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X-ray Diffraction Characterization and Electronic Structure of a Complex of Copper(II) with a Nitroxyl-β-Keto Ester: Bis[(1-oxy-2,2,6,6-tetramethylpiperidin-4-yl)pivaloylacetato]copper(II)[1]

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The crystal and molecular structure of the title compound has been determined from three-dimensional single-crystal X-ray diffraction data collected by counter techniques. The crystals of the green form are triclinic, space group $P\bar{1}$, with two formula units in the cell (a = 11.992 (1) Å, b = 12.188 (1) Å, c = 12.912 (1) Å, α = 78.03 (2)°, β = 78.96 (2)°, γ = 84.09 (2)°). The structure has been refined by least-squares methods to $R = 0.074$ and $R_w = 0.087$ for 5283 independent reflections with $F_o > 4\sigma(F_o)$. The coordination geometry about both copper(II) ions corresponds to a tetragonally distorted octahedron with a pair of β-diketonate ligands and two monodentate O-bonded nitroxyl radicals belonging to other molecules. Significant parameters of the coordinated nitroxides include Cu-O = 2.583 (5) and 3.157 (5) Å and Cu-O-N = 158.5 (4) and 139.5 (4)°. Noniterative extended Hückel calculations show that the copper-nitroxyl interaction is strongly dependent on the Cu-O-N angle.

Introduction

The stable nitroxyl free radicals, widely used as spin probes in biological systems,[3a] have been more recently included in transition-metal systems.[3b-11] These species provide a means to study interactions between nonequivalent unpaired electrons (different g values) and are important in the investigation of metal-ligand bonding.[11]

Considerable attention has been attracted by two types of such metal-nitroxyl systems: (i) the nitroxide functioning as a Lewis base is added to a previously formed metal complex; (ii) the nitroxyl group is a part of a ligand able to complex a metal ion.

The synthesis of complexes of type ii was undertaken in order to study the intramolecular interactions between the nonequivalent unpaired electrons. We recently described such a study by EPR spectroscopy in dilute solution for the the bis[(1-oxy-2,2,6,6-tetramethylpiperidin-4-yl)pivaloylacetato]copper(II) complex (Figure 1), a molecule with three paramagnetic centers. A study of the magnetic susceptibilities of this compound between 1.3 and 300 K has been reported earlier[12] and interpreted with the assumption of an exchange interaction between these three centers. The weak (+9.6 cm^{-1}) copper-nitroxyl interaction supported this interpretation as some metal-nitroxyl adducts of type i, in which the paramagnetic centers are expected to be closer, exhibit strong antiferromagnetic interactions.[5,13]

It is now common practice in the study of exchange interactions to relate the magnetic susceptibility results to the molecular structure, as determined by X-ray diffraction.

Table I. Crystallographic Data

formula: $C_{32}H_{54}N_2O_8Cu$
mol wt 658.33
cryst syst: triclinic
V = 1808.03 Å^3
space group: $P\bar{1}$
$Z = 2$
a = 11.992 (1) Å
α = 78.03 (2)°
b = 12.188 (1) Å
β = 78.96 (2)°
c = 12.912 (1) Å
γ = 84.09 (2)°
d(calcd) = 1.210 Mg m^{-3}
d(obsd) = 1.23 Mg m^{-3}
t = 20 °C
radiation: Mo Kα (λ = 0.7090 Å), graphite monochromator
cryst-detector dist: 173 mm
detector window: height, 6 mm; width, 1.5 + 1.5 tan θ
takeoff angle: 3°
scan mode: ω scan
max Bragg angle: 2° < θ < 30°
scan angle: 1.0 + 0.14 tan θ
scan speed: 0.011° s^{-1}
Test reflections: 600, 0$\bar{6}$0, $\bar{1}$06

In this paper, we report the crystal and molecular structure of the compound, which shows that the main metal-nitroxyl interactions are intermolecular. The results of an extended Hückel calculation[14] are presented.

Experimental Section

Synthesis and Physical Measurements. The compound (mp 249 °C) was prepared as previously described,[15] by the action of copper acetate on the nitroxyl bidentate ligand in a mixture of ethanol-water (50/50, v/v). The crude compound was dissolved in boiling n-heptane, and the solution was left to cool to room temperature. Large green-black crystals were obtained. Slow evaporation at room temperature of the mother liquor afforded a mixture of the same crystals along with platelike yellow ones. If n-hexane was used instead of n-heptane, one always obtained a mixture of the green and yellow crystals, both having the same elemental analysis. Further evidence of the chemical identity of the two kinds of crystals was supported by EPR spectroscopy: the spectra in dilute solution are the same and are characteristic of three interacting paramagnetic centers.[10] The presence of two kinds of crystals of the same compound can be tentatively related to the existence of a cis-trans isomerism of the molecule. A preliminary investigation of the yellow form showed a different space group ($P2_1/n$) and cell dimensions (a = 11.854 Å, b = 15.149 Å, c = 40.089 Å, β = 95.93°).

X-ray Data Collection and Structure Determination. Weissenberg photographs taken for a small *green* monocrystal (0.21 × 0.25 × 0.25 mm) showed that the compound crystallizes in the triclinic system. The same crystal was mounted on an Enraf-Nonius CAD-4 four-circle

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Table II. Atomic Coordinates ($\times 10^4$)[a]

	molecule A				molecule B			
	x	y	z	B_{eq}, Å^2	x	y	z	B_{eq}, Å^2
Cu	0	0	0	3.07	5000	5000	5000	4.97
N(1)	−2711 (4)	−4935 (4)	2072 (4)	4.76	1807 (4)	9251 (5)	2181 (4)	5.65
C(2)	−1803 (5)	−4520 (5)	2473 (5)	5.18	2985 (6)	9358 (6)	1556 (5)	7.38
C(3)	−811 (5)	−4209 (5)	1536 (5)	4.70	3821 (5)	9248 (5)	2342 (5)	6.91
C(4)	−1234 (5)	−3497 (5)	565 (5)	4.28	3626 (5)	8289 (4)	3250 (5)	3.91
C(5)	−1964 (5)	−4174 (5)	161 (5)	5.12	2459 (6)	8430 (7)	3895 (6)	5.26
C(6)	−3028 (5)	−4498 (5)	980 (6)	5.19	1521 (6)	8519 (9)	3232 (6)	5.81
C(7)	−1385 (6)	−5478 (6)	3311 (6)	7.38	3043 (7)	10487 (8)	797 (7)	8.15
C(8)	−2263 (7)	−3474 (7)	2945 (6)	7.33	3241 (7)	8432 (8)	897 (7)	8.21
C(9)	−3508 (6)	−5466 (6)	639 (7)	7.36	457 (8)	9027 (14)	3788 (9)	11.67
C(10)	−3920 (6)	−3489 (7)	1081 (8)	8.36	1258 (11)	7406 (10)	3075 (11)	10.99
O(11)	−3496 (4)	−5400 (4)	2804 (4)	6.33	1009 (4)	9536 (5)	1650 (4)	7.47
O(12)	−251 (3)	−3223 (3)	−282 (3)	4.28	4426 (3)	8342 (3)	3950 (3)	4.33
C(13)	152 (4)	−2201 (4)	−421 (4)	3.56	4848 (4)	7348 (4)	4480 (4)	3.83
C(14)	1064 (4)	−1985 (4)	−1264 (4)	3.81	5616 (4)	7468 (4)	5127 (4)	3.71
C(15)	1592 (4)	−989 (4)	−1536 (5)	3.08	6170 (4)	6567 (5)	5680 (4)	3.69
C(16)	2608 (4)	−820 (4)	−2473 (4)	3.77	7028 (5)	6723 (5)	6367 (5)	4.44
C(17)	3690 (6)	−1248 (11)	−2061 (8)	9.02	8095 (8)	6142 (11)	6025 (11)	9.66
C(18)	2528 (9)	−1376 (11)	−3346 (7)	8.05	7306 (10)	7889 (9)	6227 (11)	10.19
C(19)	2704 (11)	340 (8)	2923 (11)	9.34	6545 (10)	6321 (15)	7453 (7)	10.41
O(20)	1316 (3)	−167 (3)	−1059 (3)	3.56	6070 (3)	5537 (3)	5654 (4)	4.68
O(21)	−313 (2)	−1558 (2)	195 (3)	3.32	4522 (3)	6480 (3)	4334 (4)	4.79

[a] B_{eq} (Å^2) $= 8\pi^2(U_1U_2U_3)^{2/3}$.

Table IVA. Bond Lengths (Å) and Angles (deg) Involving the Cu Atoms[a]

	A	B		A	B
Cu-N(1)′	3.785 (5)	4.216 (5)	Cu-O(20)	1.904 (3)	1.898 (4)
Cu-O(11)′	2.583 (5)	3.157 (5)	Cu-O(21)	1.930 (3)	1.912 (4)
N(1)′-Cu-O(20)	89.9 (1)	92.9 (2)	O(11)′-Cu-O(20)	82.9 (2)	78.3 (2)
N(1)′-Cu-O(21)	89.9 (1)	83.9 (2)	O(11)′-Cu-O(21)	89.8 (2)	89.3 (2)
O(20)-Cu-O(21)	92.3 (1)	92.9 (2)	N(1)′-O(11)′-Cu	158.5 (4)	139.5 (4)

[a] A and B are the two inequivalent molecules. A primed atom (N′) means that this atom belongs to another molecule.

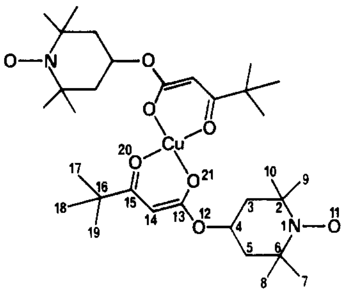

Figure 1. Chemical structure of the copper(II) complex showing the numbering of the atoms.

Table VA. Torsion Angles (deg) Involving the Ester Linkage

	A	B
C(3)-C(4)-O(12)-C(13)	−99.7 (6)	−146.5 (5)
C(5)-C(4)-O(12)-C(13)	143.0 (5)	96.1 (6)
C(4)-O(12)-C(13)-C(14)	−178.0 (5)	179.5 (4)
C(4)-O(12)-C(13)-O(21)	1.8 (8)	−0.3 (7)
O(12)-C(13)-C(14)-C(15)	179.8 (5)	−176.8 (5)
O(12)-C(13)-O(21)-Cu	−171.0 (4)	−179.8 (4)

diffractometer with monochromatized Mo Kα radiation. Accurate cell constants were derived from least-squares refinement of the setting angles of 25 reflections and are reported in Table I with other crystal data.

The intensities of 9925 independent reflections ($2 < \theta < 30°$) were collected. Three standard reflections were periodically checked and showed no significant discrepancy. The data were corrected for the Lorentz–polarization factor but not for absorption or extinction. Among the independent reflections collected, 5283 had $F_o > 4\sigma(F_o)$ and were used to refine the structural parameters.

The $P\bar{1}$ space group was expected since most metal β-diketonates are centrosymmetrically arranged around the metal ion. This was consistent with statistical and piezoelectric tests.

The Harker section of the Patterson map showed two copper ions in the unit cell related by a translation of $^1/_2$, $^1/_2$, $^1/_2$. Attempts to solve the structure by direct methods with use of MULTAN,[16] with two symbolic reflections and 499 E values greater than 1.65, gave for each E set a large part of the two molecules, but the copper atoms were shifted from their expected positions. These two molecule fragments were not related by an operation of symmetry. The combination of the Patterson and direct methods led one to place the copper atoms in 0, 0, 0 and $^1/_2$, $^1/_2$, $^1/_2$ in agreement with the expectation that the molecule is centrosymmetric.

A first refinement with 32 atoms resulted in an R value of 0.24. Then, all the missing non-hydrogen atoms were located on a difference Fourier map.

The structure was refined with the ORXFLS3 program[17] with Cu (anomalous scattering factor included), C, N, and O atoms anisotropic with use of the 5283 selected reflections. At this stage of refinement, a difference Fourier map showed significant electron densities in the positions calculated for the non methyl hydrogen atoms. They were introduced in the refinement but not refined. Finally, the R values ($R_w = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}$; $R = \sum|F_o - F_c|/\sum|F_o|$) reached the values $R_w = 0.087$ $R = 0.074$. Atomic coordinates and thermal parameters are reported in Tables II and III (Table III is in the supplementary material). Bond lengths, bond angles, and torsional angles (Tables IV and V; Tables IVB and VB are in the supplementary material) were calculated by using ORFFE,[18] and the different views were plotted by using a local adaptation of the ORTEP program.[19]

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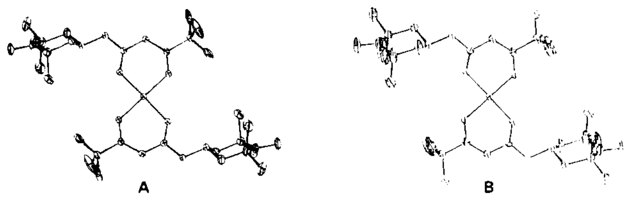

Figure 2. ORTEP drawings of molecules A and B projected in their β-diketonate plane.

Description of the Structure

One of the most characteristic features of this structure is the difference of the conformation of the two molecules in the cell (Figure 2). The planes defined by the Cu atom and the four surrounding O(ligand) atoms, are nearly orthogonal (80°). The most important conformational differences arise from the relative orientation of the piperidine rings and the *tert*-butyl groups to the central β-diketonate part of the molecule.

Inspection of Tables IV and V shows that the tetramethylpiperidine rings are identical within experimental errors and that both have the usual[20] flattened chair conformation equatorially substituted by the ester linkage. The nitroxyl groups have the expected pyramidal shape, the angle between the N(1)–O(11) bond and the C(2)–N(1)–C(6) plane being around 20° (19.3 and 21.8°). In both molecules, the C(4)–O(12)–C(13)–C(14)–C(15)–O(20)–O(21) fragment is nearly planar. The distances of these atoms to their mean plane do not exceed 0.007 and 0.02 Å in molecules A and B, respectively.

The different orientation of the piperidine ring with respect to that plane is illustrated by the C(3)–C(4)–O(12)–C(13) and C(5)–C(4)–O(12)–C(13) torsional angles. The ring is in a trans position to the Cu atom, and its mean plane makes an angle of 67° with the C(4)–O(12)–C(13) plane in both molecules. But as shown by the torsional angles (Table V), they are rotated around the C(13–O(12) bond in such a manner that they are symmetrical with respect to the plane perpendicular to the C(4)–O(12)–C(13) plane.

The observed geometry of the *tert*-butyl groups is greatly influenced by the large anisotropic thermal motion of the methyl carbon atoms. The magnitude of this motion is clear from an inspection of the thermal ellipsoids in Figure 2, where it may also be noted that the preferred direction of motion is approximately perpendicular to the C(15)–C(16) direction. The large-scale thermal motion and the shortened C–C bond lengths (e.g., C(16)–C(18) = 1.450 Å, C(16)–C(19) = 1.420 Å) suggest that the atoms of the *tert*-butyl groups are disordered on a static or dynamic basis between different conformations allowed by rotation around the C(15)–C(16) bond.

Figure 3 shows all the important bonding interactions for the two copper atoms. Six oxygen atoms are bound to each Cu(II) ion at the vertices of a tetragonally distorted octahedron. Four of these atoms belong to the two pivaloylacetate ligands and occupy the coplanar (the Cu atoms are located on a center of symmetry) equatorial coordination sites at bonding distances larger for the ester carbonyl oxygen atom O(20) than for the other one, as expected.[21] The axial coordination sites are occupied by the oxy oxygen atoms O(11)′ of two other molecules. In molecule A (Cu: 0, 0, 0), the nitroxyl oxygen atoms (Cu–O(11)′ = 2.583 (5) Å, are not directly over the copper atom but are displaced toward O(20) with resultant distortions of the O(11)′–Cu–O(ligand) angles from the expected 90° values; these idealized positions are occupied by the nitrogen atoms N(1)′ of the nitroxyl groups (N(1)′–Cu–O(ligand) = 90°). In molecule B (Cu: $^1/_2$, $^1/_2$, $^1/_2$), both the oxygen and the nitrogen atoms of the two nitroxyl groups deviate from the idealized bonding pattern. The distance from the Cu(II) ion to the O(11)′ oxygen atom is larger (3.157 (5) Å) in this case. As shown in Figure 2, the relative configurations of the nitroxide and the β-diketonate rings are very different in the two molecules. In molecule A, the mean plane of the piperidine ring is close to the *yz* plane (see Figure 3) and this configuration places the bulky methyl groups in an empty place of the space. On the other hand, in molecule B, the plane of the cyclic nitroxide is roughly in the *xz* plane and this configuration does not allow the O(11)′ oxygen atom and the copper ion to be as close as in molecule A.

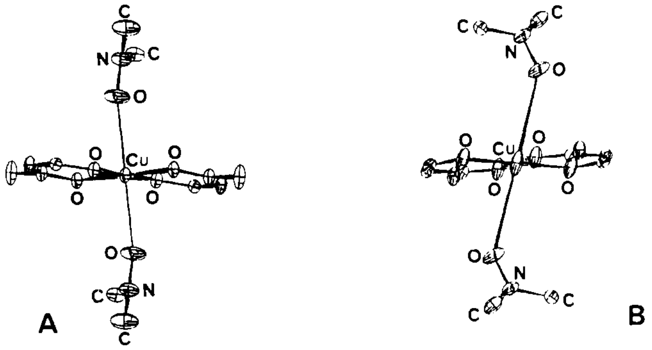

Figure 3. ORTEP drawings showing the bonding pattern of the copper atoms.

Discussion

The tendency of the central metal atom of oxygen-bonded β-diketonate complexes to increase its coordination number with Lewis bases is well documented.[22] In this copper(II) β-diketonate bis(nitroxyl), in the solid state, the copper ion increases its coordination number to 6 with the oxygen atoms of two nitroxyl groups of two other molecules acting as Lewis bases. This is not the case in some other complexes in which the central copper(II) atom is mixed-bonded to nitrogen and oxygen atoms. These compounds have been studied by X-ray diffraction;[23] the nitroxyl groups and the copper ion are far apart.

As expected, shorter distances between copper and nitroxyl groups have been observed in adducts of copper(II) hexafluoroacetylacetonate[5,13,24,25] with individual nitroxyls. In this case, the molecules have been specifically designed in order to get copper(II)–oxygen(nitroxyl)-bonded species. Although the bis(β-keto ester) complex in our example has less Lewis acid character than the hexafluoroacetylacetone analogue,[22] the copper–oxygen(nitroxyl) distance is similar in the solid state for these compounds.

The magnetic susceptibilities of the title complex, recorded over the temperature range 1.3–300 K, have been reported previously.[12] It was assumed that one copper ion and two nitroxyls were interacting. Although the crystal structure shows that the main interactions are intermolecular, the quantitative interpretation of the data still remains correct. All data were fitted by this scheme, leading to a copper–nitroxyl exchange value of +9.6 cm^{-1} and a nitroxyl–nitroxyl value of −0.01 cm^{-1}. Because of the two independent copper sites, there should be two different sets of *J* values and the values obtained for this best fit would be an average of these

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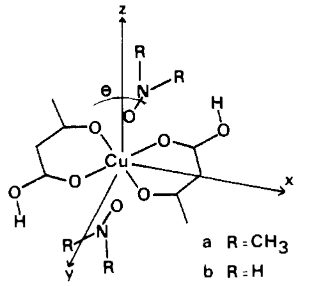

Figure 4. Molecular fragment used for extended Hückel calculations: (a) title complex; (b) complex used in the study of the variation of the overlap between the copper d_{xy} and π^* nitroxyl orbitals with the angle θ.

values. In the lattice, the distance between the nearest copper–bis(nitroxyl) sites is greater than 9 Å so we assume that the reported J values are really the values (averaged) of the isolated sites.

Surprisingly, copper–nitroxyl exchange interactions of the same order of magnitude have been reported for compounds in which the copper–nitroxyl distances, as determined by X-ray diffraction, are very different. A copper–nitroxyl exchange value of 10.5 cm^{-1} has been reported by Russian workers[23] for the copper(II) complex of a Schiff base nitroxyl in which the paramagnetic centers are separated by more than 5 Å. Such a low value might be expected from the room-temperature magnetic measurements for the adduct of copper(II) hexafluoroacetylacetonate with 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-*N*-oxy, where the copper–nitroxyl distance is 2.4 Å.[24] In a very similar complex, the adduct of the same fluorinated β-diketone with 2,2,6,6-tetramethylpiperidinyl-*N*-oxy, a large (more than 450 cm^{-1}) antiferromagnetic interaction has been found from EPR and magnetic experiments.[13] In this case, the copper–oxygen(nitroxyl) distance is 1.92 Å.[25]

This shows that the magnitude of the interactions is dramatically dependent on both the copper–nitroxyl distance and the relative orientation of the orbitals containing the unpaired electrons. We have developed noniterative extended Hückel calculations[14] on molecules A and B, in their X-ray geometries, as shown in Figure 4a. In both cases, the three unpaired electrons are found, as expected, to be respectively in the following molecular orbitals: an MO mainly localized on the copper(II) d_{xy} orbital (x and y axes are shown in Figure 4) and two quasi-degenerated nitroxyl π^* MO's, of the form $\psi_S = (\pi^*_{N_1O_1} + \pi^*_{N_2O_2})$ and $\psi_A = (\pi^*_{N_1O_1} - \pi_{N_2O_2})$. Obviously, one can define localized molecular orbitals $\psi_{N_1O_1}$ and $\psi_{N_2O_2}$ as

$$\psi_{N_1O_1} = 1/2^{1/2}(\psi_A + \psi_S) = 2^{1/2}\pi^*_{N_1O_1}$$

$$\psi_{N_2O_2} = 1/2^{1/2}(\psi_A - \psi_S) = 2^{1/2}\pi^*_{N_2O_2}$$

In both molecules, the ψ_S and ψ_A MO's are found to be equally delocalized on the two nitroxyl groups;, i.e., the contributions of the different atomic orbitals are nearly equal in $\pi^*_{N_1O_1}$ and $\pi^*_{N_2O_2}$.

Table VI. Variation of $\langle d_{xy} | \pi_{NO} \rangle$ with θ (deg) and Cu–O Bond Length (Å)

	θ		
Cu–O	0	45	90
2.56	0	1.9×10^{-4}	8.6×10^{-4}
2	0	2×10^{-3}	1.1×10^{-2}

It is a common practice to relate magnetic interactions to the overlap[13,24,25,26] and overlap density[27] between the molecular orbitals occupied by a single electron. In our example, the zero overlap found between the two nitroxyl groups would cause any magnetic interaction between the unpaired electrons occupying the π^* MO's to be very small in agreement with the experimental determination (−0.01 cm^{-1}).[12] In the case of the magnetic interaction between copper and nitroxyls, the overlap between the copper d_{xy} and the π^* nitroxyl MO's is found to be very weak (0.0002 au) for molecule A and almost zero for molecule B; the experimental weak value of +9.6 cm^{-1} [12] supports this result.

The overlap between copper and nitroxyl MO's is strongly dependent on both interatomic distances and relative orientations of the nitroxyl groups with respect to the copper xy plane. If the radical ligands are axial and oriented with respect to the square-planar Cu–β-diketonate fragment in such a way that the CNC plane lies in the yz plane (the solid-state symmetry being maintained), one can define all the possible conformations by the angle θ between the NO bond and the z axis as shown in Figure 4.

We have performed overlap calculations of the copper fragment and two H_2NO nitroxyl groups (Figure 4b) for θ = 0, 45, and 90° and two Cu–O distances (Table VI). It appears that the overlap integrals $\langle d_{xy}/\pi^*_{NO} \rangle$ increases rapidly with θ. Although the overlap remains very small for our experimental Cu–O distance (2.56 Å) in absolute value, its variation with θ is significant and one can expect a stronger exchange interaction for molecular systems with comparable Cu–O distances and favorable orientations of the nitroxyl groups. For $\theta = 0$, owing to the orthogonality of d_{xy} and π^*_{NO}, S is zero, and owing to the value of the Cu–NO distance, the coupling will be weakly ferromagnetic according to Kahn and Charlot.[27]

In molecule A, where the Cu–O(nitroxyl) distance is the smaller, the Cu–O–N angle corresponds to θ = 21.5° and the resulting coupling is expected to be small. In contrast, in molecule B, the larger overlap that would result from the larger θ angle (40.1°) is counterbalanced by the larger Cu–O(nitroxyl) distance (3.157 Å). The averaged small experimental coupling is consistent with the above model.

Synthesis and structural and magnetic studies of related systems are currently under way in our laboratory.

Registry No. Bis[(1-oxy-2,2,6,6-tetramethylpiperidin-4-yl)pivaloylacetato]copper(II), 65652-96-2.

Supplementary Material Available: Listings of anisotropic thermal parameters (Table III), bond lengths and angles (Table IVB), torsion angles (Table VB), and observed and calculated structure factors (34 pages). Ordering information is given on any current masthead page.

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