4,5}$ which lack aryl groups, and $\text{Au}(\text{CH}_2\text{PEt}_3)_2^{+,4}$ containing only Au-C bonds, have absorption bands in the region 200-350 nm assignable to $p \leftarrow d$ transitions.

In binuclear compounds the p and d orbitals on the adjacent metal centers mix so that the $p \leftarrow d$ transition⁴ is replaced by $\sigma(p_z) \leftarrow \sigma^*(d_z)$ (z axis through the metal atoms).^{1,4,6} Phosphorescence from the binuclear d¹⁰-d¹⁰ compounds $\text{Pt}_2(\text{dppm})_3$ and $\text{Pd}_2(\text{dppm})_3$ ($\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$), in which the metal atoms are three-coordinate, is attributed to this transition,¹ as is phosphorescence from d⁸-d⁸ complexes, such^{6a} as $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{4-}$, in which the metals are four-coordinate. The lifetimes of the excited states resulting from these metal-centered transitions sometimes are long enough for bimolecular reactions to occur, such as light-induced oxidative addition of CH_2Cl_2 to $\text{Pd}_2(\text{dppm})_3$ to give $\text{Pd}_2(\mu\text{-CH}_2)(\text{dppm})_2(\text{Cl})_2$ and the reaction of aryl bromide^{6b} with $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{4-}$.

Emission also has been observed from the heterobimetallic gold(I) compound $\text{AuTl}[\text{CH}_2\text{P}(\text{S})\text{Ph}_2]_2$ in solution at room temperature.⁷ Neither the Au^I nor Tl^I precursor complexes are luminescent under similar conditions, suggesting that the emission

is a result of interactions between the metals. An understanding of the metal-metal interactions and luminescent properties of homobimetallic gold compounds serves as a starting point to develop an understanding of the luminescent properties of heterobimetallic systems containing closed-shell metal ions.

Since $[\text{Au}(\text{dppm})]_2^{2+}$ is found to be strongly luminescent in solution, an SCF-X α -SW molecular orbital study of the model compound $[\text{Au}(\text{H}_2\text{PCH}_2\text{PH}_2)]_2^{2+}$ in the chair conformation (C_{2h} point group) was undertaken to determine the nature of the orbitals involved. The suggestion that a bonding interaction between the metals in $[\text{Au}(\text{dppm})]_2^{2+}$ may occur by d_{z^2} - s - p_z orbital mixing⁸ was investigated. The Au^I-ligand bonding and other details of the X α calculation, the first to be performed on a binuclear gold compound, are reported in this study. X α calculations have been performed on the dinuclear d¹⁰ compounds $[\text{Cu}(\text{HNCHNH})]_2$ and $[\text{Ag}(\text{HNCHNH})]_2$, which are planar and show metal-ligand π bonding.⁹

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