Table III. Bond Angles (deg) and Their Estimated Standard Deviations

OW–K1–OW	146.57 (7)	K1–O1–H3	109 (2)
OW–K1–O1	69.97 (4)	B1–O1–H3	109 (2)
OW–K1–O1	121.54 (5)	K2–O2–B1	127.1 (1)
OW–K1–O4	116.45 (4)	K2–O2–H4	105 (2)
OW–K1–O4	87.59 (4)	B1–O2–H4	111 (2)
OW–K1–O6	80.52 (4)	B1–O3–B3	124.2 (2)
OW–K1–O6	73.55 (4)	K1–O4–B1	94.6 (1)
O1–K1–O1	143.39 (6)	K1–O4–B2	117.0 (1)
O1–K1–O4	48.60 (4)	B1–O4–B2	123.5 (2)
O1–K1–O4	102.76 (4)	K2–O5–B2	138.1 (1)
O1–K1–O6	75.60 (4)	K2–O5–H5	98 (3)
O1–K1–O6	137.55 (4)	B2–O5–H5	115 (3)
O1–K1–O4	102.76 (4)	K1–O6–B2	118.3 (1)
O4–K1–O4	90.95 (5)	K1–O6–B3	119.1 (1)
O4–K1–O6	96.58 (4)	B2–O6–B3	118.8 (2)
O4–K1–O6	167.85 (4)	K2–O7–B3	113.2 (1)
O6–K1–O6	77.71 (5)	K2–O7–H6	93 (2)
O2–K2–O2	180.00	B3–O7–H6	117 (3)
O2–K2–O5	74.33 (5)	O1–B1–O2	110.1 (2)
O2–K2–O5	105.67 (5)	O1–B1–O3	109.3 (2)
O2–K2–O7	76.17 (4)	O1–B1–O4	108.7 (2)
O2–K2–O7	103.83 (4)	O2–B1–O3	108.1 (2)
O5–K2–O5	180.00	O2–B1–O4	110.2 (2)
O5–K2–O7	90.03 (5)	O3–B1–O4	110.5 (2)
O5–K2–O7	89.97 (5)	O4–B2–O5	118.6 (2)
O7–K2–O7	180.00	O4–B2–O6	121.5 (2)
K1–OW–H1	121 (2)	O5–B2–O6	119.9 (2)
K1–OW–H2	103 (2)	O3–B3–O6	121.2 (2)
H1–OW–H2	105 (3)	O3–B3–O7	118.1 (2)
K1–O1–B1	106.8 (1)	O6–B3–O7	120.7 (2)

The final coefficient, refined by least squares, was 0.000 000 7 (in absolute units).

The structure was solved by using direct methods. Hydrogen atoms were located and their positions and isotropic thermal parameters were refined. The structure was refined by full-matrix least squares where the function minimized was $\sum w(|F_o| - |F_c|)^2$ and the weight w is defined as $4F_o^2/\sigma^2(F_o^2)$. The standard deviation on intensities, $\sigma(F_o^2)$, is defined as follows:

$$\sigma^2(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2]/L^2$$

where S is the scan rate, C is the total integrated peak count, R is the ratio of scan time to background counting time, B is the total background count, L is the Lorentz–polarization factor, and the parameter p is a factor introduced to downweight intense reflections. Here p was set to 0.050. Scattering factors were those tabulated by Cromer and Waber.[26] Anomalous dispersion effects were included in F_c;[27] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[28] Only the 1165 reflections having intensities greater than 3.0 times their standard deviation were used in the refinements. The final cycle of refinement included 136 variable parameters and converged (largest parameter shift was 0.06 times its esd) with unweighted and weighted agreement factors of

$$R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.029$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.041$$

The standard deviation of an observation of unit weight was 1.22. The highest peak in the final difference Fourier had a height of 0.28 e/Å^3 with an estimated error based on ΔF[29] of 0.07. Plots of $\sum w(|F_o| - |F_c|)^2$ vs. $|F_o|$, reflection order in data collection, $(\sin\theta)/\lambda$, and various classes of indices showed no unusual trends. The computer was a PDP-11/60-based system. Positional parameters are listed in Table I. Bond distances and angles are collected in Tables II and III. Tables of observed and calculated structure factor amplitudes, thermal parameters, least-squares planes, and intermolecular contacts are available as supplementary material. The calculated X-ray powder pattern for Cu radiation is also available.

Acknowledgment. We thank O. L. Davis for the many powder diffraction spectra and assistance with the oven experiments and Dr. R. C. Medrud for preliminary crystal analysis and the calculated X-ray powder pattern.

Supplementary Material Available: Tables of anisotropic thermal parameters, weighted least-squares planes, and intermolecular contacts to 3.50 Å for I, the 40 most intense lines in the calculated X-ray powder pattern of I for Cu radiation, and complete X-ray powder patterns for β-KB_3O_5 and γ-KB_3O_5 and a stereoview of the unit cell of I (9 pages); a table of observed and calculated structure factors for I (4 pages). Ordering information is given on any current masthead page.

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Contribution from the Departments of Chemistry, Colorado State University, Fort Collins, Colorado 80523, University of Colorado at Denver, Denver, Colorado 80202, and University of Denver, Denver, Colorado 80208

Metal–Nitroxyl Interactions. 49. Molecular Structure and EPR Spectra of Dichloro(bis((1-pyrazolyl)methyl)(2,2,6,6-tetramethyl-1-oxy-4-piperidinyl)amine)copper(II) and EPR Studies of Copper–Nitroxyl Exchange in Related Compounds

Joseph H. Reibenspies,[1a] Oren P. Anderson,*[1a] Sandra S. Eaton,*[1b] Kundalika M. More,[1c] and Gareth R. Eaton*[1c]

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The structure of the title compound, Cu(bp-NO)Cl_2, has been investigated by single-crystal X-ray diffraction. Discrete molecules of Cu(bp-NO)Cl_2 crystallize in the monoclinic space group $P2_1/c$ ($Z = 4$), with $a = 11.737$ (4) Å, $b = 11.744$ (4) Å, $c = 15.326$ (4) Å, and $\beta = 94.03$ (2)°. In Cu(bp-NO)Cl_2, the three nitrogen atoms of the bp-NO ligand and two chloride ions surround the copper(II) ion in a distorted square pyramidal array. One of the chloride ions occupies the more weakly bound apical position (Cu–Cl1 = 2.495 (1) Å), while the second occupies a basal position (Cu–Cl2 = 2.231 (1) Å). The Cu–N(amine) bond distance (2.195 (3) Å) is much longer than the Cu–N(pyrazole) bond distances (1.965 (3), 1.957 (4) Å). The magnitude of the copper–nitroxyl exchange coupling constant, J, in a series of copper(II) complexes of spin-labeled bis(pyrazolyl)amines ranged from >3500 to <100 G. It is proposed that the magnitude of J reflects the strength of the bond between the copper(II) and the amine nitrogen that is attached to the spin label.

Introduction

Recently, it has been shown that reaction of 1-(hydroxymethyl)-3,5-dimethylpyrazole with primary amines (RNH_2) produces the bis(pyrazolyl)amine bdmp-R.[2] The structures of four transition-metal complexes of these ligands have been determined. In Ni(bdmp-ae)$(NO_3)_2$, the metal was in a distorted octahedral environment and the distance between the Ni(II) atom

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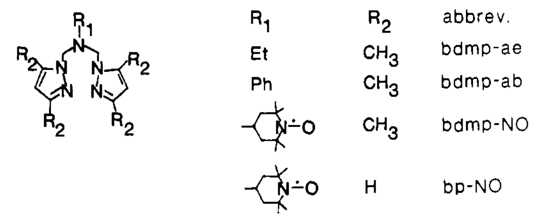

and the amine nitrogen atom was 2.128 (5) Å.[3] In Cu(bp-ae)Br_2, the metal was in a distorted square pyramidal environment and the distance between the copper(II) atom and the amine nitrogen atom was 2.191 (2) Å.[4] In Cu(bdmp-ab)Br_2, the metal was in a distorted trigonal bipyramidal environment and the distance between the Cu(II) atom and the amine nitrogen atom was 2.423 (1) Å.[5] In Co(bdmp-ab)Cl_2 the metal was in a distorted tetrahedral environment and the amine nitrogen atom was not coordinated.[5] These structures indicate that bis(pyrazolyl)amines can function as flexible bidentate or tridentate ligands and that there can be considerable variation in the length of the bond to the amine nitrogen. This raises the possibility that the bonding between Cu(II) and the amine nitrogen atom in a bis(pyrazolyl)amine complex might be sensitive to changes in the pyrazole substituents and in the anion.

The electron–electron spin–spin interaction between a paramagnetic transition metal and a nitroxyl radical is a sensitive probe of the bonding pathway between the two paramagnetic centers. It therefore appeared likely that it would be possible to use copper–nitroxyl interactions to study the binding of the amine nitrogen atom in copper complexes of a spin-labeled bis(pyrazolyl)amine. We have prepared the spin-labeled ligands bdmp-NO and bp-NO and the corresponding copper(II) complexes. EPR spectra of Cu(bp-NO)X_2 (X = Cl, Br) and Cu(bdmp-NO)X_2 (X = Cl, Br, ClO_4, BF_4) were examined. Structure determination was carried out by single-crystal X-ray diffraction.

Experimental Section

Physical Measurements. Visible spectra were obtained in dichloromethane or toluene solutions on a Cary 14 spectrometer with the OLIS modification.[6] Visible spectra are given below with band maxima in nanometers and log ϵ in parentheses. Infrared spectra were obtained in Nujol mulls or KBr pellets on a Perkin-Elmer 283B spectrometer. Melting points were obtained on a Hoover Mel-Temp apparatus. Mass spectra were obtained by fast atom bombardment (FAB) of samples in a glycerol matrix. Under these conditions the Cu(II) was reduced to Cu(I). X-Band EPR spectra were obtained with 100-kHz modulation on a Varian E9 interfaced to an IBM CS9000 or on an IBM ER200D interfaced to an IBM CS9000. Q-Band spectra were obtained on a spectrometer that has been described previously.[7] Solutions were about 1×10^{-3} M. The lines in the spectra were sufficiently broad that the spectra were not changed by degassing the samples. Spectra were obtained with microwave powers that did not cause saturation and modulation amplitudes that did not distort the line shapes.

Preparation of Ligands. Bis((3,5-dimethyl-1-pyrazolyl)methyl)-phenylamine, bdmp-ab, was prepared as reported in the literature.[2,5]

Bis((3,5-dimethyl-1-pyrazolyl)methyl)(2,2,6,6-tetramethyl-1-oxy-4-piperidinyl)amine, bdmp-NO. The spin-labeled ligand was prepared by a procedure similar to that reported for bdmp-ab.[2,5] 1-(Hydroxymethyl)-3,5-dimethylpyrazole[2] (1.26 g, 10 mmol) was added to a solution of 4-amino-2,2,6,6-tetramethylpiperidinyl-1-oxy (0.856 g, 5.0 mmol) in 1,2-dichloroethane (10 mL). The solution was stirred for 24 h. The dichloroethane layer was separated from the water layer, and the dichloroethane was removed under vacuum. The resulting red solid was recrystallized from hexane: yield 1.84 g, 95%; mp 60 °C. IR: 1560, 1465, 1380, 1320, 1240, 1200, 1100, 1030, 980, 780, 720 cm^{-1}.

Bis((1-pyrazolyl)methyl)(2,2,6,6-tetramethyl-1-oxy-4-piperidinyl)-amine, bp-NO. The ligand was prepared from 1-(hydroxymethyl)-pyrazole and 4-amino-2,2,6,6-tetramethylpiperidinyl-1-oxy by a procedure similar to that reported for bdmp-NO: yield 80%; mp 105 °C. IR: 1450, 1380, 1240, 1180, 1130, 1085, 960, 750, 615 cm^{-1}.

Preparation of Copper Complexes. Cu(bdmp-ab)Cl_2 was prepared as previously reported;[5] mp 139 °C (lit.[5] mp 140–141 °C). IR: 1600, 1555, 1465, 1415, 1385, 1315, 1280, 1210, 1180, 1125, 1060, 975, 810, 800, 770, 755, 690, 615 cm^{-1}. Vis (dichloromethane): 850 (2.36), 374 (3.13), 281 (3.64) nm. Mass spectrum: $(M - 2Cl)^+$, m/z = 442 for ^{63}Cu.

Dichloro(bis((3,5-dimethyl-1-pyrazolyl)methyl)(2,2,6,6-tetramethyl-1-oxy-4-piperidinyl)amine)copper(II), Cu(bdmp-NO)Cl_2. The complex was prepared by a procedure analogous to that reported for Cu(bdmp-ab)Cl_2.[5] $CuCl_2 \cdot 2H_2O$ (0.17 g, 1.0 mmol) was dissolved in absolute ethanol (5 mL) and treated with triethyl orthoformate (1 mL) to remove water. A solution of bdmp-NO (0.388 g, 1.0 mmol) in absolute ethanol (2 mL) was added. A green solid crystallized from the solution at room temperature within 10 min of mixing the reactants. The crystals were collected by filtration, washed with about 1 mL of absolute ethanol, and then washed several times with dry diethyl ether; yield 0.40 g, 77%. Prolonged heating under vacuum caused decomposition; mp 179 °C. IR: 1460, 1400, 1305, 1270, 1240, 1200, 1180, 1120, 1060, 975, 880, 790, 670, 610 cm^{-1}. Vis (dichloromethane): 895 (2.41), 365 (3.13) nm. Vis (1:1 dichloromethane–toluene): 900 (2.43), 360 (3.21) nm.

Dichloro(bis((1-pyrazolyl)methyl)(2,2,6,6-tetramethyl-1-oxy-4-piperidinyl)amine)copper(II), Cu(bp-NO)Cl_2. This complex was prepared from bp-NO and $CuCl_2 \cdot 2H_2O$ by a procedure similar to that used to prepare Cu(bdmp-NO)Cl_2: yield 82%; mp 168 °C. IR: 1450, 1400, 1375, 1320, 1270, 1240, 1200, 1185, 1130, 1090, 1060, 980, 870, 825, 790, 755, 680, 600 cm^{-1}. Mass spectrum: $(M - 2Cl)^+$, m/z = 395 for ^{63}Cu. Crystals used in the X-ray diffraction study were grown from absolute ethanol.

Dibromo(bis((3,5-dimethyl-1-pyrazolyl)methyl)(2,2,6,6-tetramethyl-1-oxy-4-piperidinyl)amine)copper(II), Cu(bdmp-NO)Br_2. This complex was prepared from bdmp-NO and $CuBr_2$ by a procedure similar to that used to prepare Cu(bdmp-NO)Cl_2: yield 75%; mp 158 °C. IR: 1460, 1400, 1300, 1275, 1240, 1200, 1180, 1120, 1060, 970, 880, 790, 670, 600 cm^{-1}. Vis (dichloromethane): 900 (2.80), 418 (3.31), 309 (3.80) nm. Vis (1:1 toluene–dichloromethane): 900 (2.70), 424 (3.35), 310 (3.50) nm. Vis (toluene, saturated): 895, 424, 310 nm.

Dibromo(bis((1-pyrazolyl)methyl)(2,2,6,6-tetramethyl-1-oxy-4-piperidinyl)amine)copper(II), Cu(bp-NO)Br_2. This complex was prepared from bp-NO and $CuBr_2$ by a procedure similar to that used to prepare Cu(bdmp-NO)Cl_2: yield 80%; mp 185 °C. IR: 1460, 1400, 1380, 1320, 1270, 1240, 1200, 1185, 1130, 1090, 1065, 985, 875, 830, 780, 755, 680 cm^{-1}. Vis (dichloromethane): 900 (2.18), 420 (2.60), 338 (2.94) nm.

Bis(perchlorato)(bis((3,5-dimethyl-1-pyrazolyl)methyl)(2,2,6,6-tetramethyl-1-oxy-4-piperidinyl)amine)copper(II), Cu(bdmp-NO)$(ClO_4)_2$. The complex was prepared from $Cu(ClO_4)_2$ and bdmp-NO by a procedure similar to that used to prepare Cu(bdmp-NO)Cl_2. Since the complex did not precipitate from the reaction mixture, the solvent was removed and the residue was washed with dry diethyl ether to give a green solid: yield 78%; mp 120 °C dec. IR: 1550, 1465, 1380, 1240, 1100 (vs, multiple peaks), 800, 600 cm^{-1}. Vis (dichloromethane, saturated): 610, 360 nm.

Bis(perchlorato)(bis((3,5-dimethyl-1-pyrazolyl)methyl)phenylamine)-copper(II), Cu(bdmp-ab)$(ClO_4)_2$. The complex was prepared from $Cu(ClO_4)_2$ and bdmp-ab by the procedure used to prepare Cu(bdmp-NO)$(ClO_4)_2$: yield 65%; mp 136 °C dec. IR: 1600, 1580, 1550, 1490, 1420, 1390, 1100 (vs, multiple peaks), 925, 800, 700, 625 cm^{-1}. Vis (dichloromethane, saturated): 616, 378 nm.

Bis(tetrafluoroborato)(bis((3,5-dimethyl-1-pyrazolyl)methyl)(2,2,6,6-tetramethyl-1-oxy-4-piperidinyl)amine)copper(II), Cu(bdmp-NO)$(BF_4)_2$. The complex was prepared from bdmp-NO and $Cu(BF_4)_2$ by the procedure used to prepare Cu(bdmp-NO)$(ClO_4)_2$: yield 70%; mp 117 °C dec. IR: 1550, 1460, 1390, 1300, 1240, 1120 (s), 1080 (s), 1040 (s), 790, 690, 530, 520 cm^{-1}. Vis (dichloromethane, saturated): 602 nm.

Structure Determination for Cu(bp-NO)Cl_2. Crystal data for Cu(bp-NO)Cl_2, together with details of the X-ray diffraction experiment and subsequent computations, are listed in Table I. Cell dimensions were obtained from a least-squares fit to the setting angles for 25 reflections ($2\theta_{av}$ = 17.04°) on a Nicolet R3m diffractometer.[8] The stability of the

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(8) Software used for diffractometer operations and data collection was provided with the Nicolet *R3m* diffractometer. Crystallographic computations were carried out with the SHELXTL program library, written by G. M. Sheldrick and supplied by Nicolet XRD for the Data General Eclipse S/140 computer in the crystallography laboratory at Colorado State University.

Table I. Details of the Crystallographic Experiment and Computations for $[Cu(bp\text{-}NO)Cl_2]$

formula	$C_{17}H_{27}N_6Cl_2CuO$
fw	465.9
cryst syst	monoclinic
space group	$P2_1/c$
a, Å	11.737 (4)
b, Å	11.744 (4)
c, Å	15.326 (4)
β, deg	94.03 (2)
V, Å^3	2107
temp, °C	−125 °C
Z	4
$F(000)$	968
ρ(calcd), g cm^{-3}	1.47
cryst dimens, mm	0.04 (100 → $\bar{1}$00) × 0.22 (010 → 0$\bar{1}$0) × 0.36 (001 → 00$\bar{1}$)
radiation	Mo Kα (λ = 0.7107 Å)
monochromator	graphite
μ, cm^{-1}	13.2
scan type	$\theta/2\theta$
geometry	bisecting
2θ range, deg	4.0–50.0
scan speed, deg min^{-1}	variable, 2.02–29.30
index restrictions	$-14 \le h \le 14, 0 \le k \le 14, -19 \le l \le 0$
reflecns	4229 measd, 4067 unique, 3005 used ($\|F_o\| > 2.5\sigma(\|F_o\|)$)
no. of least-squares params	256
data/params	11.7
R	0.053
R_w	0.048
GOF	1.24
g	6.3×10^{-4} (refined)
slope, norm prob plot	1.12

Table II. Fractional Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for $[Cu(bp\text{-}NO)Cl_2]$[a]

atom	x	y	z	U_{iso}[b]
Cu	1444 (1)	6562 (1)	1914 (1)	20 (1)
Cl1	−381 (1)	6954 (1)	1031 (1)	23 (1)
Cl2	2397 (1)	8138 (1)	2327 (1)	34 (1)
N1	629 (3)	6350 (3)	2979 (2)	19 (1)
N2	57 (3)	5345 (3)	2999 (2)	19 (1)
C1	496 (4)	6852 (4)	3741 (3)	26 (1)
C2	−184 (4)	6189 (4)	4245 (3)	30 (2)
C3	−443 (4)	5222 (4)	3755 (3)	24 (1)
N3	2318 (3)	6187 (3)	912 (2)	23 (1)
N4	2055 (3)	5127 (3)	579 (2)	23 (1)
C4	3173 (4)	6552 (4)	486 (3)	37 (2)
C5	3473 (5)	5754 (5)	−130 (4)	54 (2)
C6	2750 (4)	4850 (4)	−47 (3)	36 (2)
C7	143 (3)	4515 (3)	2292 (3)	20 (1)
C8	1131 (4)	4513 (4)	945 (3)	23 (1)
N5	1224 (3)	4706 (3)	1896 (2)	17 (1)
C9	2258 (3)	4136 (3)	2345 (2)	16 (1)
C10	2294 (3)	2853 (3)	2199 (3)	20 (1)
C11	3385 (4)	2289 (4)	2608 (3)	23 (1)
N6	3606 (3)	2681 (3)	3523 (2)	21 (1)
C12	3424 (4)	3874 (4)	3803 (3)	22 (1)
C13	2340 (3)	4356 (3)	3322 (3)	19 (1)
C14	3234 (4)	3844 (4)	4782 (3)	33 (2)
C15	4480 (4)	4604 (4)	3652 (3)	33 (2)
C16	3212 (4)	1005 (4)	2623 (3)	31 (2)
C17	4429 (4)	2573 (4)	2090 (3)	30 (2)
O	4317 (3)	2091 (3)	4016 (2)	35 (1)

[a] Estimated standard deviations in the least significant digits are given in parentheses. [b] U_{iso} is defined as one-third of the trace of the U_{ij} tensor.

crystal in the X-ray beam was monitored by measurement of the intensities of 3 control reflections (20$\bar{4}$, $\bar{1}$2$\bar{1}$, $\bar{2}$1$\bar{1}$) every 97 reflections. No significant change in the intensities of these 3 reflections was noted. An empirical absorption correction was performed, utilizing the intensity profiles obtained for 10 reflections as a function of ψ ($\Delta\psi$ = 15°). The range of transmission factors exhibited for the complete data set was 0.426–0.489. The merging R decreased from 0.029 before the correction to 0.0242 after correction. In addition to the absorption correction, Lorentz and polarization corrections were applied to the data.

Table III. Bond Lengths (Å) and Angles (deg) for $[Cu(bp\text{-}NO)Cl_2]$[a]

	a. Bond Lengths		
Cu–Cl1	2.495 (1)	Cu–Cl2	2.231 (1)
Cu–N1	1.965 (3)	Cu–N3	1.957 (4)
Cu–N5	2.195 (3)	N1–N2	1.360 (5)
N1–C1	1.327 (5)	N2–C3	1.342 (5)
N2–C7	1.466 (5)	C1–C2	1.388 (6)
C2–C3	1.384 (6)	N3–N4	1.372 (5)
N3–C4	1.307 (6)	N4–C6	1.343 (6)
N4–C8	1.448 (5)	C4–C5	1.392 (8)
C5–C6	1.372 (8)	C7–N5	1.461 (5)
C8–N5	1.472 (5)	N5–C9	1.509 (5)
C9–C10	1.524 (5)	C9–C13	1.516 (5)
C10–C11	1.536 (6)	C11–N6	1.482 (5)
C11–C17	1.543 (6)	C11–C16	1.523 (6)
N6–C12	1.486 (5)	N6–O	1.288 (4)
C12–C13	1.534 (6)	C12–C14	1.532 (6)
C12–C15	1.538 (6)		
	b. Bond Angles		
Cl1–Cu–Cl2	113.3 (1)	Cl1–Cu–N1	91.4 (1)
Cl1–Cu–N3	95.3 (1)	Cl1–Cu–N5	94.6 (1)
Cl2–Cu–N1	97.6 (1)	Cl2–Cu–N3	97.5 (1)
Cl2–Cu–N5	152.1 (1)	N1–Cu–N3	159.5 (1)
N1–Cu–N5	79.7 (1)	N3–Cu–N5	80.5 (1)
Cu–N1–N2	113.5 (2)	Cu–N1–C1	140.2 (3)
N2–N1–C1	106.1 (3)	N1–N2–C3	111.1 (3)
N1–N2–C7	120.0 (3)	C3–N2–C7	128.6 (3)
N1–C1–C2	110.4 (4)	C1–C2–C3	105.7 (4)
N2–C3–C2	106.7 (4)	Cu–N3–N4	112.3 (3)
Cu–N3–C4	141.4 (3)	N4–N3–C4	105.8 (4)
N3–N4–C6	110.7 (4)	N3–N4–C8	117.6 (3)
C6–N4–C8	131.7 (4)	N3–C4–C5	111.0 (5)
C4–C5–C6	105.7 (5)	N4–C6–C5	106.8 (4)
N2–C7–N5	108.2 (3)	N4–C8–N5	107.5 (3)
Cu–N5–C7	104.6 (2)	Cu–N5–C8	99.5 (2)
Cu–N5–C9	110.2 (2)	C7–N5–C8	112.4 (3)
C7–N5–C9	115.9 (3)	C8–N5–C9	112.6 (3)
N5–C9–C10	113.7 (3)	N5–C9–C13	111.5 (3)
C10–C9–C13	108.3 (3)	C9–C10–C11	113.4 (3)
C10–C11–N6	109.7 (3)	C10–C11–C17	111.6 (3)
N6–C11–C17	109.1 (3)	C10–C11–C16	108.9 (3)
N6–C11–C16	107.9 (3)	C17–C11–C16	109.5 (4)
C11–N6–C12	123.2 (3)	C11–N6–O	116.8 (3)
C12–N6–O	116.0 (3)	N6–C12–C13	109.9 (3)
N6–C12–C14	107.2 (3)	C13–C12–C14	107.8 (3)
N6–C12–C15	110.4 (3)	C13–C12–C15	111.8 (3)
C14–C12–C15	109.6 (4)	C9–C13–C12	113.9 (3)

[a] Estimated standard deviations in the least significant digits are given in parentheses.

The copper atom was located by inspection of peaks in the E map generated by the direct-methods routine SOLV. Subsequent Fourier difference electron density maps revealed all non-hydrogen ligand atoms. Neutral-atom scattering factors[9] and anomalous scattering contributions[10] were included for all atoms.

In the final model, all non-hydrogen atoms were given anisotropic thermal parameters. Hydrogen atoms were included in idealized positions (C–H = 0.96 Å, U(H) = 1.2[U_{iso}(C)]). The refinement converged ((shift/esd)$_{av}$ < 0.012, (shift/esd)$_{max}$ = 0.084 over the last 10 cycles) to yield the residual indices shown in Table I. In the final difference electron density map, the highest peak (0.54 e Å^{-3}) occurred near the copper atom. The minimum in the map was −0.64 e Å^{-3}.

Final fractional atomic coordinates for all non-hydrogen atoms of $Cu(bp\text{-}NO)Cl_2$ may be found in Table II. Bond lengths and angles for $Cu(bp\text{-}NO)Cl_2$ are given in Table III. Anisotropic thermal parameters (Table S-I), calculated hydrogen atom coordinates (Table S-II), and structure factors (calculated and observed, ×10, Table S-III), have been included as supplementary material.

Computer Simulations. The simulations of the EPR spectra were obtained with CUNO[11] for fluid-solution data and with MENO[12] for fro-

(9) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, p 99.
(10) Reference 9, p 149.
(11) Eaton, S. S.; DuBois, D. L.; Eaton, G. R. *J. Magn. Reson.* **1978**, *32*, 251.

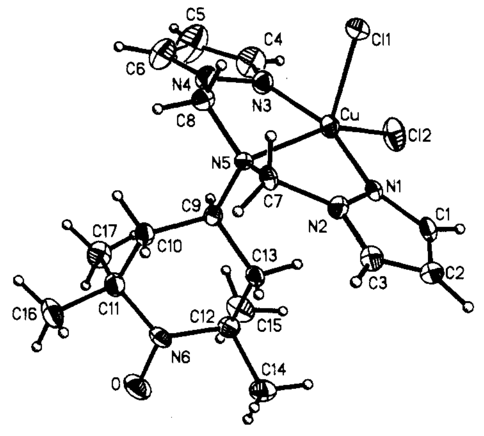

Figure 1. Thermal ellipsoid plot (50% probability) of Cu(bp-NO)Cl_2. Hydrogen atoms have been included as spheres of fixed, arbitrary radius.

zen-solution data. The exchange term in the Hamiltonian was $-JS_1 \cdot S_2$. The simulated fluid-solution spectra are not dependent on the sign of J.

Results and Discussion

Cu(bp-NO)X_2 and Cu(bdmp-NO)X_2 (X = Cl, Br). The IR spectra of the complexes had a band at 970–985 cm^{-1}. In the analogous complexes of bdmp-ab a band was reported at ca. 975 cm^{-1} when the amine nitrogen atom was weakly coordinated.[5] The band shifted to ca. 920–935 cm^{-1} when the amine nitrogen atom was not coordinated. Thus, the IR spectra of the bdmp-NO and bp-NO complexes suggested that the amine nitrogen atom was weakly coordinated. The visible spectra of Cu(bdmp-NO)X_2 (X = Cl, Br) and Cu(bp-NO)X_2 (X = Cl, Br) in fluid solution had broad d–d bands with maxima at about 900 nm (11 000 cm^{-1}). Similar broad bands at 9500–11 500 cm^{-1} were reported for the solid reflectance spectra of Cu(bdmp-R)X_2 (R = ae, ab; X = Cl, Br).[3,5] Thus, the visible spectra suggested that the spin-labeled complexes were five-coordinate but also indicated that the visible spectra might not be a sensitive monitor of small changes in the geometry. Therefore, a crystal structure was obtained for Cu(bp-NO)Cl_2 to determine the detailed geometry around the Cu(II) for comparison with the geometries of Cu(bp-ae)Br_2[4] and Cu(bdmp-ab)Br_2.[5]

Structure of Cu(bp-NO)Cl_2. The structure of one of the discrete, five-coordinate, neutral complexes, Cu(bp-NO)Cl_2, together with the numbering scheme used in the refinement, is displayed in Figure 1. The coordination geometry in this complex is best described as square pyramidal, with Cl1 occupying the apical position. This assignment is supported by the long Cu–Cl1 bond distance (2.495 (1) Å, vs. a Cu–Cl2 distance of 2.231 (1) Å), which is expected for the bond to the apical atom in a square-pyramidal array around Cu(II), and by the angular parameter τ,[13] which is 0.12 for this complex (τ = 0.0 for idealized square-pyramidal geometry and 1.0 for idealized trigonal-bipyramidal geometry).

The structure for Cu(bp-NO)Cl_2 is very similar to that reported recently for Cu(bp-ae)Br_2 (angular parameter τ = 0.12).[4] The distances from the copper(II) ions to the two types of nitrogen atoms are nearly identical for the two structures, and even the difference (0.264 Å) between the two Cu–Cl distances in Cu(bp-NO)Cl_2 is nearly the same as the corresponding difference (0.288 Å) in the Cu–Br distances in Cu(bp-ae)Br_2. The similarity in the Cu–N(amine) distances in these two structures (Cu–N5 = 2.195 (3) Å in Cu(bp-NO)Cl_2, Cu–N(amine) = 2.191 (2) Å in Cu(bp-ae)Br_2) is particularly striking, given the much shorter distances to tertiary, aliphatic amine atoms in other copper(II) complexes.[14] These similarities suggest that the coordinated

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(13) Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349.

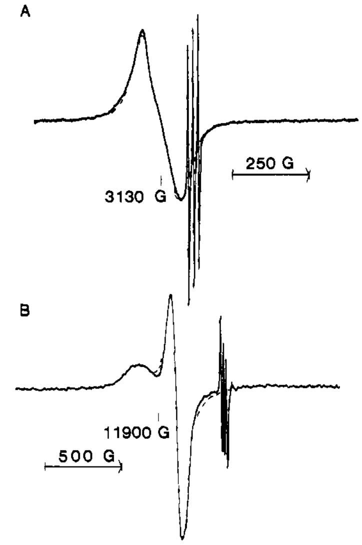

Figure 2. EPR spectra of Cu(bp-NO)Br_2 at room temperature: (A) 1000-G scan (X-band) of a solution in 1:2 toluene–dichloromethane obtained with 4-G modulation amplitude and 5-mW microwave power; (B) 2000-G scan (Q-band) of a toluene solution obtained with 12.5-G modulation amplitude and 5-mW microwave power. The dashed lines indicate regions in which the simulated spectra do not overlay the experimental data. The simulated spectra were obtained with J = 2000 G, copper and nitroxyl g values of 2.14 and 2.0059, respectively, and nuclear hyperfine splittings for copper and nitroxyl of 50 and 16 G, respectively.

halide, Cl^- or Br^-, does not have a large impact on the geometry of these complexes. However, these structures are strikingly different from the structure of Cu(bdmp-ab)Br_2,[5] in which the copper(II) ion has a distorted trigonal bipyramidal coordination environment (maximum τ = 0.77) and the Cu–N(amine) distance is 2.423 (1) Å. Two factors may contribute to the differences in the structures. The steric effects of the 3,5-dimethylpyrazole substituents on the bdmp-ab ligand may favor the trigonal bipyramidal geometry. The lower basicity of the phenyl-substituted nitrogen atom in the bdmp-ab ligand than of the aliphatic-substituted nitrogen atoms in the bp-ae or bp-NO ligands may contribute to a lengthening of the Cu–N(amine) bond that favors the trigonal bipyramidal geometry. In the Co(bdmp-ab)Cl_2 complex, the aniline nitrogen was not coordinated to Co(II), resulting in a four-coordinate, distorted tetrahedral complex,[5] while the Ni(bdmp-ae)$(NO_3)_2$ complex exhibited a distorted octahedral coordination sphere, in which the ethylamine nitrogen was coordinated.[3] These structures suggest that the basicity of the amine nitrogen is a significant factor in determining the strength of interaction between the metal ion and the amine nitrogen, although the differences between the metals and other changes in the coordination spheres may also contribute to differences in the binding of the amine nitrogen.

Other metric details of the structure of Cu(bp-NO)Cl_2 are unexceptional. The pyrazole rings are planar, as expected, with all deviations from the least-squares planes through the two rings less than 0.01 Å. The four basal coordinating atoms about copper(II) are an average of 0.18 Å from the least-squares plane through those atoms, while copper(II) is 0.35 Å above that plane. The copper(II) atom is only 0.10 Å above the plane through the three coordinating nitrogen atoms and is 0.08 Å from the plane of the pyrazole ring containing N1 and 0.19 Å from the plane of the pyrazole ring containing N2.

EPR Spectra of Cu(bp-NO)X_2 (X = Cl, Br). In dichloromethane solution the X-band spectra of Cu(bp-NO)Cl_2 and Cu(bp-NO)Br_2 had a signal at g = 2.07 with partially resolved copper hyperfine splitting of about 25 G (Figure 2A). A spectrum of Cu(bdmp-ab)Cl_2 in dichloromethane had g = 2.14 and A_{Cu} = 48 G. The spectra of Cu(bp-NO)X_2 were therefore attributed

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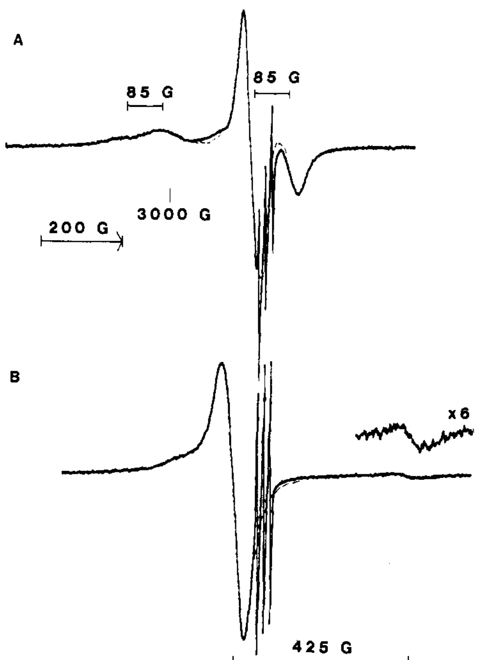

Figure 3. 1000-G scans of the X-band EPR spectra of Cu(bdmp-NO)-Cl_2: (A) spectrum in dichloromethane solution at 22 °C obtained with 5-mW microwave power and 2-G modulation amplitude; (B) spectrum in toluene solution at 10 °C obtained with 10-mW microwave power and 2-G modulation amplitude. The dashed lines indicate regions in which the simulated spectra do not overlay the experimental data. The simulated spectra were obtained with copper and nitroxyl g values of 2.13 and 2.0059, respectively, and nuclear hyperfine splittings for copper and nitroxyl of 50 and 16 G, respectively.

to exchange interaction between the copper and nitroxyl unpaired electrons that was sufficiently large relative to the g-value difference to give a signal at the average g value with half the value of A_{Cu} observed in the absence of spin-spin interaction.[15,16] The simulated spectrum was obtained with $J = 2000$ G, although larger values of J gave comparable agreement with the experimental spectrum. The sharp three-line signal at $g = 2.0$ was due to a small amount of nitroxyl that was not interacting with the copper(II) and was not included in the simulation.

A more accurate value of the electron-electron exchange coupling constant was obtained from the Q-band (35-GHz) spectrum of Cu(bp-NO)Br_2 in dichloromethane (Figure 2B). Separate signals were observed for the copper and nitroxyl "inner" lines of the AB splitting pattern. The "outer" lines were too weak to detect. At the higher frequency the g-value difference caused a larger separation between the copper and nitroxyl energy levels than that at X-band.[17] The value of J that gave one signal at the average of the copper and nitroxyl g values for Cu(bp-NO)Br_2 at X-band was not large enough to give an averaged signal at Q-band. The Q-band spectrum was simulated with $J = 2000$ G which is consistent with the X-band data. The uncertainty in the value of J was about 200 G. When the temperature was decreased, the copper "inner" line broadened substantially due to incomplete motional averaging. The position of the nitroxyl "inner" line did not shift with temperature over the range −55 to +22 °C, which indicated that the value of J was not strongly temperature dependent.

The low solubility of Cu(bp-NO)X_2 limited the range of studies that could be performed in solution. The X-band spectrum of Cu(bp-NO)Br_2 in 1:1 toluene-dichloromethane was indistinguishable from that in dichloromethane. Thus, the limited data available do not indicate a strong dependence of the EPR spectra

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(16) Eaton, S. S.; More, K. M.; Sawant, B. M.; Eaton, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 6560.
(17) Eaton, S. S.; More, K. M.; DuBois, D. L.; Boymel, P. M.; Eaton, G. R. *J. Magn. Reson.* **1980**, *41*, 150.

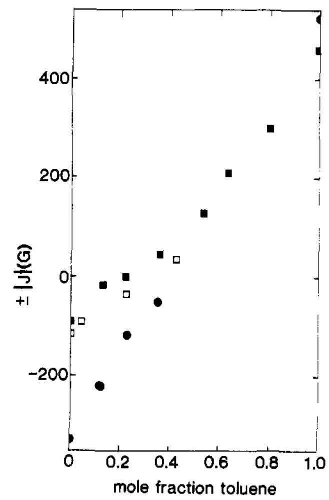


Figure 4. Plot of the electron-electron coupling constant, J, for Cu-(bdmp-NO)X_2 (X = Cl, Br) vs. the mole fraction of toluene in the solvent mixture: (■) X = Cl, second solvent dichloromethane; (●) X = Br, second solvent dichloromethane; (□) X = Cl, second solvent chloroform. The sign of J is not known so an arbitrary sign convention was used.

on solvent or temperature. Attempts to obtain spectra in frozen solution or on imbiber beads[18] resulted in aggregation of the complexes.

EPR Spectra of Cu(bdmp-NO)X_2 (X = Cl, Br). Two spectra that show the AB splitting patterns that typify the spectra of these complexes are shown in Figure 3. The value of J for the spectra in Figure 3 is 85 G. The splitting between the nitroxyl "inner" and "outer" lines is equal to J and is marked on the spectrum. The splitting of the copper lines is also equal to J but is less well-resolved due to the greater line widths of the copper lines than of the nitroxyl lines. For both pairs of signals the "inner" lines have greater intensity than the "outer" lines. The value of J for the spectrum in Figure 3B is 425 G. Comparison of the spectra in parts A and B of Figure 3 shows the characteristic changes that occur as the value of J increases—the "inner" lines move closer together and the intensity of the "outer" lines decreases. Due to the greater line width for the copper lines than for the nitroxyl lines, the copper "outer" lines were not observed in the spectrum shown in Figure 3B.

The values of J for Cu(bdmp-NO)X_2 (X = Cl, Br) were strongly dependent on solvent. When the relative proportions of toluene and dichloromethane were varied, the absolute value of J passed through a minimum. The value of J for Cu(bdmp-NO)Cl_2 also passed through a minimum as the solvent composition was varied from chloroform to toluene. One interpretation of these results is that the value of J changed sign as the solvent was varied. A plot of J vs. the mole fraction of toluene is given in Figure 4, based on an arbitrary assumption concerning the signs of the values of J. The smooth variation in the values appears to support the proposal of a change of sign. The similarity in the values of J for X = Cl and Br (Figure 4) indicated that the bonding in the complexes was not strongly dependent on the anion.

In fluid solution the X-band EPR spectra of Cu(bdmp-NO)X_2 (X = Cl, Br) were strongly dependent on temperature. The direction in which the magnitude of J changed with temperature depended on solvent. In toluene solution the magnitude of J decreased as the temperature was decreased. In chlorinated solvents and mixtures that were predominantly chlorinated solvents, the magnitude of J increased as the temperature decreased. The temperature dependence of the data is shown in Figure 5 with the same arbitrary sign convention as in Figure 4. The similarity in the slopes of the lines for all of the solvents suggests that there is a common temperature-dependent contribution to J and that contribution has the same sign as the net value of J in chlorinated solvents but is opposite to the sign of J in toluene.

(18) More, K. M.; Eaton, G. R.; Eaton, S. S. *Anal. Chem.* **1984**, *56*, 1551. More, K. M.; Eaton, G. R.; Eaton, S. S. *J. Magn. Reson.* **1984**, *59*, 497.

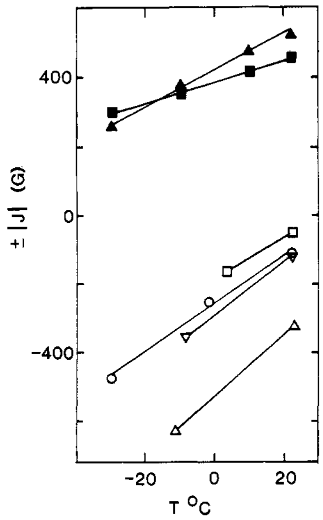
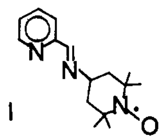


Figure 5. Plot of the temperature dependence of J for Cu(bdmp-NO)X_2 in various solvents with the same sign convention as in Figure 4: (■) X = Cl in toluene; (▲) X = Br in toluene; (□) X = Cl in 1:2 toluene–chloroform; (○) X = Cl in chloroform; (▽) X = Br 1:1 toluene–dichloromethane; (△) X = Br in dichloromethane.

In frozen toluene–dichloromethane solution the EPR spectra of Cu(bdmp-NO)X_2 (X = Cl, Br) were poorly resolved but indicated strong interaction between the copper and nitroxyl unpaired electrons, which is consistent with the rapid increase in J with decreasing temperature in fluid solution in chlorinated solvents. The relative intensity of the half-field transitions[19] for X = Cl and Br was 2.7×10^{-4}, which corresponds to a copper–nitroxyl distance of 6.5 Å. In the crystal structure of Cu(bp-NO)Cl_2 the through-space distances between the copper and the nitroxyl nitrogen and oxygen were 5.694 and 6.913 Å, respectively, for an average of 6.3 Å. The similarity between this average value and the copper–nitroxyl distance obtained from the EPR spectrum of Cu(bdmp-NO)Cl_2 suggests that the structure of Cu(bdmp-NO)Cl_2 in frozen solution does not differ greatly from the structure of Cu(bp-NO)Cl_2 observed in the crystal. It is therefore proposed that the increase in the value of J with decreasing temperature is due to a decrease in the length of the bond between the copper and the amine nitrogen.

Cu(bdmp-NO)X_2 (X = ClO_4, BF_4). In the IR spectra of these complexes there were strong peaks characteristic of the anion. The perchlorate band at 1100 cm^{-1} was split into several partially resolved peaks. The tetrafluoroborate peaks also were split (1040, 1080, 1120 and 520, 530 cm^{-1}). These splittings indicate coordination of the anions.[20] The visible spectra in dichloromethane solution had maxima at 600–610 nm (ca. 16 500 cm^{-1}), which is at substantially higher energy than was observed for five-coordinate Cu(bdmp-R)X (X = Cl, Br) (9500–11 000 cm^{-1}) and somewhat higher than reported for six-coordinated Cu(bdmp-Et)$(NO_3)_2$ (13 500 cm^{-1}).[3] The EPR spectrum of Cu(bdmp-ab)$(ClO_4)_2$ on imbiber beads had g = 2.05, 2.07, 2.24 and $A_\parallel$ = 172 G. The observation of $g_\perp < g_\parallel$ and the large value of $A_\parallel$ suggest that these complexes are four- or six-coordinate rather than five-coordinate.[21-24] At both X-band and Q-band the EPR spectra of Cu(bdmp-NO)X_2 (X = ClO_4, BF_4) in fluid solution had one signal at the average of the copper and nitroxyl g values, which indicated strong exchange between the copper and nitroxyl unpaired electrons. To obtain an averaged signal at Q-band requires $J > 3500$ G for this complex. There was no indication of solvent dependence of the spectra.

For comparison of the magnitude of J, EPR spectra were also obtained for Cu(bdmp-ab)Cl_2 bound to the spin-labeled ligand I. The amine nitrogen in this complex is expected to be strongly



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bound to the copper. The EPR spectra showed strong exchange at both X-band and Q-band, which indicates $J > 3500$ G.

Comparison of the Values of J in Fluid Solution. The largest values of J (>3500 G) were observed for Cu(bdmp-NO)X_2 (X = ClO_4, BF_4) and the complex of Cu(bdmp-ab)Cl_2 with the spin-labeled ligand I. In these complexes it is proposed that there is strong bonding between the copper and the nitrogen attached to the nitroxyl ring. Slightly smaller values of J (about 2000 G) were observed for Cu(bp-NO)X_2 (X = Cl, Br). The decrease in the value of J suggests a weaker bond between the copper and the amine nitrogen as observed in the crystal structure of Cu(bp-NO)Cl_2 (2.189 Å). These values of J were not strongly dependent on solvent or temperature. Much smaller values of J were observed for Cu(bdmp-NO)X_2 (X = Cl, Br). It is proposed that this was due to a much weaker bond between the copper and the amine nitrogen, similar to what was observed in Cu(bdmp-ab)Br_2[5] (2.423 Å). These values of J were strongly dependent on temperature, which suggests that the weak spin–spin interactions were sensitive to small changes in geometry. The weaker Cu–N(amine) bond in Cu(bdmp-NO)X_2 than in Cu(bp-NO)X_2 suggests that the steric effect of the 3,5-dimethylpyrazole substituents has a significant effect on the geometry of the complexes.

There are two potential pathways for the copper–nitroxyl exchange interaction in these complexes. When there is a bond between the copper and the amine nitrogen, exchange interaction can occur through that bond. The relative importance of ferromagnetic and antiferromagnetic contributions may depend on bond length and may vary as the geometry shifts from distorted square pyramidal to distorted trigonal bipyramidal. Interaction can also occur via the bond of the copper to the pyrazole nitrogens and through the intervening bonds to the nitroxyl ring. The presence of a CH_2 group in the latter pathway is expected to limit the value of J to a significantly smaller value than could be obtained by a strong interaction of the copper with the amine nitrogen. If the interaction of the copper with the amine nitrogen is weak, the contribution to the copper–nitroxyl interaction from the bond to the pyrazole nitrogen may be comparable in magnitude to the interaction via the amine nitrogen. If the two contributions are of opposite sign, changes in the magnitudes of the two terms could result in a change in the sign of J.

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Supplementary Material Available: Anisotropic thermal parameters (Table S-I) and calculated hydrogen atom coordinates (Table S-II) (4 pages); structure factors (Table S-III) (20 pages). Ordering information is given on any current masthead page.

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