Stable solid Cu(hp) adducts were previously obtained only with the hydrohalic acids HCl and HBr, in which case proton interaction with the ligand aza nitrogens are assumed to provide the necessary additional stability. The EPR spectrum of Cu(hp)(HCl)$_2$ was analyzed and gave $b = 0.285$ and $r = 33\%$.[1] These values are intermediate between those reported above for solid-state and frozen-solution spectra. They point to an appreciably short Cu–Cl distance and are in agreement with the relevant role ascribed to the proton–ligand interaction in stabilizing these compounds.

Finally ligand hyperfine structure was detected and is clearly resolved in the X-band spectrum of ^{63}Cu/Ni(hp)(py)$_2$. The coupling, measured on the g_x and g_z features, ranges from 0.94 to 1.20 mT and is apparently due to four almost equivalent nitrogen nuclei (nine lines with the expected intensity ratio). Upon substitution of the axial pyridines with different donors, e.g. HCl, this pattern remains unchanged[1] and is therefore attributed to the four macrocyclic nitrogens.

Metal–Nitroxyl Interactions. 35. Conformational Effects on Spin–Spin Interaction in Spin-Labeled Copper Salicylaldimines

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

A series of complexes has been prepared in which a nitroxyl spin label is attached by an amide linkage to the α-carbon of the ethylene or trimethylene bridge in derivatives of (*N,N'*-disalicylidene-1,2-ethanediaminato)copper(II) (Cu(salen)) or (*N,N'*-disalicylidene-1,3-propanediaminato)copper(II) (Cu(salpn)). EPR spectra have been examined in fluid solution as a function of temperature and solvent. Values of the electron–electron spin–spin coupling constant J were smaller for the Cu(salen) complexes (3–20 G) than for the Cu(salpn) analogues (10–92 G). Electron-donating substituents on the salicylaldehyde ring caused an increase in J for both series of complexes, and an electron-withdrawing substituent caused a decrease in J for a Cu(salpn) derivative. Decreasing temperature caused an increase in J for the Cu(salen) derivatives and a decrease in J for the Cu(salpn) derivatives. Hydrogen-bonding interaction with chloroform or 1,1,1-trifluoroethanol caused an increase in J for the Cu(salen) derivatives and a decrease in J for the Cu(salpn) derivatives. If the sign of J is the same for all the complexes, the substituent effects are similar for the two series of complexes, but the conformational changes due to temperature changes or hydrogen bonding have opposite effects for the two series of complexes.

Introduction

NMR has been used widely to study molecular conformations. Both chemical shifts and coupling constants have proven to be valuable probes. When the electron-relaxation time is sufficiently fast, NMR spectra can be obtained for paramagnetic samples. However, for slowly relaxing metals such as Cu(II), NMR spectra cannot be obtained except in special cases. EPR g values and nuclear hyperfine couplings provide information concerning the geometry of the immediate vicinity of the unpaired electron. It would be useful to have an EPR probe of more distant changes. We have recently observed that metal–nitroxyl spin–spin coupling constants (J), which can be obtained from fluid solution EPR spectra, are sensitive probes of conformational changes.[1-3] We are therefore exploring the extent to which changes in the value of J can be used to monitor structural changes in solution. The information obtained from J complements that which can be obtained from ENDOR and ESEEM studies.

We have prepared a series of spin-labeled complexes in which a nitroxyl spin label is attached by an amide linkage to the α-carbon of the ethylene or trimethylene bridge in

Cu(salen) and Cu(salpn) derivatives. The structural formulas for these compounds are
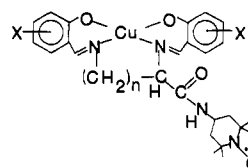
n	X	
1	H	Cu(salen-NO)
1	4-OMe	Cu(4-OMe-salen-NO)
2	H	Cu(salpn-NO)
2	3-OEt	Cu(3-OEt-salpn-NO)
2	4-OMe	Cu(4-OMe-salpn-NO)
2	4,6-(OMe)$_2$	Cu(4,6-(OMe)$_2$-salpn-NO)
2	5-Cl	Cu(5-Cl-salpn-NO)

The fluid solution EPR spectra have been examined as a function of solvent and temperature to compare the changes

(1) Sawant, B. M.; Braden, G. A.; Smith, R. E.; Eaton, G. R.; Eaton, S. S. *Inorg. Chem.* **1981**, *20*, 3349–3354.
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(3) More, K. M.; Eaton, G. R.; Eaton, S. S. *Can. J. Chem.* **1982**, *60*, 1392–1401.

in the spin–spin coupling constants that occur for the two classes of compounds.

Experimental Section

Physical Measurements. Infrared spectra were obtained in halo-carbon or Nujol mulls on a Perkin-Elmer 283B spectrometer. Electronic spectra were obtained in CHCl$_3$ solution on a Beckman Acta V spectrometer. Data are given below with wavelengths in nanometers and log ϵ in parentheses. X-band EPR spectra were obtained on a Varian E-9 spectrometer. EPR samples were prepared in dried degassed solvents with concentrations about 10^{-3} M. All spectra were obtained at microwave power levels well below saturation. g values were measured relative to that of DPPH (2.0036). Elemental analyses were performed by Spang Microanalytical Laboratory.

Preparation of Compounds. 2,3-Bis(trifluoroacetamido)propionic Acid (I). 2,3-Diaminopropionic acid hydrochloride (0.703 g, 5 mmol) was dissolved in 20 mL of water containing sodium hydroxide (0.4 g, 10 mmol). *S*-Ethyl trifluorothioacetate (2.372 g, 15 mmol) was added in one portion. The reaction mixture was stirred at room temperature for 18 h. The mixture was cooled in an ice bath, acidified with concentrated HCl, and extracted with four 100-mL portions of ether. The extract was dried over sodium sulfate. The ether was removed under reduced pressure. The product was recrystallized from ether/petroleum ether (1:3) to give a white solid: yield 1.11 g (75%); mp 178 °C; IR ν_{NH} 3300, ν_{CO} 1710 cm^{-1}.

2,4-Bis(trifluoroacetamido)butyric Acid (II). The protecting groups were attached by the procedure described above for I but using 2,4-diaminobutyric acid dihydrochloride (0.955 g, 5 mmol) and 20 mL of water containing sodium hydroxide (0.6 g, 15 mmol): yield 1.24 g (80%); mp 135 °C; IR ν_{NH} 3280, ν_{CO} 1620, 1690 cm^{-1}.

N-(2,2,6,6-Tetramethyl-1-oxy-4-piperidinyl)-2,3-bis(trifluoro-acetamido)propionamide (III). Dry triethylamine (0.10 g, 1.0 mmol) was added to a solution of I (0.296 g, 1.0 mmol) in 25 mL of anhydrous ether at 0 °C. A solution of ethyl chloroformate (0.11 g, 1.0 mmol) in 5 mL of anhydrous ether was added slowly (5 min). After the mixture was stirred for an additional 15 min at 0 °C, the ice bath was removed and stirring was continued for 2 h at room temperature. The reaction mixture was filtered, and the filtrate was cooled to 0 °C. A solution of 4-amino-2,2,6,6-tetramethylpiperidinyl-1-oxy (0.171 g, 1.0 mmol) in 20 mL of ether was added dropwise (10 min). The reaction mixture was stirred for 1 h at 0 °C and then for 4 h at 40 °C. The solvent was removed under reduced pressure. The product was dissolved in 100 mL of dichloromethane. The solution was washed with 50 mL of 1 N HCl, 50 mL of saturated sodium bicarbonate solution, and 50 mL of water. The solution was dried over sodium sulfate. Removal of the solvent gave a red oil that gave a yellow solid upon addition of ether. The solid was dissolved in chloroform, and the resultant mixture was chromatographed on silica gel. The center of the slow-moving yellow band was collected. The solvent was removed, and the resulting solid was recrystallized from dichloro-methane/ether: yield 0.21 g (47%); mp 175 °C; IR ν_{NH} 3460, 3230, ν_{CO} 1720, 1665 cm^{-1}. Anal. Calcd for C$_{16}$H$_{23}$N$_4$O$_6$F$_6$: C, 42.77; H, 5.16; N, 12.47. Found: C, 42.57; H, 5.29; N, 12.41.

N-(2,2,6,6-Tetramethyl-1-oxy-4-piperidinyl)-2,4-bis(trifluoro-acetamido)butyramide (IV). This compound was prepared from II and 4-amino-2,2,6,6-tetramethylpiperidinyl-1-oxy by a procedure analogous to that used for III; yield 0.29 g (63%); mp 193 °C; IR ν_{NH} 3440, 3220, ν_{CO} 1730, 1660 cm^{-1}. Anal. Calcd for C$_{17}$H$_{25}$N$_4$O$_4$F$_6$: C, 44.06; H, 5.44; N, 12.09. Found: C, 43.98; H, 5.40; N, 12.06.

N-(2,2,6,6-Tetramethyl-1-oxy-4-piperidinyl)-2,3-diaminopropion-amide (V). A 0.135-g portion of III (0.30 mmol) was added to 40 mL of a 7:1 mixture of 0.1 N NaOH and ethanol. The reaction mixture was stirred at room temperature for 2 h. The product was extracted into chloroform (four 50-mL portions). The CHCl$_3$ was removed under reduced pressure, and the product was dried under vacuum for 2 h to give a red oil: yield 62 mg (80%); IR ν_{NH} 3360, 3290, ν_{CO} 1660 cm^{-1}.

N-(2,2,6,6-Tetramethyl-1-oxy-4-piperidinyl)-2,4-diaminobutyramide (VI). This compound was prepared from IV by a procedure analogous to that used for V: yield 70 mg (85%); IR ν_{NH} 3360, 3290, ν_{CO} 1660 cm^{-1}.

[1-(((2,2,6,6-Tetramethyl-1-oxy-4-piperidinyl)amino)carbonyl)-N,N'-disalicylidene-1,2-ethanediaminato]copper(II), Cu(salen-NO). Salicylaldehyde (0.112 g, 1.0 mmol) was added to a solution of V (0.129 g, 0.50 mmol) in 20 mL of absolute ethanol. The reaction mixture was stirred at room temperature for 3 h. The volume was

reduced to about 10 mL under vacuum. Cupric acetate (0.10 g, 0.50 mmol) dissolved in 40 mL of warm absolute ethanol was added. The mixture was warmed to 40 °C and stirred for 30 min. The volume was reduced to about 15 mL under reduced pressure and then the solution was cooled in an ice bath for 30 min. The product was separated by filtration and recrystallized from chloroform/heptane: yield 0.150 g (57%); IR ν_{NH} 3200, ν_{CO} 1650, ν_{CN} 1620 cm^{-1}; visible spectrum (CHCl$_3$ solution) 571 (2.43), 370 (4.00), 280 (4.38). Anal. Calcd for C$_{26}$H$_{31}$CuN$_4$O$_4$: C, 59.25; H, 5.93; N, 10.63. Found: C, 59.32; H, 5.93; N, 10.71.

[1-(((2,2,6,6-Tetramethyl-1-oxy-4-piperidinyl)amino)carbonyl)-N,N'-bis(4-methoxysalicylidene)-1,2-ethanediaminato]copper(II), Cu(4-OMe-salen-NO). This compound was prepared from 2-hydroxy-*p*-anisaldehyde and V by a procedure analogous to that used for Cu(salen-NO): yield 0.18 g (61%); IR ν_{NH} 3260, ν_{CO} 1640, ν_{CN} 1620, 1605 cm^{-1}; visible spectrum (CHCl$_3$ solution) 567 (2.59), 357 (4.26), 299 (4.54), 257 (4.59). Anal. Calcd for C$_{28}$H$_{35}$CuN$_4$O$_6$: C, 57.28; H, 6.01; N, 9.54. Found: C, 57.30; H, 5.94; N, 9.62.

[1-(((2,2,6,6-Tetramethyl-1-oxy-4-piperidinyl)amino)carbonyl)-N,N'-disalicylidene-1,3-propanediaminato]copper(II), Cu(salpn-NO). This compound was prepared from salicylaldehyde and VI by a procedure analogous to that used for Cu(salen-NO): yield 0.16 g (59%); IR ν_{NH} 3270, ν_{CO} 1660, ν_{CN} 1640, 1620 cm^{-1}; visible spectrum (CHCl$_3$ solution) 610 (2.50), 378 (4.03), 278 (4.48). Anal. Calcd for C$_{27}$H$_{33}$CuN$_4$O$_4$: C, 59.93; H, 6.15; N, 10.35. Found: C, 59.77; H, 6.19; N, 10.28.

[1-(((2,2,6,6-Tetramethyl-1-oxy-4-piperidinyl)amino)carbonyl)-N,N'-bis(3-ethoxysalicylidene)-1,3-propanediaminato]copper(II), Cu(3-OEt-salpn-NO). This compound was prepared from 3-eth-oxysalicylaldehyde and VI by a procedure analogous to that used for Cu(salen-NO). In the final step of the preparation, the ethanol was removed completely under vacuum. The residue was washed with 20 mL of ether, and the product was recrystallized from chloroform: yield 0.15 g (48%); IR ν_{NH} 3250, ν_{CO} 1630, ν_{CN} 1610 cm^{-1}; visible spectrum (CHCl$_3$ solution) 600 (2.56), 395 (3.90), 291 (4.43). Anal. Calcd for C$_{31}$H$_{41}$CuN$_4$O$_6$: C, 59.17; H, 6.57; N, 8.79. Found: C, 58.91; H, 6.52; N, 8.79.

[1-(((2,2,6,6-Tetramethyl-1-oxy-4-piperidinyl)amino)carbonyl)-N,N'-bis(4-methoxysalicylidene)-1,3-propanediaminato]copper(II), Cu(4-OMe-salpn-NO). This compound was prepared from 2-hydroxy-*p*-anisaldehyde and VI by a procedure analogous to that used for Cu(salen-NO): yield 0.19 g (63%); IR ν_{NH} 3200, ν_{CO} 1630, ν_{CN} 1605 cm^{-1}; visible spectrum (CHCl$_3$ solution) 610 (2.50), 361 (4.22), 297 (4.62), 257 (4.63). Anal. Calcd for C$_{29}$H$_{37}$CuN$_4$O$_6$: C, 57.94; H, 6.20; N, 9.32. Found: C, 57.89; H, 6.12; N, 9.23.

[1-(((2,2,6,6-Tetramethyl-1-oxy-4-piperidinyl)amino)carbonyl)-N,N'-bis(4,6-dimethoxysalicylidene)-1,3-propanediaminato]copper(II), Cu(4,6-(OMe)$_2$-salpn-NO). This compound was prepared from 4,6-dimethoxysalicylaldehyde and VI by a procedure analogous to that used for Cu(salen-NO): yield 0.17 g (52%); IR ν_{NH} 3230, ν_{CO} 1645, ν_{CN} 1610 cm^{-1}; visible spectrum (CHCl$_3$ solution) 600 (2.49), 315 (4.56). Anal. Calcd for C$_{31}$H$_{41}$CuN$_4$O$_8$: C, 56.31; H, 6.25; N, 8.47. Found: C, 56.26; H, 6.20; N, 8.54.

[1-(((2,2,6,6-Tetramethyl-1-oxy-4-piperidinyl)amino)carbonyl)-N,N'-bis(5-chlorosalicylidene)-1,3-propanediaminato]copper(II), Cu(5-Cl-salpn-NO). This compound was prepared from 5-chloro-salicylaldehyde and VI by a procedure analogous to that used for Cu(salen-NO): yield 0.16 g (52%); IR ν_{NH} 3210, ν_{CO} 1650, ν_{CN} 1630 cm^{-1}; visible spectrum (CHCl$_3$ solution) 605 (2.65), 392 (4.04), 278 sh (4.45). Anal. Calcd for C$_{27}$H$_{31}$Cl$_2$CuN$_4$O$_4$: C, 53.16; H, 5.12; N, 9.18; Cl, 11.62. Found: C, 53.06; H, 5.10; N, 9.20; Cl, 11.49.

Computer Simulations. For a molecule containing two unpaired electrons and no nuclear spins, the EPR Hamiltonian for fluid solution spectra in the rapid tumbling regime is given by eq 1. The computer

$$\mathcal{H} = \beta H(g_1 S_1 + g_2 S_2) + hJS_1 S_2 \tag{1}$$

program CUNO[4,5] was used to obtain the computer simulations reported here. It uses eq 1 plus terms arising from nuclear hyperfine coupling to the copper nucleus (A_{Cu}), to nitrogens in the copper coordination sphere (A_N), and to the nitroxyl nitrogen ($A_{N'}$). Both ^{63}Cu and ^{65}Cu are included in the calculations. The values cited throughout the text

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Table I. Values of J at Room Temperature[a]

compd	solvent	J, G	$10^4 J$, cm^{-1}
Cu(salen-NO)	CH$_2$Cl$_2$	3	3
	THF	4	4
	CH$_2$Cl$_2$/CF$_3$CH$_2$OH[b]	6	6
	CHCl$_3$	7.5	7.2
	CHCl$_3$/CF$_3$CH$_2$OH[b]	14.5	13.9
	py	10[c]	10[c]
Cu(4-OMe-salen-NO)	CH$_2$Cl$_2$	4	4
	THF	4	4
	CHBr$_3$	9	9
	CHCl$_3$	11.5	11
	CH$_2$Cl$_2$/CF$_3$CH$_2$OH[b]	12.5	12.0
	CHBr$_3$/CF$_3$CH$_2$OH[b]	14	13.4
	CHCl$_3$/CF$_3$CH$_2$OH[b]	19.5	18.7
	py	10[c]	10[c]
Cu(salpn-NO)	CH$_2$Cl$_2$	44	42
	CHCl$_3$	40	38
	THF	35	34
	py	12[c]	12[c]
Cu(3-OEt-salpn-NO)	toluene	66	63
	CH$_2$Cl$_2$	56	54
	CHCl$_3$	42	40
	CH$_2$Cl$_2$/CF$_3$CH$_2$OH[b]	26	25
	CF$_3$CH$_2$OH	25[c]	25[c]
	THF	25	24
	py	5[c]	5[c]
Cu(4-OMe-salpn-NO)	toluene	78	75
	CH$_2$Cl$_2$	74	71
	THF	68	65
	CHCl$_3$	63	60
	CH$_2$Cl$_2$/CF$_3$CH$_2$OH[b]	63	60
	CH$_2$Cl$_2$/CF$_3$CH$_2$OH[d]	56	58
	CHCl$_3$/CF$_3$CH$_2$OH[b]	52	50
	1:1 toluene/pyridine	28	27
	py	5[c]	5[c]
Cu(4,6-(OMe)$_2$-salpn-NO)	toluene	66	63
	CH$_2$Cl$_2$	62	60
	THF	62	60
	CHCl$_3$	51	49
	py	30	29
Cu(5-Cl-salpn-NO)	CH$_2$Cl$_2$	27	26
	CHCl$_3$	17	16
	THF	10[c]	10[c]
	py	10[c]	10[c]

[a] Uncertainty ±1 unless otherwise noted. [b] 19:1 by volume. [c] Lines are broad. Value of J is only approximate. [d] 9:1 by volume.

for A_{Cu} refer to ^{63}Cu. The sign of J cannot be determined from these experiments. The details of the calculations have been discussed.[4,5]

To facilitate comparison with the field-swept experimental spectra, the values of J, A_M, A_N, and $A_{N'}$ are given in units of gauss in the following discussion. The conversion between hertz and gauss is given by eq 2–4. g_1 and g_2 are the copper and nitroxyl g values, respectively.

$$J\text{ (G)} = [J\text{ (Hz)}]\frac{h}{2\beta}\left(\frac{1}{g_1} + \frac{1}{g_2}\right) \qquad (2)$$

$$A_M\text{ (G)} = [A_M\text{ (Hz)}]\frac{h}{g_1\beta} \qquad (3)$$

$$A_{N'}\text{ (G)} = [A_{N'}\text{ (Hz)}]\frac{h}{g_2\beta} \qquad (4)$$

The conversion factor for A_N is the same as for A_M. The electron–electron spin–spin coupling results in AB patterns in the EPR spectra. The lines in the spectra are referred to as copper or nitroxyl depending on the nature of the transition as J approaches zero. When J is small relative to the g-value difference between the copper and nitroxyl electrons, each of the copper and nitroxyl lines is split into a doublet. In the spin-labeled copper complexes reported here, the apparent copper line widths are large due to unresolved hyperfine coupling to the nitrogens in the copper coordination sphere. Thus, for values of J less than about 30 G, spin–spin splitting was resolved for the nitroxyl lines but not for the copper lines. For larger values of J, splitting was resolved in both the copper and nitroxyl lines. The values of J
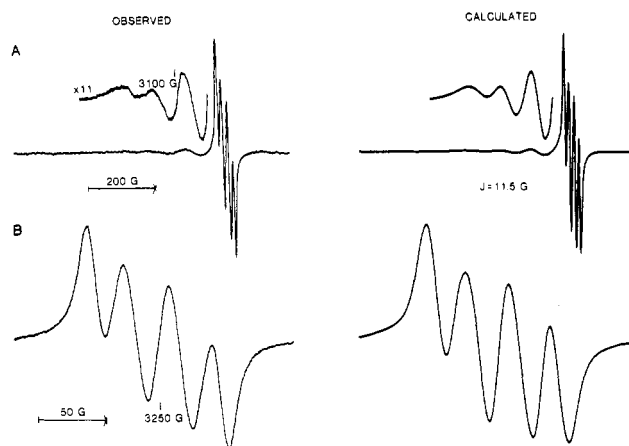

Figure 1. X-Band (9.11 GHz) EPR spectra of Cu(4-OMe-salen-NO) in CHCl$_3$ solution at room temperature and computer simulations. (A) 800-G scan of the full spectrum. The insert showing the details of the copper lines was obtained with an overall amplification 11 times greater than that used to obtain the full spectrum. (B) 100-G scan of the nitroxyl lines. The spectra were obtained with 10-mW power and 1.25-G modulation amplitude.

obtained by simulation of the spectra are given in Table I. The uncertainty in the value of J ranges from ±1 G for $J < 10$ G to ±3 G for J about 75 G.

In noncoordinating solvents the g values for Cu(salen-NO) and Cu(4-OMe-salen-NO) were 2.093–2.096 and A_{Cu} was 84–86 G. These values are in good agreement with the averages of the parameters reported for Cu(salen) doped into Ni(salen): $g = 2.096$ and $A_{Cu} = 86.7$ G.[6] For Cu(salpn-NO) and its substituted analogues, the g values were 2.106–2.108 and A_{Cu} was 73–78 G. These values are in good agreement with ones that we have reported previously for copper salicylaldimines containing 1,3-diaminopropane.[7] The slightly larger g values and smaller A_{Cu} values for Cu(salpn-NO) and its derivatives than for Cu(salen-NO) and Cu(4-OMe-salen-NO) are consistent with slightly greater distortion from planarity of the copper coordination environment for Cu(salpn-NO) than for Cu(salen-NO).[8] The hyperfine coupling to the nitrogens in the copper coordination sphere was not resolved so the value of A_N used in the simulations was assumed to be 13 G as was observed for closely related complexes.[8] The coupling of the nitroxyl electron to the nitrogen of the nitroxyl ring was 15.3–16.0 G, depending on solvent and temperature.

Results and Discussion

A series of copper salicylaldimines has been prepared in which a nitroxyl spin label is attached by an amide linkage to the α-carbon of a 1,2-diamino or 1,3-diamino bridge. The d–d transitions in the visible spectra of Cu(salen-NO) and Cu(4-OMe-salen-NO) occur at 571 and 567 nm, respectively. Under a variety of experimental conditions the d–d transition in Cu(salen) has been reported to occur at 559,[9] 565,[10] 571,[11] and 578 nm.[12] The d–d transitions in the visible spectra of Cu(salpn-NO) and its derivatives occur at 600–610 nm. Literature values for the d–d transition in Cu(salpn) are 595[12] and 602 nm.[11] Thus, the attachment of the nitroxyl spin label to the ethylene or trimethylene bridge does not appear to influence the geometry of the copper coordination sphere. The slightly lower energy for the transition in Cu(salpn-NO) and its derivatives than in Cu(salen-NO) and Cu(4-OMe-salen-

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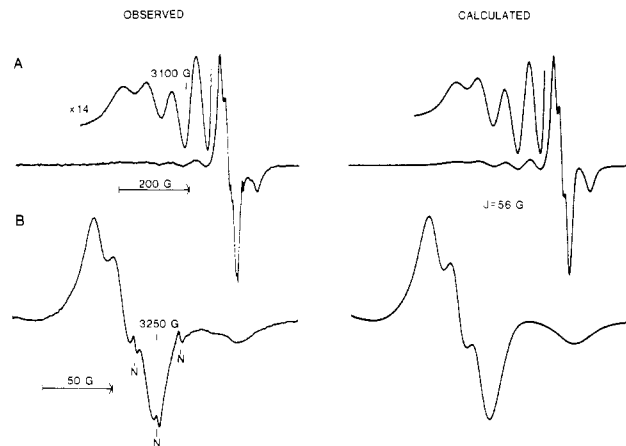(12) Batley, G. E.; Graddon, D. P. *Aust. J. Chem.* **1968**, *21*, 1473–1485.
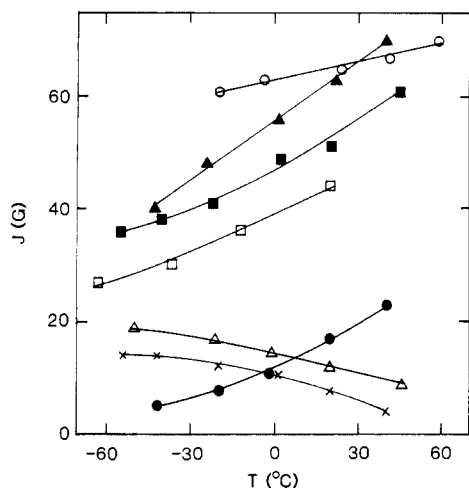
Figure 2. Plots of the values of J as a function of temperatures: (×) Cu(salen-NO); (△) Cu(4-OMe-salen-NO); (□) Cu(salpn-NO); (○) Cu(3-OEt-salpn-NO); (▲) Cu(4-OMe-salpn-NO); (■) Cu(4,6-(OMe)$_2$-salpn-NO); (●) Cu(5-Cl-salpn-NO). Data for Cu(salpn-NO) were obtained in CH$_2$Cl$_2$, data for Cu(3-OEt-salpn-NO) in toluene, and data for all other compounds in CHCl$_3$.

Figure 3. X-Band (9.11 GHz) EPR spectra of Cu(3-OEt-salpn-NO) in CH$_2$Cl$_2$ solution at room temperature and computer simulations. (A) 800-G scan of the full spectrum. The insert showing the details of the copper lines was obtained with an overall amplification 14 times greater than that used to obtain the full spectrum. (B) 100-G scan of the nitroxyl lines. The spectra were obtained with 2-mW microwave power and 0.8-G modulation amplitude. The three lines marked N are due to nitroxyl impurity that is not interacting with copper.

NO) is consistent with slightly greater distortion from planarity in the copper coordination sphere for Cu(salpn-NO) than for Cu(salen-NO).[8] A similar conclusion was obtained from a comparison of the copper g and A values as discussed above.

EPR Spectra of Cu(salen-NO) and Cu(4-OMe-salen-NO). The EPR spectrum of Cu(4-OMe-salen-NO) in CHCl$_3$ solution is shown in Figure 1. The electron–electron coupling constant (11.5 G) is about the same size as the nitroxyl nitrogen hyperfine coupling (15.7 G) so the two triplets overlap to give an apparent four-line pattern. The value of J is small relative to the line widths of the copper lines so a four-line spectrum was observed for the copper transitions with the highest field line obscured by the sharper nitroxyl lines. When the solution was cooled, the value of J increased as shown in Figure 2. Spectra obtained in other halogenated solvents indicated that the value of J increased in the order CH$_2$Cl$_2$ (4 G) < CHBr$_3$ (9 G) < CHCl$_3$ (11.5 G). Addition of CF$_3$CH$_2$OH (about 5% by volume) to each of these solutions caused the value of J to increase by 5–8 G. If the effect of CF$_3$CH$_2$OH on the value of J were due to coordination to the copper, THF would be expected to cause a similar effect on the value of J. However, the value of J in THF solution is the same as in CH$_2$Cl$_2$ so the effect of CF$_3$CH$_2$OH does not appear to be due to coordination to the copper. As discussed below, coordination of pyridine to copper caused other changes in the spectra.

The spectra of Cu(salen-NO) were similar to those of Cu(4-OMe-salen-NO) but with smaller values of J. The value of J for Cu(salen-NO) increased as solvent was varied in the order CH$_2$Cl$_2$ ≈ THF < CHCl$_3$ ≈ CH$_2$Cl$_2$/CF$_3$CH$_2$OH < CHCl$_3$/CF$_3$CH$_2$OH. This order is similar to that which was observed for Cu(4-OMe-salen-NO). The value of J for Cu(salen-NO) in CHCl$_3$ solution increased as the temperature was decreased (Figure 2) paralleling the behavior of Cu(4-OMe-salen-NO).

X-ray crystal structures have shown that CHCl$_3$ and *p*-nitrophenol form hydrogen-bonded adducts with Cu(salen).[13,14] The hydrogen bond is to one of the coordinated oxygens of the ligand. Hydrogen-bond formation decreases the "buckling" of the ethylene linkage and moves the linkage away from a gauche conformation. The effects of solvent on the values of

J for Cu(salen-NO) and Cu(4-OMe-salen-NO) suggest that hydrogen bonding may also be important in fluid solution. The hydrogen-bonding ability of chlorinated solvents increases in the order CH$_2$Cl$_2$ < CHBr$_3$ < CHCl$_3$, which is the order observed for increasing values of J. CF$_3$CH$_2$OH has a strong tendency to form hydrogen bonds, and its presence in solution also caused an increase in the value of J that was additive with the effects of the chlorinated solvents. Only one component was observed in the EPR spectra, which indicates either that all of the copper complex was hydrogen bonded to solvent or that the rate of exchange between the free and hydrogen-bonded forms was rapid on the EPR time scale. The additivity of the effects of chlorinated solvent and of CF$_3$CH$_2$OH makes the latter option appear more plausible. If the solution structures are similar to the structures in the crystals, the increase in the value of J as a result of hydrogen bonding is due to a decrease in the "buckling" of the ethylene linkage and movement away from a gauche conformation. The increase in J as temperature was decreased may indicate that the conformational changes that occur with decreasing temperature are similar to those that result from hydrogen bonding.

EPR Spectra of Cu(salpn-NO) and Derivatives. The EPR spectrum of Cu(3-OEt-salpn-NO) in CH$_2$Cl$_2$ solution is shown in Figure 3. The value of J (56 G) is larger than the nitroxyl nitrogen hyperfine splitting so the nitroxyl region of the spectrum is clearly split into inner and outer lines. The inner nitroxyl lines are sharper and more intense than the outer lines. The sharp three-line pattern in the center of the nitroxyl spectrum is due to a fraction of a percent of nitroxyl impurity that is not interacting with copper. The copper hyperfine splitting is about the same size as J so the two copper quartets superimpose to give an approximately five-line pattern, of which the high-field component is obscured by the sharper nitroxyl lines.

The values of J obtained for Cu(salpn-NO) and its derivatives are summarized in Table I and Figure 2. In each case the values of J in toluene and/or CH$_2$Cl$_2$ solution were greater than in CHCl$_3$ solution, which is the reverse of the pattern observed for Cu(salen-NO) or Cu(4-OMe-salen-NO). Similarly, addition of CF$_3$CH$_2$OH caused a decrease in the value of J for the Cu(salpn-NO) derivatives, which is the opposite of its effect on Cu(salen-NO) or Cu(4-OMe-salen-NO). Decreasing the temperature led to a decrease in the value of J (Figure 2). Thus, for each of these changes the behavior

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of the complexes with the trimethylene bridge is the reverse of that for the ethylene-bridged analogues. X-ray structural data are not available for Cu(salpn) so a detailed analysis of the effects of hydrogen bonding is not possible. The visible spectra and EPR spectra indicated that the copper coordination sphere in Cu(salpn-NO) and its derivatives is slightly more distorted from planarity than in Cu(salen-NO) which will influence the conformation at the α-carbon. The greater flexibility of the trimethylene bridge than of the ethylene bridge will also affect the conformation at the α-carbon.

In both series of complexes, addition of electron-donating substituents on the salicylaldimine ring caused an increase in J, and for Cu(5-Cl-salpn-NO), the electron-withdrawing chloro substituent caused a decrease in J. Maslen and Waters have analyzed the crystallographic data available for bis(bidentate salicylaldimine) complexes and concluded that increased electron density in the salicylaldimine ring causes changes in the hybridization of the coordinated oxygen and changes in the distortion from planarity of the complex.[15] In quadridentates the situation is complicated by the steric requirements of the ligand.[15] It would appear from the present data that the electronic effects of the ring substituents are similar for the two series of complexes and must therefore be causing somewhat different changes than those that occur due to hydrogen bonding or a decrease in temperature.

Since the sign of J is unknown, it is possible that J is positive for some of these complexes and negative for others. In the foregoing discussion it was assumed for simplicity that the sign of J was the same for all the compounds examined. If, however, the sign of J for the Cu(salen-NO) derivatives were the opposite of the sign for the Cu(salpn-NO) derivatives, then the effects of the ring substituents would be opposite for the two series while the effects of temperature and hydrogen bonding would be similar.

Possible Explanation of Conformational Effects on J. The copper unpaired electron is in the $d_{x^2-y^2}$ orbital, which is directed toward the coordinated oxygens and nitrogens. Thus, the major pathway for spin delocalization would be expected to be by σ interaction. A similar pathway was been observed for paramagnetic nickel(II) complexes.[16] Studies of ethylenediamine coordinated to nickel(II) have shown that spin delocalization onto the protons follows an approximately $\cos^2 \theta$ dependence where θ is the dihedral angle between the H–C–N and C–N–Ni planes.[16] Thus, there is substantially greater spin density on the equatorial proton than on the axial proton, and the spin densities are sensitive to changes in the chelated ethylenediamine conformation. The maximum spin delocalization at $\theta = 180°$ is similar to the "W plan", which has been observed to favor long-range spin–spin interactions.[3,17] Inspection of molecular models indicated that for both the Cu(salen-NO) and Cu(salpn-NO) derivatives, steric constraints favor an equatorial position for the bulky spin-labeled amide groups. However, in both cases the hydrocarbon backbone is substantially distorted from that of a simple ethylene linkage due to the constraints of the salicylaldimine coordination. The orientations of the substituents are not the same as on an undistorted ring. The larger values of J for the Cu(salpn-NO) derivatives than for the Cu(salen-NO) derivatives may indicate that θ is closer to $180°$ for Cu(salpn-NO) than for Cu(salen-NO) and that the greater spin density on the α-carbon leads to a greater spin–spin interaction.

In a variety of plausible conformations for these molecules, the carbonyl oxygen of the amide linkage is close to one of the coordinated nitrogens. Although the primary path for spin delocalization would be expected to involve the nitrogen σ orbitals, some unpaired spin density would be expected to be induced in the nitrogen π orbital. We have previously proposed that overlap of a carbonyl oxygen with a π system provided an alternate pathway for electron spin delocalization.[2] Such an interaction is very sensitive to small changes in molecular structure. Coordination of an axial ligand to the copper interferes sterically with such an interaction. The observation that pyridine coordination greatly reduced the spin–spin interaction for most of the complexes examined in this study is consistent with the proposal that the amide oxygen plays a role in the spin–spin interaction. However, pyridine coordination would also be expected to change the geometry at the α-carbon so the role of the carbonyl oxygen is difficult to assess. Further studies on related complexes will be required to distinguish between the possible contributions.

Line Widths. Some broadening of the nitroxyl lines is expected due to mixing of the copper and nitroxyl wave functions. That contribution to the line width is expected to increase with increasing values of J. For molecules with relatively rigid geometries nitroxyl line widths of 1.5–2 G ($J = 3$ G),[2] 6–7 G ($J = 20$ G),[18] and 8–10 G ($J = 78$ G)[1] have been observed. For molecules with more flexible geometries, population of conformations with slightly different values of J causes an uncertainty in the value of J that can cause a broadening of the lines if conformational averaging is not rapid on the EPR time scale. This contribution to the line width is frequently much greater than the contribution from mixing of the metal and nitroxyl wave functions in a static conformation.[1,2,18]

In the room-temperature EPR spectra of Cu(salen-NO) and Cu(4-OMe-salen-NO) the nitroxyl line widths in all solvents except pyridine were 7–10 G, which indicates some flexibility of the molecule but with a relatively narrow range of values of J for the accessible conformations or rapid interconversion of accessible conformations on the EPR time scale. For Cu(salpn-NO) and its derivatives in noncoordinating solvents, the nitroxyl inner lines had line widths of 11–18 G and the outer line widths were 15–23 G. The larger nitroxyl line widths for the Cu(salpn-NO) derivatives than for Cu(salen-NO) are consistent with the general pattern that line widths increase as J increases. The line widths are substantially greater than those cited above for relatively rigid molecules, which indicates considerable flexibility of these molecules. The larger line widths for the outer lines than for the inner lines occur because an uncertainty in the value of J causes a greater uncertainty in the position of the outer lines than of the inner lines.

In pyridine solution the nitroxyl lines for all of the complexes were broadened further (line widths of 25–35 G). The broadening of the lines makes an accurate determination of J difficult, but it appears that for most of the complexes pyridine coordination results in a substantial decrease in J. The large changes in the spectra in the presence of pyridine suggest that pyridine coordinates to the copper. The broadened lines may indicate that a wide variety of conformations with somewhat different values of J are accessible in the pyridine adduct or that the pyridine on–off rate is intermediate on the EPR time scale. There is one notable exception to these patterns. Pyridine has less impact on the spectrum of Cu-(4,6-(OMe)$_2$-salpn-NO) than on the other spectra. The bulky 6-substituents in this complex may interfere with the conformational changes that accompany pyridine coordination and thereby decrease the extent of pyridine coordination. For most of the complexes, THF caused little change in the value of J from that observed in CH$_2$Cl$_2$ solution. However, for Cu(5-Cl-salpn-NO) the spectra in THF were broadened and similar

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to the spectra in pyridine solution. These results suggest that there is some coordination of THF to this complex but not to the other complexes. The electron-withdrawing Cl may decrease the coordinating ability of the salicylaldimine sufficiently that formation of a 5-coordinate species becomes more favorable.

Conclusions

The EPR spectra of these Cu(salen-NO) and Cu(salpn-NO) derivatives indicate that exchange interactions through saturated linkages are strongly dependent upon the detailed molecular conformation. Thus, they can be useful probes of structural changes and weak molecular interactions.

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Structure of the Iron Pentacarbonyl Anion

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Full structure calculations using an atom superposition and electron delocalization molecular orbital theory show the form of the (square-pyramidal) iron pentacarbonyl anion where the bent apical carbonyl ligand eclipses a basal one has a slight edge in stability over the staggered conformation. The bending is dominated by the singly occupied molecular orbital that is mainly of apical carbonyl π^* character. On bending, an iron 4p orbital is allowed by symmetry to mix in and stabilize this orbital, an effect not noted in a Walsh analysis by Hoffmann et al. The angle of bending, 121–125°, is supported by an EPR study by Fairhurst et al. We also find the basal carbonyl ligands bend down 5–15° to maximize d–π^* stabilization.

Introduction

There are excellent reasons to believe the apical carbonyl ligand will bend in the iron pentacarbonyl anion, on the basis of a Walsh diagram and analysis by Hoffmann et al.[1] and the recent EPR study of Fairhurst et al.[2] for Fe(CO)$_5^-$ in a Cr(CO)$_6$ matrix. The direction of this bending has not been explored in the model theoretical study and was not resolved by EPR. The nature of the singly occupied molecular orbital is unclear in that according to the Walsh analysis of ref 1 it appears to have d$_{yz}$ metal character (coordinates are defined in Figure 1) while Fairhurst et al. favor d$_{z^2}$.

We have completed full structure predictions for Fe(CO)$_5^-$ for two orientations. We also find the basal ligands bend down a few degrees. In this paper we examine these and other properties of Fe(CO)$_5^-$ within the framework of molecular orbital theory.

Method

We use an atom superposition and electron delocalization molecular orbital (ASED–MO) technique. This theory uses the electrostatic theorem[3] for forces on nuclei in molecules within a molecular electronic charge density partitioning model. The density is broken into rigid free-atom parts and an electron delocalization bond charge part. As atoms bond together to form a molecule, the forces on the nuclei are integrated, yielding a repulsive energy due to the rigid-atom densities and the atomic nuclei and an attractive energy due to electron delocalization.[4a] The sum is exactly the molecular binding energy. The atom superposition component is evaluated from the atomic density

functions. At equilibrium, the Laplacian of this component contains harmonic, cubic, and quartic stretching force constants to good accuracy.[4b] The electron delocalization energy has been found to be well approximated by a one-electron molecular orbital energy. A Hamiltonian similar in form to that of extended Hückel is used.[4c] The ASED–MO theory has been used for numerous predictions of structures, force constants, and electronic properties of molecules, surfaces, and solids. The parameters used in the present study were also used in an earlier analysis of the structure and bonding in (cyclobutadiene)iron tricarbonyl.[5] They are given in Table I.

Results and Discussion

Our fully optimized eclipsed and staggered iron pentacarbonyl anion structures may be seen in Figure 2. The energies are practically identical, with the eclipsed form only 0.03 eV more stable. The orbitals and bonding analysis are found to be the same for both conformations, so we will treat only the eclipsed one, except to note the slight differences in other structure parameters of the two forms. The apical Fe–C–O angle is 121° for the eclipsed and 125° for the staggered conformation, both supporting the estimate of 119° by Fairhust et al. based on their EPR data. The basal CO–Fe–CO angles are 152 and 159° for the eclipsed and 155° for the staggered form, close to the typical value of 150° quoted by Rossi and Hoffmann.[6] We find ligand-kinking distortions are destabilizing.

For each orientation, the apical CO bond length is 0.10 Å longer than the basal CO lengths, an indication that the unpaired electron in this d^9 anion is described by a molecular orbital with apical CO π^* character. It may also be noted in Figure 2 that the distance between Fe and C of the apical CO is 0.10–0.12 Å longer than the others. This suggests the

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