Contribution from the Departments of Chemistry, University of Denver,
Denver, Colorado 80208, and the University of Colorado at Denver, Denver, Colorado 80202

# Metal–Nitroxyl Interactions. 13. Substituent Effects on Electron–Electron Coupling in Spin-Labeled Copper Salicylaldimines

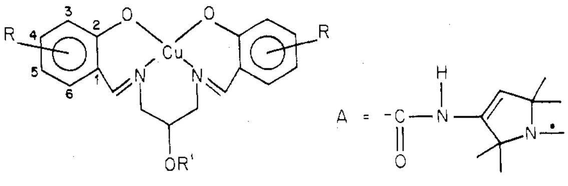
K. M. MORE, G. R. EATON,* and S. S. EATON

*Received March 16, 1979*

Seven new spin-labeled copper salicylaldimines have been prepared with electron-donating and -withdrawing groups on the salicylaldehyde ring. Resolved electron–electron coupling was observed in the room-temperature solution EPR spectra with values ranging from 5.5 G (0.000 53 $cm^{-1}$) to 25.7 G (0.002 47 $cm^{-1}$). Values of $J$ are dependent on temperature and solvent and on the ring substituent.

## Introduction

Spin–spin interactions between unpaired electrons are important contributors to the EPR spectra of many systems of current interest. The case of nitroxyl free radicals interacting with paramagnetic transition-metal complexes have been reviewed recently.[1] As part of a study of metal–nitroxyl interactions we have reported resolved electron–electron coupling in a variety of spin-labeled copper complexes.[2–6] In the present paper we report the preparation and EPR study of a series of spin-labeled copper salicylaldimines, I–VII, with



I, R = 3-OMe; R′ = A
II, R = 4-OMe; R′ = A
III, R = 5-OMe; R′ = A
IV, R = 3-OEt; R′ = A
V, R = 4,6-$(OMe)_2$; R′ = A
VI, R = 5-Cl; R′ = A
VII, R = 4,6-$Cl_2$; R′ = A
VIII, R = H; R′ = A
IX, R = 5-*t*-Bu; R′ = A
X, R = 3-OMe; R′ = H
XI, R = 4-OMe; R′ = H
XII, R = 5-OMe; R′ = H
XIII, R = 3-OEt; R′ = H
XIV, R = 4,6-$(OMe)_2$; R′ = H
XV, R = Cl; R′ = H
XVI, R = 4,6-$Cl_2$; R′ = H
XVII, R = 5-*t*-Bu; R′ = H
XVIII, R = 3-OMe; R′ = CONHPh
XIX, R = 4-OMe, R′ = CONHPh
XX, R = 5-OMe; R′ = CONHPh
XXI, R = 3-OEt; R′ = CONHPh
XXII, R = 4,6-$(OMe)_2$; R′ = CONHPh
XXIII, R = 5-Cl; R′ = CONHPh
XXIV, R = 4,6-$Cl_2$; R′ = CONHPh
XXV, R = H; R′ = CONHPh

a range of electron-donating and -withdrawing groups on the salicylaldimine ring. Results are compared with those obtained previously for VIII and IX. Complexes X–XXV were also studied to obtain comparison information on analogous systems with diamagnetic ligands.

## Experimental Section

**Physical Measurements.** All spectra were obtained in dry, purified solvents. Infrared spectra were recorded in Nujol mulls on a Perkin-Elmer 337 grating spectrometer. Visible spectra were obtained in dichloromethane, tetrahydrofuran, and pyridine solutions on a Beckman Acta V spectrometer using 5.0 × $10^{-4}$–3.0 × $10^{-3}$ M solutions.[4] Data are given below with wavelengths in nanometers and log $\epsilon$ in parentheses. Magnetic susceptibilities were measured at room temperature on a Bruker Faraday balance with 1-μg senstivity using $HgCo(SCN)_4$ as calibrant.[7] Values of $\mu_{eff}$ in Bohr magnetons are given below with the temperature at which the measurement was made, and the diamagnetic correction[8] ($\chi^{dia}$) used in the calculation is given in parentheses. cgs-emu/mol units are used throughout. A temperature-independent paramagnetism (TIP) of 60 × $10^{-6}$ was assumed for Cu(II) as previously discussed.[4] EPR spectra were obtained on a Varian E-9 as described previously.[4]

**Preparation of Compounds.** The copper complexes X–XVI were prepared by the method reported for XVII.[9] Yields and characterization data for individual compounds are given below.

**(2-Hydroxy-*N*,*N*′-bis(3-methoxysalicylaldiminato)-1,3-diaminopropane)copper(II) (X):** yield 90%; IR $\nu_{OH}$ 3420 $cm^{-1}$; $\mu_{eff}$ = 1.79 $\mu_B$ (22 °C, $\chi^{dia} = -197.5 \times 10^{-6}$); visible spectrum (pyridine solution) 602 (2.41), 385 (4.01). Anal. Calcd for $C_{19}H_{20}CuN_2O_5$: C, 54.35; H, 4.80; N, 6.67. Found: C, 54.38; H, 4.73; N, 6.77.

**(2-Hydroxy-*N*,*N*′-bis(4-methoxysalicylaldiminato)-1,3-diaminopropane)copper(II) (XI):** yield 90%; IR $\nu_{OH}$ 3250 $cm^{-1}$; $\mu_{eff}$ = 1.80 $\mu_B$ (22 °C, $\chi^{dia} = -197.5 \times 10^{-6}$); visible spectrum (pyridine solution) 620 (2.32), 365 (4.08). Anal. Calcd for $C_{19}H_{20}CuN_2O_5$: C, 54.35; H, 4.80; N, 6.67. Found: C, 54.39; H, 4.80; N, 6.77.

**(2-Hydroxy-*N*,*N*′-bis(5-methoxysalicylaldiminato)-1,3-diaminopropane)copper(II) (XII):** yield 85%; IR $\nu_{OH}$ 3180 $cm^{-1}$; $\mu_{eff}$ = 1.78 $\mu_B$ (22 °C, $\chi^{dia} = -197.5 \times 10^{-6}$); visible spectrum (pyridine solution) 612 (2.35), 390 (4.05). Anal. Calcd for $C_{19}H_{20}CuN_2O_5$: C, 54.35; H, 4.80; N, 6.67. Found: C, 54.06; H, 4.74; N, 6.71.

**(2-Hydroxy-*N*,*N*′-bis(3-ethoxysalicylaldiminato)-1,3-diaminopropane)copper(II) (XIII):** yield 80%; IR $\nu_{OH}$ 3380 $cm^{-1}$; $\mu_{eff}$ = 1.82 $\mu_B$ (22 °C, $\chi^{dia} = -222.2 \times 10^{-6}$); visible spectrum (pyridine solution) 606 (2.36), 385 (4.08). Anal. Calcd for $C_{21}H_{24}CuN_2O_5$: C, 56.30; H, 5.40; N, 6.25. Found: C, 56.06; H, 5.13; N, 6.24.

**(2-Hydroxy-*N*,*N*′-bis(4,6-dimethoxysalicylaldiminato)-1,3-diaminopropane)copper(II) (XIV):** yield 92%; IR $\nu_{OH}$ 3350 $cm^{-1}$; $\mu_{eff}$ = 1.80 $\mu_B$ (22 °C, $\chi^{dia} = -230.4 \times 10^{-6}$); visible spectrum (pyridine solution) 610 (2.33), 358 (4.07). Anal. Calcd for $C_{21}H_{24}CuN_2O_7$: C, 52.55; H, 5.04; N, 5.84. Found: C, 52.27; H, 5.02; N, 5.85.

**(2-Hydroxy-*N*,*N*′-bis(5-chlorosalicylaldiminato)-1,3-diaminopropane)copper(II) (XV):** yield 90%; IR $\nu_{OH}$ 3270 $cm^{-1}$; $\mu_{eff}$ = 1.79 $\mu_B$ (22 °C, $\chi^{dia} = -198.9 \times 10^{-6}$); visible spectrum (pyridine solution) 620 (2.34), 387 (4.10). Anal. Calcd for $C_{17}H_{14}Cl_2CuN_2O_3$: C, 47.62; H, 3.29; N, 6.53; Cl, 16.54. Found: C, 47.74; H, 3.39; N, 6.44; Cl, 16.68.

**(2-Hydroxy-*N*,*N*′-bis(4,6-dichlorosalicylaldiminato)-1,3-diaminopropane)copper(II) (XVI):** yield 90%; IR $\nu_{OH}$ 3430 $cm^{-1}$; $\mu_{eff}$ = 1.81 $\mu_B$ (22 °C, $\chi^{dia} = -233.2 \times 10^{-6}$); visible spectrum (pyridine solution) 623 (2.33), 385 (4.14). Anal. Calcd for $C_{17}H_{12}Cl_4CuN_2O_3$: C, 41.03; H, 2.43; N, 5.63; Cl, 28.50. Found: C, 41.08; H, 2.48; N, 5.70; Cl, 28.60.

The spin-labeled copper complexes I–VII were prepared by the method reported for VIII and IX.[4] Yields and characterization data for individual compounds are given below.

**(2-(*N*-(2,2,5,5-Tetramethyl-3-pyrrolinyl-1-oxy)carbamato)-*N*,*N*′-bis(3-methoxysalicylaldiminato)-1,3-diaminopropane)copper(II) (I):** yield 80%; IR $\nu_{NH}$ 3150 $cm^{-1}$, $\nu_{CO}$ 1720 $cm^{-1}$; $\mu_{eff}$ = 2.41 $\mu_B$ (20 °C, $\chi^{dia} = -292.2 \times 10^{-6}$); visible spectrum ($CH_2Cl_2$ solution) 610 (2.51), 391 (3.96), 290 (4.51), 240 (4.75); (THF solution) 600 sh (2.30), 385 (4.00), 284 (4.42), 235 (4.76); (pyridine solution) 595 (2.34), 381 (4.87). Anal. Calcd for $C_{28}H_{33}CuN_2O_7$: C, 55.95; H, 5.53; N, 9.32. Found: C, 56.08; H, 5.77; N, 9.66.

**(2-(*N*-(2,2,5,5-Tetramethyl-3-pyrrolinyl-1-oxy)carbamato)-*N*,*N*′-bis(4-methoxysalicylaldiminato)-1,3-diaminopropane)copper(II) (II):** yield 89%; IR $\nu_{NH}$ 3160 $cm^{-1}$, $\nu_{CO}$ 1725 $cm^{-1}$; $\mu_{eff}$ = 2.48 $\mu_B$ (20 °C, $\chi^{dia} = -292.2 \times 10^{-6}$); visible spectrum ($CH_2Cl_2$ solution) 608 (2.40), 357 (4.15), 293 (4.56), 255 (4.59), 230 (4.60); (THF solution) 615 (2.42), 359 (4.35), 290 (4.66), 255 (4.74), 230 (4.79); (pyridine solution) 614 (2.33), 361 (4.27). Anal. Calcd for $C_{28}H_{33}CuN_2O_7$: C, 55.95; H, 5.53; N, 9.32. Found: C, 55.87; H, 5.45; N, 9.38.

**(2-(*N*-(2,2,5,5-Tetramethyl-3-pyrrolinyl-1-oxy)carbamato)-*N*,*N*′-bis(5-methoxysalicylaldiminato)-1,3-diaminopropane)copper(II)**

---

* To whom correspondence should be addressed at the University of Denver.

0020-1669/79/1318-2492$01.00/0

**(III)**: yield 65%; IR $\nu_{NH}$ 3150 cm$^{-1}$, $\nu_{CO}$ 1720 cm$^{-1}$; $\mu_{eff}$ = 2.45 $\mu_B$ (22 °C, $\chi^{dia} = -292.2 \times 10^{-6}$); visible spectrum ($CH_2Cl_2$ solution) 595 (2.46), 402 (4.07), 278 sh (4.39), 260 sh (4.56), 229 (4.79); (THF solution) 615 (2.49), 408 (4.15), 282 sh (4.34), 257 sh (4.56), 230 (4.82); (pyridine solution) 603 sh (2.37), 405 (4.08). Anal. Calcd for $C_{28}H_{33}CuN_4O_7$: C, 55.95; H, 5.53; N, 9.32. Found: C, 55.95; H, 5.36; N, 9.36.

**(2-(*N*-(2,2,5,5-Tetramethyl-3-pyrrolinyl-1-oxy)carbamato)-*N*,*N*′-bis(3-ethoxysalicylaldiminato)-1,3-diaminopropane)copper(II) (IV)**: yield 52%; IR $\nu_{NH}$ 3200 cm$^{-1}$, $\nu_{CO}$ 1720 cm$^{-1}$; $\mu_{eff}$ = 2.45 $\mu_B$ (20 °C, $\chi^{dia} = -315.9 \times 10^{-6}$); visible spectrum ($CH_2Cl_2$ solution) 615 (2.50), 391 (4.00), 291 (4.51), 240 (4.75); (THF solution) 605 sh (2.31), 387 (4.03), 282 (4.45), 236 (4.77); (pyridine solution) 600 (2.29), 385 (4.02). Anal. Calcd for $C_{30}H_{37}CuN_4O_7$: C, 57.27; H, 5.93; N, 8.90. Found: C, 57.07; H, 5.78; N, 8.75.

**(2-(*N*-(2,2,5,5-Tetramethyl-3-pyrrolinyl-1-oxy)carbamato)-*N*,*N*′-bis(4,6-dimethoxysalicylaldiminato)-1,3-diaminopropane)copper(II) (V)**: yield 65%; IR $\nu_{NH}$ 3170 cm$^{-1}$, $\nu_{CO}$ 1720 cm$^{-1}$; $\mu_{eff}$ = 2.39 $\mu_B$ (22 °C, $\chi^{dia} = -325.2 \times 10^{-6}$); visible spectrum ($CH_2Cl_2$ solution) 594 (2.37), 344 (4.12), 311 (4.55); (THF solution) 606 (2.35), 358 (4.03), 299 (4.36); (pyridine solution) 605 (2.23), 355 (4.18). Anal. Calcd for $C_{30}H_{37}CuN_4O_9$: C, 54.50; H, 5.64; N, 8.47. Found: C, 54.53; H, 5.52; N, 8.40.

**(2-(*N*-2,2,5,5-Tetramethyl-3-pyrrolinyl-1-oxy)carbamato)-*N*,*N*′-bis(5-chlorosalicylaldiminato)-1,3-diaminopropane)copper(II) (VI)**: yield 70%; IR $\nu_{NH}$ 3270 cm$^{-1}$, $\nu_{CO}$ 1730 cm$^{-1}$; $\mu_{eff}$ = 2.46 $\mu_B$ (22 °C, $\chi^{dia} = -293.6 \times 10^{-6}$); visible spectrum ($CH_2Cl_2$ solution) 605 (2.38), 384 (4.00), 273 sh (4.32), 235 (4.73); (THF solution) 618 (2.44), 386 (4.21), 235 (4.95); (pyridine solution) 615 (2.33), 386 (4.14). Anal. Calcd for $C_{26}H_{27}Cl_2CuN_4O_5$: C, 51.20; H, 4.46; N, 9.18; Cl, 11.62. Found: C, 51.17; H, 4.57; N, 9.20; Cl, 11.58.

**(2-(*N*-(2,2,5,5-Tetramethyl-3-pyrrolinyl-1-oxy)carbamato)-*N*,*N*′-bis(4,6-dichlorosalicylaldiminato)-1,3-diaminopropane)copper(II) (VII).** This complex was prepared several times with varying reaction times and varying excess of nitroxyl isocyanate, but an analytical sample could not be obtained. However, the impurity did not appear to have any significant impact on the IR, visible, or EPR spectra: yield 52–70%; IR $\nu_{NH}$ 3255 cm$^{-1}$, $\nu_{CO}$ 1740 cm$^{-1}$; $\mu_{eff}$ = 2.30–2.36 $\mu_B$ ($\chi^{dia} = -328.0 \times 10^{-6}$); visible spectrum ($CH_2Cl_2$ solution) 609 (2.37), 390 (4.04), 281 (4.42), 238 (4.74); (pyridine solution) 616 (2.26), 391 (4.06). Anal. Calcd for $C_{26}H_{25}Cl_4CuN_4O_5$: C, 46.00; H, 3.71; N, 8.25; Cl, 20.89. Found (range for three preparations): C, 44.55–45.91; H, 3.98–4.04; N, 7.55–7.77; Cl, 19.63–20.56. The low values of the magnetic susceptibility suggest that the impurity is not another spin-labeled copper complex. Since the chlorine analyses were consistently low, the impurity cannot be the starting material VII.

The phenylcarbamate complexes XVIII–XXIV were prepared by the method reported for XXV.[4] Yields and characterization data are given below for individual compounds.

**(2-(*N*-Phenylcarbamato)-*N*,*N*′-bis(3-methoxysalicylaldiminato)-1,3-diaminopropane)copper(II) (XVIII)**: yield 80%; IR $\nu_{NH}$ 3200 (b), $\nu_{CO}$ 1710 cm$^{-1}$; $\mu_{eff}$ = 1.85 $\mu_B$ (23 °C, $\chi^{dia} = -255.3 \times 10^{-6}$); visible spectrum ($CH_2Cl_2$ solution) 615 (2.47), 391 (3.93), 290 (4.46), 240 (4.79); (THF solution) 600 sh (2.26), 385 (3.83), 284 (4.27), 239 (4.67); (pyridine solution) 600 (2.36), 384 (3.99). Anal. Calcd for $C_{26}H_{25}CuN_3O_6$: C, 57.93; H, 4.67; N, 7.79. Found: C, 58.05; H, 4.74; N, 7.90.

**(2-(*N*-Phenylcarbamato)-*N*,*N*′-bis(4-methoxysalicylaldiminato)-1,3-diaminopropane)copper(II) (XIX)**: yield 75%; IR $\nu_{NH}$ 3170 cm$^{-1}$, $\nu_{CO}$ 1705 cm$^{-1}$; $\mu_{eff}$ = 1.78 $\mu_B$ (22 °C, $\chi^{dia} = -255.4 \times 10^{-6}$); visible spectrum ($CH_2Cl_2$ solution) 608 (2.34), 354 (4.24), 292 (4.60), 255 (4.66), 235 (4.72); (pyridine solution) 616 (2.26), 359 (4.23). Anal. Calcd for $C_{26}H_{25}CuN_3O_6$: C, 57.93; H, 4.67; N, 7.79. Found: C, 58.05; N, 4.64; N, 7.90.

**(2-(*N*-Phenylcarbamato)-*N*,*N*′-bis(5-methoxysalicylaldiminato)-1,3-diaminopropane)copper(II) (XX)**: yield 80%; IR $\nu_{NH}$ 3160 cm$^{-1}$, $\nu_{CO}$ 1700 cm$^{-1}$; $\mu_{eff}$ = 1.78 $\mu_B$ (22 °C, $\chi^{dia} = -255.4 \times 10^{-6}$); visible spectrum (pyridine solution) 610 (2.24), 390 (3.93). Anal. Calcd for $C_{26}H_{25}CuN_3O_6$: C, 57.93; H, 4.67; N, 7.79. Found: C, 57.84; H, 4.74; N, 7.82.

**(2-(*N*-Phenylcarbamato)-*N*,*N*′-bis(3-ethoxysalicylaldiminato)-1,3-diaminopropane)copper(II) (XXI)**: yield 48%; IR $\nu_{NH}$ 3230 cm$^{-1}$ (b), $\nu_{CO}$ 1705 cm$^{-1}$; $\mu_{eff}$ = 1.78 $\mu_B$ (20 °C, $\chi^{dia} = -279.1 \times 10^{-6}$); visible spectrum ($CH_2Cl_2$ solution) 615 (2.44), 391 (3.93), 287 (4.42), 240 (4.76); (THF solution) 615 sh (2.30), 385 (3.98), 282 (4.42), 241 (4.81); (pyridine solution) 603 (2.30), 382 (4.07). Anal. Calcd for $C_{28}H_{29}CuN_3O_6$: C, 59.30; H, 5.15; N, 7.41. Found: C, 59.32; H, 4.99; N, 7.67.

**(2-(*N*-Phenylcarbamato)-*N*,*N*′-bis(4,6-dimethoxysalicylaldiminato)-1,3-diaminopropane)copper(II) (XXII)**: yield 70%; IR $\nu_{NH}$ 3190 cm$^{-1}$, $\nu_{CO}$ 1715 cm$^{-1}$; $\mu_{eff}$ = 1.82 $\mu_B$ (22 °C, $\chi^{dia} = -288.3 \times 10^{-6}$); visible spectrum ($CH_2Cl_2$ solution) 595 (2.35), 350 sh (4.09), 312 (4.54), 230 (4.64). Anal. Calcd for $C_{28}H_{29}CuN_3O_8$: C, 56.14; H, 4.88; N, 7.01. Found: C, 55.96; H, 4.84; N, 7.08.

**(2-(*N*-Phenylcarbamato)-*N*,*N*′-bis(5-chlorosalicylaldiminato)-1,3-diaminopropane)copper(II) (XXIII)**: yield 75%; IR $\nu_{NH}$ 3160 cm$^{-1}$, $\nu_{CO}$ 1715 cm$^{-1}$; $\mu_{eff}$ = 1.72 $\mu_B$ (22 °C, $\chi^{dia} = -256.8 \times 10^{-6}$); visible spectrum ($CH_2Cl_2$ solution) 600 (2.29), 385 (3.76), 278 sh (4.10), 238 (4.51); (THF solution) 610 (2.58), 386 (4.08), 238 (4.86); (pyridine solution) 613 (2.31), 390 (4.10). Anal. Calcd for $C_{24}H_{19}Cl_2CuN_3O_4$: C, 52.62; H, 3.50; N, 7.67; Cl, 12.94. Found: C, 52.36; H, 3.55; N, 7.54; Cl, 12.68.

**(2-(*N*-Phenylcarbamato)-*N*,*N*′-bis(4,6-dichlorosalicylaldiminato)-1,3-diaminopropane)copper(II) (XXIV)**: yield 85%; IR $\nu_{NH}$ 3160 cm$^{-1}$, $\nu_{CO}$ 1695 cm$^{-1}$; $\mu_{eff}$ = 1.75 $\mu_B$ (22 °C, $\chi^{dia} = -291.1 \times 10^{-6}$); visible spectrum ($CH_2Cl_2$ solution) 611 (2.27), 391 (4.03), 281 (4.42), 239 (4.76); (THF solution) 620 (2.31), 388 (4.11), 237 (4.86); (pyridine solution) 618 (2.26), 390 (4.06). Anal. Calcd for $C_{24}H_{17}Cl_4CuN_3O_4$: C, 46.74; H, 2.77; N, 6.81; Cl, 22.99. Found: C, 46.69; H, 2.83; N, 6.63; Cl, 23.05.

**Computer Simulations.** The EPR spectra of the copper complexes with diamagnetic ligands were simulated by using a computer program which included first-order nitrogen hyperfine coupling, first-order Breit–Rabi corrections for the coupling to the copper nucleus,[10] dependence of intensity on *g* value,[11] and line widths that varied with copper nuclear spin as $A + Bm_I + Cm_I^2$.[12] The EPR spectra of the spin-labeled copper complexes were simulated by using the computer program CUNO.[13] The Hamiltonian used was

$$\begin{aligned}\mathcal{H} = {} & g_1\beta H\hat{S}_{1Z} + g_2\beta H\hat{S}_{2Z} + hJ\hat{S}_{1Z}\hat{S}_{2Z} + (hJ/2) \times \\ & (\hat{S}_{1+}\hat{S}_{2-} + \hat{S}_{1-}\hat{S}_{2+}) + hA_{Cu}\hat{S}_{1Z}\hat{I}_{1Z} + hA_N\hat{S}_{1Z}\hat{I}_{2Z} + hA_{N'}\hat{S}_{2Z}\hat{I}_{3Z} + \\ & (hA_{Cu}/2)(\hat{S}_{1+}\hat{I}_{1-} + \hat{S}_{1-}\hat{I}_{1+}) - g_{N1}\beta_N H\hat{I}_{1Z} - g_{N2}\beta_N H\hat{I}_{2Z}\end{aligned}$$

where $g_1$ and $g_2$ are the *g* values of the copper and nitroxyl electrons in the absence of interaction; $S_1$ and $S_2$ refer to the copper and nitroxyl electron spins, respectively; *J* is the electron–electron coupling constant in hertz; $I_1$, $I_2$, and $I_3$ refer to the copper nuclear spin, the nuclear spins of the coordinated nitrogens, and the nuclear spin of the nitroxyl nitrogen, respectively; $A_{Cu}$ is the copper electron–copper nucleus coupling constant in hertz; $A_N$ is the coupling constant in hertz between the copper electron and the nuclear spins of the coordinated nitrogens; $A_{N'}$ is the coupling constant in hertz between the nitroxyl electron and the nuclear spin of the nitroxyl nitrogen; and all other symbols are defined as in ref 14. The first seven terms in the Hamiltonian were treated exactly and the last three were treated as a perturbation to second order for the transition energies and to first order for the transition probabilities. This is analogous to the treatment of the "ABMX" system commonly encountered in NMR. In the following discussion transitions are labeled as "copper" or "nitroxyl" according to the nature of the transitions as $J \rightarrow 0$. The spectra were calculated at constant frequency, including the dependence of intensity on *g* value.[11] The adjustable parameters were treated as follows. Values of $g_1$, $A_{Cu}$, and $A_N$ were estimated by simulation of the EPR spectra of a closely related copper complex with a diamagnetic ligand in the same solvent—i.e., X and XVIII were used as models for the copper electron in I in the absence of electron–electron coupling. $g_2$ and $A_{N'}$ were assigned to be equal to the values observed for the same nitroxyl group in the same solvent. Adjustment of the above parameters did not improve the agreement between observed and calculated spectra. The value of *J* was determined by the separation between the "inner" and "outer" sets of lines in the "nitroxyl" region. The "copper" lines were sufficiently broad that small variations in *J* did not have a major impact on the appearance of the "copper" lines. Line widths of the "copper" lines were fit to $A + Bm_I + Cm_I^2$ where $m_I$ is the copper nuclear spin. Line widths of the "nitroxyl" lines were fit to $A + Bm_I + Cm_I^2$ where $m_I$ is the nitroxyl nitrogen nuclear spin. Values of *A*, *B*, and *C* were different for the "inner" and "outer" "nitroxyl" lines. Both $^{63}Cu$ and $^{65}Cu$ were included in all calculations.

## Results and Discussion

The copper complexes I–VII and XVIII–XXIV were prepared by reaction of isocyanates with the alcohol groups in X–XVI, producing substituted carbamates as evidenced by

Table I. EPR Spectra of Copper Complexes with Diamagnetic Ligands

| complex | R | solvent | $g$[a] | $A_{\mathrm{Cu}}$,[b] G | $A_{\mathrm{N}}$,[c] G | $A$[d] | $B$[d] | $C$[d] |
|---|---|---|---|---|---|---|---|---|
| XIV | 4,6-(OMe)$_2$ | THF | 2.1060 | 77.1 | 13.5 | 26.9 | 14.3 | 3.4 |
| XI | 4-OMe | THF | 2.1080 | 75.0 | 13.4 | 25.3 | 13.3 | 3.5 |
| XVII[e] | 5-*t*-Bu | THF | 2.1087 | 74.3 | 13.4 | 25.7 | 13.6 | 2.9 |
| XIII | 3-OEt | THF | 2.1094 | 74.0 | 13.4 | 26.2 | 12.2 | 2.9 |
| X | 3-OMe | THF | 2.1101 | 74.0 | 13.4 | 28.7 | 12.8 | 3.2 |
| XII | 5-OMe | THF | 2.1108 | 74.0 | 13.4 | 25.8 | 11.9 | 2.8 |
| XV | 5-Cl | THF | 2.1111 | 73.3 | 13.4 | 24.5 | 12.9 | 3.7 |
| XVI | 4,6-Cl$_2$ | THF | 2.1149 | 71.0 | 13.4 | 27.8 | 14.4 | 3.4 |
| XIII | 3-OEt | $CHCl_3$ | 2.1051 | 75.2 | 13.4 | 30.7 | 16.2 | 3.3 |
| XIII | 3-OEt | $CH_2Cl_2$ | 2.1062 | 75.0 | 13.4 | 26.6 | 12.5 | 2.6 |
| XIII | 3-OEt | 9:1 toluene-THF | 2.1074 | 74.0 | 13.4 | 26.2 | 13.5 | 3.4 |
| XIII | 3-OEt | $Me_2SO$ | 2.1190 | 77.0[f] | 13.4[f] | 54.5[f] | 26.4[f] | 2.19[f] |
| XIII | 3-OEt | py | 2.1225 | 63.0[f] | 13.0[f] | 50.0[f] | 27.2[f] | 3.88[f] |

[a] Uncertainty ±0.0007. [b] Uncertainty ±0.2 G, unless otherwise noted. The value given is for $^{63}$Cu; value for $^{65}$Cu is 1.07 times the value given. [c] Uncertainty ±0.2 G. [d] $A$, $B$, and $C$ are the line width parameters; see text. Values given are for 100% Lorentzian lines. [e] Data from ref 4. [f] Value uncertain due to incomplete motional averaging.

the loss of the characteristic OH stretch in the IR and the appearance of NH and CO stretches characteristic of substituted carbamates. The frequencies of these stretches are included in the Experimental Section.

**Magnetic Susceptibility.** The room-temperature magnetic moments of solid samples of the copper complexes with diamagnetic ligands X–XVI and XVIII–XXIV fall in the range 1.72–1.82 $\mu_B$. These values are comparable to those previously observed for XVII and XXV.[4] For the spin-labeled copper complexes I–VII the room-temperature magnetic moments fall in the range 2.39–2.48 $\mu_B$. These values are similar to those found for other spin-labeled copper complexes with $J \ll kT$.[4-6]

**Electronic Spectra.** The ultraviolet and visible spectra of the complexes with diamagnetic ligands and of the spin-labeled complexes are given in the Experimental Section. For each of the R groups it was found that the electronic spectra of the spin-labeled complex were very similar to the spectra of the copper complexes with diamagnetic ligands, which indicated that the spin label had not significantly perturbed the electronic structure of the complex.

Where permitted by solubility, electronic spectra were obtained in dichloromethane ($CH_2Cl_2$), tetrahydrofuran (THF), and pyridine solution. Except for the d–d band near 600 nm there was no significant solvent dependence of the spectra. The maximum shift in the d–d band with solvent was about 20 nm, indicating that any interaction with the solvent as a fifth ligand, for either oxygen or nitrogen donors, has a small effect on the electronic spectra.[4,15] It should also be noted that the d–d band is broad and poorly resolved from the tail of the higher intensity bands which occur at higher energy, so the band position is at best accurate to ±5 nm.

For all of the ring substituents examined, the d–d transitions in $CH_2Cl_2$ solution occurred in the range 594–616 nm, showing little dependence on the electron-donating or -withdrawing properties of the substituents. The energy of the $\pi \rightarrow \pi^*$ transition, which is partially localized on the azomethine linkage,[16] was considerably more sensitive to the substituent effects. Electron-donating groups in the 4- and 6-positions shifted the band to higher energy while electron-donating groups in the 3- and 5-positions shifted it to lower energy. The extremes observed were 344 nm (R = 4,6-OMe$_2$) and 402 nm (R = 5-OMe). These shifts in the transition energy were substantially larger than those observed in some related substituted salicylaldimine ligands[17] where shifts in electron density may be counterbalanced by changes in intramolecular hydrogen bonding. Alternating effects of ring substituents on the stereochemistry of nickel salicylaldimines have been discussed.[18]

It might be expected that the frequency of the Schiff base C–N stretch would also have provided an indication of the substituent effects on the coordinating nitrogens. However, there is a phenyl ring vibration which occurs near 1600 cm$^{-1}$. Due to partial overlap of these vibrations in many of the IR spectra and to difficulties in assigning the two bands, the assessment of the impact of the substituents on the frequency of the C–N stretch is not straightforward.

**EPR Spectra.** The EPR spectra of the copper complexes with diamagnetic ligands X–XXV showed the usual four-line pattern due to coupling of the electron to the spin $^3/_2$ copper nucleus. Line widths decreased toward high field. Partially resolved superhyperfine splitting due to coupling to the two nitrogens in the copper coordination sphere was observable in all cases for the highest field line and in some cases was also detectable on the second-highest field transition. Parameters obtained by computer simulation of the EPR spectra of X–XVII are given in Table I. Electron-donating substituents on the salicylaldimine ring resulted in lower $g$ values and higher values of $A_{\mathrm{Cu}}$ than were observed in the complexes with electron-withdrawing substituents. The extreme values were observed for R = 4,6-OMe$_2$ ($g$ = 2.1060, $A_{\mathrm{Cu}}$ = 77.1 G) and R = 4,6-Cl$_2$ ($g$ = 2.1149, $A_{\mathrm{Cu}}$ = 71.0 G). Unlike the substituent effects on the electronic spectra, there did not appear to be any effect of substituent position (3, 4, 5, or 6) on the EPR spectra.

The effect of solvent on the EPR spectra was examined for the copper complex XIII, with R = 3-OEt (Table I). As observed for other copper complexes,[6,7,15] the $g$ values increased and $A_{\mathrm{Cu}}$ decreased as the donor ability of the solvent increased.

The EPR spectrum of the spin-labeled copper complex VII with R = 4,6-Cl$_2$ is shown in Figure 1A. An expanded presentation of the "nitroxyl" region of the spectrum is shown in Figure 1B. The "nitroxyl" region is clearly not the usual three-line pattern. As seen by the agreement between the observed and calculated spectra, the observed pattern is consistent with an electron–electron coupling constant, $J$, of 25.7 G (0.00247 cm$^{-1}$). A small amount of free nitroxyl (i.e., not interacting with copper) was present in the sample (~3%) due to decomposition of the complex. Even in carefully purified solvents a small amount of decomposition was frequently observed.

The value of $J$ was found to vary little with ring substituent, as indicated in Table II. Although in THF solution the values of $J$ ranged from 5.5 to 16.0 G, there does not appear to be a simple correlation between the electronic nature of R and the value of $J$. The value of $J$ in the unsubstituted complex was 6.4 G. For all the 3- and 5-substituents the value of $J$ in THF solution fell within the range 10.3–13.0 G. The spread was greater for 4- and 6-substituents. For the electron-donating 4-OMe and 4,6-(OMe)$_2$ groups, the values of $J$ were 5.5 and 6.0 G, respectively, whereas for the electron-withdrawing 4,6-dichloro substituents the value of $J$ was 16.0 G.

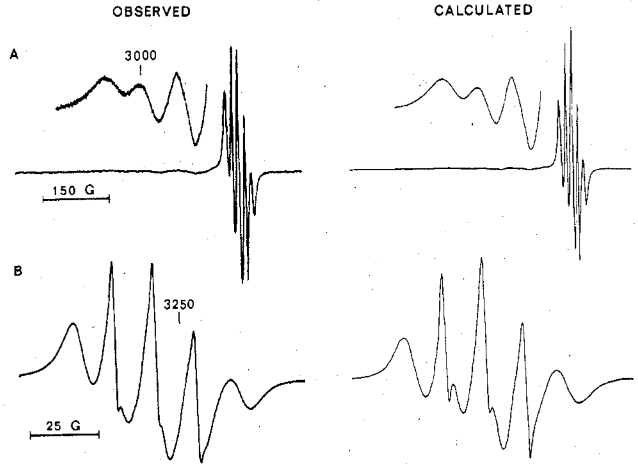


**Figure 1.** X-Band (9.102 GHz) EPR spectra of the spin-labeled copper complex VII in $CH_2Cl_2$ solution and computer simulations: (A) full spectrum, 650 G scan, 125 G/min scan rate, 10 mW, 0.8 G modulation amplitude; expanded "copper region", 375 G scan, 125 G/min scan rate, 30 mW, 2.0 G modulation amplitude; (B) "nitroxyl" region, 100 G scan, 12.5 G/min scan rate, 10 mW, 0.8 G modulation amplitude. A small amount of free nitroxyl (~3%) is present in the experimental spectra and included in the simulations.

**Table II.** Electron-Electron Coupling in the Spin-Labeled Copper Complexes

| complex | R | solvent | $J$,[a] G | $J$,[a] $cm^{-1}$ |
|---|---|---|---|---|
| II | 4-OMe | THF | 5.5 | 0.000 53 |
| VIII | H | THF | 6.4[b] | 0.000 61[b] |
| V | 4,6-$(OMe)_2$ | THF | 6.0 | 0.000 58 |
| VI | 5-Cl | THF | 10.3 | 0.000 99 |
| I | 3-OMe | THF | 11.0 | 0.001 06 |
| III | 5-OMe | THF | 11.0 | 0.001 06 |
| IX | 5-*t*-Bu | THF | 11.8[b] | 0.001 13[b] |
| IV | 3-OEt | THF | 13.0 | 0.001 25 |
| VII | 4,6-$Cl_2$ | THF | 16.0 | 0.001 54 |
| VIII | H | $CH_2Cl_2$ | 7.5[b] | 0.000 72[b] |
| I | 3-OMe | $CH_2Cl_2$ | 11.3 | 0.001 08 |
| V | 4,6-$(OMe)_2$ | $CH_2Cl_2$ | 11.4 | 0.001 09 |
| IV | 3-OEt | $CH_2Cl_2$ | 19.3 | 0.001 85 |
| VII | 4,6-$Cl_2$ | $CH_2Cl_2$ | 25.7 | 0.002 47 |
| IV | 3-OEt | $CHCl_3$ | 18.4 | 0.001 76 |
| IV | 3-OEt | $Me_2SO$ | 17.5 | 0.001 68 |
| IV | 3-OEt | py | 16.0 | 0.001 54 |
| IV | 3-OEt | 9:1 toluene-THF | 15.8 | 0.001 51 |

[a] Values obtained by computer simulation. [b] Value taken from ref 4.

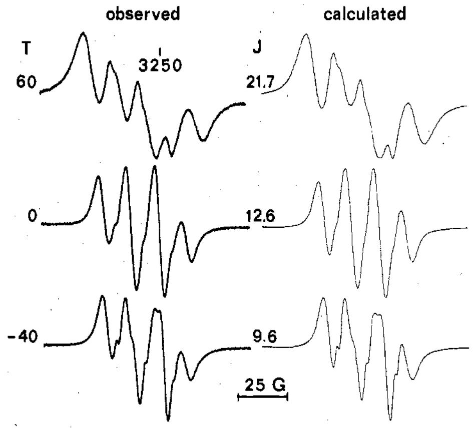


**Figure 2.** X-Band (9.102 GHz) EPR spectra of the spin-labeled copper complex IX in 10:1 toluene-THF solution at three temperatures and computer simulations; 100 G scans, 25 G/min scan rate, 10 mW, 0.2 G modulation amplitude. Values of $J$ are in gauss. A small amount of free nitroxyl (~2%) is observed in the experimental spectra and included in the simulation.

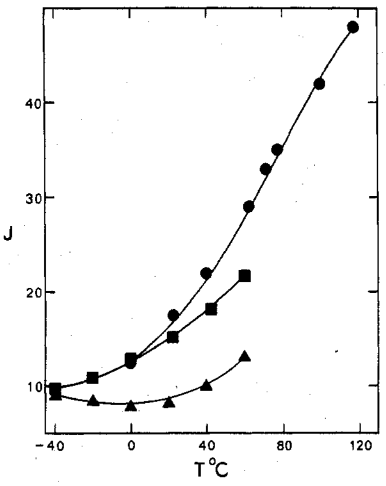


**Figure 3.** Temperature dependence of the electron-electron coupling constant, $J$, in gauss for spin-labeled copper complexes II and IX: ●, IX, R = 5-*t*-Bu, in toluene solution; ■, IX, R = 5-*t*-Bu, in 10:1 toluene-THF solution; ▲, II, R = 4-OMe in 9:1 toluene-THF solution.

Although the data for the two 4,6-disubstituted complexes might have suggested a pattern of increasing $J$ with increased electronegativity, the significance of this observation was decreased by the similarity in $J$ for R = 4,6-dimethoxy and for the unsubstituted complex. Clearly the value of $J$ did not correlate with the electron-donating and -withdrawing character of R as observed for the $g$ value and copper hyperfine coupling constant $A_{Cu}$. Neither did the values of $J$ demonstrate the opposite effects of the 3,5- and 4,6-substituents which were observed in the electronic spectra.

The dependence of $J$ on solvent was also examined (Table II). For the five cases examined, the value of $J$ in THF solution was smaller than in $CH_2Cl_2$ solution. However, the magnitude of the solvent effect varied considerably. The change in $J$ from THF to $CH_2Cl_2$ solution was less than 1 G for R = 3-OMe and about 10 G for R = 4,6-$Cl_2$. A more extensive series of solvents was examined for R = 3-OEt, and $J$ was found to decrease in the order $CH_2Cl_2 > CHCl_3 > Me_2SO >$ py > 9:1 toluene-THF > THF. Since the solvent dependence of the $g$ values and of $A_{Cu}$ for the diamagnetic complex with R = 3-OEt (XXI) indicated that axial ligation increased in the order $CHCl_3 < CH_2Cl_2 <$ 9:1 toluene-THF < THF < $Me_2SO$ < py, it appeared that the effects of solvent on $J$ did not correlate with increasing axial ligation. The impact of solvent on $J$ observed in this case does not correspond to either of the patterns observed previously for spin-labeled derivatives of Cu(baen)[6] or Cu(batm).[5] For each of the three types of compounds the solvent influences are different. In the current study the value of $J$ was smallest in THF and largest in $CH_2Cl_2$, but THF and $CH_2Cl_2$ gave intermediate values of $J$ in the two prior studies. The largest values of $J$ for spin-labeled Cu(baen)[6] and Cu(batm)[5] were in $Me_2SO$ and pyridine, respectively, but these solvents gave intermediate values for $J$ for the spin-labeled copper salicylaldimine IV. Thus the solvent influence must reflect specific solvent-solute interactions, which vary from system to system.

The temperature dependence of $J$ was studied for R = 5-*t*-Bu (IX) and R = 4-OMe (II). The "nitroxyl" region of the EPR spectra of complex IX at several temperatures is shown in Figure 2. Values of $J$ as a function of temperature for both II and IX are plotted in Figure 3. For R = 5-*t*-Bu in toluene or 10:1 toluene-THF solution, the value of $J$ increased rapidly as the temperature was increased. However, for R = 4-OMe in 9:1 toluene-THF the value of $J$ changed by less than ca. 1 G between -40 and +30 °C and then increased slightly at higher temperatures. Both results are in

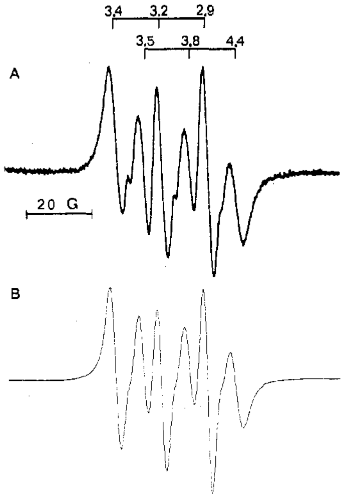


**Figure 4.** X-Band (9.102 GHz) EPR spectrum (A) of the spin-labeled copper complex, II, in 9:1 toluene–THF solution at −20 °C and computer simulation (B); 100 G scan, 12.5 G/min scan rate, 1 mW, 0.63 G modulation amplitude. The line widths of the six "nitroxyl" lines as obtained by computer simulation are indicated above the corresponding lines in the experimental spectrum.

marked constrast with the behavior of $J$ in spin-labeled Cu(baen).[6] In that case $J$ decreased markedly as the temperature was increased.[6]

Our studies to date indicate that a number of factors influence the magnitude of $J$.[2-6] Since the effects of temperature and solvent vary from system to system, it is not clear what conditions should be used to make comparisons between different types of complexes. However, even with these uncertainties it is clear that the magnitude of $J$ for this series of complexes is substantially smaller than for the spin-labeled copper complexes Cu(baen) ($J$ = 475–520 G[6]), Cu(batm) ($J$ = 300–415 G for one isomer[5]), and Cu(porphyrin) ($J$ = 77–92 G[3]). In the spin-labeled copper salicylaldimines the nitroxyl group is only slightly further away from the copper than in the three other types of complexes. However there is a rough correlation between the magnitude of $J$ and the amount of orbital interaction one might intuitively expect on the basis of simplified models of electron delocalization. For example, in the complexes reported in this paper two saturated carbons intervene between the copper and the pyrroline ring, whereas some degree of delocalization involving all of the atoms between the pyrroline ring and the atom coordinated to copper can be envisioned in the other cases cited above. We have preliminary results on other systems which indicate that there is no simple dependence of $J$ on distance, number of bonds, or type of bonds. The complexity of the molecules precludes any meaningful quantum-mechanical estimation of $J$ at this time.

The "nitroxyl" region of the EPR spectrum of the complex with R = 4-OMe (II) at −20 °C in 9:1 toluene–THF is shown in Figure 4. Since the value of $J$ (8.5 G) is about half the value of $A_{N'}$, the "inner" and "outer" triplets are clearly resolved, and line widths can be accurately determined for each component as indicated in the figure. For the "inner" triplet the line widths decrease to higher field, but for the "outer" triplet the line widths increase to higher field. A similar pattern of line width variations is also observed in other spectra where the individual components are well resolved. The explanation for this variation in relaxation times is currently under investigation.

**Acknowledgment.** This work was supported in part by the National Institutes of Health (Grant GM 21156). Elemental analysis were performed by Spang Microanalytical Laboratory. We thank Dr. D. L. Dubois for useful discussions during the early part of this work.

**Registry No.** I, 70749-62-1; II, 70749-63-2; III, 70749-64-3; IV, 70775-21-2; V, 70749-65-4; VI, 70749-66-5; VII, 70749-67-6; X, 70775-22-3; XI, 70749-68-7; XII, 70749-69-8; XIII, 70749-70-1; XIV, 70749-71-2; XV, 70749-72-3; XVI, 70749-73-4; XVIII, 70749-74-5; XIX, 70775-23-4; XX, 70749-75-6; XXI, 70749-76-7; XXII, 70749-77-8; XXIII, 70749-78-9; XXIV, 70749-79-0.

## References and Notes

(1) Eaton, G. R., Eaton, S. S. *Coord. Chem. Rev.* **1978**, *32*, 207–62.
(2) Boymel, P. M.; Chang, J. R.; DuBois, D. L.; Greenslade, D. J.; Eaton, G. R.; Eaton, S. S. *J. Am. Chem. Soc.* **1977**, *99*, 5500–1.
(3) Braden, G. A.; Trevor, K. T.; Neri, J. M.; Greenslade, D. J.; Eaton, G. R.; Eaton, S. S. *J. Am. Chem. Soc.* **1977**, *99*, 4854–5.
(4) DuBois, D. L.; Eaton, G. R.; Eaton, S. S. *J. Am. Chem. Soc.* **1978**, *100*, 2686–9.
(5) DuBois, D. L.; Eaton, G. R.; Eaton, S. S. *Inorg. Chem.* **1979**, *18*, 75–9.
(6) DuBois, D. L.; Eaton, G. R.; Eaton, S. S. *J. Am. Chem. Soc.* **1979**, *101*, 2624–7.
(7) Brown, D. B.; Crawford, V. H.; Hall, J. W.; Hatfield, W. E. *J. Phys. Chem.* **1977**, *81*, 1303–6.
(8) Boudreaux, E. A., Mulay, L. N., Eds., "Theory and Applications of Molecular Paramagnetism"; Wiley: New York, 1976.
(9) Dey, K. *Indian J. Chem.* **1971**, *9*, 887–8.
(10) Goodman, B. A.; Raynor, J. B. *Adv. Inorg. Chem. Radiochem.* **1970**, *13*, 224–5.
(11) Aasa, R.; Vänngård, T. *J. Magn. Reson.* **1975**, *19*, 308–15.
(12) McConnell, H. *J. Chem. Phys.* **1956**, *25*, 709–11; Kivelson, D. *J. Chem. Phys.*, **1960**, *33*, 1094–106.
(13) Eaton, S. S.; Eaton, G. R.; DuBois, D. L. *J. Magn. Reson.* **1978**, *32*, 251–63.
(14) Wertz, J. E.; Bolton, J. R. "Electron Spin Resonance"; McGraw-Hill: New York, 1972; Chapter 3 and Appendix C.
(15) Yokoi, H. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 3037–40. Yokoi, H.; Addison, A. W. *Inorg. Chem.* **1977**, *16*, 1341–9.
(16) Crawford, S. M. *Spectrochim. Acta* **1963**, *19*, 255–70. Downing, R. S.; Urbach, F. L. *J. Am. Chem. Soc.* **1969**, *91*, 5977–83.
(17) Charette, J.; Falthansl, G.; Teyssie, Ph. *Spectrochim. Acta* **1964**, *20*, 597–618. Boucher, L. J. *J. Inorg. Nucl. Chem.* **1974**, *36*, 531–6.
(18) Maslen, H. S.; Waters, T. N. *Coord. Chem. Rev.* **1975**, *17*, 172–4.