

complex observed by Day and McClung<sup>11</sup> where pyridine and dtas<sup>-</sup> were involved in formation of the mixed-ligand complex.) For this case, one can expect the metal hyperfine constants and *g* of the mixed-ligand complexes to have values comparable to those of VO(dtc)<sub>2</sub>, VO(dtp)<sub>2</sub>, and VO(dtas)<sub>2</sub>.<sup>6-8</sup> The observed values for the complexes identified as mixed-ligand

complexes are consistent with this expectation. The next-neighbor hyperfine splitting observed provides additional confirmation of the identification.

**Registry No.** VO(dtp)<sub>2</sub>, 41523-86-8; VO(dtas)<sub>2</sub>, 37448-72-9; VO(dtp)(dtas), 79483-63-9; VO(dtc)(dtas), 79483-64-0.

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## Crystal and Molecular Structure of Dipolar Spin-Coupled Dimers of an Irregularly Pentacoordinate Copper(II) Complex, [Cu(5-MeIn)(DBM)]

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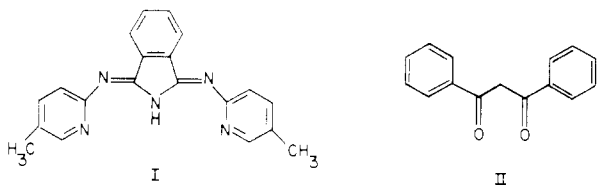
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Ternary complexes of copper(II) with the anions of dibenzoylmethane (II) and 1,3-bis(2-pyridylimino)isoindolines were synthesized. Mononuclear pentacoordinate structures are assigned to the compound III with the 5-methylpyridyl ligand (I) as well as the 4-methylpyridyl and nonmethylated complexes V and IV. The X-ray crystal structure of the 5-methylated complex III attributes it to the space group *P*2<sub>1</sub>/*n*, with a final *R* factor of 0.047. The coordination geometry is neither square pyramidal nor trigonal bipyramidal but an intermediate structure, in which the more distant of the dibenzoylmethanate oxygen atoms could be considered to approximate the axial donor of a square pyramid. The 5-methylated complex, III, packs uniquely in the crystal lattice as symmetry-related pairs of molecules, in which the isoindolinate ligands are cofacial, with a Cu-Cu separation of 4.453 Å. Within this noncovalent dimer, a spin-exchange process operates, so that the solid state of III exhibits the electron spin resonance spectrum of a spin-coupled triplet system, though the susceptibility obeys a Curie-Weiss law above 77 K. All of III-V are irregularly pentacoordinate in nondonor solvents.

### Introduction

Our interest in five-coordinate copper(II) complexes as possible models for the active sites of some copper-containing proteins<sup>2</sup> has led us to synthesize a number of compounds with stereochemistries based upon trigonal symmetries.<sup>3</sup> We have prepared complexes by combination, on the copper(II) ion, of a tridentate chelating agent with a bidentate one, distortions away from *C*<sub>4v</sub> symmetry being assisted where possible by the use of sterically constraining substituents.

During the course of this work it was found that the complex formed with the anions of the ligands 1,3-bis((5-methyl-2-pyridyl)imino)isoindoline (5-MeInH, I) and dibenzoylmethane



(HDBM, II) exhibited a solid-state, powder ESR spectrum suggestive of magnetically coupled copper(II) centers. Microanalytical data for the complex were consistent with the formulation Cu(5-MeIn)(DBM), and an examination of molecular models indicated that regular trigonal-bipyramidal geometry would not be unfavorable. No mode for coordinative dimerization (ligand bridging) was apparent. In order to examine possible pathways for magnetic coupling, we have determined the crystal and molecular structure of the complex. The results of the study are reported here together with some of the results of solution and solid-state ESR measurements.

Table I. Crystal Data for Cu(5-MeIn)(DBM)

|                           |                       |                                                                           |                  |
|---------------------------|-----------------------|---------------------------------------------------------------------------|------------------|
| dimens                    | 0.32 × 0.31 × 0.12 mm | no. of reflctns used to determine cell constants and their 2σ limits, deg | 25, 20 < 2θ < 30 |
| mol wt                    | 613.17                | <i>Z</i>                                                                  | 4                |
| cell constants            |                       | $\rho_{\text{calc}}$ , g cm <sup>-3</sup>                                 | 1.411            |
| <i>a</i> , Å              | 20.520 (4)            | $\mu$ , cm <sup>-1</sup>                                                  | 7.59             |
| <i>b</i> , Å              | 11.187 (2)            |                                                                           |                  |
| <i>c</i> , Å              | 12.658 (3)            |                                                                           |                  |
| $\beta$ , deg             | 96.83 (5)             |                                                                           |                  |
| <i>V</i> , Å <sup>3</sup> | 2885.12               |                                                                           |                  |

### Experimental Section

The preparation of the ligands is described elsewhere.<sup>4,5</sup> Commercial dibenzoylmethane (Aldrich) was used without further purification.

The compound (dibenzoylmethanato)(1,3-bis((5-methyl-2-pyridyl)imino)isoindolato)copper(II) (III) was prepared by refluxing copper(II) acetate hydrate (0.60 g, 3 mmol), 5-MeInH (0.98 g, 3 mmol), HDBM (0.67 g 3 mmol), and Et<sub>3</sub>N (0.60 g, 6 mmol) in MeOH solution (80 mL) for 30 min. The green precipitate was collected by filtration and crystallized from DMF (*N,N*-dimethylformamide). The yield was essentially quantitative. Anal. Calcd for C<sub>35</sub>H<sub>27</sub>CuN<sub>5</sub>O<sub>2</sub>: C, 68.6; H, 4.44; N, 11.4. Found: C, 68.4; H, 4.44; N, 11.6. A crystal suitable for structure determination was obtained by slowly cooling a DMF solution of the complex.

[Cu(In)(DBM)] (IV) and [Cu(4-MeIn)(DBM)] (V) were prepared in an analogous fashion. In the latter case, crystallization was effected at 255 K, and the yield was considerably lower. Anal. Calcd for C<sub>33</sub>H<sub>23</sub>CuN<sub>5</sub>O<sub>2</sub> (IV): C, 67.7; H, 3.96; N, 12.0. Found: C, 67.8; H, 3.95; N, 11.9. Calcd for C<sub>35</sub>H<sub>27</sub>CuN<sub>5</sub>O<sub>2</sub> (V): C, 68.6; H, 4.44. Found: C, 68.9; H, 4.39.

Electron spin resonance spectra were obtained at 77 K and ambient temperature with a Varian Associates E-12 X-band spectrometer. Microanalyses were performed by Canadian Microanalytical Service Ltd. Variable-temperature magnetic susceptibility was performed

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**Table II.** Data Collection and Refinement Details for Cu(5-MeIn)(DBM)

|                                                                           |                                     |
|---------------------------------------------------------------------------|-------------------------------------|
| diffractometer                                                            | Philips PW1100                      |
| monochromator                                                             | graphite                            |
| radiation ( $\lambda$ , Å)                                                | Mo K $\alpha$ (0.710 69)            |
| method                                                                    | $\theta$ - $2\theta$                |
| scan width, deg                                                           | 1.00                                |
| scan speed, deg min <sup>-1</sup>                                         | 2.4                                 |
| bkgd time, s                                                              | 2 × 20                              |
| no. of stds                                                               | 3                                   |
| standardization period                                                    | 2 h                                 |
| 2 $\theta$ limits of data, deg                                            | 6 < 2 $\theta$ < 54                 |
| no. of data collected                                                     | 2223                                |
| rel transmission factors (full data set)                                  | 0.968–0.794                         |
| no. of data used in final refinement                                      | 2074, with $ F_o  > 6\sigma( F_o )$ |
| no. of data/no. of variables                                              | 5.3                                 |
| $R_1 = \Sigma   F_o  -  F_c   / \Sigma  F_o $                             | 0.047                               |
| $R_2 = [\Sigma w( F_o  -  F_c )^2 / \Sigma w F_o ^2]^{1/2}$               | 0.048                               |
| max residual electron density on difference Fourier map, e/Å <sup>3</sup> | 0.53                                |

<sup>a</sup> The function minimized was  $\Sigma w(|F_o| - |F_c|)^2$ , where  $w = 1/\sigma(F_o)^2$ . <sup>b</sup> Relative intensities and their standard deviations were calculated as  $S - tB$  and  $\sigma(I) = [S + t^2B + p^2(S + tB^2)]^{1/2}$ , where  $S$  is the total peak scan count,  $B$  is the total background scan count,  $t$  is the ratio of peak to background scan times, and  $p$  is a constant, here taken as 0.04 to account for other sources of error.<sup>7,8</sup>

by Dr. A. B. P. Lever at York University.

**Crystal Examination and Data Collection.** The crystal data showed the systematic absences  $0k0$  ( $k = 2n + 1$ ) and  $h0l$  ( $h + l = 2n + 1$ ) and symmetry, establishing  $P2_1/n$  as the unique space group.<sup>6</sup> The refined cell constants and other pertinent crystal data are presented in Table I. The routine aspects of data collection are presented in Table II.

Statistical analysis of the standard reflections indicated that there was no crystal decomposition during the course of data collection. Semiempirical absorption corrections based on pseudoellipsoid model<sup>9</sup> and 384 azimuthal scan data from 12 independent reflections were applied.

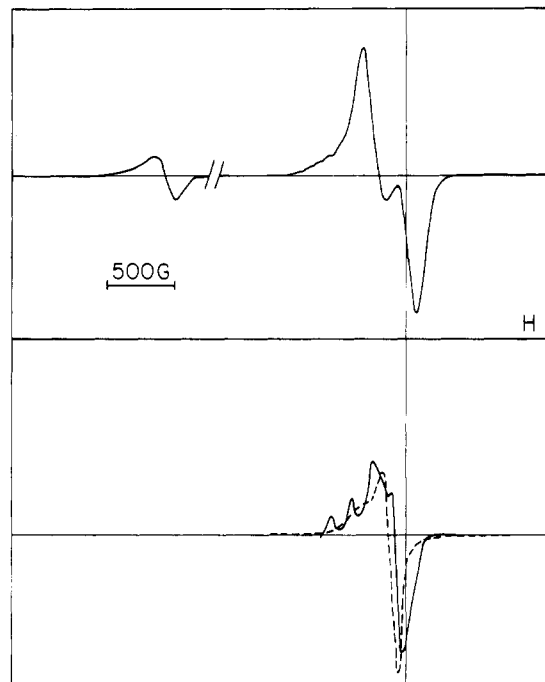
**Solution and Refinement of the Structure.** The structure was solved by the Patterson method and was refined by blocked full-matrix least squares with complex neutral-atom scattering factors<sup>10</sup> and weights =  $1/[\sigma^2(F)]$ . A difference Fourier map then revealed the positions of all hydrogen atoms. The phenyl and methine hydrogen atom positions were established geometrically assuming a C–H bond distance of 1.08 Å. The methyl hydrogen positions taken from the  $F_o - F_c$  synthesis were used as a starting set to produce standard tetrahedral geometry and subsequently refined as rigid groups. The spectroscopically determined C–H bond distance of 1.08 Å was used to obtain realistic and consistent contact distances. (Refinement of the H atoms with C–H = 0.95 Å<sup>11</sup> gave a marginal improvement in  $R$  factor = 0.045 with common  $U_{iso}$  values of 0.055 (8) Å<sup>2</sup> (sp<sup>2</sup> C–H) and 0.120 (15) Å<sup>2</sup> (sp<sup>3</sup> C–H).)

The refined parameters included anisotropic thermal parameters for the nonhydrogen atoms. The final positional and thermal parameters for all atoms, together with their estimated standard deviations, are listed in Tables V–VII (supplementary material).

The observed and calculated structure factor amplitudes are tabulated as supplementary material. Computations were performed using the SHELX76 system by G. M. Sheldrick and ORTEP2 by C. K. Johnson.

## Results and Discussion

X-Band ESR spectra have been obtained for Cu(5-MeIn)(DBM) in powder form and in solution at 77 K and ambient



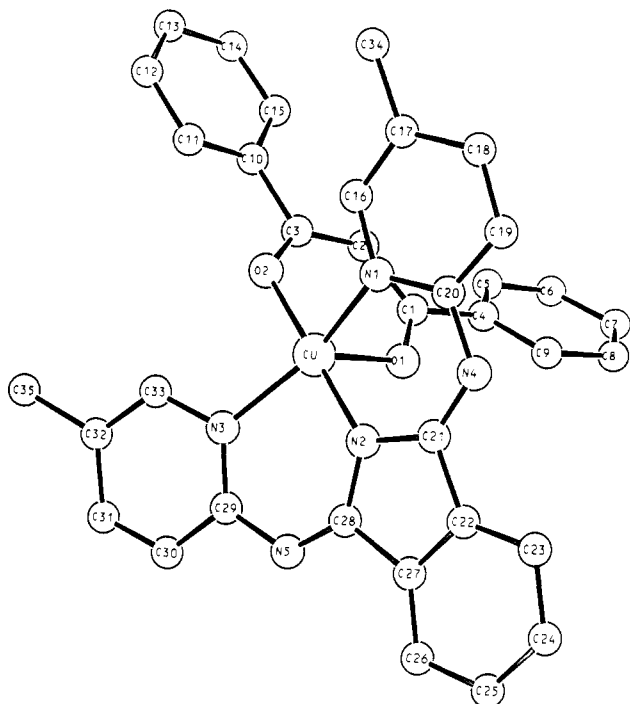
**Figure 1.** X-Band ESR spectra: upper panel, Cu(5-MeIn)(DBM) powder at 295 K with the low-field end at 50 $\times$  gain; lower panel, Cu(IIn)(DBM) (broken trace) powder at 295 K and Cu(4-MeIn)(DBM) (solid trace) in toluene/dichloromethane at 77 K. The vertical line indicates  $g = 2$ .

temperature. The spectrum of the powdered complex (Figure 1) shows the features characteristic of a dimeric copper system<sup>12</sup> with resonances centered about both  $\sim 3300$  G and  $\sim 1650$  G, corresponding to  $\Delta M_s = \pm 1$  and  $\Delta M_s = \pm 2$  transitions, respectively. In addition, the  $\Delta M_s = \pm 1$  signal exhibits five copper hyperfine lines of average separation 77 G (vide infra). Lowering the sample temperature to 77 K produced no effect on the shape of the high-field signal but allowed the detection, at high gain, of four, poorly resolved copper hyperfine lines of average separation 85 G, on the low-field side of the  $\Delta M_s = \pm 2$  signal. The overall appearance of the spectrum is similar to those previously reported for the dimeric complexes  $[\text{Cu}_2(\text{tren})_2(\text{BiIm})](\text{BPh}_4)_2$ ,<sup>13</sup> for which the intradimer exchange parameter,  $|J|$ , was estimated to be less than  $0.5 \text{ cm}^{-1}$ , and  $[\text{Cu}_2(\text{cyclops})_2\text{N}_3]\text{ClO}_4$ ,<sup>14</sup> for which  $J = -0.56 \text{ cm}^{-1}$ .

The complex is sparingly soluble in chloroform or toluene/dichloromethane, in which the ambient-temperature spectrum ( $g_0 = 2.11$ ,  $A_0 = 0.0071 \text{ cm}^{-1}$ ) shows no obvious signs of coupling apart from the usual Cu and <sup>14</sup>N hyperfine structure. In low-temperature glasses, the spectrum is very similar to those of the nonmethylated and 4-methyl analogues,  $[\text{Cu}(\text{IIn})(\text{DBM})]$  and  $[\text{Cu}(4\text{-MeIn})(\text{DBM})]$ . The ESR spectrum of these (e.g., Figure 1) in the solid state shows no sign of the exchange coupling displayed by the title compound. The solution glass spectra (e.g., Figure 1) of all the species are indicative of monomeric structures. Overlap between the low- and high-field regions renders accurate analysis difficult without simulation. However, for  $[\text{Cu}(4\text{-MeIn})(\text{DBM})]$ ,  $g_3$  (2.230) and, particularly, the low value of  $A_3$  ( $0.0613 \text{ cm}^{-1}$ ) are indicative of low-symmetry structures for these molecules in solution. It is worth noting that the magnitude of  $A_3$  is

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**Figure 2.** Representation of an individual molecule of Cu(5-Melin)(DBM), with the atom numbering scheme shown. The DBM anion lies across the rear of the diagram, at the upper right. Hydrogens omitted for clarity.

**Table III.** Molecular Dimensions in the Coordination Group for Cu(5-Melin)(DBM)

| (a) Distances, Å <sup>a</sup>  |           |                         |           |
|--------------------------------|-----------|-------------------------|-----------|
| Cu-O(1)                        | 2.178 (5) | Cu-N(1)                 | 2.056 (5) |
| Cu-O(2)                        | 1.954 (4) | Cu-N(2)                 | 1.904 (5) |
| Cu...Cu <sup>1</sup>           | 4.453 (2) | Cu-N(3)                 | 2.050 (5) |
| Cu...N(4)                      | 3.338     | Cu...N(1 <sup>1</sup> ) | 3.971 (5) |
| Cu...N(5)                      | 3.337     |                         |           |
| (b) Angles, Deg                |           |                         |           |
| O(1)-Cu-O(2)                   | 88.1 (2)  | O(1)-Cu-N(1)            | 94.3 (2)  |
| O(1)-Cu-N(2)                   | 90.7 (2)  | O(1)-Cu-N(3)            | 110.1 (2) |
| O(2)-Cu-N(1)                   | 91.6 (2)  | O(2)-Cu-N(2)            | 178.3 (2) |
| O(2)-Cu-N(3)                   | 90.2 (2)  | N(1)-Cu-N(2)            | 89.7 (2)  |
| N(1)-Cu-N(3)                   | 155.6 (2) | N(2)-Cu-N(3)            | 89.0 (2)  |
| (c) Polyhedral Edge Lengths, Å |           |                         |           |
| O(1)...O(2)                    | 2.876     | O(1)...N(1)             | 3.106     |
| O(1)...N(2)                    | 2.911     | O(1)...N(3)             | 3.465     |
| O(2)...N(1)                    | 2.876     | N(1)...N(2)             | 2.795     |
| O(2)...N(3)                    | 2.837     | N(2)...N(3)             | 2.774     |
| N(1)...N(3)                    | 4.013     |                         |           |

<sup>a</sup> *i* denotes the symmetry transformation  $-x, -y, 2-z$ .

almost twice the value observed in the powder spectrum, as expected for a monomer-dimer copper(II) system.<sup>14</sup>

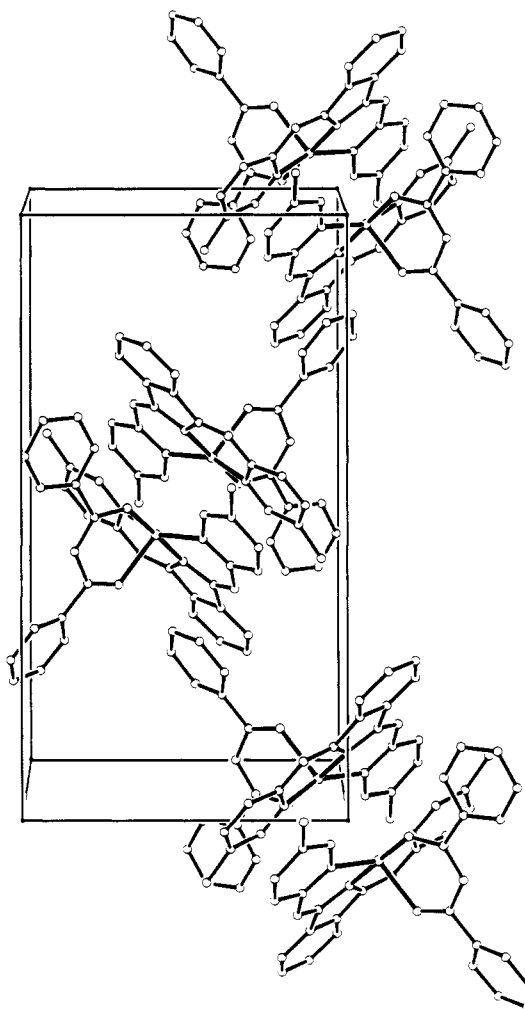
No other, stronger exchange processes occur in the solid state. Between 77 and 300 K, the magnetic susceptibility of III obeys the Curie-Weiss law, with  $C = 0.49$ ,  $\theta = 18$  K.

The ESR data for Cu(5-Melin)(DBM) provide good evidence for the presence, in the solid state, of dimeric units exhibiting a weak superexchange interaction between copper centers. Other examples of dimeric copper complexes of known structure, exhibiting exchange interactions, contain, without exception, a bridging atom or group of atoms through which a magnetic interaction may be mediated. In order to examine possible pathways for electron exchange in Cu(5-Melin)(DBM), we have determined the crystal and molecular structure of the complex.

The atom numbering scheme of the Cu(5-Melin)(DBM) molecule is shown in Figure 2. Distances and angles pertaining to the coordination environment of copper are given

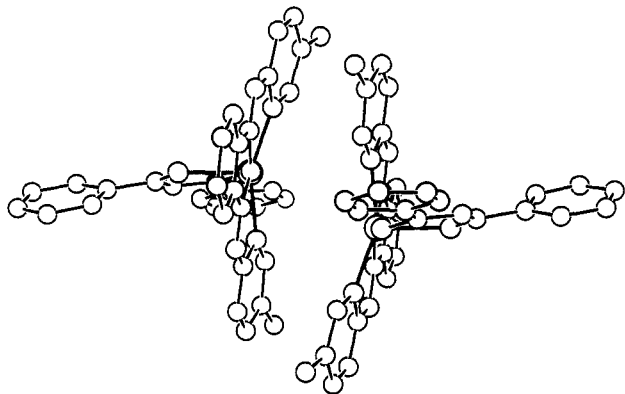
**Table IV.** Bond Lengths (Å) and Bond Angles (Deg) for the Dibenzoylmethane and 1,3-Bis((5-methyl-2-pyridyl)imino)isoindoline Ligands in Cu(5-Melin)(DBM)

| (a) Dibenzoylmethane Ligand                              |            |                   |            |
|----------------------------------------------------------|------------|-------------------|------------|
| C(1)-O(1)                                                | 1.258 (9)  | C(3)-O(2)         | 1.292 (9)  |
| C(1)-C(2)                                                | 1.427 (9)  | C(3)-C(2)         | 1.368 (10) |
| C(1)-C(4)                                                | 1.496 (10) | C(3)-C(10)        | 1.511 (9)  |
| C(1)-O(1)-Cu                                             | 124.3 (4)  | C(3)-O(2)-Cu      | 127.5 (4)  |
| C(2)-C(1)-O(1)                                           | 124.5 (6)  | C(2)-C(3)-O(2)    | 127.4 (6)  |
| C(4)-C(1)-O(1)                                           | 117.4 (6)  | C(10)-C(3)-O(2)   | 112.5 (6)  |
| C(3)-C(2)-C(1)                                           | 125.6 (7)  |                   |            |
| (b) 1,3-Bis((5-methyl-2-pyridyl)imino)isoindoline Ligand |            |                   |            |
| N(4)-C(21)                                               | 1.292 (10) | C(20)-N(4)        | 1.394 (9)  |
| C(21)-C(22)                                              | 1.487 (10) | C(21)-N(2)        | 1.376 (9)  |
| C(22)-C(27)                                              | 1.377 (11) | C(27)-C(28)       | 1.491 (10) |
| C(28)-N(2)                                               | 1.372 (9)  | C(28)-N(5)        | 1.294 (10) |
| N(5)-C(29)                                               | 1.394 (9)  | C(29)-N(3)        | 1.352 (9)  |
| N(1)-C(20)                                               | 1.371 (8)  |                   |            |
| C(16)-N(1)-Cu                                            | 118.9 (4)  | C(21)-N(4)-C(20)  | 124.4 (6)  |
| C(20)-N(1)-C(16)                                         | 116.9 (6)  | C(22)-C(21)-N(2)  | 107.9 (6)  |
| C(18)-C(17)-C(16)                                        | 115.4 (6)  | C(21)-N(2)-Cu     | 124.5 (5)  |
| C(34)-C(17)-C(18)                                        | 122.8 (7)  | C(28)-N(2)-C(21)  | 109.7 (5)  |
| C(20)-C(19)-C(18)                                        | 119.9 (7)  | C(27)-C(22)-C(21) | 107.4 (6)  |
| N(4)-C(20)-N(1)                                          | 123.3 (6)  | C(24)-C(23)-C(22) | 114.7 (8)  |
| C(20)-N(1)-Cu                                            | 123.3 (4)  | N(5)-C(28)-N(2)   | 130.5 (6)  |
| N(1)-C(20)-N(4)                                          | 123.4 (6)  | C(29)-N(5)-C(28)  | 123.6 (6)  |
| N(4)-C(21)-N(2)                                          | 129.7 (6)  | C(29)-N(3)-Cu     | 124.9 (4)  |
| C(28)-N(2)-Cu                                            | 123.7 (5)  | N(5)-C(29)-N(3)   | 122.9 (6)  |



**Figure 3.** Unit cell contents viewed along *c* axis. The *a* axis is vertically disposed.

in Table III. Selected bond lengths and angles for the dibenzoylmethane and 1,3-bis((5-methyl-2-pyridyl)imino)isoindoline ligand anions are given in Table IV, while least-



**Figure 4.** Interacting pair of Cu(5-MeIn)(DBM) molecules. For clarity of presentation, the hydrogen atoms are omitted.

squares planes and intermolecular contact distances are given in Tables IX and X, respectively. Molecular packing within the unit cell is shown in Figure 3.

The structure consists of discrete Cu(5-MeIn)(DBM) molecules in which the copper atom is coordinated to the deprotonated pyrrole and pyridine nitrogen atoms of 5-MeIn and the two oxygen atoms of DBM. The geometry of the molecule may best be described as intermediate between trigonal bipyramidal and square pyramidal. The almost linear O(2)-Cu-N(2) angle of  $178.3^\circ$  is consistent with regular trigonal-bipyramidal geometry, but the three bond angles in the trigonal plane are greatly distorted from the expected value of  $120^\circ$ . In particular, the N(1)-Cu-N(3) angle of  $155.6^\circ$  suggests<sup>15</sup> a distortion toward square-pyramidal stereochemistry in which the atoms N(1)-N(3) and O(2) comprise the basal plane. The choice of atom O(1) as apical donor is supported by the significantly longer Cu-O(1) distance of 2.178 Å relative to 1.954 Å for Cu-O(2) and 2.056 Å for Cu-N(1), the longer of the Cu-N distances. The Cu-O and Cu-N bond lengths are otherwise comparable to those reported previously for related systems.<sup>16,17</sup>

The 5-MeIn ligand is not overall planar, the pyridine rings defined by N(1) and N(3) being twisted 6 and  $9^\circ$ , respectively, with respect to the pyrrole ring. Bond lengths and angles for DBM are not unusual and are similar to values previously reported.<sup>17</sup> As found previously,<sup>17</sup> the phenyl groups are twisted with respect to the CuO(1)O(2) chelate ring by  $29$  and  $7^\circ$  for the phenyl rings containing C(4) and C(10), respectively.

The dimeric nature of Cu(5-MeIn)(DBM), inferred from the solid-state ESR data, is revealed by examination of the unit cell contents (Figure 3). The molecules are packed in symmetry-related pairs with a Cu-Cu separation of 4.453 (2) Å (Figure 4). If the geometry of the Cu(5-MeIn)(DBM) molecule is regarded as a distorted square pyramid, the packing of the dimers may be described as basal plane to basal plane.

A notable feature of the structure is the lack of any close contacts, either within or between dimers which may be regarded as bonding interactions. The closest *intradimer* contact is 2.994 Å between atoms N(5) and H'(342). The closest *interdimer* contact is 2.286 Å between the hydrogen atoms H(23) and H'(25) (see Table IV for symmetry relationships). We are led to the conclusion, therefore, that crystal packing forces, presumably of an attractive  $\pi$  type, are responsible for the dimeric arrangement of the molecules. This is concordant with the observation that this 5-methylated derivative is less soluble than its nonmethylated congener (IV) and markedly less so than the very soluble 4-methyl isomer (V). It seems that the intermolecular interaction contributes to the lattice energy of III. The spectroscopic and chemical evidence thus suggest that the unusual structural features of the Cu(5-MeIn)(DBM) lattice are not shared by V or IV, which are its isomer and a homologue, respectively.

In the light of the structure determination, it is apparent that electron exchange between the copper(II) centers is not mediated through any sort of inter- or intradimer bridging interaction. In addition, the Cu-Cu separation within each dimer appears large enough to render the possibility of direct overlap between copper orbitals somewhat unlikely. Given the presence of magnetically coupled, yet apparently isolated, copper(II) atoms, we conclude that the coupling is purely dipolar ("through-space") in nature. Such a mechanism has been utilized previously,<sup>18</sup> in connection with NMR studies, to explain magnetic interactions that occur between atoms separated by a distance too great to be considered a chemical bond. The splitting between the center of the hyperfine structure near 2800 G and a weak feature on the highest field edge of the  $g = 2$  region is ca. 870 G, which corresponds to  $D \approx 0.0420 \text{ cm}^{-1}$ , and a computed value of  $r = 4.1 \text{ Å}$  for the Cu-Cu distance in a simple dipolar model.<sup>19</sup>

Spin exchange has recently been observed in crystals of (*meso*-tetraphenylporphyrinato)copper(II),<sup>20</sup> where the  $\Delta M_s = 2$  line is observed. As in (phthalocyaninato)copper(II),<sup>21</sup> though, the current interpretation involves interaction amongst at least three coppers(II).

Cu(5-MeIn)(DBM) thus appears to constitute the first example of pairwise dipolar coupling in a copper system of known structure.

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**Registry No.** III, 79682-03-4; IV, 79682-04-5; V, 79682-05-6.

**Supplementary Material Available:** Tables V (nonhydrogen atom positional parameters), VI (nonhydrogen atom anisotropic thermal parameters), VII (hydrogen atom positional and isotropic thermal parameters), VIII (remaining bond lengths and angles for ligands), IX (least-squares planes and their deviations), X (intermolecular contact distances less than 3.5 Å) and XI (observed and calculated structure factors) (23 pages). Ordering information is given on any current masthead page.

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