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Magnetic Interactions in Chloro-Bridged Dimers. Structural Characterization of Aquadichlorobis(2-methylpyridine)copper(II) and Bis[dichlorobis(2-methylpyridine)copper(II)]

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The synthesis and crystal and molecular structure of the complex aquadichlorobis(2-methylpyridine)copper(II), Cu(2-pic)$_2$Cl$_2$(OH$_2$), CuC$_{12}$H$_{16}$Cl$_2$N$_2$O, has been determined from three-dimensional X-ray counter data. The complex crystallizes in the triclinic space group $P\bar{1}$ with two molecules in a cell of dimensions a = 8.464 (4) Å, b = 12.552 (4) Å, c = 7.345 (2) Å, α = 93.45 (2)°, β = 113.56 (3)°, and γ = 99.52 (3)°. The structure has been refined by least-squares methods to a final R factor (on F) of 0.026 on the basis of 2576 independent data. The crystal structure of the complex bis[dichlorobis(2-methylpyridine)copper(II)], [Cu(2-pic)$_2$Cl$_2$]$_2$, [CuC$_{12}$H$_{14}$Cl$_2$]$_2$, has been redetermined with use of counter data. This complex also crystallizes in the triclinic space group $P\bar{1}$, with one dimeric formula unit in a cell of dimensions a = 8.647 (2) Å, b = 10.985 (3) Å, c = 8.440 (2) Å, α = 106.99 (2)°, β = 113.88 (2)°, and γ = 70.43 (2)°. The structure has been refined to a final value of the R factor (on F) of 0.031 on the basis of 1737 independent intensities. The aqua complex is a five-coordinate tetragonal-pyramidal monomer, with two trans-pyridine and two trans-chloride ligands in the base plane and the water molecule at the apex. The anhydrous complex is dimeric, with tetragonal-pyramidal geometry at each copper center. The centrosymmetric dimers are formed by very weak axial coordination to one copper center by a chloride ligand, which is in the base plane of the adjacent copper atom. The axial Cu–Cl distance (r) of 3.364 (1) Å is very long, as is the Cu–Cu' separation of 4.404 (1) Å in the dimers. The magnetic properties of dimers of this general type are discussed in terms of their structures, and the influence of r and of the bridging Cu–Cl–Cu' angle are noted.

Introduction

The structural and magnetic properties of copper(II) complexes of the type CuL$_2$X$_2$ have been the subjects of numerous recent publications; this is particularly true for the cases where L is pyridine or a substituted pyridine.[1-14] Much of this work has been concerned with the correlation of the structural properties of these complexes with their magnetic properties. One of our interests has been in the investigation of the structural and magnetic behavior of halogen-bridged dimers of copper(II), and since the 2-methylpyridine complexes [Cu(2-pic)$_2$X$_2$]$_2$ form such dimeric species,[2,3] we have been particularly intrigued by them.[3,10]

The magnetic properties of the chloro complex [Cu(2-pic)$_2$Cl$_2$]$_2$, which we reported earlier, are consistent with a weakly antiferromagnetic interaction in which the ground-state singlet lies 7.4 cm^{-1} lower in energy than the lowest triplet state. The structure of [Cu(2-pic)$_2$Cl$_2$]$_2$ was originally determined by Duckworth and Stephenson[2] on the basis of visually estimated Weissenberg film data obtained from several different crystals that gradually decomposed in the X-ray beam. Consequently, while the overall structure was unambiguously determined by these workers, the metrical parameters could not be obtained with the precision that would

normally be possible. In order to include this complex in our attempted structural–magnetic correlation, therefore, we have redetermined this crystal structure using counter methods and one crystal that showed no sign of decomposition during the data collection.

In the process of synthesizing suitable crystals of [Cu(2-pic)$_2$Cl$_2$]$_2$, we also synthesized a new complex of formulation Cu(2-pic)$_2$Cl$_2$(OH$_2$). Several complexes have previously been identified in the copper halide–pyridine system, including several isomers of Cu(py)$_2$X$_2$,[1,6] Cu$_2$(py)$_2$X$_4$,[4] and Cu$_4$(py)$_4$OX$_6$,[15] and in the copper halide–4-methylpyridine system,[6] but to our knowledge this is the first documentation of such behavior with 2-methylpyridine. We have, therefore, also determined the crystal structure of this complex in order to characterize it more fully.

Experimental Section

Synthesis of Cu(2-pic)$_2$Cl$_2$(OH$_2$). In an attempt to obtain crystals of [Cu(2-pic)$_2$Cl$_2$]$_2$ more stable than those obtained previously, we modified the published[2] preparation. To a solution of 1.35 g (0.01 mol) of anhydrous copper(II) chloride in 30 mL of methanol was added a solution of 1.86 g (0.02 mol) of 2-methylpyridine in 30 mL of

	[Cu(2-pic)$_2$-Cl$_2$(OH$_2$)]	[Cu(2-pic)$_2$Cl$_2$]$_2$	
		this work	ref 2[a]
a, Å	8.464 (4)	8.647 (2)	8.58 (5)
b, Å	12.552 (4)	10.985 (3)	10.99 (5)
c, Å	7.345 (2)	8.440 (2)	8.50 (5)
α, deg	93.45 (2)	106.99 (2)	106.6 (10)
β, deg	113.56 (3)	113.88 (2)	114.8 (10)
γ, deg	99.52 (3)	70.43 (2)	69.9 (5)
V, Å^3	698.6 (10)	679.2 (5)	670.6
μ(Mo K$\bar{\alpha}$), cm^{-1}	19.9	20.4	20.4
Z	2	1	1
D_{obsd}, g cm^{-3}	1.58	1.58	1.58
D_{calcd}, g cm^{-3}	1.611	1.568	1.59

[a] We report here the reduced cell derived from the data in ref 2.

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methanol. The resulting mixture was stirred for several minutes with gentle heating and filtered to remove the yellow-green precipitate; the blue filtrate was then allowed to stand at room temperature for a few hours, filtered, and subsequently placed in a freezer. Blue, prismatic crysals precipitated in less than 24 h. Preliminary crystallographic examination (vide infra) demonstrated that these crystals are not the same as those previously studied,[2] and subsequent crystallographic analysis (vide infra) demonstrated that they are Cu(2-pic)₂Cl₂(OH₂).

Synthesis of [Cu(2-pic)₂Cl₂]₂. The complex was synthesized by the method of Duckworth and Stephenson.[2] To a solution of 0.85 g (0.005 mol) of copper chloride dihydrate in 30 mL of absolute ethanol was added an excess of an ethanol solution of 2-methylpyridine. The solution was warmed with stirring and filtered to remove the green precipitate. The blue-green solution was immediately placed in a freezer; dark blue crystals formed after a few days. Preliminary crystallographic examination (vide infra) suggested that these crystals were the same as those previously studied.[2]

X-ray Data Collection and Reduction. (a) Cu(2-pic)₂Cl₂(OH₂). A prismatic crystal was mounted on a glass fiber in arbitrary orientation and placed on an Enraf-Nonius CAD-4 automatic diffractometer. Preliminary examination indicated that the crystals belong to the triclinic crystal system, the cell chosen being consistent only with the space groups $P\bar{1}$ (C_i^1) or $P1$ (C_1^1). The former was confirmed by the subsequent successful refinement of the structure. Accurate cell constants were obtained by least-squares methods and are listed in Table I along with additional crystal data.

Diffraction data were collected on the CAD-4 diffractometer equipped with molybdenum radiation (λ(Mo K$\bar{\alpha}$) = 0.7107 Å) and a graphite monochromator. A unique set of data ($\pm h, +k, \pm l$) in the range $2 \leq 2\theta \leq 55°$ was collected by the ω–θ scan technique. The intensities and their standard deviations were corrected for Lorentz–polarization effects and absorption. A total of 3201 independent reflections was processed of which 2576 had $I \geq 3\sigma(I)$; only these latter data were considered observed and used in subsequent calculations.

(b) [Cu(2-pic)₂Cl₂]₂. Data collection and reduction were carried out as described above. The complex again crystallizes in the triclinic space group $P\bar{1}$ (C_i^1), and the cell constants are compared with those obtained previously[2] in Table I. The observed and calculated densities are 1.58 and 1.568 g cm⁻³, respectively, for one dimeric formula unit per cell. Hence, in space group $P\bar{1}$ the dimers are constrained to lie on crystallographic inversion centers. The data collection was carried out as above, except that data with ($\pm h, \pm k, +l$) were collected. Data reduction was also carried out as described above. A total of 3112 independent data was obtained, of which 1737 had $I > 3\sigma(I)$; only these latter data were used in the refinement.

Solution and Refinement of the Structures. Both structures were solved by the heavy-atom method. All least-squares calculations were carried out on F, the function minimized being $\sum w(|F_o| - |F_c|)^2$ where the weights, w, are assigned as $4F_o^2/\sigma^2(I)$. In the calculation of the structure factors, F_c, the neutral-atom scattering factors were taken from ref 16a. The effects of the anomalous dispersion of all atoms were included. The values of $\Delta f'$ and $\Delta f''$ were taken from ref 16b.

Cu(2-pic)₂Cl₂(OH₂). The position of the copper atom was determined from a three-dimensional Patterson map. All other non-hydrogen atoms were located in a subsequent difference Fourier map. Anisotropic, least-squares refinement of these positions gave values of the usual agreement factors $R = \sum ||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$ of 0.042 and 0.057. The positions of the 16 independent hydrogen atoms were discovered in a subsequent difference Fourier map. The final cycles of least squares involved anisotropic refinement of the nonhydrogen atoms and isotropic refinement of the hydrogen atoms and converged to final values of R and R_w of 0.026 and 0.029, respectively. In the final cycle, no parameter experienced a shift of more than 0.33σ, which is taken as evidence of convergence. A final difference Fourier map was featureless, with no peak higher than 0.13 e Å⁻³. No correction for secondary extinction appeared necessary, so none was applied. The positional parameters derived from the final cycle, along with their standard deviations as estimated from the inverse matrix, are presented in Table II.

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Table II. Positional Parameters for [Cu(2-pic)₂Cl₂(OH₂)]

atom	x	y	z
Cu	0.19280 (3)	0.22787 (2)	0.10325 (4)
Cl(1)	0.17598 (6)	0.12457 (5)	-0.17822 (8)
Cl(2)	0.21615 (7)	0.34703 (5)	0.36681 (8)
O	0.1335 (2)	0.0837 (1)	0.3017 (2)
N(1)	-0.0596 (2)	0.2400 (1)	-0.0479 (2)
N(11)	0.4512 (2)	0.2243 (1)	0.2332 (2)
C(6)	-0.1898 (3)	0.1629 (2)	-0.0477 (3)
C(5)	-0.3642 (3)	0.1704 (2)	-0.1345 (3)
C(4)	-0.4076 (2)	0.2598 (2)	-0.2256 (3)
C(3)	-0.2760 (3)	0.3380 (2)	-0.2300 (3)
C(2)	-0.1012 (2)	0.3268 (2)	-0.1423 (3)
C(7)	0.0436 (3)	0.4071 (2)	-0.1540 (4)
C(61)	0.4962 (3)	0.1311 (2)	0.2984 (3)
C(51)	0.6677 (3)	0.1183 (2)	0.3840 (3)
C(41)	0.7987 (3)	0.2035 (2)	0.4039 (3)
C(31)	0.7559 (3)	0.2985 (2)	0.3361 (3)
C(21)	0.5808 (2)	0.3079 (2)	0.2517 (3)
C(71)	0.5318 (3)	0.4094 (2)	0.1753 (4)
H(6)	-0.152 (2)	0.106 (2)	0.019 (3)
H(5)	-0.442 (3)	0.116 (2)	-0.128 (3)
H(4)	-0.519 (3)	0.265 (2)	-0.279 (3)
H(3)	-0.294 (2)	0.396 (2)	-0.287 (3)
H(7)	0.002 (3)	0.461 (2)	-0.236 (3)
H(7)'	0.134 (2)	0.436 (2)	-0.032 (3)
H(7)''	0.100 (3)	0.376 (2)	-0.218 (3)
H(61)	0.410 (2)	0.081 (2)	0.288 (3)
H(51)	0.682 (3)	0.052 (2)	0.417 (3)
H(41)	0.914 (3)	0.193 (2)	0.456 (4)
H(31)	0.836 (2)	0.358 (2)	0.344 (3)
H(71)	0.624 (3)	0.453 (2)	0.175 (4)
H(71)'	0.443 (4)	0.394 (3)	0.043 (4)
H(71)''	0.475 (3)	0.445 (2)	0.244 (4)
H(W1)	0.149 (3)	0.107 (2)	0.404 (4)
H(W2)	0.063 (3)	0.031 (2)	0.263 (4)
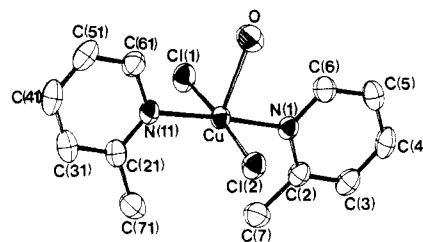
Figure 1. View of the complex [Cu(2-pic)₂Cl₂(OH₂)], showing the atomic labeling scheme used. Thermal ellipsoids here and in the subsequent figure are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity.

[Cu(2-pic)₂Cl₂]₂. For our convenience, the structure was solved as above; naturally, it would have been equally easy to convert the positional parameters in ref 2 to our reduced cell and use them as the initial basis for refinement. Refinement was also conducted as above, the final least-squares cycles again involving anisotropic refinement of nonhydrogen atoms and isotropic refinement of the 14 hydrogen atoms. Consequently, in the final cycle of least squares there were 1737 observations and 210 variables; no parameter shifted by more than 0.11σ, which is taken as evidence of convergence. The final values of R and R_w are 0.031 and 0.029, respectively. No correction for the effects of secondary extinction was necessary, and none was made. A final difference Fourier contained no peak higher than 0.14 e Å⁻³, and the map was featureless. The atomic positional parameters derived from the last cycle of least squares, along with their standard deviations as estimated from the inverse matrix, are presented in Table III. Listings of the atomic thermal parameters and of the observed and calculated structure amplitudes for both structures are available as supplementary material.

Descriptions of the Structures

Cu(2-pic)₂Cl₂(OH₂). The complex consists of monomeric, five-coordinated units that are well separated from each other in the crystals. A view of a single molecule is shown in Figure

Table III. Positional Parameters for $[Cu(2\text{-pic})_2Cl_2]_2$

atom	x	y	z
Cu(1)	-0.11041 (5)	0.21409 (4)	0.03638 (5)
Cl(1)	-0.35338 (10)	0.33188 (9)	-0.14000 (10)
Cl(2)	0.13388 (9)	0.08662 (8)	0.20706 (9)
N(1)	-0.2466 (3)	0.2113 (2)	0.1794 (3)
N(11)	0.0289 (3)	0.2370 (2)	-0.0888 (3)
C(6)	-0.3119 (4)	0.1088 (3)	0.1418 (4)
C(5)	-0.4050 (4)	0.0980 (3)	0.2332 (4)
C(4)	-0.4282 (4)	0.1935 (4)	0.3711 (4)
C(3)	-0.3626 (4)	0.2999 (4)	0.4095 (4)
C(2)	-0.2737 (4)	0.3085 (3)	0.3116 (4)
C(7)	-0.2009 (5)	0.4230 (4)	0.3497 (5)
C(61)	0.0045 (4)	0.1733 (3)	-0.2549 (4)
C(51)	0.0980 (4)	0.1772 (4)	-0.3506 (4)
C(41)	0.2219 (4)	0.2471 (3)	-0.2733 (4)
C(31)	0.2444 (4)	0.3146 (3)	-0.1069 (4)
C(21)	0.1452 (3)	0.3108 (3)	-0.0142 (4)
C(71)	0.1587 (4)	0.3901 (4)	0.1655 (5)
H(6)	-0.286 (3)	0.047 (3)	0.058 (3)
H(5)	-0.446 (3)	0.026 (3)	0.199 (4)
H(4)	-0.489 (4)	0.189 (3)	0.439 (4)
H(3)	-0.376 (3)	0.360 (3)	0.492 (3)
H(61)	-0.079 (3)	0.126 (2)	-0.300 (3)
H(51)	0.078 (3)	0.134 (3)	-0.451 (3)
H(41)	0.292 (3)	0.253 (3)	-0.333 (3)
H(31)	0.317 (3)	0.359 (2)	-0.049 (3)
H(7)	-0.229 (5)	0.485 (4)	0.417 (5)
H(7)'	-0.072 (5)	0.400 (4)	0.401 (5)
H(7)''	-0.212 (5)	0.454 (3)	0.265 (5)
H(71)	0.234 (4)	0.434 (3)	0.204 (4)
H(71)'	0.051 (3)	0.443 (3)	0.168 (3)
H(71)''	0.205 (4)	0.326 (3)	0.248 (4)

Table IV. Internuclear Separations (Å) in $[Cu(2\text{-pic})_2Cl_2(OH_2)]$ and $[Cu(2\text{-pic})_2Cl_2]_2$

atoms	$[Cu(2\text{-pic})_2Cl_2(OH_2)]$	$[Cu(2\text{-pic})_2Cl_2]_2$	
		this work	ref 2
Cu–Cl(1)	2.314 (1)	2.253 (1)	2.21 (1)
Cu–Cl(2)	2.296 (1)	2.287 (1)	2.26 (1)
Cu–N(1)	2.013 (1)	2.011 (2)	2.02 (1)
Cu–N(11)	2.016 (1)	2.005 (2)	1.98 (1)
Cu–X[a]	2.500 (1)	3.364 (1)	3.37 (1)
Cu–Cu'		4.404 (1)	4.41 (1)

[a] X represents the apical atom; this is O for $[Cu(2\text{-pic})_2Cl_2(OH_2)]$ and Cl(2)' for the dimer.

Table V. Internuclear Angles (Deg) in $[Cu(2\text{-pic})_2Cl_2(OH_2)]$ and $[Cu(2\text{-pic})_2Cl_2]_2$

atoms	$[Cu(2\text{-pic})_2\text{-}Cl_2(OH_2)]$	$[Cu(2\text{-pic})_2Cl_2]$	
		this work	ref 2
Cl(1)–Cu–Cl(2)	173.66 (2)	177.58 (5)	176.8[b]
Cl(1)–Cu–N(1)	89.37 (4)	90.05 (7)	89.4 (9)
Cl(1)–Cu–N(11)	87.90 (4)	89.38 (7)	91.5 (9)
Cl(1)–Cu–X[a]	101.87 (5)	98.21 (3)	98.2 (7)
Cl(2)–Cu–N(1)	89.97 (4)	90.17 (7)	90.2 (9)
Cl(2)–Cu–N(11)	92.16 (4)	90.67 (7)	89.3 (9)
Cl(2)–Cu–X[a]	84.47 (5)	79.37 (3)	78.6 (7)
N(1)–Cu–N(11)	173.98 (5)	173.39 (12)	173.8[b]
N(1)–Cu–X[a]	96.39 (5)	94.82 (7)	92 (1)
N(11)–Cu–X[a]	89.42 (5)	91.77 (7)	94 (1)
Cu–Cl(2)–Cu'		100.63 (3)	101.4 (7)

[a] See footnote to Table IV. [b] Value calculated from the data in ref 2.

1. As can be seen in this figure, the complex adopts the (4 + 1) tetragonal-pyramidal geometry with the water molecule at the apical site; the basal sites are occupied by two trans-pyridine nitrogen atoms and two trans-chloride ions. The geometry at copper is only slightly distorted from that of an ideal tetragonal pyramid. The four basal atoms Cl(1), Cl(2), N(1), and N(11) are coplanar, with no atom deviating from the least-squares plane by more than 0.015 (2) Å. As is expected for this geometry,[2,3,17,18] the copper atom sits 0.11 Å above this plane, toward the apical ligand; the methyl group carbon atoms C(7) and C(71) lie on the other side (below) this plane and presumably block approach to the sixth coordination site. The cis angles in the basal plane range from 87.90 (4) to 92.16 (4)°, while the trans angles are 173.66 (2) and 173.98 (2)°. The Cu–O bond is not exactly perpendicular to this plane, the oxygen atom tilting toward Cl(2) and N(11) and away from Cl(1). The Cu–N bond lengths of 2.013 (1) and 2.016 (1) Å are very similar to those found in related complexes, as are the Cu–Cl distances of 2.296 (1) and 2.314 (1) Å. The Cu–O distance of 2.500 (1) Å is relatively short for an apical atom in a copper(II) tetragonal pyramid. The bond lengths and angles in the inner coordination sphere of the complex are compared with those in the related dimer in Tables IV and V, respectively.

The presence of the apical water molecule above the copper atom and the two methyl groups below the base plane presumably precludes the formation of dimeric species of the type found in the absence of the water molecule (vide infra). In principle, however, such a dimeric complex could be synthesized if the methyl group were absent, i.e., in the case of $Cu(py)_2Cl_2(OH_2)$. This complex has not yet been synthesized to our knowledge. However, the relative ease with which the

present complex was formed in the apparent absence of added water would suggest that the syntheses of a variety of complexes of the formulation $CuL_2Cl_2(OH_2)$ should be possible, and the stereochemical arguments above may indicate that many such complexes will be dimeric. The presence of the coordinated water molecule will certainly prevent the formation of higher aggregates such as those found in $Cu(py)_2Cl_2$.[1]

The geometry of the 2-methylpyridine ligands is normal. The two six-membered rings are planar, with no atom deviating from the least-squares plane by more than 0.014 (2) Å in one ring and 0.006 (2) Å in the other. The exocyclic methyl carbon atoms are slightly out of these planes, the deviations being 0.094 (2) and 0.030 (3) Å, respectively. The two pyridine planes are not exactly coplanar, the dihedral angle between them being 9.4°. Both pyridine rings are nearly perpendicular to the base plane of the copper complex, the torsional angles being 82.9 and 73.5° for the two pyridine planes. Hence, the angles here between the normals to the pyridine and copper planes are greater than those of 59.7 and 58.2° found in the polymeric $Cu(4\text{-pic})_2Cl_2$ and $Cu(py)_2Cl_2$ systems,[1c,9] respectively. The values here are, however, comparable to those of 70.6 and 84.3° in $[Cu(2\text{-pic})_2Cl_2]_2$ (vide infra). The bond lengths and angles in the ligands are available as supplementary material.

Inversion-related monomers appear to be joined by a pair of hydrogen bonds between the apical water molecule of one complex and a chloride ligand of the other complex. The O···Cl distances and H···Cl distances and associated O–H···Cl angle are 3.173 (2) Å, 2.41 (1) Å, and 171°, which are well within the ranges observed for other O–H···Cl hydrogen bonds.[19,20] It is noteworthy in Table V that the Cu–O vector is tilted toward Cl(2), so that O–Cu–Cl(2) is acute while O–Cu–Cl(1) is obtuse. This tilt brings the oxygen atom closer

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Table VI. Structural and Magnetic Properties of Tetragonal-Pyramidal Dichloro-Bridged Copper(II) Dimers

complex[a]	Cu–Cl' (r), Å	Cu–Cu' Å	Cu–Cl–Cu' (φ), deg	φ/r	2J, cm⁻¹	ref
[Cu(PAN)Cl]₂	2.647 (1)	3.416	87.79 (3)	33.17		21
[Cu(DMGH)Cl₂]₂	2.698	3.445	88.0	32.62	+6.3	22, 23
[Cu(DMEN)Cl₂]₂	2.734 (3)	3.458 (3)	86.13 (8)	31.50	−2.1	17, 26
[Cu(BTMH)Cl₂]₂	2.735 (2)	3.631 (3)	92.83 (5)	33.94		27
[Cu(9M6MP)Cl₂]₂	2.737 (1)	3.519 (1)	88.17	32.21		28
[Cu(AETA)Cl₂]₂	2.767 (5)	3.592	90.1 (2)	32.56		29
[Cu(BBTE)Cl₂]₂	2.825 (2)	3.749 (2)	94.22 (5)	33.35		30
[Cu(TMPD)Cl₂]₂	2.980 (1)	3.958 (1)	96.5 (1)	32.38		31
[Cu(TMSO)Cl₂]₂	3.020 (2)	3.737 (2)	88.5 (1)	29.30	−17.0	32
[Cu(TMEN)Cl₂]₂	3.147 (4)	4.089 (4)	96.8 (1)	30.76	−5.6	26, 33
[Cu(2-pic)₂Cl₂]₂	3.364 (1)	4.404 (1)	100.63 (3)	29.91	−7.4	10, this work

[a] Abbreviations: PAN = 1-(2-pyridylazo)-2-naphtholate; DMGH = dimethylglyoxime; DMEN = N,N-dimethylethylenediamine; 9M6MP = 9-methyl-6-mercaptopurine; AETA = N-(2-aminoethyl)thiophene-2-carboxaldimine; BBTE = BuSCH₂CH₂SBu; TMSO = tetramethylene sulfoxide; TMEN = N,N,N',N'-tetramethylethylenediamine; BTMH = benzoyltrimethylhydrazine; TMPD = N,N,N',N'-tetramethyl-o-phenyl-enediamine.
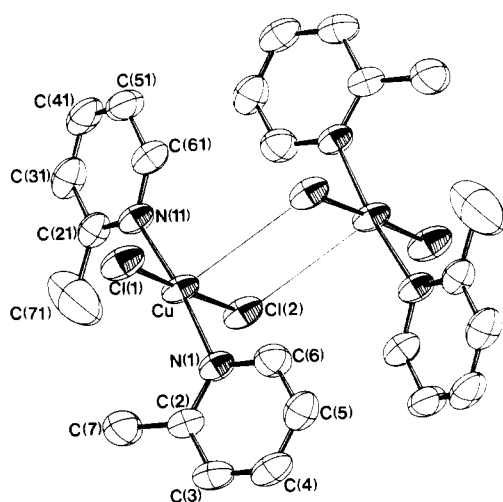

Figure 2. View of the dimeric unit in [Cu(2-pic)₂Cl₂]₂.

to Cl(1) of the inversion-related molecule to which it forms the hydrogen bond, and hence the distortion of the geometry at copper may be ascribable to this effect.

[Cu(2-pic)₂Cl₂]₂. As was previously deduced,[2] the complex consists of dichloro-bridged dimeric units; a view of a single dimer is given in Figure 2. The geometry at the copper(II) centers is again tetragonal pyramidal, with the base plane formed by the trans-nitrogen atoms of the two 2-picoline ligands and two trans-chloride ligands as in the monomer; in the present case, however, the fifth (apical) site is occupied by a chloride ligand, which is in the base plane of the neighboring copper ion. There is a crystallographic inversion center in the middle of the dimer.

The geometry at copper is more highly distorted than that in the monomer. The four basal atoms are not coplanar, there being a slight but significant tetrahedral distortion such that the two chloride ligands are displaced by 0.080 (1) and 0.083 (1) Å on one side of the least-squares plane while the two nitrogen atoms are 0.081 (2) and 0.082 (2) Å on the other side. A similar result was noted[3] in the corresponding bromo complex, [Cu(2-pic)₂Br₂]₂, the deviations there being 0.07 Å. The copper atom lies more nearly in the least-squares plane, being displaced by 0.034 (1) Å toward the apical ligand; the methyl carbon atoms C(7) and C(71) lie 2.475 (4) and 2.411 (4) Å, respectively, on the other side of this plane and again block approach to the sixth coordination site.

The bond lengths and bond angles involving the copper atoms in the complex are compared with those found in the earlier study[2] and those in the monomer in Tables IV and V. The Cu–Cl and Cu–N distances in the base plane are normal, with the bond from the copper to the bridging ligand Cl(2) (2.287 (1) Å) slightly longer than that to the terminal ligand

Cl(1) (2.253 (1) Å) as expected. The apical Cu–Cl(2)' bond of 3.364 (1) Å is extremely long and is longer than that found in any other tetragonal-pyramidal dichloro-bridged copper(II) dimer. The bridging Cu–Cl(2)–Cu' angle of 100.63 (3)° is also the largest such value, and consequently the Cu–Cu' separation of 4.404 (1) Å is far in excess of that in any of these dimeric complexes. These three latter values can be compared with those of 101.4 (7)°, 3.37 (1) Å, and 4.41 (1) Å reported earlier.[2] The bridging geometry observed here is compared with that in all other tetragonal-pyramidal dichloro-bridged copper(II) dimers in Table VI.

The geometry of the 2-methylpyridine ligands is normal and is comparable to that observed in the monomer. The two six-membered rings are planar, with no atom deviating from the least-squares plane by more than 0.014 (4) Å in one ring and by 0.017 (3) Å in the other. The exocyclic methyl carbon atoms, C(7) and C(71), lie 0.023 (4) and 0.113 (4) Å out of their respective least-squares planes. The dihedral angle between the two pyridine planes is 25.3°; in the bromo analogue[3] this dihedral angle is 17.2° while in the monomer it is only 9.4°. As was noted earlier, the torsional angles between the pyridine planes and the base plane of the copper are 70.6 and 84.3°. The bond lengths and angles in the ligands are available as supplementary material.

In the absence of any potential donor atom, there is no hydrogen bonding in the crystals of [Cu(2-pic)₂Cl₂]₂.

Discussion

The development of appropriate theoretical models for understanding both energetic and physical phenomena in exchange-coupled paramagnetic clusters and the relationship between structural, chemical, and magnetic properties has been

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greatly aided by recent systematic studies on several different series of transition-metal compounds.[12,34-43] Several theoretical discussions of aspects of orbital interactions and the formation of wave functions appropriate to the exchange process have recently appeared,[38,39,44-47] but these analyses have not yet yielded a quantitative or even semiquantitative structure–magnetism correlation.

Exchange coupling in copper(II) systems is largely an isotropic phenomenon, and Heisenberg exchange theory is consequently appropriate for the analysis of the properties of copper(II) dimers. For a bimetallic complex the exchange-coupling constant is a measure of the energy separation between the singlet and triplet states and is not necessarily a measure of the strength of the exchange interaction. Hoffmann and co-workers[45] have shown that the singlet–triplet splitting is given by

$$E_T - E_S = -2K_{ab} + (e_1 - e_2)^2/(J_{aa} - J_{ab}) \qquad (1)$$

where K_{ab} is the molecular exchange integral, J_{aa} and J_{ab} are the one- and two-center Coulomb repulsion integrals, and e_1 and e_2 are the one-electron energies of the orbitals that are involved in the exchange coupling. Hoffmann and co-workers have pointed out that the exchange and Coulomb integrals are relatively insensitive to subtle structural distortion and substituent effects, and as a result, the singlet–triplet splitting is largely determined by the energy difference $(e_1 - e_2)$. As has been noted both by us[34-36] and by others,[37-39,45] this term is determined by the structure of the bridging unit. Structural and magnetic data now exist for five examples of chloride-bridged parallel-planar copper(II) dimers, which are listed in Table VI. It may be seen by inspection of these data that the angles at the bridging chloride ion range from 86 to over 100°. While the in-plane copper chloride bond distances are nearly constant at 2.27 ± 0.04 Å, the out-of-plane bond distances vary from 2.65 Å in the 1-(2-pyridylazo)-2-naphtholate compound[21] to 3.36 Å in the 2-methylpyridine compound. It may reasonably be concluded on the basis of the results of the work on the hydroxo-bridged complexes[34-36] and theoretical calculations[38,39,44,45,48] that the exchange-coupling constant will be dependent on the magnitude of the angle at the bridge, ϕ, as well as the bond length in the superexchange pathway. It may be predicted on orbital overlap considerations, alone, that an increase in the bond distances will be accompanied by a decrease in the magnitude of the exchange-coupling constant. These results and considerations suggest that the exchange-coupling constants might be examined in terms of the quotient ϕ/r_o, where r_o is the long, out-of-plane bond distance. Further
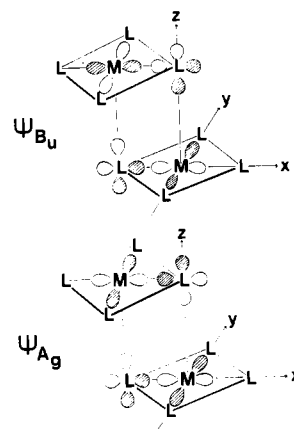

Figure 3. σ antibonding orbitals for parallel-planar dimers, showing the symmetric and antisymmetric combinations. The combination of d_{z^2} orbitals is omitted for clarity.

refinements on the correct structural parameters will probably require that r_o be raised to some power n or that an exponential expression of the form $\exp(-br_o)$ be adopted,[48] but sufficient data do not exist at this time to justify these refinements.

A structural model that is appropriate for the analysis of the experimental results for the parallel-planar dimers is shown in Figure 3. The symmetry of the idealized model is C_{2h}, and the symmetric and antisymmetric combinations of σ antibonding orbitals transform as A_g and B_u. The appropriate linear combinations of metal orbitals and ligand orbitals may be constructed accordingly.[49] The analysis of the magnetic data for the parallel-planar complexes is complicated by an additional structural feature, that being a wide variation in the out-of-plane bond distance. Furthermore, additional metal orbitals become involved in the exchange mechanism. The A_g and B_u combinations of the d_{z^2} orbitals are not shown in Figure 3 since their inclusion would unnecessarily complicate the drawing. However, it is easy to visualize the appropriate combinations. It is now possible to summarize the metal and ligand orbitals that are primarily involved in the exchange-coupling mechanism; these are the σ antibonding $d_{x^2-y^2}$ orbitals, the d_{z^2} orbitals on the metal, and the ligand p_x and p_y orbitals. The ligand s orbitals are of secondary importance because of the relatively larger difference in energy between these orbitals and the metal orbitals. It must also be recognized that the energies of the highest occupied molecular orbitals are influenced by the nature of the ligands that are not primarily involved in the exchange process since the symmetry of the exchange-coupled unit is relatively low.

Extended Hückel molecular orbital calculations have been carried out on a number of model systems of chloro-bridged, parallel-planar copper(II) complexes,[50] and the results are in qualitative agreement with the experimental observations. In fact, if the input parameters in the calculations are properly selected, the experimental observations can be nearly duplicated. These results suggest that the angle at the bridge is the most important factor in determining the sign of the exchange-coupling constant, but the bond distances in the superexchange pathway are significant factors in determining the magnitude of J. This, in turn, implies that a family of J vs. ϕ/r curves should exist. With continued research efforts designed to improve theoretical models and to obtain a greater number of experimental examples, the nature of the relationship between the structural properties and the exchange-coupling constant for this series of compounds can be refined. Attempts are now being made to obtain magnetic data for

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those compounds listed in Table VI that have been structurally but not magnetically characterized, as well as to obtain new examples for analysis.

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# Synthesis and Structural Characterization of the Primary-Amine-Substituted Phosphines $(C_6H_5NH)_3P$ and $[(C_6H_5NH)_2P]_2NC_6H_5$

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The new primary-amine-substituted diphosphines $[(C_6H_5NH)_2P]_2NC_6H_5$ and $(C_6H_5NH)_3P$ have been obtained from the transamination of $[(C_2H_5)_2N]_3$ with aniline. ^{31}P NMR spectral evidence for intermediate formation of $[(C_2H_5)_2N]_2P(NHC_6H_5)$ and $[(C_2H_5)_2N]P(NHC_6H_5)_2$ has been obtained. The structure of $[(C_6H_5NH)_2P]_2NC_6H_5$ as the diethyl ether monosolvate and $(C_6H_5NH)_3P$ have been established by single-crystal X-ray studies. Crystals of $(C_6H_5NH)_3P$ are hexagonal, space group $P6_3$, with $a = b = 11.449$ (3) Å, $c = 7.488$ (2) Å, $Z = 2$, $d_{calcd} = 1.20$ g cm^{-3}, and $d_{obsd} = 1.21$ g cm^{-3} (20 °C, Mo Kα). The crystal structure, solved by direct methods, refined anisotropically to $R_F = 0.053$ and $R_{wF} = 0.071$ and 935 independent observed reflections. $(C_6H_5NH)_3P$ has C_3 molecular symmetry. The C–N and P–N distances and N–P–N angles are 1.393 (10) Å, 1.697 (7) Å, and 99.5 (4)°, respectively. Crystals of $[(C_6H_5NH)_2P]_2NC_6H_5 \cdot (C_2H_5)_2O$ are monoclinic, space group $P2_1/n$, with $a = 9.193$ (4) Å, $b = 21.154$ (8) Å, $c = 16.624$ (5) Å, $\beta = 96.64$ (3)°, $Z = 4$, $d_{calcd} = 1.23$ g cm^{-3}, and $d_{obsd} = 1.25$ g cm^{-3} (20 °C, Mo Kα). The crystal structure, solved by direct methods, refined anisotropically to $R_F = 0.075$ and $R_{wF} = 0.085$ for 1403 independent observed reflections. $[(C_6H_5NH)_2P]_2NC_6H_5$ has approximate C_{2v} molecular symmetry in the crystal, a structure in which the N_2P–N–PN_2 conformation is twisted slightly from eclipsed phorphorus lone-pair electrons. Mean bond distances are as follows: $C_6H_5(H)N$–P, 1.70 (1) Å; C_6H_5N–P, 1.67 (1) Å; C–N, 1.41 (1) Å. Mean bond angles are as follows: $C_6H_5(H)N$–P–NHC_6H_5, 94.9 (5)°; $C_6H_5(H)N$–P–NC_6H_5, 105.3 (6)°; P–N–P, 117.7 (5)°; P–N(H)–C_6H_5, 121.1 (5)°; P–N–C, 124.9 (5)°. $(C_6H_5NH)_3P$ is stable in the solid; in solution it reacts rapidly to establish equilibrium with $[(C_6H_5NH)_2P]_2NC_6H_5$ and $C_6H_5NH_2$. $[(C_6H_5NH)_2P]_2NC_6H_5$ in the absence of $C_6H_5NH_2$ is stable for extended periods in solution, reacting only slowly to more highly condensed products.

Primary-amine-substituted phosphines, because of their N–H bond functionality, are potential intermediates for the synthesis of a wide variety of aminophosphine compounds; however, because of their high reactivity they are seldom isolated. Trissubstituted phosphines, i.e., $(RNH)_3P$ (R = H, alkyl, aryl), often invoked as reaction intermediates, are sufficiently labile to have eluded isolation and unambiguous structural characterization.[2-7]

Trianilinophosphine has been reported,[8-10] but the early accounts of its isolation appear doubtful.[6,11] Recently, Trishin and co-workers[12] reported preparation of $(C_6H_5NH)_3P$ by $[(C_2H_5)_2N]_3P$–$C_6H_5NH_2$ transamination according to eq 1;

$$[(C_2H_5)_2N]_3P + 3C_6H_5NH_2 \rightarrow$$
$$3(C_2H_5)_2NH + (C_6H_5NH)_3P \quad (1)$$
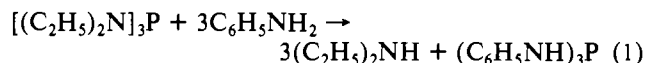
however, their characterization data were insufficient to leave characterization unequivocal and their study did not establish properties of $(C_6H_5NH)_3P$ in solution. Recently, we have reexamined the reaction of $[(C_2H_5)_2N]_3P$ with aniline, in order to clarify the nature of the reaction products. We find that the products are $(C_6H_5NH)_3P$ (**1**) and a new diphosphine $[(C_6H_5NH)_2P]_2NC_6H_5$ (**2**). Preliminary accounts of this work have been reported.[13] Our study of the isolation, solution behavior, and X-ray structural characterization of these compounds is reported below.

Experimental Section

Apparatus and Materials. All manipulations requiring inert atmosphere were carried out in N_2-flushed glovebags or standard Schlenk apparatus.[14] Infrared, ^1H NMR (90.0 MHz), and mass spectra were obtained with a Perkin-Elmer 337G, a Varian EM390, and a Varian MAT CH-5 spectrometers, respectively. Phosphorus-31 NMR spectra were obtained with a JEOL-PFT 100 spectrometer equipped with standard probe accessories. ^1H NMR chemical shifts were measured relative to internal $(CH_3)_4Si$; values downfield from the standard given positive (+δ) values. ^{31}P NMR chemical shifts were measured relative

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