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Magnetic Properties and Molecular Structure of Copper(II) Complexes of 2,3-Pyrazinedicarboxamide

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The synthesis, crystal structures, and magnetic properties of several copper(II) complexes of 2,3-pyrazinedicarboxamide [L = $C_4H_2N_2(CONH_2)_2$] are reported. The crystal structures of $CuL_2(OH)_2 \cdot 2H_2O$ and $[CuLCl_2]_2$ were determined from single crystal x-ray diffraction using counter methods, and the magnetic susceptibility of these complexes plus the complex $CuL_2(ClO_4)_2$ were studied over the temperature range 6–300 K. $CuL_2(OH)_2 \cdot 2H_2O$ crystallizes as a monomeric complex with hydrogen bonding between the uncoordinated water molecules and the pyrazine carboxamide groups. $[CuLCl_2]_2$ crystallizes as a dimeric complex with an inversion center. The $CuLCl_2$ coordination sphere is square planar. The dimer is formed by two bridging chlorines to form a five coordinate copper(II) unit. The magnetic properties of $CuL_2(OH)_2 \cdot 2H_2O$ and $CuL_2(H_2O)_2$ are consistent with simple Curie Law. The magnetic susceptibility for the chlorine bridged dimer $[CuLCl_2]_2$ exhibits antiferromagnetic coupling ($g = 2.11$, $J = -11.5$ cm^{-1}). Crystal data for $CuL_2(OH)_2 \cdot 2H_2O$: space group $P2_1/c$, $a = 9.733(1)$, $b = 7.928(2)$, $c = 14.848(2)$ Å, $\beta = 123.51(1)°$, $z = 2$, $d_{calc} = 1.76$ g/cm^3, $d_{obs} = 1.78 \pm 0.1$ g/cm^3, $R = 0.079$ for 1125 reflections; crystal data for $[CuLCl_2]_2$: space group $P2_1/c$, $a = 6.327(1)$ Å, $b = 19.910(5)$ Å, $c = 7.572(2)$ Å, $\beta = 95.86(2)°$, $z = 2$, $d_{calc} = 2.10$ g/cm^3, $d_{obs} = 2.10 \pm 0.01$ g/cm^3, $R = 0.056$ for 840 reflections.

Introduction

Previous reports of cobalt(II) [1], copper(II) [2–5], and iron(II) [5] complexes of pyrazinecarboxylic acids (*1*, *2*) have shown a variety of structural and magnetic properties. The metal bridging capabilities of pyrazine are well documented and studies of pyrazine bridged complexes have shown pyrazine to be an active bridging ligand in the enhancement of electron transfer processes [6–12] as well as magnetic exchange [13–17]. We have been studying the properties of substituted pyrazine ligands with respect to the bonding and magnetism of divalent transition metal complexes. Substituted pyrazine may act as a chelating ligand bridging two metals [2, 18, 19] or as a non-bridging chelate [1, 3–5]. When the substituted pyrazine ligand (*e.g.*, pyrazinecarboxylic acid, *1*, 2,3-pyrazinedicarboxylic acid, *2*, or 2,3-pyrazinedicarboxamide, *3*) is a non-bridging chelate, there are often significant intermolecular contacts through the uncoordinated functional groups on the pyrazine ring which result in magnetic interactions between paramagnetic metal centers [4, 5]. Also, when the complexes of copper(II) chloride are prepared in acidic solutions, the substituted pyrazine ligands show a propensity for dimer formation with the complexes having the general formula $[CuLCl_2]_2$ [3].

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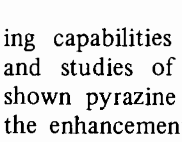

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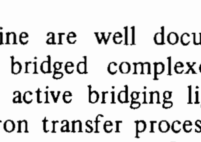

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In this report we extend our study of the structures, bonding, and magnetism of substituted pyrazine ligands to the copper(II) complexes of 2,3-pyrazinedicarboxamide (*3*). We report on the x-ray crystal structures of $[CuLCl_2]_2$ and $CuL_2(OH)_2 \cdot 2H_2O$ and the powder magnetic susceptibility measurements from 6–300 K for $[CuLCl_2]_2$,

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$CuL_2(OH)_2 \cdot 2H_2O$ and $CuL_2(ClO_4)_2$, where L is 2,3-pyrazinedicarboxamide.

Experimental

Syntheses

Preparation of [$CuLCl_2$]$_2$

Equal molar amounts of hydrated copper(II) chloride and 2,3-pyrazinedicarboxamide (obtained from Pfaltz and Bauer, Inc. and used as received) were dissolved in 6N hydrochloric acid solutions. The two solutions were then mixed and allowed to stand in a beaker covered with a watch glass. After several days, green crystals of $[CuLCl_2]_2$ were deposited.

Preparation of $CuL_2(OH)_2 \cdot 2H_2O$

A 10 mmol sample of 2,3-pyrazinedicarboxamide was dissolved in 150 ml of distilled water and 10 ml of 0.1 N NaOH. A 10 mmol sample of hydrated copper(II) chloride was dissolved in 25 ml of distilled water. The two solutions were mixed and medium blue crystals of $CuL_2(OH)_2 \cdot 2H_2O$ were deposited a few days later.

Preparation of $CuL_2(ClO_4)_2$

A 0.06 mol sample of 2,3-pyrazinedicarboxamide was dissolved in approximately 100 ml of distilled water and 2 ml of concentrated perchloric acid. A 0.06 mol sample of copper(II) perchlorate was dissolved in 5 ml of distilled water. The 2,3-pyrazinedicarboxamide/perchloric acid solution was filtered and allowed to drip into the copper(II) perchlorate solution. Dark blue crystals precipitated immediately.

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 $CuL_2(ClO_4)_2$ has been reported previously and has the monomeric structure illustrated in Fig. 1 [20]. A single crystal of $CuL_2(OH)_2 \cdot 2H_2O$ having no dimension greater than 0.35 mm and a single crystal of $[CuLCl_2]_2$ with approximate dimensions of 0.22 mm × 0.20 mm × 0.08 mm were mounted on a General Electric XRD-5 diffractometer. Systematic extinctions of (OkO), k = 2n + 1 and (hOl), h = 2n + 1 and successful refinement of each structure verified the space group choices as $P2_1/c$.

Lattice constants for $[CuLCl_2]_2$ were determined by a least squares fit of 40 carefully measured 2θ values of the copper $K\alpha_1$ and $K\alpha_2$ doublet for reflections with 2θ greater than 60°. 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. The data were corrected for absorption as a function of ϕ and background as a function of 2θ.

The structure was determined by the usual heavy atom techniques [21]. Six hydrogen atom coordinates were obtained from a difference Fourier map and not allowed to vary in further least squares refinements. Addition of an anomalous dispersion correction in the copper and chlorine scattering factor curves and further refinement of all non-hydrogen atoms led to a final R = 5.6%.

Lattice constants for $CuL_2(OH)_2 \cdot 2H_2O$ were determined by a least squares fit of 13 carefully measured 2θ values of 2θ greater than 54° under fine conditions (2° take off angle and 0.05° slit). The resultant lattice constants and their esds' are listed in Table I.

The measurement of the experimental density for $CuL_2(OH)_2 \cdot 2H_2O$ indicated that there were two molecules in the unit 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 for the other 14 non-hydrogen atoms. The structure was refined using a block-diagonal least-squares program with isotropic temperature factors. A difference electron density map was calculated to find the hydrogen atom coordinates. Refinements continued using anisotropic temperature factors for the non-hydrogen atoms and $1/\sigma^2$ weights*. Addition of an anomalous dispersion correction in the copper scattering factor curve and further refinement of all non-special position and non-hydrogen coordinates and thermal parameters led to a final R = 7.9%.

Magnetic Measurements

Magnetic susceptibilities were measured on an alternating force magnetometer (AFM) [22, 23] from 6 to 300 K. The calibration of the instrument and measurement techniques are described elsewhere [2].

Results

The final least-squares coordinates with esd's for each parameter are summarized for $[CuLCl_2]_2$ and $CuL_2(OH)_2 \cdot 2H_2O$ in Table II. Tables IIC and IID (supplementary material) contain the final least-squares coordinates and thermal parameters

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*σ is based entirely on counting statistics. In both structures reflections were considered statistically significant by the criterion $[I_{Ni} - 2\sigma(I_{Ni})] - [I_{Co} - 2\sigma(I_{Co})] > 500$.

TABLE I. Experimental Details for $[CuLCl_2]_2$ and $CuL_2(OH)_2 \cdot 2H_2O$.

	$[CuLCl_2]_2$	$CuL_2(OH)_2 \cdot 2H_2O$
MW of asymmetric unit	300.49	465.65
Space group	$P2_1/c$	$P2_1/c$
Cell constants	a = 6.327(1) Å b = 19.910(5) Å c = 7.572(2) Å β = 95.86(2)°	a = 9.733(1) Å b = 7.298(2) Å c = 14.848(2) Å β = 123.57(1)°
$V(Å^3)$	949.0	878.7
Radiation	CuK_α, =1.5405 Å	CuK_α, =1.5405 Å
Max. 2θ, (deg.)	120	140
Number of reflections collected	1408	1584
Number of reflections above	840 (60%)	1125 (71%)
Calcd density g/cm^3	2.10	1.76
Measured density	2.10 ± 0.01 (by flotation in CCl_4/CH_3I)	1.78 ± 0.01 (by flotation in CH_3I/C_6H_5Cl) C_6H_5Cl)
R for all reflections above	5.6%	7.9%

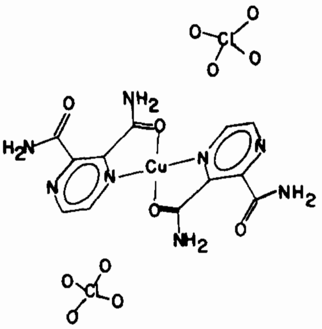

Fig. 1. Molecular structure of $CuL_2(ClO_4)_2$.

with esd's for these complexes. Figure 2 shows a schematic drawing of one molecular unit of $[CuLCl_2]_2$ while Fig. 3 shows a schematic drawing of one molecular unit of $CuL_2(OH)_2 \cdot 2H_2O$.

The 2,3-pyrazinedicarboxamide ligand has six possible coordinating sites of which two, N1 and O8, involve coordination to the copper atom in $CuLCl_2$. The coordination sphere about the metal atom is distorted square pyramid (4 + 1) resulting from the formation of two single chlorine atom bridges between metal atoms forming a dimer related by an inversion center. The distortion in the coordination plane is primarily due to constraints imposed by the bidentate ligand resulting in the formation of a five membered ring at the copper atom (N1–Cu–O8 78.6(3)°). There are no apparent intermolecular contacts in the unit cell; however, an intramolecular hydrogen bond exists between the uncoordinated oxygen, O11, and the nitrogen atom, N9, from the adjacent carboxamide group of the ligand (2.63(1) Å). Additional structural parameters for $[CuLCl_2]_2$ are listed in Table III.

Two sites, N1 and N9, in the 2,3-pyrazinedicarboxamide ligand are coordinated to the copper atom in $CuL_2(OH)_2 \cdot 2H_2O$. The additional coordination of two hydroxide ions to a single copper atom results in a monomeric unit with a tetragonally distorted octahedral coordination sphere. The distortion in the coordination plane is evidenced by the N9–Cu–N1 angle (81.8(3)°) resulting from the formation of the five membered ring required at the metal atom by the bidentate ligand. There are two uncoordinated water molecules in the unit cell that are hydrogen bonded to the carboxamide oxygen, O8. Additionally, there is a two dimensional intermolecular hydrogen bond network forming sheets of monomers parallel to the $(\bar{1}01)$ plane. Another hydrogen bond exists between the coordinated water oxygen, O13, and the carboxamide oxygen, O11, of the uncoordinated carboxamide group (2.81(1) Å) in an adjacent molecule. Since each monomeric unit has two O11 atoms and two O13 atoms each molecule is involved in four intermolecular hydrogen bonds as shown in the stereo view in Fig. 4.

It is interesting to note the differences in the coordination of the 2,3-pyrazinedicarboxamide ligand to copper(II) in these complexes. In $CuLCl_2$ and $CuL_2(ClO_4)_2$, the carboxamide groups are coordinated to the copper ions through the oxygen atoms (O8 in $CuLCl_2$) while in $CuL_2(OH)_2 \cdot 2H_2O$, the carboxamide group is coordinated to the copper atom through the nitrogen atom, N9. Another difference between the two complexes is in the presence of an intramolecular hydrogen bond in $CuLCl_2$ and

TABLE II. Fractional Atomic Coordinates.

$[CuLCl_2]_2$ Atom	x	y	z
Cu	0.9615(3)	−0.0030(1)	0.2410(2)
CL1	1.2608(5)	−0.0174(2)	0.1121(4)
CL2	0.8955(5)	−0.1115(2)	0.2823(4)
O8	0.7363(12)	0.0188(4)	0.3927(11)
O11	0.4538(13)	0.2251(4)	0.4197(11)
N1	0.9656(14)	0.0986(5)	0.2356(12)
N4	0.9245(15)	0.2343(5)	0.2083(13)
N9	0.5122(16)	0.0960(5)	0.4757(13)
N12	0.6461(17)	0.3110(5)	0.3309(14)
C2	0.8024(18)	0.1300(6)	0.3064(15)
C3	0.7860(18)	0.2001(6)	0.2911(15)
C5	1.0822(19)	0.2039(6)	0.1457(17)
C6	1.0999(19)	0.1363(7)	0.1544(16)
C7	0.6782(18)	0.0810(6)	0.4001(15)
C10	0.6131(18)	0.2447(6)	0.3570(15)
H5	1.1256(0)	0.2321(0)	0.0833(0)
H6	1.2220(0)	0.1115(0)	0.0972(0)
H9	0.4800(0)	0.1400(0)	0.4800(0)
H9′	0.4200(0)	0.0600(0)	0.5300(0)
H12	0.5200(0)	0.3400(0)	0.3000(0)
H12′	0.7600(0)	0.3350(0)	0.3700(0)
$CuL_2(OH_2 \cdot 2H_2O$			
Cu	1.0000(0)	0.5000(0)	0.5000(0)
O8	0.7984(6)	0.4045(8)	0.1883(4)
O11	0.4410(6)	0.1787(8)	0.0654(4)
O13	1.1457(6)	0.2062(8)	0.5391(4)
O14	0.9715(7)	−0.0165(8)	0.3540(4)
N1	0.7925(7)	0.3512(8)	0.4209(4)
N4	0.5331(7)	0.1184(9)	0.2917(5)
N9	0.9636(6)	0.5066(8)	0.3568(4)
N12	0.6660(8)	0.0124(9)	0.1445(5)
C2	0.7487(9)	0.3133(10)	0.3206(5)
C3	0.6182(9)	0.1961(10)	0.2562(5)
C5	0.5772(10)	0.1600(11)	0.3911(6)
C6	0.7148(9)	0.2685(10)	0.4597(5)
C7	0.8459(10)	0.4155(11)	0.2860(6)
C10	0.5696(9)	0.1299(11)	0.1455(6)
H5	0.5035(0)	0.1089(0)	0.4206(0)
H6	0.7485(0)	0.3059(0)	0.5361(0)
H9	1.0735(0)	0.4600(0)	0.3677(0)
H9′	0.9600(0)	0.6400(0)	0.3400(0)
H12	0.7200(0)	0.0300(0)	0.1050(0)
H12′	0.6944(0)	−0.1119(0)	0.1850(0)
H13	0.2400(0)	0.2500(0)	0.5350(0)
H14	0.9750(0)	0.1200(0)	0.3600(0)
H14′	1.0400(0)	−0.0500(0)	0.3250(0)

TABLE III. Additional Structural Parameters for $[CuLCl_2]_2$.

Cu–Cu′	3.733(1) Å
Cl1–Cu–O8	168.3(3)°
Cl1–Cu–N1	96.1(3)°
Cl1–Cu–Cl1′	88.2(1)°
Cl2–Cu–N1	167.2(3)°
Cl1′–Cu–O8	101.2(3)°
Cl1–Cu–Cl2′	100.6(1)°
Cu–Cl1–Cu′	91.8(1)°

$CuL_2(ClO_4)_2$ stabilizing the relative orientation of the two carboxamide groups. In $CuL_2(OH)_2 \cdot 2H_2O$ this hydrogen bond is not present.

Magnetic susceptibility measurements were carried out on these complexes in order to determine the extent of magnetic interactions which can occur. The magnetic data of polycrystalline samples of $CuLCl_2$, $CuL_2(OH)_2 \cdot 2H_2O$ and $CuL_2(ClO_4)_2$ are tabulated in Table IIIA (supplementary material) and are plotted in Fig. 5 and 6. Figure 5 is plotted as inverse magnetic susceptibility and effective magnetic moment as a function of temperature. Since the inverse magnetic susceptibility plots of both $CuL_2(OH)_2 \cdot 2H_2O$ and $CuL_2(ClO_4)_2$ are linear as a function of temperature, the Curie–Weiss Law (eqn. 1) was used to fit the data of these complexes

$$\chi = \frac{Ng^2\mu_\beta^2 S(S+1)}{3k(T-\theta)} \qquad (1)$$

The lines through the inverse magnetic susceptibility data points in Fig. 5 are the fit of the data to equation 1 with $S = 1/2$ for copper(II). The fitted parameters for both complexes are listed in Table IV.

Figure 6 is a plot of the molar magnetic susceptibility and the effective magnetic moment as a function of temperature for the dimeric complex $[CuLCl_2]_2$. The maximum in the molar susceptibility at approximately 22 K and the decrease in the effective magnetic moment are both indicative of antiferromagnetic coupling within the structural dimer of $[CuLCl_2]_2$. The Heisenberg–Dirac–Van Vleck Hamiltonian may be used to describe the magnetic interaction in a molecule with two interacting paramagnetic centers,

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

where for a copper(II) dimer, $S_1 = S_2 = 1/2$. Using the Hamiltonian in eqn. (2), a closed form equation first derived by Bleaney and Bowers [24] may be obtained,

$$\chi = \frac{Ng^2\mu_\beta^2}{kT} \; \frac{2e^x}{1+3e^x} \qquad (3)$$

where $x = -2J/kT$. The line through the points in Fig. 6 is the fit of the dimer susceptibility data to eqn. (3) with the parameters listed in Table IV.

Discussion

The magnetic data for the two monomeric complexes showed essentially Curie-like temperature dependent behavior. The effective magnetic moment

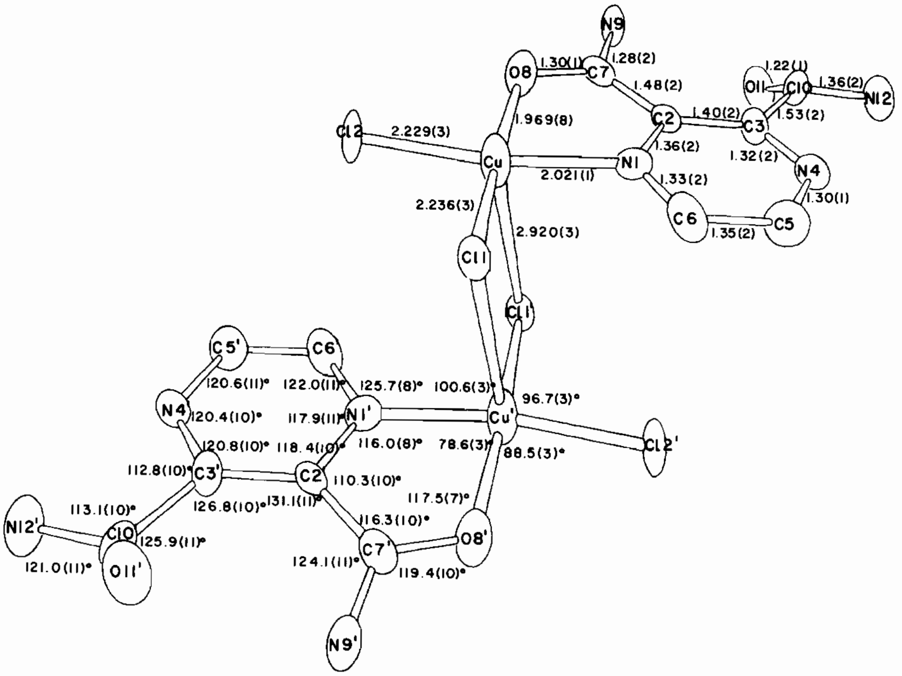

Fig. 2. Molecular structure of $[CuLCl_2]_2$.

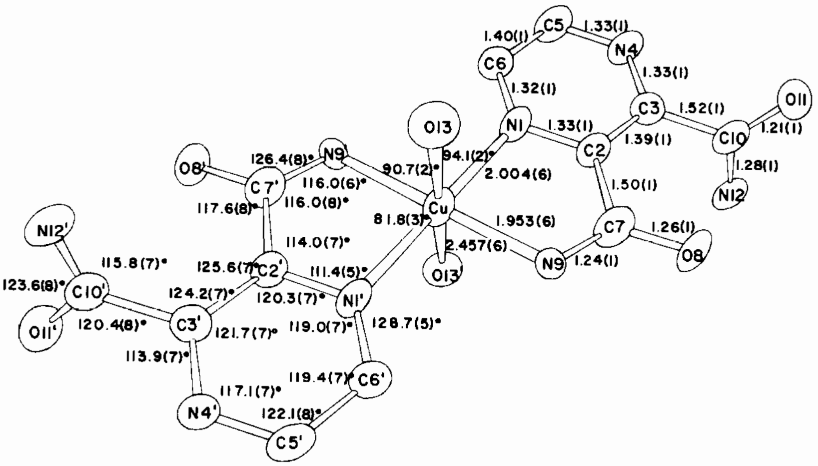

Fig. 3. Molecular structure of $CuL_2(OH)_2 \cdot 2H_2O$.

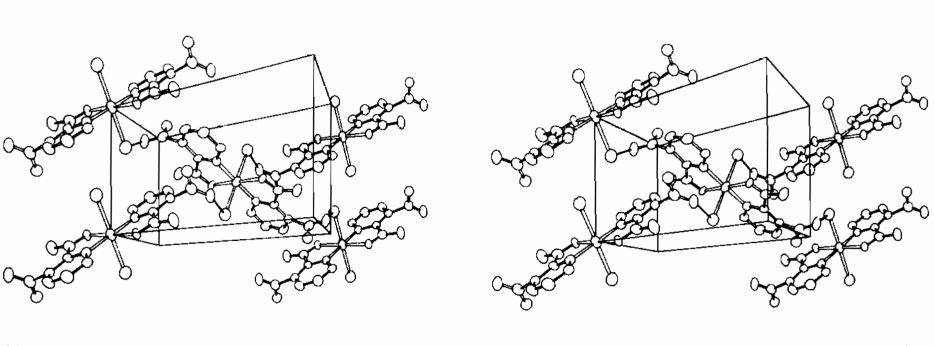

Fig. 4. Stereo view of packing diagram for $CuL_2(OH)_2 \cdot 2H_2O$, showing intermolecular hydrogen bonds.

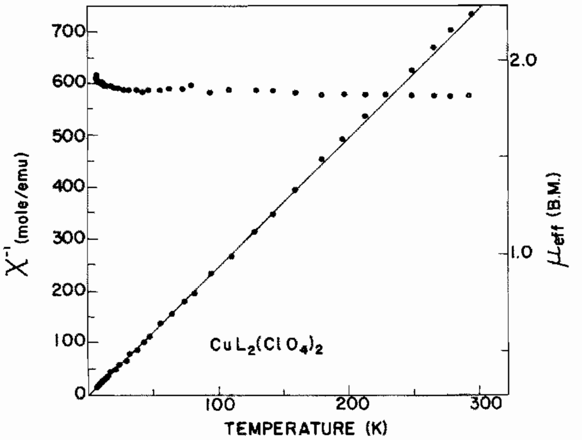

Fig. 5. Inverse magnetic susceptibility and effective magnetic moment of $CuL_2(OH)_2 \cdot 2H_2O$ plotted as a function of temperature. The line through the point is the best fit of the data to the Curie–Weiss law (eqn. 1) as described in the text.

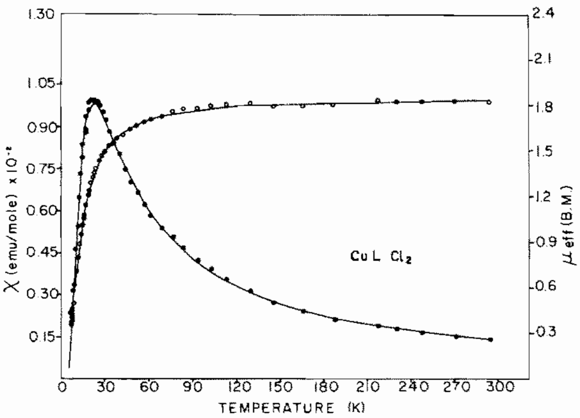

Fig. 6. Magnetic susceptibility and effective magnetic moment of $[CuLCl_2]_2$ plotted as a function of temperature. The smooth curve is the fit of the data to eqn. (3) as described in the text.

for $CuL_2(OH)_2 \cdot 2H_2O$ appears to be invariant as a function of temperature. This behavior is indicative of a classical paramagnet following the Curie Law. A fit of the data to the Curie–Weiss law gave a Weiss constant nearly equal to zero (θ = 0.26 K).

The $CuL_2(ClO_4)_2$ complex was also fit to Curie–Weiss law ($\theta = 0.52$ K) and shows a very slight increase in the effective magnetic moment as the temperature approaches 0 K as shown in Fig. 5. The x-ray crystal structure reported by Mondal and Ray [20] describes a monomeric molecular unit with no apparent magnetic exchange pathways. Since the authors did not report hydrogen atom coordinates in their paper, we calculated the probable hydrogen atom coordinates from their reported atomic coordinates in order to determine if a hydrogen bonded pathway was present. The hydrogen atoms generated in this manner were not in acceptable orientations for participation in a hydrogen bonding network. The lack of observable superexchange pathway is consistent with the very small magnetic interaction parameters in each of the monomeric complexes.

Dimer formation by the complex $[CuLCl_2]_2$ follows the same chemical trend exhibited by copper(II) and pyrazinecarboxylic acid when prepared in acidic medium [4]. Although the pyrazinecarboxylic acid dimer crystallized without a center of symmetry, it is very similar to the centrosymmetric pyrazinedicarboxamide dimer reported here. Some structural details of the copper chlorine bridge for the two dimers are listed in Table V.

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 Fig. 7. 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* [26]. Recent empirical tabulations of chlorine bridged dimers by Hatfield *et al.* [25, 27] indicate that chlorine bridged complexes of type *2* (and possibly those of type *1* as well) appear to require a distance parameter in addition to the simple angular dependence. Hatfield has shown in a small set of single atom bridged complexes that the magnetic coupling parameter J shows a close correlation to the ratio of the bridging angle and the internuclear separation (ϕ/r) rather than just the bridging angle alone. This

TABLE IV. Magnetic Parameters for $[CuLCl_2]_2$, $CuL_2(OH)_2 \cdot 2H_2O$ and $CuL_2(ClO_4)_2$.

Compound	g	J(cm^{-1})	θ(K)	Model
$[CuLCl_2]_2$	2.11(2)	−11.5(2)		Simple dimer
$CuL_2(OH)_2 \cdot 2H_2O$	2.28(2)		0.3(2)	Curie–Weiss S = 1/2
$CuL_2(ClO_4)_2$	2.09(2)		0.5(2)	Curie–Weiss S = 1/2

TABLE V. Structural Details of the Cu–Cl Bridge.

	Cl–Cu–Cl	r	ϕ/r	J(cm^{-1})
$[CuLCl_2]_2$	91.8°	2.920 Å	31.4	−11.5(2)
$CuL'Cl_2$	88°	2.81 Å	31	−6.11
	86°	2.89 Å	29	

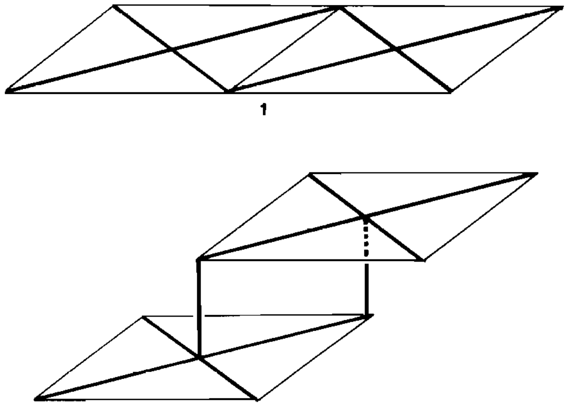

Fig. 7. Schematic diagram illustrating two types of bridging geometries common for copper(II) ions: (1) coplanar bridge and (2) perpendicular plane bridge.

observation is a result of their attempts to reconcile the magnetic exchange parameters and bridging geometries of set of complexes bridged by the third row elements of the periodic table. The values for ϕ/r for the chlorine bridged dimers reported in Table V are for complexes of bridging type *2* (Fig. 7). However, these values are not within the range predicted by the recent compiled tabulation of ϕ/r and J. While the correlation between these parameters may indeed be valid in some situations, the number of different parameters which can affect the magnetic exchange makes such correlations risky at best.

The absence of pyrazine bridging in the two monomeric pyrazinedicarboxamide complexes reported here is not surprizing in view of our previous reports on the bonding geometries of substituted pyrazine ligands. We have reported several other complexes of substituted pyrazine ligands coordinated to both copper(II) and iron(II). Only one of these complexes exhibited a direct pyrazine bridge, although several of the others exhibited bridging geometries involving other coordination groups. A carboxylate bridging pathway observed in the isomorphous complexes ML_2', where HL′ = pyrazinecarboxylic acid, and the chlorine bridged complex reported here are examples of bridged metals that accommodate nonbridging pyrazine ligands. Table VI summarizes the magnetic parameters for this series of complexes. It is interesting to note the variety of different magnetic and structural models in this series of complexes.

References

1 C. J. O'Connor and E. Sinn, *Inorg. Chem., 20,* 545 (1981).
2 C. J. O'Connor, C. L. Klein, R. J. Majeste and L. M. Trefonas, *Inorg. Chem., 21,* 64 (1982).
3 C. L. Klein, L. M. Trefonas, C. J. O'Connor and R. J. Majeste, *Cryst. Str. Comm., 10,* 891 (1981).
4 C. L. Klein, R. J. Majeste, L. M. Trefonas and C. J. O'Connor, *Inorg. Chem., 21,* 1891 (1982).
5 C. L. Klein, R. J. Majeste, L. M. Trefonas and C. J. O'Connor, *J. Chem. Soc., Dalton,* in press.
6 C. Creutz and H. Taube, *J. Am. Chem. Soc., 91,* 3988 (1969); *95,* 1086 (1973).

TABLE VI. Summary of Magnetic Parameters for Cu(II) and Fe(II) Complexes of Pyrazinecarboxylic Acid (HL′) and 2,3-pyrazinedicarboxylic Acid (H_2L'').

Compound	g	J(cm^{-1})	θ(K)	Model	Ref.
$[Cu(HL')Cl_2]_2$	2.23			Dimer S = 1/2	5
CuL_2'	2.11		0.59	Curie–Weiss S = 1/2	5
	2.12	0.42		Heisenberg–Chain S = 1/2	5
$CuL_2'(H_2O)_2$	2.15		0.30	Curie–Weiss S = 1/2	5
	2.15	0.23		Heisenberg–Chain S = 1/2	5
CuL″HC	2.28	1.2		Heisenberg–Chain S = 1/2	3
	2.28	0.97		Molecular Field Chain S = 1/2	3
	2.28		1.4	Curie–Weiss S = 1/2	3
$CuHL_2''(H_2O)_3$	2.32		−0.16	Curie–Weiss S = 1/2	6
$FeL_2'(H_2O)_2$	2.13		11.7	Curie–Weiss S = 1/2	6
	2.12	−0.8		Fisher–Chain S = 2	6
$FeL_2''(H_2O)_3$	2.16		−2.23	Curie–Weiss S = 2	6
$FeL_2''(H_2O)_3$	2.16		8.69*	Zero Field Splitting S = 2	6

*8.69 is actually the value for D/k, the energy for the zero field splitting.

7 J. K. Beattie, N. S. Hush and P. R. Taylor, *Inorg. Chem.*, *15*, 992 (1976).

8 T. J. Meyer, M. J. Powers, D. J. Salmon and R. W. Callahan, *J. Am. Chem. Soc.*, *99*, 1064 (1977).

9 T. J. Meyer, *Acc. Chem. Res.*, *11*, 94 (1978).

10 J. A. Baumann, D. J. Salmon, S. T. Wilson and T. J. Meyer, *Inorg. Chem.*, *18*, 2472 (1979).

11 P. W. Charreck, M. Goldstein, E. M. McPartlin, W. E. Unsworth, *Chem. Comm.*, 1634 (1971).

12 J. M. Malin, D. A. Ryan and T. V. O'Halloran, *J. Am. Chem. Soc.*, *100*, 2097 (1978).

13 M. Inoue and M. Kubo, *Coord. Chem. Rev.*, *21*, 1 (1976).

14 H. W. Richardson, J. R. Wasson and W. E. Hatfield, *Inorg. Chem.*, *16*, 484 (1977).

15 A. B. Blake and W. E. Hatfield, *J. Chem. Soc., Dalton Trans.*, 863 (1978).

16 M. S. Haddad, D. N. Hendrickson, J. P. Cannady, R. S. Drago and D. S. Bieckza, *J. Am. Chem. Soc.*, *101*, 898 (1979).

17 J. Darriet, M. S. Haddad, E. N. Duesler and D. N. Hendrickson, *Inorg. Chem.*, *18*, 2679 (1979).

18 H. E. Toma, *J. Inorg. Nucl. Chem.*, *38*, 431 (1976); *37*, 785 (1975).

19 H. E. Toma and L. A. Oliveira, *Inorg. Chim. Acta*, *33*, 2143 (1979).

20 M. Mondal and S. Ray, *Acta Cryst.*, *B33*, 2297 (1977).

21 The conventional reliability index

$$R = \frac{\Sigma \| kF_o | - | F_c \|}{\Sigma | kF_o |}$$

is cited throughout the paper. Scattering factors for carbon, nitrogen, oxygen, chlorine and copper are taken from the paper by D. T. Cromer and J. T. Waber, *Acta Cryst.*, *18*, 104 (1965), while that for hydrogen is from International Tables for X-Ray Crystallography, Vol. III, Kynoch Press, Birmingham, England, 1968.

22 C. J. O'Connor, *Prog. Inorg. Chem.*, *29*, 203 (1982).

23 R. T. Lewis, *Rev. Sci. Instrum.*, *42*, 31 (1971).

24 B. Bleaney and K. D. Bowers, *Proc. Roy. Soc.*, *A214*, 451 (1952).

25 W. E. Hatfield, R. R. Weller, J. W. Hall, *Inorg. Chem.*, *19*, 3825 (1980).

26 V. H. Crawford, H. W. Richardson, J. R. Wasson, D. J. Hodyson, W. E. Hatfield, *Inorg. Chem.*, *15*, 2107 (1976).

27 W. E. Marsh, W. E. Hatfield and D. J. Hodgson, *Inorg. Chem.*, *21*, 2679 (1982).