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Crystal Structure and Magnetic Properties of Bis(pyrazine)copper(II) Perchlorate, $Cu(pyz)_2(ClO_4)_2$, a Two-Dimensional Heisenberg Antiferromagnet

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The crystal and molecular structure of $Cu(pyz)_2(ClO_4)_2$, where pyz is pyrazine, has been determined by using heavy-atom, least-squares, X-ray methods for 1027 reflections measured on a computer-automated four-circle diffractometer. The complex crystallizes in the space group $C2/m$ in a unit cell with $\alpha = 14.123$ (4) Å, $b = 9.781$ (2) Å, $c = 8.984$ (2) Å, $\beta = 147.12$ (2)°, $\rho_{obsd} = 2.08$ (1) g/cm^3, and $\rho_{calcd} = 2.09$ g/cm^3. The structure was refined to final discrepancy indices of $R = 0.052$ and $R_w = 0.069$. The complex consists of sheets of copper(II) ions bridged by ambidentate pyrazine ligands. The distance between two adjacent sheets is 7.012 Å. The dihedral angle between the plane of each pyrazine ligand and the sheet in which it is located is 66.1°. The coordination geometry about each copper(II) ion is that of a tetragonally elongated octahedron, where each copper(II) ion is bonded strongly [Cu–N = 2.062 (3) Å] to four pyrazine ligands and weakly [Cu–O = 2.373 (12) Å] to two perchlorate ions. The magnetic susceptibility vs. temperature data (4.2–285 K) were least-squares fit to a theoretical equation for a two-dimensional Heisenberg antiferromagnet.

Introduction

Pyrazine (pyz) and derivatives have been shown to bridge copper(II) ions, forming one-dimensional chains.[5] Hatfield and co-workers[6–9] have studied a variety of such compounds and have established with structural data that the orientation of the π system of pyrazine relative to the copper(II) ion coordination plane is important in determining whether or not a magnetic exchange interaction is propagated.

Several two-dimensional exchange-interacting transition-metal compounds have been structurally and magnetically characterized.[10–14] However, the bridge between the metal ions in all of these two-dimensional compounds consists of a single atom such as an oxygen atom or a halide ion. The compound $Co(pyz)_2Cl_2$ represents a rare two-dimensional polymeric system where the extended pyrazine unit bridges between the metal ions in a sheet.[15] In a very recent paper,[16] we reported that the compound $Cu(pyz)_2(ClO_4)_2$ is involved in an antiferromagnetic exchange interaction. In this paper, we report the single-crystal X-ray structure of $Cu(pyz)_2(ClO_4)_2$, as well as a reevaluation of the magnetic susceptibility data. It is shown that the structure of the compound is that of a two-dimensional polymeric network and that the magnetism data are best fit to a two-dimensional Heisenberg model.

Experimental Section

Compound Preparation and Physical Measurements. The preparation of $Cu(pyz)_2(ClO_4)_2$ was carried out according to details given before.[16] Crystals were obtained by slow evaporation of a water solution. Physical measurements were carried out as described in a previous paper.[16] Susceptibility measurements were carried out on polycrystalline samples at a field of 13 kG. The magnetic susceptibility was studied as a function of magnetic field at 4.2 K in the range 13–32 kG.

Crystal Measurements. A crystal of $Cu(pyz)_2(ClO_4)_2$ with dimensions of 0.12 × 0.12 × 0.08 mm was used for data collection. The cell dimensions were obtained by a least-squares fit to the automatically centered settings for 15 reflections on a Syntex P2$_1$ four-circle automatic diffractometer equipped with a graphite monochromator.[17] Data collection showed systematic absences $h + k = 2n + 1$ for hkl consistent with the space groups $C2$, Cm, and $C2/m$. The structure solution shows the correct space group is $C2/m$. Examination of three standard reflections, which were monitored every 57 reflections, showed no evidence for crystal deterioration. Lorentz and polarization corrections were applied to the data. Absorption corrections were unnecessary due to the small linear absorption coefficient. Additional details are given in Table I.

Table I. Experimental Data for the X-ray Diffraction of $Cu(pyz)_2(ClO_4)_2$

Crystal Parameters

$a = 14.123$ (4) Å	$Z = 2$
$b = 9.781$ (2) Å	mol wt 422.6
$c = 8.984$ (2) Å	ρ(calcd) = 2.09 g cm^{-3}
$\beta = 147.12$ (2)°	ρ(obsd) = 2.08 (1) g cm^{-3} [a]
space group $C2/m$	$V = 672.8$ Å^3

Measurement of Intensity Data

radiation: Mo K$\bar{\alpha}$, λ 0.710 69 Å
monochromator: graphite crystal
takeoff angle: 6.2°
X-ray beam collimator diameter: 1.0 mm
cryst dimens: 0.12 × 0.12 × 0.08 mm
cryst orientatn: random
reflctns measd: ($\pm h,k,l$)
max 2θ: 70°
scan type: θ–2θ
scan speed: 1–5° min^{-1}
base width: 1.8° in 2θ
background time/scan time: 0.3
standards monitored/reflctns: 3/57
reflctns collected: 1561 unique reflections, 1027 with $F^2 > 4\sigma(F^2)$

[a] Flotation in chloroform–bromoform.

Structure Solution and Refinement. The structure was solved by the heavy-atom technique using 1027 reflections with $F^2 > 4\sigma(F^2)$ in $C2/m$. The positions of all the nonhydrogen atoms except for O(3) of the perchlorate anion were located. As the refinement proceeded, it became clear that the anion was disordered about the mirror plane. The disorder resulted in the smearing out of O(3) which lies off the mirror plane. The average positions of Cl, O(1), and O(2) are on the symmetry plane and fit the expected geometry of the anion. Since attempts to sort out the disorder failed, the position of O(3) was calculated and not allowed to vary in the least-squares refinement. The same model was tested in both the space groups $C2$ and Cm and was judged to be inappropriate in these space groups because unreasonable interatomic distances resulted.

The hydrogen atom positions were obtained from Fourier difference maps. The final cycle of full-matrix least-squares refinement led to the discrepancy factors of $R = 0.052$ and $R_w = 0.069$, where

$$R = \sum||F_o| - |F_c||/\sum|F_o|$$

$$R_w = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$$

The final value of $[\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, where m is the number of reflections and n is the number of variables, is 1.62. The neutral atom scattering curves were taken from the analytical expression used in ref 18. Anomalous dispersion factors for Cu and Cl were included. A final difference map showed three peaks greater than two-thirds of a hydrogen atom. One of these peaks was 0.9 Å from O(3) with a density of 1.6 of a hydrogen atom. The other two were ca. 1 Å from the Cl atom with densities of 0.9 of a hydrogen atom.

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Table II. Final Positional Parameters[a] for $Cu(pyz)_2(ClO_4)_2$ Including Hydrogen Atoms[b]

atom	*x*	*y*	*z*
Cu	0.000 (0)	0.0000 (0)	0.000 (0)
N(1)	0.1457 (4)	0.1500 (3)	0.2952 (6)
C(1)	0.2505 (5)	0.2675 (4)	0.6481 (8)
C(2)	0.1459 (5)	0.1699 (4)	0.4433 (7)
Cl	−0.2984 (2)	0.000 (0)	−0.0581 (3)
O(1)	−0.1844 (8)	0.0000 (0)	0.2144 (11)
O(2)	−0.2018 (7)	0.0000 (0)	−0.0661 (10)
O(3)	−0.4037 (0)	0.1169 (0)	−0.1915 (0)
H(1)	0.247 (6)	0.280 (5)	0.752 (9)
H(2)	0.068 (6)	0.126 (5)	0.413 (10)

[a] Standard deviations of the least significant figures are given in parentheses and are given in this fashion in succeeding tables. [b] The hydrogen atoms in $Cu(pyz)_2(ClO_4)_2$ were located in the Fourier map.

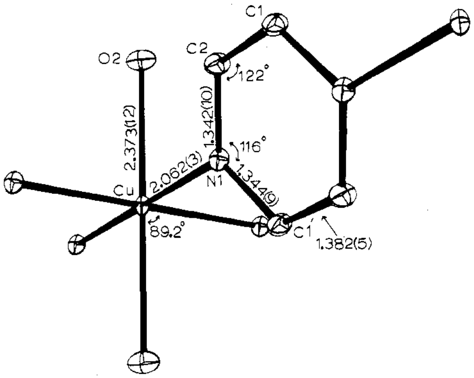

Figure 1. ORTEP plot of the inner coordination sphere about the copper(II) ion in $Cu(pyz)_2(ClO_4)_2$. One pyrazine is also shown.

Final positional and anisotropic thermal parameters for $Cu(pyz)_2(ClO_4)_2$ are given in Tables II and III, respectively.

Results and Discussion

Crystal Structure of $Cu(pyz)_2(ClO_4)_2$. Heavy-atom techniques were used to solve the structure of $Cu(pyz)_2(ClO_4)_2$. Table IV lists the principal *inter*atomic distances and angles. The structure of $Cu(pyz)_2(ClO_4)_2$ is made of parallel sheets, each consisting of an infinite square array of copper(II) ions bridged by bidentate pyrazine groups. Each copper(II) ion is bonded strongly to four nitrogen atoms from four different pyrazine ligands and weakly to two oxygen atoms from two perchlorate ions.

The coordination geometry about each copper(II) ion is that of a tetragonally elongated octahedron, as illustrated in Figure 1. The basal plane of four nitrogen atoms is a perfect square with a mean Cu–N distance of 2.062 (3) Å. This bond length is longer than that reported for the one-dimensional polymer $[Cu(NO_3)_2(pyz)]_x$,[19] where Cu–N = 1.984 (4) Å, and shorter than that reported for the analogous $[Cu(hfac)_2(pyz)]_x$ polymer,[20] where Cu–N = 2.529 (9) Å. Also, this bond length is shorter than that of the Co–N distance [2.18 (1) Å] reported[15] for the structurally similar $Co(pyz)_2Cl_2$. In the axial sites of the coordination geometry of the copper(II) ion in $Cu(pyz)_2(ClO_4)_2$ there are two Cu–O bonds with a length of 2.373 (12) Å, a length which signals weak bonding of the copper(II) ion to the two perchlorate ions. The present bond length is not very much different from that [2.379 (13) Å] reported[21] for the compound $[Cu_2(TMDT)_2(ClO_4)_2]ClO_4$, where TMDT is 1,1,7,7-tetramethyldiethylenetriamine.

The pyrazine ring in $Cu(pyz)_2(ClO_4)_2$ is essentially planar; see Table V. The dimensions of the ring (see Figure 1) compare well with those reported for $Co(pyz)_2Cl_2$,[15] $[Cu(hfac)_2(pyz)]_x$ and $Cu_2(hfac)_2(pyz)$,[20] $[(NH_3)_5Ru(pyz)Ru(NH_3)_5]^{5+}$ ion,[22] and $[Cu(NO_3)_2(pyz)]_x$.[19] For example, in $[Cu(hfac)_2(pyz)]_x$ the C–C distance is 1.38 (2) Å and the two N–C distances are 1.33 (1) Å.

The pyrazine rings in $Cu(pyz)_2(ClO_4)_2$ are canted relative to the $Cu-N_4$ coordination plane, i.e., the sheet. The dihedral angle is 66.1°. Figure 2 shows a stereoscopic plotting of a section of a sheet. The distance between two adjacent sheets is 7.012 Å.

An interesting aspect of the structure of $Cu(pyz)_2(ClO_4)_2$ is the relatively large Cu–O(2)–Cl angle (see Table IV, footnote *d*). This is an unusual situation, for such a Cu–O–Cl angle is generally ca. 130° as is found in $Cu(NH_2CH_2CH_2SCH_3)_2(ClO_4)_2$.[23] Examination of the packing diagram shows that the ClO_4^- ion in $Cu(pyz)_2(ClO_4)_2$ is experiencing a tight fit in the lattice. The Cu–O(2)–Cl angle is large apparently to minimize nonbonded interactions between ClO_4^-

Table III. Anisotropic Thermal Parameters[a] for $Cu_2(pyz)_2(ClO_4)_2$

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	0.0052 (1)	0.0018 (1)	0.0071 (3)	0.0000 (0)	0.0049 (2)	0.0000 (0)
N(1)	0.0056 (4)	0.0032 (2)	0.0101 (9)	−0.0002 (2)	0.0060 (6)	−0.0002 (4)
C(1)	0.0102 (6)	0.0041 (3)	0.0203 (13)	−0.0018 (4)	0.0131 (8)	−0.0025 (5)
C(2)	0.0084 (6)	0.0046 (3)	0.0180 (13)	−0.0022 (4)	0.0109 (8)	−0.0033 (5)
Cl	0.0070 (2)	0.0169 (3)	0.0185 (6)	0.0000 (0)	0.0099 (3)	0.0000 (0)
O(1)	0.0211 (13)	0.0173 (9)	0.0292 (23)	0.0000 (0)	0.0227 (16)	0.0000 (0)
O(2)	0.0137 (8)	0.0087 (5)	0.0341 (21)	0.0000 (0)	0.0200 (13)	0.0000 (0)
O(3)	0.0799 (30)	0.0884 (36)	0.1470 (64)	0.0734 (29)	0.1024 (43)	0.0903 (41)

atom	*B*, Å²	atom	*B*, Å²
H(1)	2.3 (10)	H(2)	1.6 (9)

[a] The form of the anisotropic thermal ellipsoid is given by $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$. Thermal parameters for the hydrogen atoms were varied isotropically.

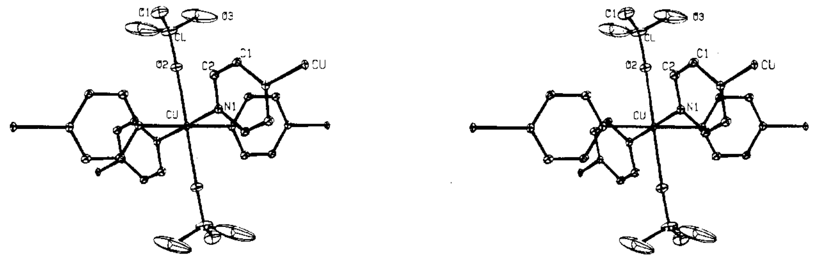

Figure 2. Stereoscopic ORTEP plotting of a section of the sheet structure in $Cu(pyz)_2(ClO_4)_2$.

Table IV. Principal Interatomic Distances (Å) and Angles (deg) for $Cu(pyz)_2(ClO_4)_2$

		Distances	
Cu-N(1)	2.062 (3)	C(1)-H(1)	0.99 (10)
Cu-O(2)	2.373 (12)	C(2)-H(2)	0.98 (10)
N(1)-C(1)′	1.344 (9)	Cl-O(1)	1.400 (7)
N(1)-C(2)	1.342 (10)	Cl-O(2)	1.426 (13)
C(2)-C(1)	1.382 (5)	Cl-O(3)[e]	1.400 (1)
		Angles	
N(1)-Cu-N(1)[a]	89.2 (2)	N(1)-C(1)′-C(2)′	121.6 (6)
N(1)-Cu-N(1)[b]	180.0 (2)	C(2)′-C(1)′-H(1)′	120 (4)
N(1)-Cu-N(1)[c]	90.8 (2)	N(1)-C(2)-H(2)	126 (4)
N(1)[a]-Cu-N(1)[b]	90.8 (2)	N(1)-C(2)-C(1)	122.0 (5)
N(1)[b]-Cu-N(1)[c]	89.2 (2)	H(2)-C(2)-C(1)	112 (4)
O(2)-Cu-O(2)[b]	180.0 (3)	O(1)-Cl-O(2)	110.2 (5)
O(2)-Cu-N(1)	89.2 (2)	O(1)-Cl-O(3)	109.3 (4)
Cu-N(1)-C(1)′	120.4 (4)	O(2)-Cl-O(3)	109.3 (3)
Cu-N(1)-C(2)	123.1 (4)	O(3)-Cl-O(3)[c]	109.5 (2)
C(1)′-N(1)-C(2)	116.4 (5)	Cl-O(2)-Cu[d]	170.6 (5)
N(1)-C(1)′-H(1)′	118.0 (4)		

[a] Atom with coordinates $-x, y, -z$. [b] Atom with coordinates $-x, -y, -z$. [c] Atom with coordinates $x, -y, z$. [d] According to our treatment of the disorder of the ClO_4^- ion, the Cl atom occurs in the mirror plane of the ClO_4^- ion. The difference Fourier map shows that the Cl atom cannot be off by more than 0.35 Å from the mirror plane. This deviation on both sides of the mirror plane would lead to an angle of 160°. Therefore, the Cu-O(2)-Cl angle lies in the range of 160-170°. [e] Position of O(3) fixed at tetrahedral angle and distance from Cl of 1.400 Å.

Table V. Least-Squares Planes for $Cu(pyz)_2(ClO_4)_2$

atom	distance, Å	atom	distance, Å
Pyrazine Plane: $-0.3276x + 0.6645y - 0.6717z = -0.0690$			
N(1)	0.004 (3)	H(1)	0.01 (6)
C(1)′	−0.007 (5)	H(1)	−0.01 (6)
C(2)	−0.006 (5)	H(2)	−0.10 (6)
C(1)	+0.007 (5)	H(2)′	+0.10 (6)
N(1)′	−0.004 (3)		
Coordination Plane of Copper: $-0.9930x - 0.0009y - 0.1179z = 0.0$			
		plane from next sheet	
Cu	0.000 (0)	Cu	−7.012 (0)
N(1)	0.000 (7)	N(1)	−7.012 (7)
N(1)[a]	0.000 (7)	N(1)[a]	−7.012 (7)
N(1)[b]	0.000 (7)	N(1)[b]	−7.012 (7)
N(1)[c]	0.000 (7)	N(1)[c]	−7.012 (7)

[a–c] See Table IV.

Table VI. Experimental and Calculated Magnetic Susceptibility Data for $Cu(pyz)_2(ClO_4)_2$[a]

	$10^3\chi_M$, cgsu		μ_{eff}/Cu, μ_B	
T, K	obsd	calcd[b]	obsd	calcd[b]
285.5	1.388	1.382	1.78	1.78
244.6	1.568	1.599	1.75	1.77
203.7	1.875	1.190	1.75	1.76
162.8	2.322	2.327	1.74	1.74
122.5	3.032	2.999	1.72	1.71
102.8	3.590	3.489	1.72	1.69
86.1	4.100	4.046	1.68	1.67
76.9	4.464	4.435	1.66	1.65
67.0	4.967	4.943	1.63	1.63
55.9	5.623	5.661	1.58	1.59
50.2	6.089	6.111	1.56	1.57
44.1	6.652	6.670	1.53	1.53
41.1	6.967	6.973	1.51	1.51
38.2	7.292	7.299	1.49	1.49
35.0	7.668	7.682	1.46	1.47
31.5	8.108	8.133	1.43	1.43
28.4	8.515	8.560	1.39	1.39
26.6	8.790	8.816	1.37	1.37
24.7	9.043	9.089	1.34	1.34
22.6	9.274	9.389	1.29	1.30
21.5	9.426	9.542	1.27	1.28
20.3	9.578	9.702	1.25	1.25
19.1	9.718	9.850	1.22	1.23
17.7	10.00	10.00	1.19	1.19
16.4	10.07	10.11	1.15	1.15
15.6	10.11	10.16	1.12	1.13
14.9	10.14	10.19	1.10	1.10
14.0	10.21	10.21	1.07	1.07
13.1	10.26	10.19	1.04	1.03
12.1	10.27	10.12	1.00	0.99
11.1	10.21	9.985	0.95	0.94
10.1	10.04	9.775	0.90	0.89
9.1	9.969	9.483	0.85	0.83
8.0	9.425	9.072	0.78	0.76
7.0	8.691	8.562	0.70	0.69
5.9	7.666	7.980	0.60	0.61
4.2	6.679	7.901	0.47	0.51

[a] Diamagnetic correction used: -165×10^{-6} cgsu. [b] Least-squares fitting to eq 1 for a two-dimensional Heisenberg model. Least-squares fit parameters: $J = -5.3$ cm^{-1} and $g = 2.107$.

ions which are bonded to copper(II) ions on adjacent sheets. The O(1)···O(1) distance between ClO_4^- ions bonded to the two copper(II) ions with positions of (x, y, z) and ($-x$, y, $1 - z$) is 2.9 Å. This value is less than twice the van der Waals radius of the oxygen atom (r = 1.5 Å). The two O(1) atoms are within a repulsive distance and any reduction of the Cu–O(2)–Cl angle would increase the repulsion.

Magnetic Susceptibility and EPR. As reported previously,[16] the compound $Cu(pyz)_2(ClO_4)_2$ gives a magnetic susceptibility vs. temperature curve indicative of an antiferromagnetic exchange interaction throughout the temperature range of 285–4.2 K. The curve has a relatively sharp maximum at 12.1 K. The susceptibility data were previously fit to a theoretical equation for a tetramer of copper(II) ions and it was concluded that the compound is either tetrameric or that the tetramer model is an approximation to the model needed for a polymeric sheet structure. A reevaluation of the magnetic susceptibility data is in order in view of the crystal structure which shows that $Cu(pyz)_2(ClO_4)_2$ has a sheet structure.

The susceptibility data for $Cu(pyz)_2(ClO_4)_2$ were least-squares fit to the high-temperature series-expansion expression for a two-dimensional square-planar antiferromagnet of Rushbrooke and Wood.[24] The susceptibility expression used in the fitting of the data was taken from the paper of Lines[25] and is given in eq 1. In this expression, $x = kT/|J|$. As has

$$\chi = \frac{Ng^2\beta^2}{4kT}\left[1\bigg/\left(1 + \frac{2}{x} + \frac{2}{x^2} + \frac{1.333}{x^3} + \frac{0.250}{x^4} - \frac{0.4833}{x^5} + \frac{0.003797}{x^6}\right)\right] \quad (1)$$

already been pointed out by Landee, Roberts, and Willet,[26] the J reported in Lines' paper is equal to $2J$ as reported by Rushbrooke and Wood. In the above equation, $2J$ is the constant in the Hamiltonian.

As can be seen in Figure 3, the least-squares fit of the susceptibility data for $Cu(pyz)_2(ClO_4)_2$ to the above theoretical equation is excellent. The parameters obtained are $J = -5.3$ cm^{-1} and $g = 2.107$. Therefore, the two-dimensional Heisenberg model seems to be a good representation of the magnetic behavior of $Cu(pyz)_2(ClO_4)_2$. The observed and calculated data are given in Table VI. The magnetic susceptibility at 4.2 K was found to be independent of the magnetic field between 13 and 32 kG.

The X-band and Q-band EPR spectra of $Cu(pyz)_2(ClO_4)_2$ are typical of a square-planar or elongated octahedral coordination geometry for a copper(II) ion. An axial spectrum with $g_{\parallel} = 2.275$ and $g_{\perp} = 2.061$ is seen. This agrees with the X-ray structure. The orbital ground state of the copper(II) ion is $d_{x^2-y^2}$, where the CuN_4 plane is the xy plane.

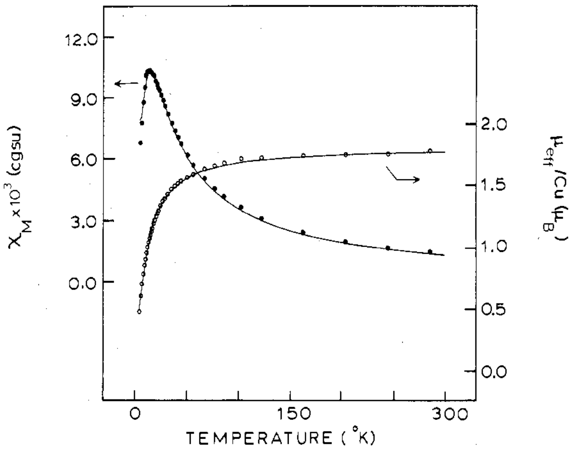

Figure 3. Experimental molar paramagnetic susceptibility (●) and effective magnetic moment (○) per Cu(II) ion vs. temperature for $Cu(pyz)_2(ClO_4)_2$. The solid lines represent the least-squares fit to a theoretical susceptibility equation for a two-dimensional Heisenberg antiferromagnet.

It has been proposed[7] that, for pyrazine-bridged copper(II) systems where the ground state is $d_{x^2-y^2}$, the overlap between the $d_{x^2-y^2}$ orbital and the pyrazine π orbitals determines the magnitude of antiferromagnetic exchange interaction. The CNDO/2 molecular orbital calculations carried out in our previous paper[16] show that the $\pi(b_{1g})$ orbital is the highest occupied pyrazine π molecular orbital, in agreement with previous work.[7] The $\pi(b_{1g})$ orbital of pyrazine is mainly carbon in character. If the pyrazine ring is coplanar with the copper(II) coordination plane, then the π system of pyrazine would be orthogonal to the $d_{x^2-y^2}$ orbital and no antiferromagnetic interaction would be observed. This was invoked as the reason for the absence of an antiferromagnetic magnetic exchange interaction in polymeric $[Cu(pyzA)_2(ClO_4)_2]_n$, where pyzA is pyrazine-2-carboxamide.[8] The crystal structure[27] of this polymer shows that the pyrazine plane is coplanar with the coordination plane of the copper(II) ion.

Canting of the pyrazine ring relative to the *xy* coordination plane leads to an overlap of the $\pi(b_{1g})$ orbital with the copper(II) $d_{x^2-y^2}$ orbital. This case was observed for polymeric $[Cu(NO_3)_2(pyz)]_x$ where the pyrazine ring is canted by 50° relative to the *xy* plane.[7] This compound shows an antiferromagnetic interaction with $J = -7.4$ cm^{-1}.[6] As mentioned above, in $Cu(pyz)_2(ClO_4)_2$ the pyrazine ring is tilted by 66.1° relative to the *xy* coordination plane and this leads to an antiferromagnetic interaction with $J = -5.3$ cm^{-1}.

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Registry No. $Cu(pyz)_2(ClO_4)_2$, 71106-29-1.

Supplementary Material Available: The final values of $|F_o|$ and $|F_c|$ for $Cu(pyz)_2(ClO_4)_2$ (8 pages). Ordering information is given on any current masthead page.

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