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Relation between Magnetic, Spectroscopic, and Structural Properties of Bis[chloro(*N*-isopropyl-2-hydroxybenzylidene)aminato-μ-*O*-copper(II)] and Bis(*N*-isopropyl-2-hydroxybenzylideneaminato)copper(II)

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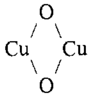
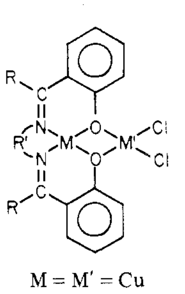
The crystal and molecular structure of the dimeric complex bis[chloro(*N*-isopropyl-2-hydroxybenzylidene)aminato-μ-*O*-copper(II)], $[Cu(ips)Cl]_2$, has been determined ($P\bar{1}$, $Z = 2$, $a = 7.432$ (4) Å, $b = 7.867$ (9) Å, $c = 10.740$ (4) Å, $\alpha = 81.87$ (5)°, $\beta = 84.52$ (4)°, $\gamma = 63.41$ (6)°, $V = 551$ Å^3, $R = 4.0\%$, 2480 reflections), and the structure of the monomeric bis(*N*-isopropyl-2-hydroxybenzylideneaminato)copper(II), $Cu(ips)_2$, has been redetermined ($Pcab$, $Z = 8$, $a = 12.830$ (3) Å, $b = 14.596$ (9) Å, $c = 20.714$ (4) Å, $V = 3879$ Å^3, $R = 4.2\%$, 1587 reflections). The ligand environments are distorted from square-planar toward tetrahedral, the distortion being greater in the case of the monomeric complex which is closer to tetrahedral than planar. Thus, in $Cu(ips)_2$ the steric constraint which is the main cause of distortion from planarity outweighs the combination of the lesser steric effects but slightly greater electrostatic repulsion in $[Cu(ips)Cl]_2$. The results are in good keeping with the hypothesis that the strength of antiferromagnetic interaction between the copper atoms (as measured by the singlet–triplet separation, $-2J$) in $[Cu(ips)Cl]_2$ and related complexes is decreased with increasing tetrahedral distortion. Comparison with related binuclear complexes suggests that the isopropyl substituent is responsible for the distortion of the copper environment in $[Cu(ips)Cl]_2$ and therefore also for the relatively small $-2J$ value and a downfield shift of characteristic d–d transitions. Changes in Cu–O–Cu bridging angles are found to be relatively unimportant in such complexes.

Introduction

Binuclear copper(II) complexes have been shown to exhibit antiferromagnetic interactions which depend more on the immediate environment of the

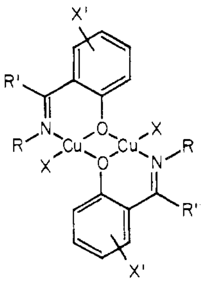


bridge than upon any other factors.[1-8] It has been found that the ligand stereochemistry about the copper atom is of particular importance, with distortion from a planar to a tetrahedral environment being the main reason for the dramatic decrease in the antiferromagnetic interaction. It appears that this is true whether the "tetrahedral" distortion is applied to one of the two copper atoms of the binuclear molecule as in compounds of type **1** or to both copper atoms in the centrosymmetric molecules of type **2**.



M = M' = Cu

1



2

For compounds of type **2**, the antiferromagnetic coupling (given by $|J|$, where $-2J$ is the singlet–triplet separation) between the copper atoms appears to fall into two groups according to the nitrogen substituents. When R is *sec*-alkyl or methyl, $|J|$ is much less than for R = *n*-alkyl.[6] Structural studies[2-4] have related this effect to distortions of the environment of the copper atoms from planarity for R = methyl and R = *n*-alkyl, though no structural work had been done on any complexes with bulky nitrogen substituents. We report here the crystal and molecular structures of complex **2**, with R = isopropyl ($[Cu(ips)Cl]_2$), and of the parent bis(salicylaldimine) complex $Cu(ips)_2$, together with a general correlation between the structural and magnetic properties of a series of binuclear complexes and a comparison between the metal environments in $[Cu(ips)Cl]_2$ and its parent Schiff base complex. A previous structural study[12] had been carried out on the $Cu(ips)_2$ compound in which a final R of 10.4 was obtained with esd's of the relevant coordinations being close to 0.01 Å and 1°. In view of the inherently greater accuracy obtainable in data collected with a diffractometer, it was thought desirable to re-collect the data and refine this structure to obtain more accurate parameters and facilitate comparisons between the two compounds.

Experimental Section

The compounds were synthesized by published methods[6,12,13] and were recrystallized from chloroform/ethanol mixtures to give well-formed green-black crystals. Suitable crystals were chosen by examination via precession photography and were mounted on glass fibers with epoxy cement. Densities were determined by flotation in an aqueous potassium iodide solution.

Crystal data for $Cu(ips)_2$: mol wt 388, space group $Pcab$, $a = 12.830$ (3) Å, $b = 14.596$ (9) Å, $c = 20.714$ (4) Å, $\alpha = \beta = \gamma = 90°$, $V = 3879$ Å^3, $Z = 8$, $\mu(\text{Mo K}\alpha) = 11.8$ cm^{-1}, $d_{\text{calcd}} = 1.329$ g cm^{-3}, $d_{\text{obsd}} = 1.331$ g cm^{-3}, $F(000) = 1624$. Crystal data for $[Cu(ips)Cl]_2$: mol wt 524, space group $P\bar{1}$, $a = 7.432$ (4) Å, $b = 7.867$ (9) Å, $c = 10.740$ (4) Å, $\alpha = 81.87$ (5)°, $\beta = 84.52$ (4)°, $\gamma = 63.41$ (6)°, $V = 551$ Å^3, $Z = 1$, $\mu(\text{Mo K}\alpha) = 22.6$ cm^{-1}, $d_{\text{calcd}} = 1.551$ g cm^{-3}, $d_{\text{obsd}} = 1.566$ g cm^{-3}.

The Enraf-Nonius program SEARCH was used to obtain 15 accurately centered reflections which were then used in the program INDEX to obtain an orientation matrix for data collection and also preliminary cell dimensions. Refined cell dimensions and their estimated standard deviations were obtained from least-squares refinement of 15 accurately centered reflections. For $Cu(ips)_2$, systematic absences occurred for $0kl$ for l odd, $h0l$ for h odd, and $hk0$ for k odd, uniquely indicating the centric space group $Pcab$, a nonstandard setting of $Pbca$ (No. 61 in ref 14), obtained by rotation of the axis labels. The mosaicity of each crystal was examined by the ω-scan technique and judged to be satisfactory.

Collection and Reduction of Data. In each case diffraction data were collected at 292 K on an Enraf-Nonius four-circle CAD4 diffractometer controlled by a PDP8/M computer, using Mo Kα radiation from a highly oriented graphite crystal monochromator. The θ–2θ scan technique was used to record the intensities for all reflections for which $0° > 2\theta > 50°$. Scan widths (SW) to include the peaks from the reflections were calculated from the formula $SW = A + B \tan \theta$, where A is estimated from the mosaicity of the crystal and B is to allow for the increase in width of peak due to Kα_1–Kα_2 splitting. For the two crystals, the values of A and B were 0.60° and 0.20°, respectively. This calculated scan angle is extended at each side by 25% for background determination (BG1 and BG2). The net count (NC) is then calculated from the total count (TOT) as NC = TOT

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

a. [Cu(ips)Cl]$_2$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	−0.002 45 (5)	−0.070 85 (4)	0.140 53 (3)	0.027 00 (7)	0.017 83 (5)	0.007 86 (3)	−0.015 45 (9)	0.000 69 (7)	−0.005 86 (6)
Cl	−0.245 9 (1)	0.034 0 (1)	0.286 20 (7)	0.029 9 (2)	0.025 5 (1)	0.009 16 (6)	−0.021 0 (2)	0.003 8 (2)	−0.009 2 (1)
O	0.082 8 (3)	−0.165 7 (2)	−0.021 5 (2)	0.033 5 (5)	0.015 1 (3)	0.007 6 (2)	−0.012 9 (6)	0.000 8 (5)	−0.005 6 (4)
N	0.212 1 (4)	−0.297 6 (3)	0.227 3 (2)	0.027 6 (5)	0.021 9 (4)	0.008 4 (2)	−0.018 4 (7)	−0.002 0 (6)	−0.003 6 (5)
C(1)	0.273 2 (4)	−0.494 6 (4)	0.055 8 (3)	0.021 5 (5)	0.018 2 (4)	0.010 6 (3)	−0.015 9 (7)	0.003 0 (6)	−0.006 1 (6)
C(2)	0.165 0 (4)	−0.353 7 (3)	−0.039 2 (3)	0.024 2 (5)	0.017 4 (4)	0.009 7 (2)	−0.018 3 (7)	0.004 1 (6)	−0.006 7 (5)
C(3)	0.142 9 (4)	−0.407 9 (4)	−0.152 6 (3)	0.027 9 (6)	0.019 4 (5)	0.009 9 (3)	−0.018 2 (8)	0.000 4 (7)	−0.006 3 (6)
C(4)	0.228 4 (4)	−0.599 9 (4)	−0.171 8 (3)	0.029 2 (6)	0.022 9 (5)	0.011 6 (3)	−0.024 6 (8)	0.004 7 (7)	−0.013 0 (6)
C(5)	0.336 7 (5)	−0.739 0 (4)	−0.078 5 (3)	0.030 1 (7)	0.017 9 (5)	0.014 7 (3)	−0.017 8 (9)	0.003 8 (8)	−0.010 9 (6)
C(6)	0.360 8 (4)	−0.686 0 (4)	0.032 1 (3)	0.025 6 (7)	0.017 5 (5)	0.013 3 (3)	−0.013 0 (8)	0.000 7 (8)	−0.005 1 (7)
C(7)	0.307 1 (4)	−0.456 1 (4)	0.177 6 (3)	0.024 9 (6)	0.020 8 (5)	0.010 5 (3)	−0.017 7 (8)	−0.001 3 (7)	−0.002 4 (6)
C(8)	0.283 1 (6)	−0.294 6 (5)	0.352 5 (3)	0.039 1 (9)	0.031 4 (7)	0.009 1 (3)	−0.021 7 (12)	−0.007 8 (8)	−0.003 3 (8)
C(9)	0.165 9 (7)	−0.357 6 (6)	0.456 9 (4)	0.051 6 (12)	0.044 7 (10)	0.010 4 (4)	−0.036 8 (17)	−0.001 9 (11)	0.001 8 (10)
C(10)	0.276 4 (5)	−0.104 3 (5)	0.363 1 (3)	0.039 4 (8)	0.041 6 (7)	0.011 1 (3)	−0.038 1 (11)	−0.002 2 (8)	−0.015 2 (7)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
H(3)	0.076 (4)	−0.321 (3)	−0.207 (2)	3.8 (6)	H(91)	0.242 (6)	−0.519 (5)	0.449 (4)	9.0 (11)
H(4)	0.209 (4)	−0.629 (4)	−0.246 (3)	4.5 (6)	H(92)	0.222 (6)	−0.369 (6)	0.537 (4)	10.2 (12)
H(5)	0.385 (5)	−0.854 (4)	−0.087 (3)	6.6 (8)	H(93)	0.019 (6)	−0.268 (6)	0.456 (4)	9.7 (12)
H(6)	0.441 (5)	−0.784 (4)	0.087 (3)	6.7 (9)	H(101)	0.342 (5)	−0.078 (4)	0.299 (3)	6.4 (8)
H(7)	0.433 (4)	−0.580 (4)	0.219 (3)	5.1 (7)	H(102)	0.134 (5)	0.007 (5)	0.371 (4)	8.1 (10)
H(8)	0.431 (5)	−0.403 (4)	0.358 (3)	6.8 (9)	H(103)	0.330 (5)	−0.114 (4)	0.435 (3)	6.6 (8)

b. Cu(ips)$_2$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.064 72 (7)	0.125 70 (7)	0.193 66 (5)	0.005 71 (6)	0.006 67 (5)	0.002 88 (3)	0.0020 (1)	−0.0007 (1)	−0.0006 (1)
O(1)	0.057 1 (4)	0.178 3 (4)	0.276 6 (2)	0.005 3 (4)	0.007 9 (4)	0.002 8 (2)	0.0022 (7)	−0.0020 (5)	−0.0020 (4)
O(2)	0.149 6 (4)	0.136 4 (4)	0.120 6 (2)	0.007 0 (4)	0.006 7 (4)	0.002 9 (2)	0.0026 (8)	0.0019 (5)	0.0004 (5)
N(1)	−0.065 1 (4)	0.184 6 (4)	0.162 5 (3)	0.005 8 (4)	0.006 4 (4)	0.001 7 (2)	0.0021 (9)	−0.0019 (6)	−0.0004 (5)
N(2)	0.113 2 (5)	0.001 8 (4)	0.217 0 (3)	0.007 1 (5)	0.007 5 (5)	0.002 6 (2)	0.0048 (9)	−0.0003 (6)	0.0013 (6)
C(1)	−0.111 5 (5)	0.248 6 (5)	0.269 1 (3)	0.006 9 (6)	0.004 7 (4)	0.001 7 (2)	−0.0011 (10)	0.0001 (7)	0.0001 (7)
C(2)	−0.017 5 (5)	0.227 0 (5)	0.303 6 (4)	0.005 4 (5)	0.004 8 (5)	0.003 4 (3)	−0.0000 (9)	0.0007 (8)	0.0009 (8)
C(3)	−0.006 2 (6)	0.260 3 (6)	0.366 7 (4)	0.008 7 (7)	0.008 0 (6)	0.001 6 (2)	0.0014 (12)	−0.0012 (8)	−0.0023 (7)
C(4)	−0.084 4 (7)	0.310 7 (6)	0.393 4 (4)	0.011 8 (9)	0.007 7 (6)	0.002 5 (3)	0.0008 (14)	−0.0004 (9)	−0.0029 (7)
C(5)	−0.177 2 (6)	0.329 5 (6)	0.362 2 (4)	0.010 8 (8)	0.008 8 (6)	0.002 2 (3)	0.0057 (13)	0.0016 (9)	−0.0023 (7)
C(6)	−0.188 7 (5)	0.299 1 (5)	0.302 3 (4)	0.005 8 (6)	0.006 8 (5)	0.003 6 (3)	0.0043 (10)	0.0003 (9)	0.0004 (8)
C(7)	−0.127 2 (5)	0.226 8 (5)	0.201 7 (4)	0.004 2 (5)	0.005 4 (5)	0.003 6 (3)	0.0005 (9)	−0.0004 (8)	0.0001 (8)
C(8)	−0.097 4 (6)	0.175 6 (6)	0.095 7 (4)	0.006 1 (7)	0.010 5 (7)	0.003 0 (3)	0.0037 (12)	−0.0004 (8)	0.0000 (8)
C(9)	−0.086 3 (7)	0.079 2 (7)	0.072 1 (4)	0.011 1 (9)	0.011 6 (7)	0.004 1 (3)	0.0011 (15)	−0.0043 (10)	−0.0069 (9)
C(10)	−0.036 8 (7)	0.245 5 (8)	0.055 1 (4)	0.012 7 (10)	0.013 8 (8)	0.002 5 (3)	0.0108 (16)	−0.0005 (9)	0.0021 (9)
C(1′)	0.220 9 (6)	−0.015 5 (5)	0.121 1 (4)	0.006 8 (6)	0.007 2 (6)	0.002 4 (3)	0.0037 (11)	−0.0004 (8)	−0.0004 (7)
C(2′)	0.207 5 (5)	0.071 6 (6)	0.095 7 (4)	0.005 3 (6)	0.007 8 (6)	0.002 4 (3)	−0.0015 (11)	−0.0003 (7)	−0.0005 (7)
C(3′)	0.262 2 (6)	0.088 9 (6)	0.038 7 (4)	0.007 6 (6)	0.007 3 (6)	0.003 5 (3)	−0.0001 (12)	−0.0024 (8)	0.0002 (7)
C(4′)	0.327 6 (6)	0.027 3 (6)	0.009 7 (4)	0.008 3 (7)	0.010 9 (8)	0.003 1 (3)	0.0011 (14)	0.0017 (9)	−0.0037 (9)
C(5′)	0.337 6 (7)	−0.056 9 (7)	0.036 6 (4)	0.009 9 (8)	0.009 5 (7)	0.005 0 (4)	0.0089 (13)	−0.0020 (10)	−0.0047 (9)
C(6′)	0.285 0 (6)	−0.078 7 (6)	0.090 8 (4)	0.010 0 (8)	0.008 8 (7)	0.003 6 (3)	0.0048 (13)	0.0005 (9)	−0.0001 (9)
C(7′)	0.172 4 (6)	−0.044 3 (6)	0.178 5 (4)	0.008 2 (7)	0.006 5 (6)	0.003 8 (3)	0.0045 (11)	−0.0024 (9)	0.0011 (7)
C(8′)	0.074 7 (7)	−0.045 0 (7)	0.275 2 (4)	0.010 9 (8)	0.013 0 (8)	0.004 7 (4)	0.0116 (15)	0.0045 (10)	0.0064 (9)
C(9′)	0.138 4 (9)	−0.038 8 (10)	0.329 9 (4)	0.015 6 (11)	0.031 8 (15)	0.002 6 (4)	−0.0167 (23)	−0.0069 (10)	0.0056 (13)
C(10′)	−0.039 2 (7)	−0.029 8 (6)	0.284 2 (4)	0.012 6 (9)	0.008 4 (7)	0.004 1 (4)	−0.0017 (14)	0.0036 (10)	0.0010 (8)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
H(3)	0.064 (4)	0.238 (4)	0.390 (2)	5 (2)	H(3′)	0.252 (3)	0.137 (3)	0.022 (2)	2 (1)
H(4)	−0.077 (4)	0.336 (3)	0.431 (2)	4 (1)	H(4′)	0.363 (4)	0.042 (4)	−0.033 (2)	5 (2)
H(5)	−0.232 (4)	0.367 (4)	0.382 (3)	5 (2)	H(5′)	0.373 (4)	−0.097 (3)	0.022 (2)	4 (2)
H(6)	−0.242 (3)	0.311 (3)	0.281 (2)	2 (1)	H(6′)	0.288 (4)	−0.140 (4)	0.112 (3)	7 (2)
H(7)	−0.188 (4)	0.255 (4)	0.180 (2)	5 (1)	H(7′)	0.186 (4)	−0.103 (4)	0.188 (2)	6 (2)
H(8)	−0.171 (4)	0.192 (4)	0.094 (3)	6 (2)	H(8′)	0.103 (4)	−0.107 (4)	0.279 (2)	6 (2)
H(91)	−0.128 (6)	0.029 (5)	0.103 (3)	11 (3)	H(91′)	0.202 (4)	−0.047 (4)	0.330 (3)	8 (2)
H(92)	−0.103 (4)	0.071 (4)	0.036 (2)	5 (2)	H(92′)	0.128 (6)	0.016 (5)	0.342 (3)	12 (3)
H(93)	−0.006 (5)	0.054 (5)	0.070 (3)	9 (2)	H(93′)	0.110 (5)	−0.080 (5)	0.370 (4)	12 (3)
H(101)	−0.047 (5)	0.310 (5)	0.075 (3)	9 (2)	H(101′)	−0.080 (4)	−0.040 (4)	0.246 (3)	7 (2)
H(102)	0.038 (5)	0.230 (5)	0.056 (3)	10 (2)	H(102′)	−0.069 (5)	−0.059 (5)	0.326 (3)	9 (2)
H(103)	−0.058 (4)	0.248 (4)	0.012 (3)	7 (2)	H(103′)	−0.055 (5)	0.031 (4)	0.294 (3)	9 (2)

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

− 2(BG1 + BG2). Reflection data were considered insignificant if intensities registered less than 8 counts above background on a rapid prescan, such reflections being rejected automatically (coded as unobserved) by the computer.

The intensities of four standard reflections, monitored at 100 reflection intervals for each crystal, showed no greater fluctuations during the data collection than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz and polarization effects and for absorption. After averaging of the intensities of equivalent reflections, the data were reduced to 2317 and 2552 independent intensities for Cu(ips)$_2$ and [Cu(ips)Cl]$_2$ respectively, of which 1587 and 2480 had $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics.[15] These data were used in the final refinement of the structural parameters.

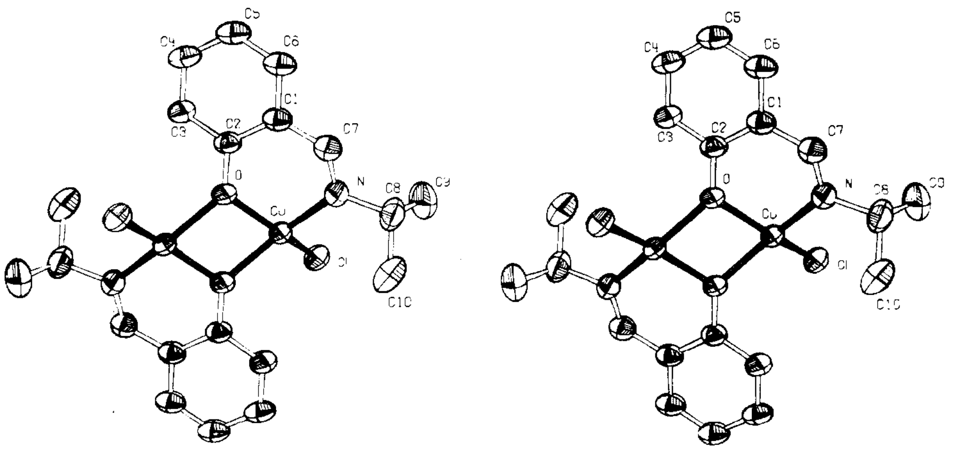


Figure 1. Stereoscopic view of $[Cu(ips)Cl]_2$.

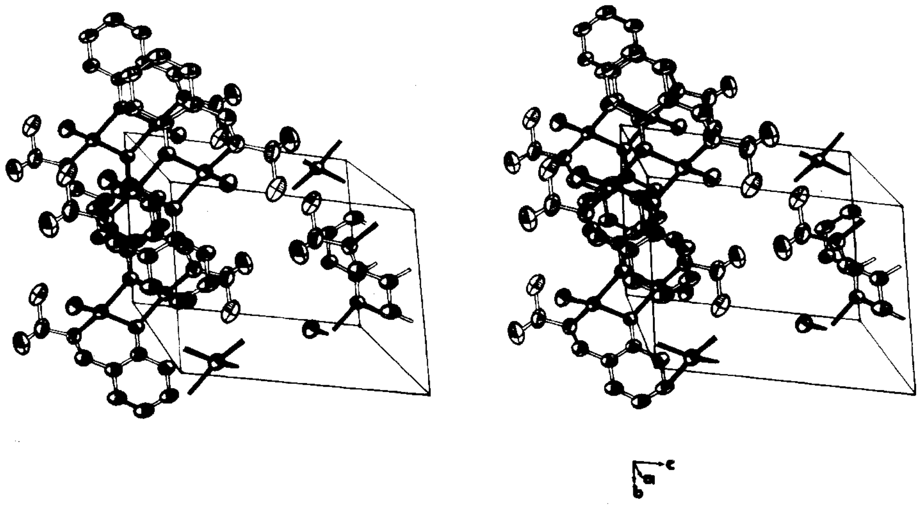


Figure 2. Molecular packing in unit cell of $[Cu(ips)Cl]_2$.

Table II. Bond Lengths (Å)

	$[Cu(ips)Cl]_2$	$Cu(ips)_2$	
		1st ligand	2d ligand
Cu-Cu[a]	3.067 (1)		
Cu-Cl	2.209 (1)		
Cu-O	1.928 (1)	1.887 (4)	1.874 (4)
Cu-O′	1.976 (1)		
Cu-N	1.965 (1)	1.984 (5)	1.974 (5)
O-C(2)	1.352 (2)	1.318 (6)	1.311 (7)
N-C(7)	1.288 (2)	1.296 (6)	1.292 (7)
N-C(8)	1.496 (2)	1.454 (8)	1.473 (8)
C(1)-C(2)	1.399 (2)	1.439 (7)	1.386 (8)
C(1)-C(6)	1.406 (2)	1.414 (7)	1.388 (8)
C(1)-C(7)	1.450 (2)	1.449 (8)	1.409 (9)
C(2)-C(3)	1.390 (2)	1.404 (8)	1.401 (9)
C(3)-C(4)	1.384 (2)	1.363 (8)	1.370 (8)
C(4)-C(5)	1.379 (3)	1.383 (8)	1.36 (1)
C(5)-C(6)	1.356 (3)	1.329 (8)	1.351 (9)
C(8)-C(9)	1.511 (3)	1.497 (9)	1.401 (9)
C(8)-C(10)	1.484 (3)	1.536 (9)	1.492 (9)

[a] Nonbonded.

Solution and Refinement of the Structures. Full-matrix least-squares refinement was based on F, and the function minimized was $\sum w(|F_o| - |F_c|)^2$. The weights w were taken as $[2F_o/\sigma(F_o^2)]^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The atomic scattering factors for nonhydrogen atoms were taken from Cromer and Waber[16] and those for hydrogen from Stewart et al.[17] The effects of anomalous dispersion were included in F_c using Cromer and Ibers' values[18] for $\Delta f'$ and $\Delta f''$. Agreement factors are defined as $R = \sum\||F_o| - |F_c\||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

For the $Cu(ips)_2$ complex, all nonhydrogen atom positions were those obtained from ref 7 and refined with isotropic temperature factors until convergence with R = 11.7% and R_w = 16.4%. Introduction of anisotropic temperature factors produced R = 6.9% and R_w = 12.3%. An analysis of the data at this point showed that the (002) reflection was suffering from severe extinction and was subsequently excluded from refinement, giving improved values for R and R_w of 5.8% and 8.6%, respectively. A Fourier difference map now revealed hydrogen atoms, which were included as isotropic atoms for three cycles of refinement and thereafter held fixed. At convergence, R = 4.2% and R_w = 4.8%.

The $[Cu(ips)Cl]_2$ structure was solved by conventional heavy-atom methods. The position of the copper atom was obtained from the Patterson map and subsequent refinement followed by difference maps enabled location of all nonhydrogen atoms (R = 11.0%, R_w = 14.5%). Introduction of anisotropic temperature factors gave R = 5.2% and R_w = 6.2%. A Fourier difference map now revealed hydrogen atom positions. Inclusion of isotropic hydrogen atoms in the refinement gave R = 4.0% and R_w = 4.2%. A structure factor calculation with all observed and unobserved reflections included (no refinement) gave R = 5.9% and 4.4% for $Cu(ips)_2$ and $[Cu(ips)Cl]_2$ respectively; on this basis it was decided that careful measurement of reflections rejected automatically during data collection would not significantly improve the results. A final Fourier difference map was featureless. Tables of the observed structure factors are available.[19]

Results and Discussion

Final positional and thermal parameters for the atoms are given in Table I. Tables II and III contain the bond lengths and angles. The digits in parentheses in the tables are the estimated standard deviations in the least significant figures quoted and were derived from the inverse matrix in the course of least-squares refinement calculations. Figure 1 is a stereoscopic pair view of $[Cu(ips)Cl]_2$, while Figure 2 shows the

Table III. Bond Angles (deg)

	$[Cu(ips)Cl]_2$	$Cu(ips)_2$	
		1st ligand	2d ligand
Cl–Cu–O	148.16 (4)		
Cl–Cu–O′	99.32 (3)		
Cl–Cu–N	104.31 (4)		
O–Cu–O′	76.44 (4)	137.2 (2)	
O–Cu–N	92.97 (5)	94.4 (2)	95.3 (2)
O(1)–Cu–N(2)		99.6 (2)	
O(2)–Cu–N(1)		100.9 (2)	
N–Cu–N(2)		137.9 (2)	
Cu–O–Cu′	103.56 (4)		
Cu–O–C(2)	124.08 (9)		
		130.2 (4)	126.0 (5)
Cu–O–C(2′)	132.23 (9)		
Cu–N–C(7)	122.1 (1)	121.3 (4)	120.8 (5)
Cu–N–C(8)	122.3 (1)	120.8 (4)	121.4 (5)
C(7)–N–C(8)	115.5 (1)	117.7 (6)	117.6 (6)
C(2)–C(1)–C(6)	118.4 (2)	117.4 (6)	120.9 (8)
C(2)–C(1)–C(7)	124.7 (1)	123.3 (7)	122.7 (7)
C(6)–C(1)–C(7)	116.8 (2)	119.2 (7)	116.5 (8)
O–C(2)–C(1)	120.4 (1)	120.1 (7)	125.8 (7)
O–C(2)–C(3)	120.1 (2)	120.6 (7)	119.1 (8)
C(1)–C(2)–C(3)	119.6 (1)	118.3 (7)	115.1 (7)
C(2)–C(3)–C(4)	120.3 (2)	119.4 (7)	124.1 (8)
C(3)–C(4)–C(5)	120.2 (2)	123.5 (7)	118.2 (8)
C(4)–C(5)–C(6)	120.1 (2)	117.9 (7)	120.7 (8)
C(1)–C(6)–C(5)	121.4 (2)	123.5 (6)	121.1 (8)
N–C(7)–C(1)	126.6 (2)	128.6 (6)	128.9 (7)
N–C(8)–C(9)	110.0 (2)	111.7 (6)	116.1 (8)
N–C(8)–C(10)	110.8 (2)	108.6 (6)	111.2 (7)
C(9)–C(8)–C(10)	113.7 (2)	113.4 (7)	117.5 (8)

Table IV. Closest Nonhydrogen Intermolecular Contacts

Molecule 1	Molecule 2	Distance, Å	Symmetry transformation
		$[Cu(ips)Cl]_2$	
Cu	C(5)	3.546 (2)	$-x, -1-y, -z$
	C(4)	3.596 (2)	$-x, -1-y, -z$
O	C(5)	3.534 (2)	$-x, -1-y, -z$
C(1)	C(1)	3.419 (3)	$1-x, -1-y, -z$
	C(3)	3.513 (2)	$-x, -1-y, -z$
		$Cu(ips)_2$	
O(1)	C(6)	3.315 (7)	$\frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}-z$
C(1)	C(10′)	3.549 (9)	$x, \frac{1}{2}+y, \frac{1}{2}-z$
C(10)	C(3′)	3.548 (10)	$x-\frac{1}{2}, \frac{1}{2}+y, \frac{1}{2}-z$

molecular packing in the unit cell of this complex. As is evident from Figure 2 and the closest intermolecular contacts (Table IV), the complexes $[Cu(ips)Cl]_2$ and $Cu(ips)_2$ consist of discrete dimeric and monomeric molecules, respectively. The molecules of $[Cu(ips)Cl]_2$ are so well separated that the observed magnetic exchange interactions[6] must be considered to be intramolecular.

The Cu–Cl distance of 2.209 Å in $[Cu(ips)Cl]_2$ is normal and compares with 2.202 Å for Cu–Cl in the two analogous type **2** complexes, with X = Cl, whose structures have so far been determined.[2,4] The Cu–O separations of 1.928 and 1.976 Å and the phenolic C–O distance of 1.352 Å are significantly longer in $[Cu(ips)Cl]_2$, due to the increase from 2 to 3 in the coordination number of the oxygen upon binucleation, than the corresponding Cu–O and C–O bonds in $Cu(ips)_2$, which average 1.881 and 1.315 Å, respectively. A probable compensating effect of these bond elongations is the slightly longer Cu–N distance of 1.965 Å in $[Cu(ips)Cl]_2$ than those of 1.984 and 1.974 Å in $Cu(ips)_2$. The other intraligand bond distances are normal for this type of compound.[4,5,7,12] The Cu_2O_2 bridging group is exactly planar because of the crystallographic center of inversion at its center. The average C–H distances are as expected:[20] 0.96 Å for $[Cu(ips)Cl]_2$ and 0.95 Å for $Cu(ips)_2$, or 0.95 Å averaged over both compounds.

The copper environment in $[Cu(ips)Cl]_2$ is the closest to tetrahedral so far observed in any complex of type **2**; the dihedral angle, τ, between the planes CuOCu′O′ and CuNClCu′N′Cl′ (planes 1 and 2 in Table V), is larger than in other complexes of **2** or in complexes of type **3** (Table VI). τ values of 0 and 90° are necessary but not sufficient conditions for planar and tetrahedral metal environments, respectively. In this case, the same angle is obtained if plane 2 is recalculated without the Cu atoms (plane 3 in Table V) or if it is replaced by the CuNCl plane (plane 5 in Table V, angle τ'). By comparison, in the parent monomer $Cu(ips)_2$, the dihedral angle (τ') between the two (ips) ligand planes is more than 60°—two-thirds of the way to tetrahedral by the angular

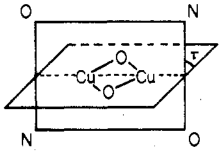


Table V

Coefficients of Least-Squares Planes $AX + BY + CZ = D$ for $[Cu(ips)Cl]_2$ and $Cu(ips)_2$

Plane	Atoms	A	B	C	D	Distances from plane, Å
1[a]	Cu, Cu′, O, O′	−0.9969	−0.0020	−0.0783	0	Cu, 0; Cu′, 0; O, 0; O′, 0
2[a]	Cu, Cu′, Cl, Cl′ N, N′	−0.7481	−0.6248	−0.2236	0	Cu, −0.0405; Cu′, 0.0405; Cl, 0.0107; Cl′, −0.0107; N, 0.0114; N′, −0.0114
3[a]	Cl, Cl′, N, N′	−0.7481	−0.6235	−0.2273	0	Cl, 0; Cl′, 0; N, 0; N′, 0; Cu, −0.0465
4a[a]	Cu, O, N, C(1), C(2), C(7)	0.9387	0.2128	−0.2712	−0.3953	Cu, −0.1893; O, 0.2238; N, 0.0851; C(1), −0.1350; C(2), −0.0636; C(7), 0.0790
$4b_1$[b]		0.4612	0.8394	−0.2877	0.8377	Cu, −0.0686; O(1), 0.0376; N(1), 0.0710; C(1), −0.0572; C(2), 0.0299; C(7), −0.0126
$4b_2$[c]		−0.7721	−0.3479	−0.5319	−3.4702	Cu, 0.0517; O(2), −0.0373; N(2), −0.0539; C(1′), 0.0239; C(2′), −0.0036; C(7′), 0.0193
5[a]	Cu′, Cl′, N′	−0.7459	−0.6124	−0.2621	0.1023	Cu′, 0; Cl′, 0; N′, 0, Cu, −0.2047

Interplanar Angles, Deg

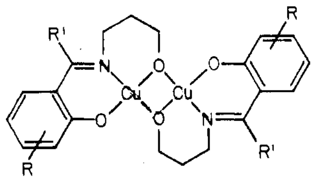
	Planes						
	1–2	1–3	1–5	2–3	2–5	3–5	$4b_1$–$4b_2$
$[Cu(ips)Cl]_2$	40.1	40.1	40.1	0.2	2.3	2.1	
$Cu(ips)_2$							60.3

[a] $[Cu(ips)Cl]_2$. [b] $Cu(ips)_2$–first ligand. [c] $Cu(ips)_2$–second ligand.

Table VI. Some Magnetic and Structural Features

Complex										
Type	Formula	$-J/\mathrm{cm}^{-1}$	τ/deg	Cu–O–Cu/deg	Cu–Cu/Å	Ref	R	R′	X	X′
3a	$Cu_2Cl_2O_4N_2C_{20}H_{20}$		13.7	103.7	3.026	21	5-Cl	H		
3b	$Cu_2O_8N_4C_{20}H_{20}$	>400	9.6	103.5	3.009	21	$3\text{-}NO_2$	H		
3c	$Cu_2O_4N_2C_{28}H_{26}$		10.4	104.0	3.031	21	5,6-benzo	H		
3d	$Cu_2O_4N_2C_{22}H_{26}$		7.0	104.2	3.035	22	H	CH_3		
3e	$Cu_2O_8N_4C_{20}H_{20}$	>500	4.0	106.0	3.030	22	$5\text{-}NO_2$	H		
2b	$Cu_2Cl_2O_2N_2C_{18}H_{20}$	240	33.1	103.3	3.051	4	C_2H_5	H	Cl	H
2c	$Cu_2Cl_2Br_2O_2N_2C_{34}H_{34}$	220	35.5	101.2	3.019	5	C_4H_9	C_6H_5	Br	5-Cl
2d	$Cu_2Br_2O_2N_2C_{18}H_{20}$	205	35.7	104.6	3.05	4	C_2H_5	H	Br	H
2e	$Cu_2Cl_2O_2N_2C_{16}H_{16}$	146, 149[b]	39.3	102.2	3.041	4	CH_3	H	Cl	H
2a	$Cu_2Cl_2O_2N_2C_{20}H_{24}$	145	40.1	103.5	3.067	*a*	$CH(CH_3)_2$	H	Cl	H

[a] Present work. [b] Two samples; see ref 4.



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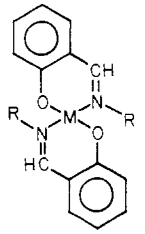

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criterion (again planar requires 0° and tetrahedral 90°). This result confirms the hypothesis on which the original structural predictions in type **2** complexes were based:[1,6,23] the copper environments in type **2** and **4** complexes can be at least partially controlled via the R-group size, and the control is finer in **2** than in **4**. Thus, in type **4** complexes, the combination of the greater steric constraint and some ligand electrostatic repulsion (O_2N_2) outweighs the lesser steric but slightly greater electrostatic (O_2NCl here) effects in type **2** complexes.

An effect of binucleation of the Schiff base ligand is observed in the six-membered ring formed from the copper atoms and the O–C(2)–C(1)–C(7)–N fragments in $Cu(ips)_2$ and $[Cu(ips)Cl]_2$. In the monomer $Cu(ips)_2$, these rings (planes 1 and 2 in Table V) are essentially planar, the pseudotetrahedral metal environment being formed by the large dihedral angle (τ') between them. In the binuclear $[Cu(ips)Cl]_2$, these six-membered rings (planes 4 in Table V) are markedly distorted from planarity, to preserve the planarity of the central Cu_2O_2 fragment. This is also evident from Figure 1.

A decrease in the strength of antiferromagnetic interaction (given by $|J|$) in type **2** complexes occurs together with a decrease in the energy of ligand field transitions in the region 18 000–8000 cm^{-1}, and both of these observations coincide with increased bulkiness of R and apparently anomalously with R = CH_3.[1,6] The structural data[4,21,22] indicate that the decreasing values of $|J|$ and the ligand field energies are, without exception, indicators of increasing tetrahedral distortion (τ).

The present results fit well into the correlation drawn between decreasing antiferromagnetic interaction and increasing τ (Table VI). In $[Cu(ips)Cl]_2$, $|J| = 145$ cm^{-1} and $\tau = 40.1°$, while the same complex with R = ethyl in place of iospropyl (**2b**) has $|J| = 240$ cm^{-1} and $\tau = 33.1°$. The Cu–O–Cu bridging angles[7] do not differ significantly between the two complexes, nor do any structural features. Thus, the differences in the magnetic properties of the two complexes can be attributed *entirely* to the change in tetrahedral distortion (i.e., $|J|$ vs. τ). Comparison of $[Cu(ips)Cl]_2$ with the R = CH_3 analogue, **2e**, suggests that the latter complex has a slightly lower $|J|$ than it should, based on τ alone. This decrease in $|J|$ can be attributed to a 1.3° decrease in Cu–O–Cu, but only limited quantitative significance is attached to this observation, pending more accurate magnetic susceptibility data.

Although Table VI contains some (but not the only) exceptions to the expected[24] relation between J and the Cu–O–Cu angle, this correlation has been observed to hold in a wide range of complexes.[7] Thus both the environment of the metal (τ) and that of the bridging ligand (Cu–O–Cu), i.e., the electronic structure of the entire bridging unit and its immediate vicinity, must be taken into account in considering any of the plausible superexchange mechanisms[7,11,24,25] proposed for such systems. In particular, we will demonstrate[26] that variations of the direction of the bond to nonmetallic atoms attached to the bridging ligand can dramatically affect the strength and sign of the interaction.

No significant correlation is observed between J and the Cu–Cu distance in Table VI. If anything, there is a slight but not consistent trend to *weaker* antiferromagnetic interaction with closer approach of the metals.

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Registry No. $Cu(ips)_2$, 38956-95-5; $[Cu(ips)Cl]_2$, 21688-42-6.

Supplementary Material Available: A listing of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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