$Nb_6I_{11}$,[43] $Ta_6Cl_{15}$,[44] and $Mo_6Cl_{12}$.[45] Such differences, however, are not common to all cluster compounds. For example, in $W_6Br_{16}$[46] there are no differences between the average W–Br bond lengths for inner and outer Br ligands, and in $[Zr_2I_9]^{3-}$,[47] where the $ZrI_6$ octahedra share faces, the differences are actually reversed. The overall average Re–P distances of 2.411 Å in $Re_2P_5$ and 2.421 Å in $Re_6P_{13}$ are close to the average Re–P distance of 2.402 Å in $ReP_4$[8] and within the range of Re–P distances found in many molecular inorganic compounds.[8,48]

The P–P distances cover the range from 2.095 to 2.265 Å in $Re_2P_5$ (2.142 to 2.291 in $Re_6P_{13}$). To our knowledge the P(3)–P(8) distance of 2.095 Å is the shortest P–P distance found in any transition-metal polyphosphide. Even shorter P–P distances are observed sometimes in molecular compounds where they can be rationalized with some double-bond character.[49]

Planar, nearly equilateral rhomboidal clusters of metal atoms were found before in $CsNb_4Cl_{11}$,[50] in $[Re_4(CO)_{16}]^{2-}$,[51,52] and in several heteronuclear molecular related compounds with clusters of the composition $T_2M_2$ (T = Mn, Re; M = Ga, In, Ge, Sn).[53,54] More examples are known for nonplanar "butterfly" clusters of four metal atoms. The reviews by King,[55] Vahrenkamp,[56] Lewis and Johnson,[57] and Tachikawa and Muetterties[58] give references to some ten clusters with such tetranuclear cores in molecular inorganic compounds. Simon[59] has pointed out that condensed butterfly clusters can be regarded as building elements in many solid-state compounds such as $Hf_3P_2$, $Nb_8P_5$, or $Mo_4P_3$. We wish to conclude that we too believe that the division in "solid-state" and "molecular" inorganic chemistry—caused by some differences in preparation and characterization methods and deepened by tradition—should be overcome at least as regards structural chemistry.[60]

**Acknowledgment.** We want to thank Dipl.-Chem. M. Möller and Dr. U. Flörke (Universität Dortmund) for the collection of the single-crystal diffractometer data and for electrical conductivity measurements. Professor R. Hoppe and Dr. G. Meyer (Universität Giessen) supported the magnetic measurements. We also acknowledge financial aid by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie.

**Registry No.** $Re_2P_5$, 80878-10-0.

**Supplementary Material Available:** Listings of structure factor amplitudes, anisotropic thermal parameters, and a Guinier powder pattern of $Re_2P_5$ (28 pages). Ordering information is given on any current masthead page.

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# Magnetic Properties and Molecular Structure of Copper(II) Complexes of Pyrazinecarboxylic Acid

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Several copper complexes of pyrazinecarboxylic acid (HL = $C_4H_3N_2COOH$) have been prepared. The crystal structures of $CuL_2$ and $CuL_2(H_2O)_2$ were determined from single-crystal X-ray diffraction using counter methods, and the magnetic properties of these complexes plus the complex $[Cu(HL)Cl_2]_2$ were studied over the temperature range 6–300 K with an alternating force magnetometer. $CuL_2(H_2O)_2$ consists of six coordinated (distorted octahedral) copper(II) ions with $L^-$ acting as a bidentate ligand and axially coordinated water molecules. $CuL_2$ is also a six-coordinate structure similiar to that of $CuL_2(H_2O)_2$ but with the axial positions now occupied by the carboxylate oxygens of a neighboring molecule to form a structural linear chain. The magnetic properties for $CuL_2$ and $CuL_2(H_2O)_2$ indicate weak ferromagnetic interactions are present. The magnetic data for $[Cu(HL)Cl_2]_2$ show that the chlorine bridged dimer is antiferromagnetically coupled ($g = 2.23$, $J/k = -8.79$ K). Crystal data for $CuL_2(H_2O)_2$: space group $P2_1/c$, $Z = 2$, $a = 5.438$ (1) Å, $b = 10.880$ (2) Å, $c = 10.385$ (2) Å, $\beta = 98.24$ (1)°, $V = 608.1$ Å$^3$, 1023 reflections. Crystal data for $CuL_2$: space group $P2_1/c$, $Z = 2$, $a = 5.0340$ (4) Å, $b = 15.3316$ (12) Å, $c = 7.0707$ (9) Å, $\beta = 106.627$ (9)°, $V = 523.3$ Å$^3$, 869 reflections.

## Introduction

Pyrazine is an excellent bridging ligand when coordinated to transition metals and has been extensively studied as an active ligand in the course of electron-transfer and magnetochemistry research.[2-12] Binuclear and polynuclear systems which have a bridging pathway composed of a conjugated bonding network are of interest to experimental magneto-

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chemists because this type of bridging ligand permits a study of the mechanism of magnetic coupling over extended distances. Carboxylate ligands as well as pyrazine ligands are equally capable of bridging and providing exchange pathways when paramagnetic metals are involved. By coordination of one oxygen atom to each metal, a three-atom bridge may be formed as in the binuclear complexes of Cu(II),[13-15] Cu(I),[16] Co(II),[17,18] Rh(II),[19,20] Cr(II),[21] Mo(II),[22,23] Pd(II),[24] Ru(II),[25] and Ni(II).[26,27] Magnetic exchange through single atom bridges has been much more thoroughly studied.[27] From these studies, it has been shown through empirical tabulations that the magnitude of the bridging angle correlates with the magnitude of the antiferromagnetic interaction for copper(II) complexes.[28]

In our laboratory, we have been studying the effects of substituted pyrazine ligands on the bonding and magnetic properties of some divalent transition-metal complexes.[29-31] In this work we have synthesized an unusual series of copper(II) complexes in which copper(II), when mixed with pyrazinecarboxylic acid (HL) under various experimental conditions, forms a dimer, a weakly coordinated one-dimensional chain, and a monomeric complex crystallizing in a hydrogen-bonded lattice with stronger hydrogen bonds along one dimension. The dimer complex has the formula $[Cu(HL)Cl]_2$, where HL = pyrazinecarboxylic acid ($C_4H_3N_2COOH$). The bridge is formed by two shared chlorine ligands,[29] and the complex exhibits antiferromagnetic behavior. The weakly coordinated linear chain complex has the formula $CuL_2$ with the bridge consisting of a three-atom carboxylate unit of the ligand. This complex exhibits weak ferromagnetic interactions. The third complex has the formula $CuL_2(H_2O)_2$. The axial water molecules are hydrogen bonded to the neighboring complexes in three dimensions but with a shorter hydrogen-bonded pathway along one dimension. The hydrogen-bonded complex also shows weak ferromagnetic behavior. We report on the X-ray crystal structures of $CuL_2$ and $CuL_2(H_2O)_2$ and the powder magnetic susceptibility measurements from 6 to 300 K for $CuL_2$, $CuL_2(H_2O)_2$, and $[Cu(HL)Cl_2]_2$.

**Table I.** Experimental Details for $[CuL_2]$ and $[CuL_2(H_2O)_2]$

| | $[Cu(C_5H_3N_2O_2)_2]$ | $[Cu(C_5H_3N_2O_2)_2(H_2O)_2]$ |
|---|---|---|
| $M_r$ of asymmetric unit | 186.63 | 204.65 |
| space group ($Z$) | $P2_1/c$ | $P2_1/c$ |
| extinctions | $h0l$ ($l = 2n + 1$<br>$0k0$ ($k = 2n + 1$) | $h0l$ ($l = 2n + 1$)<br>$0k0$ ($k = 2n + 1$) |
| cell constants | $a = 5.0340$ (4) Å,<br>$b = 15.3316$ (12)<br>$c = 7.0707$ (9) Å,<br>$\beta = 106.627$ (9)° | $a = 5.438$ (1) Å,<br>$b = 10.880$ (2) Å,<br>$c = 10.385$ (2) Å,<br>$\beta = 98.24$ (1)° |
| $V$, Å$^3$ | 523.3 | 608.1 |
| radiation | Cu K$\alpha$, $\lambda = 1.5405$ | Cu K$\alpha$, $\lambda = 1.5405$ Å |
| max $2\theta$, deg | 145 | 140 |
| no. of reflctns collected | 1148 | 1160 |
| no. of reflctns above $\sigma$ | 869 | 1023 |
| calcd density, g cm$^{-3}$ | 1.97 | 1.89 |
| measd density, g cm$^{-3}$ | 1.99 (1) (flotation in $CH_3I/CCl_4$) | 1.90 (1) |
| $R_F$ for all reflctns above $\sigma$ | 0.069 | 0.074 |

## Experimental Section

**Synthesis. Preparation of the Complexes $CuL_2$ and $CuL_2(H_2O)_2$, Where HL = Pyrazinecarboxylic Acid.** A 5-mmol sample of pyrazinecarboxylic acid was dissolved in approximately 150 mL of $H_2O$. A 5-mmol sample of hydrated copper(II) chloride was dissolved in 25 mL of $H_2O$. The solutions were mixed, and dark blue platelike crystals of $CuL_2$ suitable for X-ray analysis were deposited after standing overnight. Medium blue crystals of $CuL_2(H_2O)_2$ were deposited a few days later.

**Preparation of the Complex $[Cu(HL)Cl_2]_2$.** A 25-mmol sample of pyrazinecarboxylic acid was dissolved in 30 mL of concentrated hydrochloric acid. A 25-mmol sample of hydrated copper(II) chloride was dissolved in 40 mL of $H_2O$. The two solutions were mixed, and green platelike crystals were deposited overnight. For each of the experiments described in this report, the crystals used for X-ray and magnetic susceptibility studies were obtained from the same preparation.

**Crystal Structure Determination.** The structure determination of $[Cu(HL)Cl_2]_2$ has been reported previously.[29] Single crystals of $CuL_2$ and $CuL_2(H_2O)_2$ having no dimension greater than 0.35 mm were selected for X-ray analysis. The crystals were mounted on a General Electric XRD-490 fully automated diffractometer. Extinctions of $k$ odd for ($0k0$) and $l$ odd for ($h0l$) characterized the space group as $P2_1/c$ for both complexes.

In the case of $CuL_2$, lattice constants were determined by a least-squares fit of 70 carefully measured $2\theta$ values of $2\theta$ greater than 100° under fine conditions (1° takeoff angle and 0.05° slit). The resultant lattice constants and their estimated standard deviations (esd's) are listed in Table I. Three-dimensional intensity data were collected by the stationary-crystal, stationary-counter method using balanced nickel and cobalt filters with copper K$\alpha$ radiation.

Lattice constants for $CuL_2(H_2O)_2$ were determined by a least-squares fit of 26 carefully measured $2\theta$ values of the copper K$\alpha_1$ and K$\alpha_2$ doublet for reflections with $2\theta$ greater than 66°. The resultant lattice constants and their esd's are listed in Table I.

For both $CuL_2$ and $CuL_2(H_2O)_2$, measurement of the experimental density indicated that there were two molecules in the cell, and therefore the copper atom occupied special positions within the cell. With the copper atoms at 0, 0, 0 and 0, $^1/_2$, $^1/_2$, a Fourier map was phased and used to find the coordinates of the other nonhydrogen atoms. The structures were refined with a block-diagonal least-squares[32] program with isotropic temperatures factors and unit weights

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Table II. Final Least-Squares Coordinates with Estimated Standard Deviations for $CuL_2$ and $CuL_2(H_2O)_2$

| atom | x/a | y/b | z/c | atom | x/a | y/b | z/c |
|---|---|---|---|---|---|---|---|
| | | | A. $CuL_2(H_2O)_2$ | | | | |
| Cu | 1.0000 (0) | 0.5000 (0) | 0.5000 (0) | C5 | 0.6516 (14) | 0.8483 (6) | 0.5365 (7) |
| O8 | 1.2214 (9) | 0.5634 (4) | 0.3794 (4) | C6 | 0.7198 (13) | 0.7270 (6) | 0.5602 (6) |
| O9 | 1.2986 (11) | 0.7318 (4) | 0.2705 (5) | C7 | 1.1859 (12) | 0.6776 (5) | 0.3465 (6) |
| O10 | 0.6905 (9) | 0.4761 (4) | 0.3133 (5) | H3 | 1.0038 (0) | 0.9125 (0) | 0.3262 (0) |
| N1 | 0.8863 (10) | 0.6750 (5) | 0.4979 (5) | H5 | 0.5212 (0) | 0.8855 (0) | 0.5847 (0) |
| N4 | 0.7526 (13) | 0.9173 (5) | 0.4522 (6) | H6 | 0.6406 (0) | 0.6778 (0) | 0.6252 (0) |
| C2 | 0.9948 (12) | 0.7419 (5) | 0.4133 (6) | H10 | 0.8000 (0) | 0.5300 (0) | 0.2650 (0) |
| C3 | 0.9232 (14) | 0.8634 (6) | 0.3912 (7) | H101 | 0.5200 (0) | 0.5050 (0) | 0.2800 (0) |
| | | | B. $CuL_2$ | | | | |
| Cu | 1.0000 (0) | 0.0000 (0) | 0.0000 (0) | C5 | 0.3422 (15) | −0.2293 (5) | 0.3183 (11) |
| O8 | 0.3309 (9) | 0.0689 (3) | 0.1051 (7) | C6 | 0.1519 (13) | −0.1755 (4) | 0.1943 (10) |
| O9 | 0.7710 (9) | 0.0550 (3) | 0.2845 (8) | C7 | 0.5350 (14) | 0.0277 (4) | 0.2227 (10) |
| N1 | 0.2134 (11) | −0.0936 (3) | 0.1710 (8) | H3 | 0.8277 (**)[a] | −0.0972 (51) | 0.4685 (**) |
| N4 | 0.5916 (13) | −0.2017 (4) | 0.4253 (9) | H5 | 0.3038 (**) | −0.2955 (45) | 0.3355 (**) |
| C2 | 0.4683 (13) | −0.0641 (4) | 0.2713 (10) | H6 | −0.0314 (**) | −0.1924 (47) | 0.1425 (**) |
| C3 | 0.6507 (13) | −0.1182 (5) | 0.4014 (10) | | | | |

[a] The two asterisks refer to a standard deviation greater than 99.

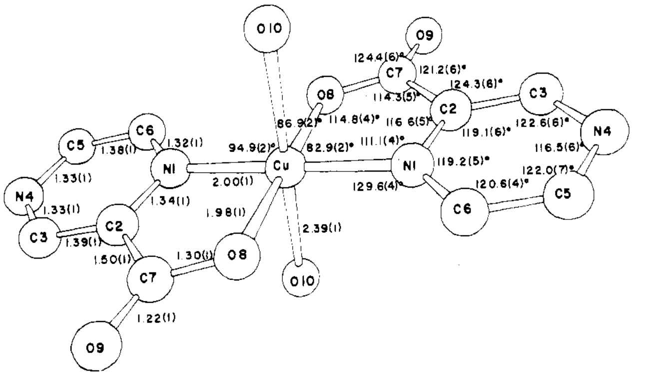

**Figure 1.** Schematic drawing of one molecular unit of $CuL_2(H_2O)_2$ including bonding distances and angles.

to a value of $R = 0.152$ for $CuL_2$ and $R = 0.157$ for $CuL_2(H_2O)_2$. A difference electron density map was calculated to find the hydrogen atom coordinates for both structures. Refinements continued with anisotropic temperature factors for the nonhydrogen atoms.

Addition of an anomalous dispersion correction in the copper scattering factor curve and further refinement of all nonspecial position coordinates and temperature factors led to a final reliability index of $R = 0.069$ for $CuL_2$. The coordinates and isotropic temperature factors for the $CuL_2(H_2O)_2$ hydrogen atoms were not allowed to vary. Continued refinement led to a final $R = 0.074$.

**Magnetic Measurements.** Magnetic susceptibilities were measured on an alternating force magnetometer (AFM)[31,33] from 6 to 300 K. The calibration of the instrument and measurement techniques are described elsewhere.[31]

## Results

The final least-squares coordinates with estimated standard deviations for each paramenter are summarized for $CuL_2(H_2O)_2$ and $CuL_2$ in Table II. Table IIC,D (supplementary material) contains the final least-squares coordinates and thermal parameters with estimated standard deviations for these complexes. The estimated standard deviations (esd's) for Cu–O and Cu–N distances are 0.005 Å and 0.2° for angles around the Cu atoms in both complexes. Figure 1 shows a schematic drawing of one molecular unit of $CuL_2(H_2O)_2$ while Figure 2 shows a schematic drawing of one molecular unit of $CuL_2$. Figure 3 shows three consecutive molecular units with the bridging distance and angles indicated for $CuL_2$.

Each pyrazinecarboxylic acid ligand has four possible coordination sties of which two, N1 and O8, involve coordination to the copper atom in $CuL_2(H_2O)_2$. The coordination of two water molecules to a single copper atom results in a monomeric unit with a distorted octahedral coordination sphere. The largest single contribution to the distortion is evidenced by the O8–Cu–N1 angle resulting from the formation of the five-membered ring required at the metal atom by the bidentate ligand (82.9 (2)° in $CuL_2(H_2O)_2$ and 84.5 (2)° in $CuL_2$).

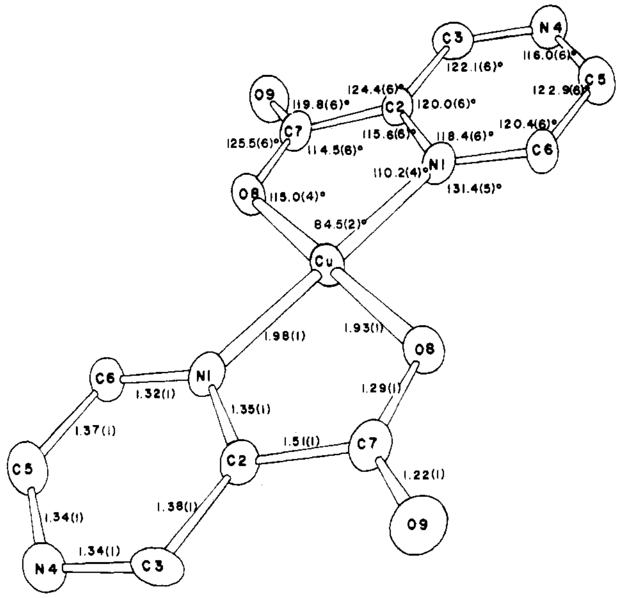

**Figure 2.** Schematic drawing of one molecular unit of $CuL_2$ including bonding distances and angles.

While three sites in the pyrazinecarboxylate ligand are coordinated in $CuL_2$, N1 and O8 are coordinated to one copper atom and O9 is weakly coordinated to an equivalent copper atom that is translated one unit cell in the x direction, thus forming a one-dimensional chain through a carboxylate bridge. There are two infinite chains in the unit cell, and each propogates along the (100) axis as shown in Figure 3. Although the Cu–Cu distance between the chains, 3.53 (1) Å, is less than the Cu–Cu distance within a single chain, 5.037 (1) Å, there is no apparent interchain-exchange pathway. There also are no nonhydrogen contact distances less than 3.403 (1) Å between the two chains, and, therefore, the observed magnetic exchange is expected to be solely intrachain exchange over the temperature region studied in this report. The orientation of neighboring chains of $CuL_2$ in the crystalline lattice is illustrated in Figure 4, which shows a packing diagram of $CuL_2$.

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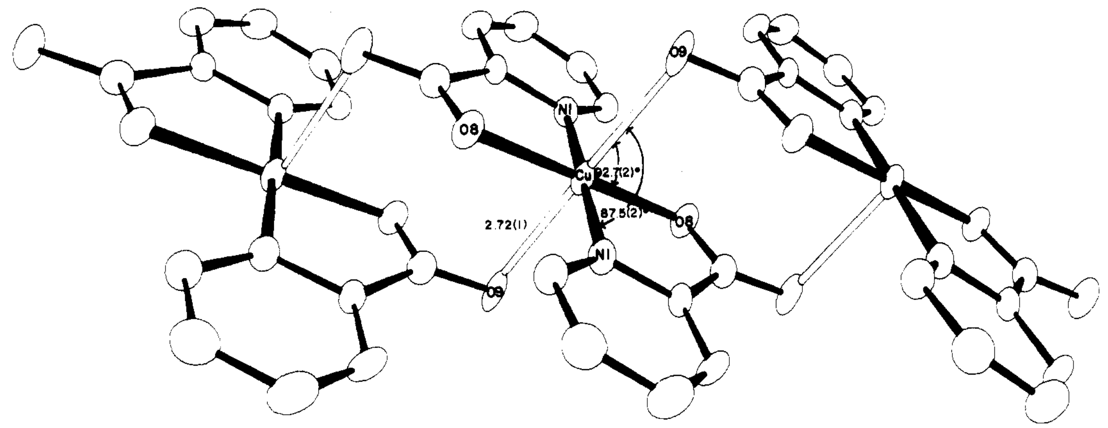

**Figure 3.** Schematic drawing of three consecutive molecular units of $CuL_2$ including bridging distances and angles.

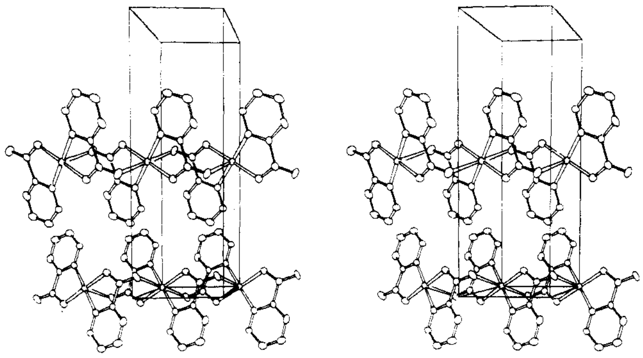

**Figure 4.** Stereoview packing diagram for $CuL_2$.

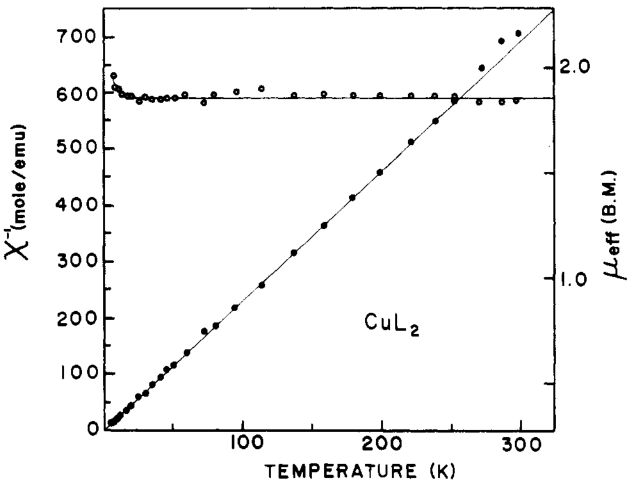

**Figure 5.** Inverse magnetic susceptibility and effective magnetic moment plotted as a function of temperature for $CuL_2$. The line through the points is the best fit as described in text.

The copper atom in $CuL_2$ is hexacoordinate. The axial coordination is due to a weak coordination of the copper ion with the carboxylate group of a neighboring molecule, thus forming a distorted octahedral coordination sphere. The coordination distances for N1 and O8 in both complexes are similar to those previously reported for copper(II) complexes whereas the Cu–O9 coordination distance of 2.72 (1) Å is considerably longer than the usual carbonyl oxygen to copper distance of 1.94 (1) Å.[34]

The average conjugated C–C bond distances (1.385 ± 0.005 and 1.375 ± 005 Å for $CuL_2(H_2O)_2$ and $CuL_2$, respectively) and the average conjugated C–N bond distances (1.330 and 1.335 ± 0.015 Å) compare favorably to the accepted literature

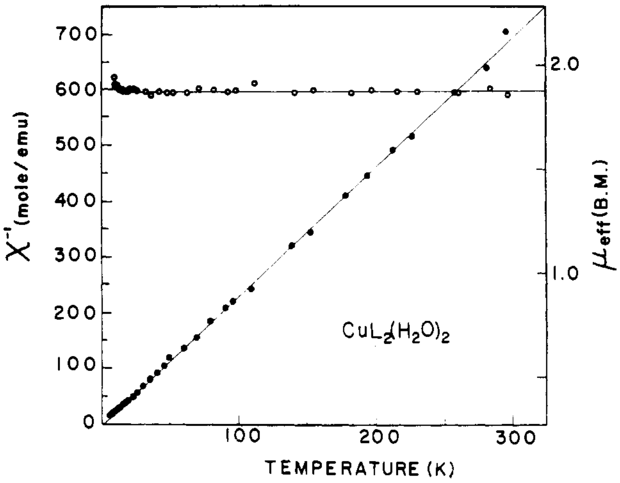

**Figure 6.** Inverse magnetic susceptibility and effective magnetic moment plotted as a function of temperature for $CuL_2(H_2O)_2$. The line through the points is the best fit as described in text.

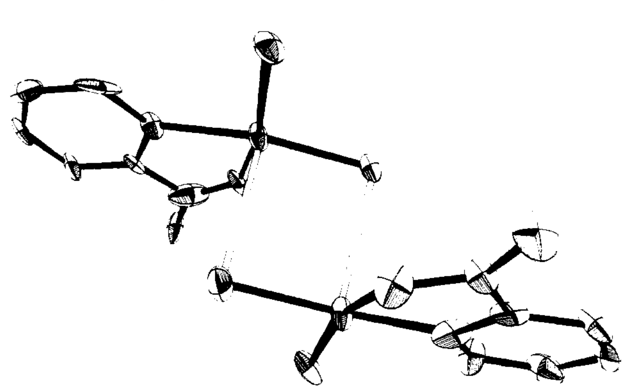

**Figure 7.** ORTEP diagram of a dimer unit of $[Cu(HL)Cl_2]_2$.

values[35] (1.396 and 1.334 Å). The averages of the NCC angles (121.1 ± 2.0 and 121.3 ± 1.6°) also compare favorably to the literature value of 122.4 ± 1°. The C7–O9 carbonyl bond distances (1.22 ± 0.02 and 1.22 ± 0.02 Å) compare favorably with the 1.215-Å[34] literature value while the C7–O8 distances (1.30 ± 0.02 and 1.29 ± 0.02 Å) are shorter than the comparable literature references with the usual distance of 1.322 Å.

Magnetic susceptibility measurements were carried out on these complexes in order to determine the extent of magnetic interactions which are expected to occur in these complexes. The magnetic data of polycrystalline samples of $CuL_2$, $CuL_2(H_2O)_2$, and $(Cu(HL)Cl_2)_2$ are tabulated in Table III

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(34) "Molecular Structures and Dimensions", Interatomic Distances, 1960–1965; Vol. A1.

(35) *Spec. Publ.—Chem. Soc.* **1958**, *No. 11*; *Suppl.* **1964**.

Table IV. Magnetic Parameters for $CuL_2$, $CuL_2(H_2O)_2$, and $[Cu(HL)Cl_2]_2$

| compd | $g$ | $\Theta$, K | $J/k$, K | model |
|---|---|---|---|---|
| $CuL_2$ | 2.11 ± 0.01 | 0.59 ± 0.02 | | $S = {}^1/_2$, Curie–Weiss |
| $CuL_2$ | 2.115 ± 0.010 | | 0.60 ± 0.02 | $S = {}^1/_2$, Heisenberg chain |
| $CuL_2(H_2O)_2$ | 2.15 ± 0.01 | 0.30 ± 0.02 | | $S = {}^1/_2$, Curie–Weiss |
| $CuL_2(H_2O)_2$ | 2.146 ± 0.010 | | 0.33 ± 0.02 | $S = {}^1/_2$, Heisenberg chain |
| $[Cu(HL)Cl_2]_2$ | 2.23 ± 0.01 | | −8.79 ± 0.05 | $S = {}^1/_2$, Dimer |

(supplementary material) and are plotted in Figures 5–7. Figures 5 and 6 are plotted as inverse susceptibility and effective magnetic moment as a function of temperature. Since the inverse susceptibility plot is linear as a function of temperature, the Curie–Weiss Law (eq 1) was used in fits of the data of these complexes.

$$\chi = Ng^2\mu_B{}^2S(S+1)/3k(T-\Theta) \qquad (1)$$

The lines through the inverse susceptibility data points in Figures 5 and 6 are the Curie–Weiss fits of the data with $S = {}^1/_2$ for copper(II). The results of the fit are shown in Table IV. The increase of the effective magnetic moment at low temperatures and the positive value of the Weiss constant for both $CuL_2$ and $CuL_2(H_2O)_2$ are indicative of ferromagnetic coupling along the structural linear chain. The molecular field exchange constant may be obtained from the values of theta extrapolated for the high-temperature regions of the data in the Curie–Weiss fit.[33] The molecular field value of $J/k$ for an $S = {}^1/_2$ linear chain is equal to the Weiss constant.

There is no exact solution to the Van Vleck equation for a one-dimensional magnetic chain, however, the series expansion for the $S = {}^1/_2$ Heisenberg ferromagnetic linear chain has been calculated by Baker et al.[36] The magnetic data for both $CuL_2$ (structural linear chain) and $CuL_2(H_2O)_2$ (hydrogen-bonded linear chain, vide infra) were fit to Baker's series expansion, and the result of this fit is shown as the smooth curve through the effective magnetic moment data in Figures 5 and 6.

The use of the linear-chain model to fit these data is very tentative. While both Curie–Weiss and the linear-chain fits are consistent with ferromagnetic interactions, the interaction parameters are very small and the moment curve shows an increase at only the lowest measured temperatures. It will be necessary to analyze the magnetic properties of these complexes at much lower temperatures if the appropriate magnetic models are to be assigned with any certainty.

$[Cu(HL)Cl_2]_2$ crystallizes in space group $P2_1/c$ and has the dimer structure illustrated in Figure 7. The details of this structure are reported elsewhere.[29] Figure 8 is a plot of the molar susceptibility which is indicative of strong antiferromagnetic coupling within the structural dimer of $[Cu(HL)Cl_2]_2$.

For a molecule with two interacting paramagnetic centers, the Heisenberg–Dirac–Van Vleck exchange Hamiltonian is written as eq 2. Substitution of this operator into the Van Vleck equation with $S_1 = S_2 = {}^1/_2$ for a copper(II) basis set yields the Bleaney–Bowers equation[37] for the magnetic susceptibility:

$$\mathcal{H} = -2JS_1 \cdot S_2 \qquad (2)$$

$$\chi = \frac{Ng^2\mu_B{}^2}{kT}\,\frac{2e^x}{1+3e^x} \qquad (3)$$

where $x = -2J/kT$. The line through the points in Figure 8 is the Bleaney–Bowers fit for the dimer susceptibility with the parameters listed in Table IV.

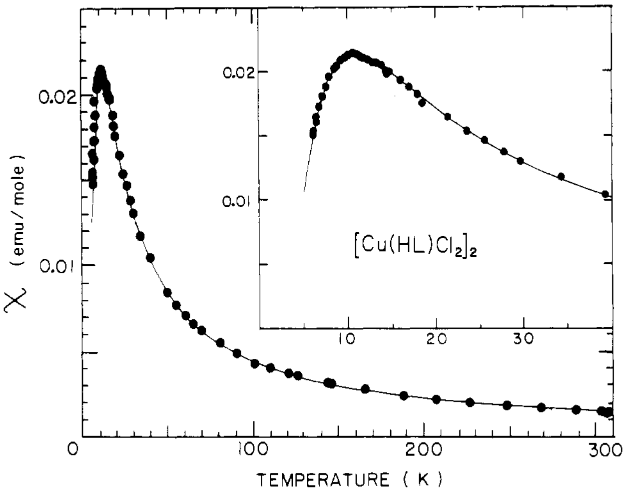

Figure 8. Magnetic susceptibility plotted as a function of temperature for $[Cu(HL)Cl_2]_2$. The curve through the points is the best fit of the data to the copper(II) dimer equation.

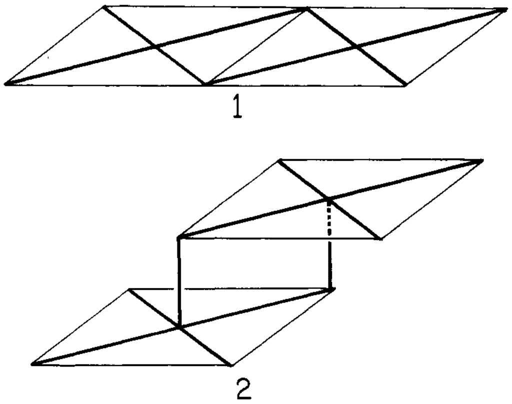

Figure 9. Schematic diagram illustrating two types of bridging geometries common for copper(II) ions: (1) coplanar bridge and (2) perpendicular plane bridge.

## Discussion

Copper(II) is well-known to distort from octahedral symmetry due to Jahn–Teller forces and to form tetragonally distorted octahedral six-coordinate complexes as well as square-planar four-coordinate and square-pyramidal five-coordinate complexes. As a result of these structures, two types of bridging geometries are possible for doubly bridged centrosymmetric copper(II) ions, as illustrated in Figure 9. These bridging geometries are coplanar bridging for four-, five-, and six-coordination (1) and perpendicular plane bridging for five- and six-coordination (2). A linear correlation between magnetic coupling and the angle of the bridge has been demonstrated by empirical tabulation of the structural and magnetic parameters of complexes of type 1.[28] Recent empirical tabulations by Hatfield et al.[38,39] indicate that complexes of type

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[36] Baker, G. A., Jr.; Rushbrooke, G. S.; Gilbert, H. E. *Phys. Rev. A* **1964**, *135*, 1272.

[37] Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London, Ser. A* **1952**, *214*, 451.

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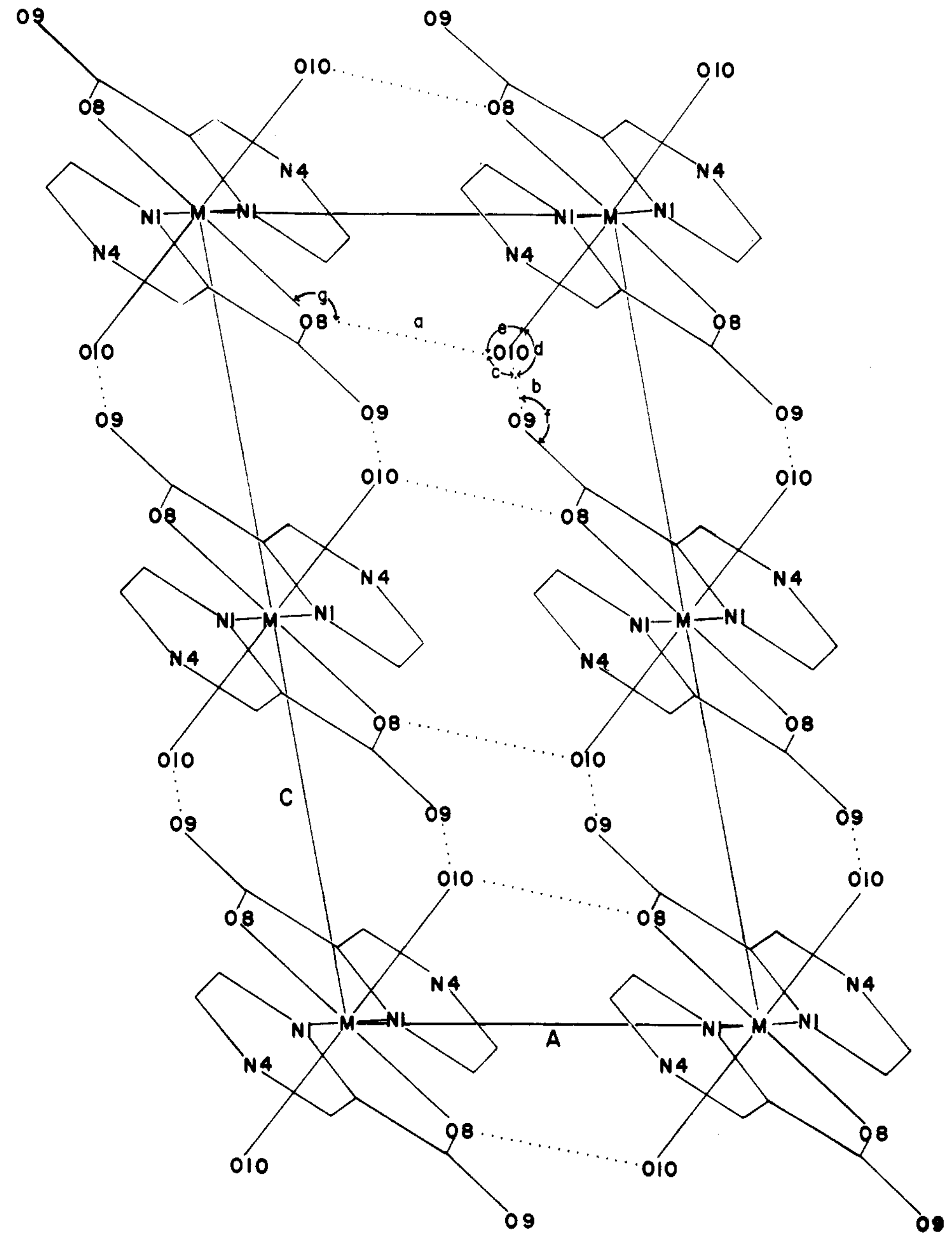

**Figure 10.** Unit cell projection on to the (*h*0*l*) plane of $CuL_2(H_2O)_2$ including hydrogen bonded distances and angles indicated in Table V.

2 (and possibly those of type 1 as well) appear to require a distance parameter in addition to the simple angular dependence. This observation is a result of their attempts to reconcile the magnetic exchange parameters and bridging geometries of an expanded set of complexes.

Each of the complexes reported here can be grouped into the second bridging category, illustrated in Figure 9. The magnetic exchange in $[Cu(HL)Cl_2]_2$ is propagated through a single atom bridge, while $CuL_2$ has an extended three-atom bridge and $CuL_2(H_2O)_2$ bridging involves hydrogen bonding. The dimer $[Cu(HL)Cl_2]_2$ has a perpendicular plane single-atom bridge which results in very strong antiferromagnetic coupling. In this complex, the average bridging angle (Cu–Cl–Cu) is 87.3° and the internuclear copper–copper distance is 3.547(4) Å. The second complex, $CuL_2$, is a perpendicular plane bridging complex with a direct three-atom carboxylate bridge which forms a linear chain along the *a* axis. There are no apparent structural interchain interactions in this complex, and the result is a fairly isolated one-dimensional unit in the lattice. The Cu–O9-C7 bridging angle is 101.8 (5)°, and the entire pyrazine ligand is essentially planar. The copper–copper distance within the chain is 5.037 (1) Å.

Table V. Hydrogen-Bonded Interaction Distances (Å) and Angles (Deg) for $CuL_2(H_2O)_2$[a]

| | | | |
|---|---|---|---|
| $a = 2.90$ (1) | | $b = 2.80$ (1) | |
| O10-H10 | 1.05 (1) | O8-H10 | 1.88 (1) |
| O10-H10 | 1.02 (1) | O9-H10′ | 1.86 (1) |
| $c = 116.4$ (3) | | $f = 134.1$ (5) | |
| $d = 108.1$ (3) | | $g = 132.2$ (2) | |
| $e = 108.3$ (4) | | | |
| H10-O10-H10 | 115.6 (3) | O9-H10′-O10 | 152.2 (3) |
| O8-H10-O10 | 161.1 (4) | | |

[a] See Figure 10 for numbering scheme.

The third complex $CuL_2(H_2O)_2$ involves a fairly extensive hydrogen-bonding network. This is illustrated schematically in Figure 10. There are, however, two distinct types of hydrogen bonds. The shorter H-bond pathway involves O10- - -O8 hydrogen bonding and a simple Cu–OH···O–Cu bridge. This pathway results in a one-dimensional chain along the *a* axis. The other pathway consists of O10- - -O9 contacts along

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(39) Hatfield, W. E., paper presented at the American Chemical Society Mid-Atlantic Regional Meeting in Washington, D.C., Jan 1981; see Abstracts, No. 221.

(011) and (0$\bar{1}$1) to complete the three-dimensional interaction. The secondary hydrogen-bonded contacts involve a five-atom rather than a three-atom bridge and are expected to have a smaller contribution to the overall magnetic exchange. These interaction distances and angles as well as other pertinent hydrogen-bonding distances and angles appear in Table V.

The nature of magnetic interactions propagated over extended distances has been an area of study and speculation over the past few years.[40–43] The research of Hendrickson et al. indicate that there is no direct general relationship between the separation of the magnetic centers and the magnitude of the magnetic coupling.[41–43] More recently, Hendrickson, Stucky, et al. have also shown that saturated carbons as well as conjugated pathways are capable of propagating magnetic exchange.[44–46] They observe magnetic coupling between magnetic centers separated by several angstroms and propagated over pathways which involve saturation carbons.[44] However, the efficiency of a given pathway appears to be stronger when there is a fully conjugated pathway in the bridging skeleton.

The copper(II) complexes of pyrazinecarboxylate reported here, and a previously reported copper(II) complex of pyrazinedicarboxylate,[31] are additional examples of magnetic exchange propagated over extended distances. Moreover, these complexes show that ferromagnetic interactions may be propagated over extended distances. Lower temperature studies must be completed before the nature of the magnetic interactions in the lattice-coupled complexes can be unambiguously determined.

**Registry No.** $CuL_2$, 33135-89-6; $CuL_2(H_2O)_2$, 74172-03-5; $[Cu(HL)Cl_2]_2$, 79900-51-9.

**Supplementary Material Available:** Listings of final least-squares coordinates with thermal parameters for $CuL_2$ and $CuL_2(H_2O)_2$ (Table IIC,D), magnetic data from 6 to 300 K for $CuL_2$, $CuL_2(H_2O)_2$, and $[Cu(HL)Cl_2]_2$ (Table III), and observed and calculated structure factor amplitudes for $CuL_2$ and $CuL_2(H_2O)_2$ (17 pages). Ordering information is given on any current masthead page.

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# Preparation and Structural Characterization of Dipalladium(II) Tetrakis(6-methyl-2-oxypyridine), $[Pd_2(mhp)_4]$

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Palladium(II) acetate reacts with sodium 6-methyl-2-oxypyridine, Na(mhp), in $CH_2Cl_2$ to give a material of empirical formula $Na_2Pd(mhp)_3(O_2CCH_3)$. Subsequent treatment of this material with methanol produces the dimeric complex $[Pd_2(mhp)_4]$. The dimer crystallizes in the space group *Pbca*, with $a = 15.625$ (2) Å, $b = 16.126$ (2) Å, $c = 18.831$ (2) Å, and $Z = 8$. Refinement, based on 3243 unique diffractometer data, gave $R = 0.054$. Four mhp ligands bridge a pair of palladium(II) atoms, which are separated by 2.546 (1) Å. The properties of this molecule are discussed with respect to those of other $[M_2(mhp)_4]$ complexes and the nature of the Pd(II)–Pd(II) interaction. $[Pd_2(mhp)_4]$ is considered to possess no net direct formal metal–metal bond.

## Introduction

Complexes of the type $[M_2(mhp)_4]$, where M = Cr, Mo, W,[2] Ru,[3] or Rh[4,5] and Hmhp = 6-methyl-2-hydroxypyridine, have been prepared and structurally characterized in the last few years. These complexes are of particular interest since they contain metal–metal bonds that are among the shortest observed for each metal. The molecules have approximate $D_{2d}$ symmetry, with M–O and M–N bonds arranged trans to their own kind so that each metal atom is bonded to two oxygen and two nitrogen atoms as well as to the other metal atom. The positions of the two methyl groups at each end of the metal–metal bond effectively prevent the binding of additional axial ligands to the metal atoms.

Recently, we reported that, in the case of a dirhodium(II) center, it is possible for *three* mhp ligands to have their nitrogen atoms attached to one rhodium atom, with only *one* nitrogen atom bonded to the other rhodium atom.[6] A twist distortion in the ligand arrangement about the Rh–Rh bond reduces the steric interactions of the three methyl groups at one end of the molecule and, simultaneously, allows one axial ligand to bind at the other end. We found that, in two such cases, mhp itself can act as the axial ligand: in $[Rh_2(mhp)_4(Hmhp)]\cdot 0.5C_7H_8$, a fifth mhp ligand, protonated at nitrogen, is attached through its oxygen atom; in $[(Rh_2(mhp)_4)_2]\cdot 2CH_2Cl_2$, two dimeric units are linked together, one bridging mhp ligand of each unit being also axially bound to the other unit through its oxygen atom. A similar 3:1 arrangement of mhp ligands

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