

# Activation of the Carbon $\beta$ -Site in Nonlinear Pseudohalides by Coordination. Crystal, Molecular, and Electronic Structure of a Bis{bis(methoxycarbimido)aminato}copper(II) Complex

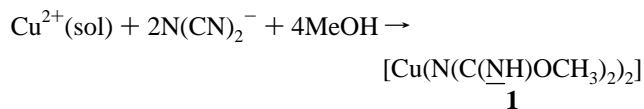
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## Introduction

In the system Cu(II)–dicyanamide–methanol–water–pyridine violet-red crystals are formed.<sup>1</sup> They do not contain pyridine and dicyanamide (as one could expect on the basis of usual coordination mode of pseudohalides)<sup>2</sup> but a new chelate ligand formed through a nucleophilic addition of the methanol molecule to the coordinated dicyanamide:



This reaction is promoted by a coordinative activation of the carbon  $\beta$ -site of the nonlinear pseudohalide  $\text{N}(\text{CN})_2^-$ . Under activation we assume a bending of the linear  $\text{N}\equiv\text{C}\beta\text{--X}$  arm of the pseudohalide (sp hybridized carbon) *via* N-coordination which alters the carbon  $\beta$ -site to be  $\text{sp}^2$  hybridized with an unsaturated valency and thus ready for a nucleophilic attack. Some more examples of this reaction pathway, leading to a new chelate formation in the coordination sphere, we have reported so far: by reacting  $\text{NCO}^-$  and pyrazole derivatives the coligand isomer formation in the coordination sphere of Cu(II), by reacting  $\text{C}(\text{CN})_2(\text{NO})^-$  and methanol in the presence of Ni(II), and by reacting *o*-NC–pyridine and methanol in the presence of Ni(II).<sup>3</sup>

Complex **1**, abbreviated as  $[\text{CuL}_2]$  with  $\text{L} = \text{N}(\text{C}(\text{NH})\text{OCH}_3)_2$ , is studied in more detail: its crystal and molecular structure is refined, and the electronic and ESR spectra, magnetic susceptibility data, and molecular orbital calculations are presented. The reason for a detailed study of **1** lies in the fact that its skeleton is isoelectronic with well-characterized  $\beta$ -diketonates, like  $[\text{Cu}(\text{acac})_2]$ .<sup>4</sup> The title complex has some features of  $[\text{Cu}(\text{biuret})_2]$ . The new ligand represents a fragment of the phthalocyanine core, and owing to four N-donor atoms, it is

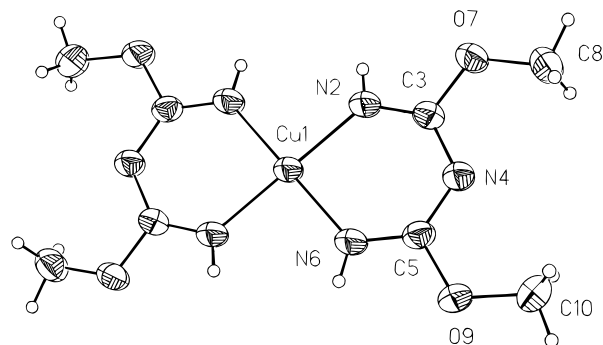


Figure 1. Molecular structure of **1** showing the atom numbering.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **1**

Cu(1)–N(2)	1.942(1)	C(3)–O(7)	1.354(2)
N(2)–C(3)	1.300(2)	O(7)–C(8)	1.434(2)
C(3)–N(4)	1.333(2)	C(5)–O(9)	1.364(2)
N(4)–C(5)	1.325(2)	O(9)–C(10)	1.436(2)
C(5)–N(6)	1.297(2)	N(2)–H(2)	0.71(2)
N(6)–Cu(1)	1.948(1)	N(6)–H(6)	0.78(2)
C(8)–H(81)	0.97(3)	C(10)–H(101)	0.96(3)
C(8)–H(82)	0.93(2)	C(10)–H(102)	0.88(3)
C(8)–H(83)	0.85(3)	C(10)–H(103)	0.88(3)
N(2)–Cu(1)–N(6)	91.87(6)	N(2)–C(3)–O(7)	115.5(1)
Cu(1)–N(2)–C(3)	127.1(1)	C(3)–O(7)–C(8)	117.8(1)
N(2)–C(3)–N(4)	128.5(1)	N(4)–C(5)–O(9)	115.6(1)
C(3)–N(4)–C(5)	120.1(1)	C(5)–O(9)–C(10)	117.2(1)
N(4)–C(5)–N(6)	129.0(1)	Cu(1)–N(2)–H(2)	125(2)
C(5)–N(6)–Cu(1)	126.8(1)	Cu(1)–N(6)–H(6)	123(2)

promising in model studies in connections to bioinorganic chemistry. In parallel we prepared an analogous Co(III) complex,  $[\text{CoL}_3]$ , whose properties were compared with the  $\beta$ -diketonate complex  $[\text{Co}(\text{acac})_3]$ .<sup>5</sup>

## Results and Discussion

**X-ray Structure.** The crystal structure of **1** consists of discrete molecules (Figure 1). The copper atom is located in the center of symmetry and it is coordinated by four nitrogen atoms in a square planar manner, forming two six-membered metallocycles. The N(2)–C(3) and N(6)–C(5) distances of 1.300(2) and 1.297(2) Å and C(3)–N(4) and C(5)–N(4) of 1.333(2) and 1.325(4) Å, respectively, indicate a strongly delocalized  $\pi$ -bonding system (Table 1). The torsion angles N(6)–C(5)–O(9)–C(10) and N(2)–C(3)–O(7)–C(8) are 179.92(2) and 177.83(2)°, respectively. There is no evidence for hydrogen bonds in the crystal structure; only weak out of the plane contacts,  $\text{Cu}\cdots\text{N}(4)$  at a distance of 3.73 Å exist between different units.

The N–H bond lengths seem to be apparently short (0.71 and 0.78 Å). Such a finding, however, could be an artifact of the X-ray structure determination which reflects the positions of the electron density maxima rather than the internuclear distances (when the N–H bond is strongly polar or the H atom bears a high positive charge). This point has been clarified by molecular orbital calculations. Using slightly idealized structure (the bond lengths and bond angles equal for the chemically equivalent atoms) the distances N–H = 1.044 and C–H = 1.100 Å were received as a result of a geometry optimization.

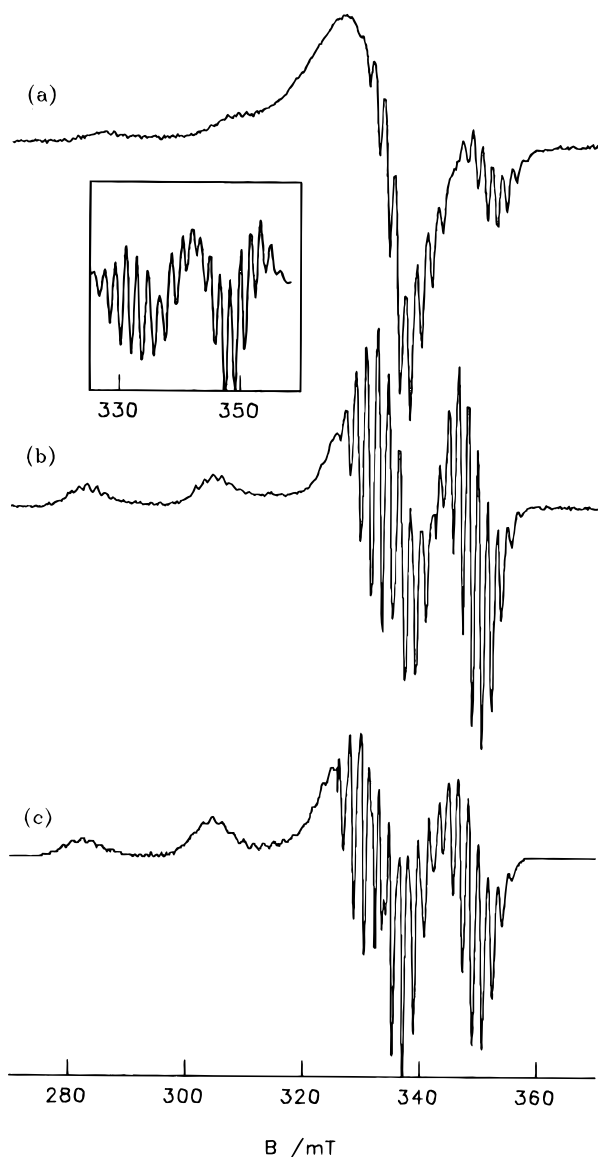
**Bonding Characteristics.** The Wiberg (bond-order) index  $W_{\text{Cu}–\text{N}(2)} = 0.75$  shows that the coordination bond is weaker than a single bond; owing to the conjugation the N–C bonds exhibit a partially multiple character,  $W_{\text{N}(2)–\text{C}(3)} = 1.43$  and

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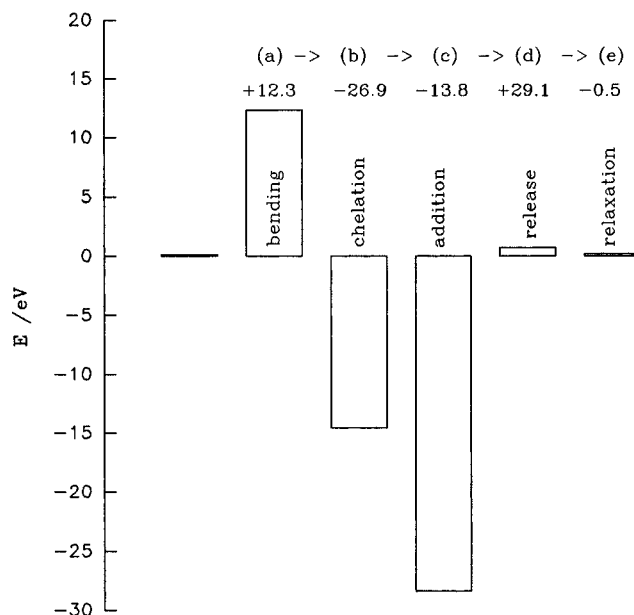


**Figure 2.** ESR spectra of a frozen (100 K) solution of **1**: (a) toluene solution; (b) 0.1 M pyridine added; (c) computer simulation. The inset shows the second derivative of the high-field part.

$W_{C(3)-N(4)} = 1.30$ ; the other bonds are single. The aminato nitrogen atom bears the most negative charge,  $Q_{N(4)} = -0.56$ , whereas its neighboring carbon atoms are strongly positively charged,  $Q_{C(3)} = +0.60$ . The N-H bond is polar as  $Q_{N(2)} = -0.56$  and  $Q_H = +0.14$  and the hydrogen atom acidic. The net  $p_z$ -orbital populations  $N_z = 6.0$  refer to ideal aromaticity of the ligand ring. The C(3) atom is an electrophilic center since  $N_z(C3) = 0.75$ . The d-orbital population of  $d^{9.15}$  confirms behavior like a Cu(II) system.

**Electronic Spectrum.** Using the coordinate system with the  $x$ -axis bisecting the N2a-Cu-N2b angle the possible d-d electronic transitions are  $\Delta_1(d_z^2 \rightarrow d_{xy})$ ,  $\Delta_2(d_{x^2-y^2} \rightarrow d_{xy})$ ,  $\Delta_3(d_{yz} \rightarrow d_{xy})$  and  $\Delta_4(d_{xz} \rightarrow d_{xy})$ . Within the range of 11 000–25 000  $\text{cm}^{-1}$  the electronic spectrum (in Nujol) exhibits a broad band centered at 20 400  $\text{cm}^{-1}$  with a shoulder at 17 500  $\text{cm}^{-1}$ . The deconvolution to three gaussian curves gave  $\Delta_3$ ,  $\Delta_4 = 20\,400$  (0.56)  $\text{cm}^{-1}$ ,  $\Delta_2 = 17\,500$   $\text{cm}^{-1}$ , (0.29)  $\text{cm}^{-1}$ , and  $\Delta_1 = 12\,300$  (0.01)  $\text{cm}^{-1}$  (relative intensities in parentheses).

DMSO, DMF, and pyridine solutions of **1** have almost the same electronic spectra, being identical with the spectrum in the Nujol suspension ( $\Delta_4 = 20\,400$   $\text{cm}^{-1}$ ,  $\epsilon = 35$   $\text{M}^{-1}$   $\text{cm}^{-1}$ ;  $\Delta_2 = 18\,000$   $\text{cm}^{-1}$ ,  $\epsilon = 28$   $\text{M}^{-1}$   $\text{cm}^{-1}$ ). **1** in toluene solution



**Figure 3.** Calculated energy profile for the model pathway.

**Table 2.** ESR Parameters of **1** from Computer Simulation<sup>a</sup>

conditions	$g_{\perp}$	$g_{\parallel}$	$ A_{\perp} $	$ A_{\parallel} $	$ A_{\perp}N $	$ A_{\parallel}N $
(1) toluene, 100 K	2.046	2.158	64	675	49	40
(2) toluene/pyridine (0.1 M), 100 K	2.049	2.161	64	660	50	35
conditions	$g_{\text{iso}}$	$ A_{\text{iso}} $	$ A_{\text{iso}}N $			
(3) toluene, room temperature	2.081	268	50			

<sup>a</sup> The hyperfine splitting constants  $|A|$  are given in units of MHz.

exhibits a slight shift of the intense band maximum to 19 900  $\text{cm}^{-1}$ . These data indicate that the complex is essentially inert to ligation in axial positions. In the planar  $[\text{Cu}(\text{acac})_2]$  complex, for comparison,  $\Delta_4 = 18\,000$   $\text{cm}^{-1}$ ,  $\Delta_3 = 15\,600$   $\text{cm}^{-1}$ , and  $\Delta_1 = 14\,500$   $\text{cm}^{-1}$  transitions were identified in single-crystal polarized spectra whereas in  $\text{CHCl}_3$  solution only two maxima at 18 810 and 15 190  $\text{cm}^{-1}$ . The spectra of  $\beta$ -diketonates, in general, are solvent-dependent owing to coordination of the solvent molecule (in the case of  $[\text{Cu}(\text{acac})_2 \cdot \text{py}]$  the two components are shifted to 15 300 and 12 500  $\text{cm}^{-1}$ ).<sup>4</sup>

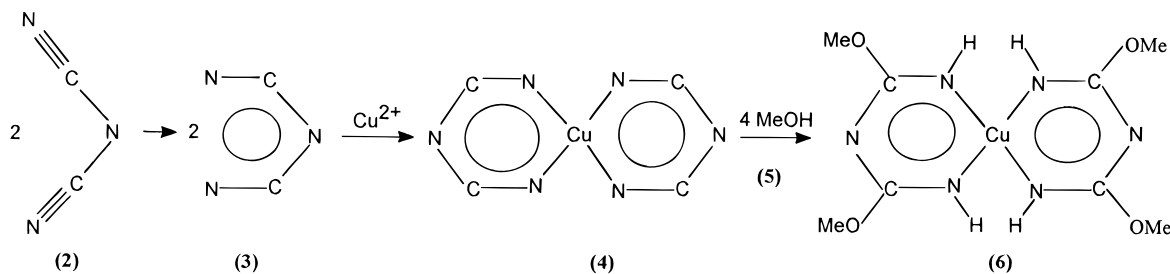
**Electron Spin Resonance.** The frozen toluene solution ESR spectrum of **1** shows only two of four low-field parallel components of the copper hyperfine structure which are well separated from the much stronger perpendicular portion of the spectrum (Figure 3). Each parallel hyperfine band is further split into lines separated by ca. 40 MHz (theoretically four equivalent  $^{14}\text{N}$  nuclei would give nine superhyperfine lines). The perpendicular part of the spectrum is more complex. This is due not only to the superhyperfine structure, but also to the presence of overshoot lines.<sup>6</sup>

Magnetic parameters obtained by a computer simulation show (Table 2) a large value of  $|A_{\parallel}|$  and a rather low value of  $g_{\parallel}$  which match well with those found for square planar copper(II) complexes with four donor nitrogen atoms.<sup>7</sup>

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## Scheme 1



Addition of 0.1 M pyridine to toluene solution results in a better resolution of the ESR spectrum of **1** at 100 K (Figure 2); the magnetic parameters, however, alter only slightly: decrease in  $|A_{\parallel}|$ , and increase in  $g_{\parallel}$ . The electron donation  $\text{py} \rightarrow \text{Cu}$  causes a back-donation to the in-plane ligands L which results in a decrease of the Cu–L covalency.<sup>8,9</sup>

Spin Hamiltonian parameters were used to estimate the molecular orbital coefficient  $\alpha$  entering the in-plane orbital  $\psi(b_{1g}) = \alpha d_{xy} - \alpha' \varphi(b_{1g})$ . An iterative procedure gave the value of  $\alpha^2 = 0.86$  which is comparable with the calculated spin densities:  $\rho(d_{xy}) = 0.834$ ,  $\rho(\text{Cu}) = 0.809$  and  $\rho(\text{N2}) = 0.045$ .

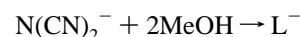
**Magnetic Susceptibility.** Within the range of 77 to 300 K the volume susceptibility  $\chi$  of **1** obeys the extended Curie–Weiss law for paramagnetic substances which can be rewritten into the form

$$\chi = (\rho/M)[N_A \mu_0 \mu_B^2/k] [S(S+1)/3] g_{\text{av}}^2 / (T - \Theta) + \alpha$$

(all the symbols adopting their usual meaning, SI units). A nonlinear regression gave the Weiss constant  $\Theta = -7.74$  K, temperature independent contribution  $\alpha = 40.7 \times 10^{-6}$  (dimensionless) and  $g_{\text{av}}(\text{MS}) = 2.089$ . The last value matches well with that obtained from ESR spectra:  $g_{\text{av}}(\text{ESR}) = 2.084$ . The effective magnetic moment  $\mu_{\text{eff}}/\mu_B = 1.81$  is slightly higher relative to the spin-only value (1.73).

**Model Reaction Pathway.** The *ab initio* energy profile along a model reaction pathway was considered as it would proceed in five steps (Scheme 1). (a) The dicyanamide activation (bending and stretching) requires an energy amount  $\Delta E = E(2) - E(3) = 6.2$  eV. For the free  $\text{N}(\text{CN})_2^-$  ion the following structural data were calculated (observed for  $\text{KN}(\text{CN})_2$ ):<sup>10</sup> N–C = 1.310 Å (1.304, 1.309, 1.317) Å, N–C = 1.147 Å (1.155, 1.156 Å), NCN = 180.0° (172.8°) and CNC = 119.2° (120.3°). (b) Chelation leading to the bis(dicyanamide) copper(II) complex,  $[\text{Cu}(\text{N}(\text{CN})_2)_2]$  is favorable as energy gained is  $\Delta E = E(4) - 2E(3) - E(\text{Cu}^{2+}) = -26.9$  eV. It seems reasonable that dicyanamide will “bend” and “chelate” simultaneously with energy release of  $\Delta E = E(4) - 2E(2) - E(\text{Cu}^{2+}) = -14.6$  eV. (c) Addition of four methanol molecules is associated with energy stabilization  $\Delta E = E(6) - E(4) - 4E(5) = -13.8$  eV. This step is supported by the electrophilicity of the carbon atom which is raised by the coordination of  $\text{N}(\text{CN})_2^-$ . Nucleophilicity of the  $\text{MeO}^-$  group may be enhanced in the presence of pyridine. The total stabilization energy is  $\Delta E = E(6) - E(\text{Cu}^{2+}) - 2E(2) - 4E(5) = -28.4$  eV. (d) The ligand release (complex splitting) requires  $\Delta E = 2E(\text{L}^-) + E(\text{Cu}^{2+}) - E(6) = +29.1$  eV. (e) The liberated anion  $\text{L}^-$  (**7**) can relax to its optimum geometry (**8**) with energy decrease  $\Delta E = E(8) - E(7) = -0.25$  eV.

The energy gained for the overall reaction



is  $\Delta E = +0.10$  eV at the SCF level and  $\Delta E = -0.24$  eV when the MP2 correlation energy is included (Figure 3).

**Conclusions.** New chelate Cu(II) complex prepared by reacting dicyanamide with methanol is formed *via* an activation (bending) of the  $\beta$ -C site of the coordinated  $\text{N}(\text{CN})_2^-$  which becomes ready for a nucleophilic attack. The new metalocycle is an electronic analogue of the  $\beta$ -diketonates but it generates a stronger ligand field.<sup>5</sup> A planar molecular structure determined by the X-ray diffraction is seen in the axial nature of the ESR spectra. The spin density at the in-plane  $d_{xy}$  orbital is partly delocalized over the donor set of nitrogen atoms. The long axial contacts in the solid state, the stability in solutions against pyridine and ammonia, and the insensitivity of the electronic and ESR spectra against the nature of the solvent are in firm harmony with the concept of the equatorial–axial interactions in metal complexes: a strong chelation effect implies a very low tendency to ligate in the axial position.<sup>11</sup>

## Experimental Section

**Synthesis.** All chemicals were of analytical grade. The system of  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{KN}(\text{CN})_2$ , pyridine, methanol, and water in molar ratios of 1:2:25:30:60 was left for a week at room temperature. The dark blue color (assigned to the pyridine complex,  $\Delta = 14\,900$   $\text{cm}^{-1}$ ,  $\epsilon = 68$   $\text{M}^{-1} \text{cm}^{-1}$ ) changed gradually to violet and finally violet-red crystals precipitated. Anal. Calcd for  $\text{C}_8\text{H}_{16}\text{CuN}_6\text{O}_4$  (found): C, 29.68 (29.91); H, 4.98 (5.03); N, 25.95 (25.78); Cu, 19.62 (19.54). Complex **1** dissolves slightly in toluene and chloroform, better in dimethyl sulfoxide and dimethylformamide and even better in pyridine. All solutions have a violet-red color. The addition of ammonia to DMF solution of the complex does not lead to ammine complex formation but to the precipitation of **1**.

**Physical Measurements.** The electronic spectrum of **1** in Nujol suspension was taken at room temperature (Carl-Zeiss, model M800, lower limit 11 000  $\text{cm}^{-1}$ ). The ESR spectra were recorded at X-band frequency (Bruker, Model ER 200 D SRC) using dried solvents. The magnetic parameters associated with the ESR spectra were determined by computer simulation using an axially symmetric spin Hamiltonian appropriate to tetragonal symmetry.<sup>12</sup> The temperature dependence of the volume magnetic susceptibility on powdered sample was recorded by AC susceptometer (LakeShore, model 7221;  $f = 222.2$  Hz,  $H_{\text{AC}} = 800$   $\text{Am}^{-1}$ ). The data set (110 points) was corrected for demagnetization and for a signal of the sample holder.<sup>13</sup>

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**Table 3.** Crystal Data, Data Collection, and Refinement of the Structure of **1**

formula	C <sub>8</sub> H <sub>16</sub> CuN <sub>6</sub> O <sub>4</sub>
fw	323.90
cryst syst	monoclinic
cryst size, mm	0.057 × 0.255 × 0.770
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> , Å	10.012(1)
<i>b</i> , Å	5.667(1)
<i>c</i> , Å	11.534(1)
$\beta$ , deg	99.71(2)
<i>V</i> , Å <sup>3</sup>	650.5(1)
<i>Z</i>	2
<i>d</i> (calc), g cm <sup>-3</sup>	1.653
$\mu$ , cm <sup>-1</sup>	17.0
index ranges	-14 < <i>h</i> < +14, -7 < <i>k</i> < +1, -16 < <i>l</i> < +16
scan range, deg	1.7 < 2 $\theta$ < 60
no. of indep reflns	4249
abs cor	SHELX77
min/max transm	0.561/0.952
no. of params refined	120
R1/wR2, <sup>a</sup> %	2.59, 7.19
<i>S</i>	1.082

<sup>a</sup> wR2 =  $(\sum |w(F_o^2 - F_c^2)|^2 / \sum [wF_o^4])^{1/2}$ . R1 =  $\sum ||F_o| - |F_c|| / \sum |F_o|$ . Weight =  $1/[\sigma^2(F_o^2) + (0.0431P)^2 + 0.1400P]$  where  $P = (F_o^2 + 2F_c^2)/3$ .

**X-ray Crystallography.** A summary of crystal data and structure refinement is presented in Table 3. The data set was collected on STOE-STADI4 diffractometer,  $\theta$ -2 $\theta$  scan mode, graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71069$  Å). Coordinates of the non-hydrogen atoms were taken from ref 1. A total of 120 variable parameters (including hydrogen atoms) were used in the full-matrix least-squares refinement on  $F^2$ .

**Molecular Orbital Calculations.** The SCF-LCAO-MO calculations have been done using the *ab initio* package in the RHF as well as UHF variants for open shell systems (*D*<sub>2h</sub> symmetry assumed). Basis set: double- $\zeta$  Huzinaga set (8s4p) contracted to [4s2p] with polarization functions for main row elements, Wachters set (14s9p5d) contracted to [8s5p3d] for Cu atom.<sup>15</sup> In the geometry optimized at the SCF level the MP2 corrections improved the total molecular energy for metal free systems. Population analysis: shared-electron-number with multicenter (SEN-*n*) corrections.<sup>16</sup>

Geometry optimization on **1** was done by a nonempirical quasi-relativistic INDO/1 method.<sup>17</sup> The spin densities for the UHF approach were projected in order to eliminate admixtures of the higher spin multiplicity components. The bonding properties were characterized by the Wiberg indices  $W_{A-B}$ .<sup>18</sup>

**Supporting Information Available:** Tables of crystallographic data, atomic coordinates, thermal parameters, bond distances, and bond angles for **1**, tables of *ab initio* molecular energies and charges, and a figure showing a stereoscopic unit cell packing diagram (8 pages). Ordering information is given on any current masthead page.

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