discussions with Dr. S. F. Rice and Professor D. S. Martin. Several infrared spectroscopic measurements were performed in Professor G. R. Rossman's laboratory at Caltech. This work was supported by National Science Foundation Grant CHE81-20419.

Registry No. $Rh_2(O_2CCH_3)_4(OH_2)_2$, 29998-99-0; $Li_2Rh_2(O_2CCH_3)_4Cl_2 \cdot 8H_2O$, 88945-58-8; $Rh_2(O_2CCH_3)_4Cl_2^{2-}$, 71844-86-5; $Rh_2(O_2CCH_3)_4Br_2^{2-}$, 88945-59-9; $Rh_2(O_2CCH_3)_4I_2^{2-}$, 88968-31-4.

Supplementary Material Available: Listings of Gaussian amplitudes of the non-hydrogen atoms and observed and calculated structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

Contribution from the Istituto di Teoria e Struttura Elettronica e Comportamento Spettrochimico
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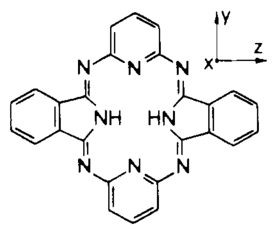
Hemiporphyrazine, a Porphyrin-Related Macrocycle That Induces Rhombically Compressed Stereochemistries: Structure and Properties of Bis(pyridine)(hemiporphyrazinato)nickel(II)

E. AGOSTINELLI, D. ATTANASIO,* I. COLLAMATI,* and V. FARES

Received May 24, 1983

The title compound crystallizes in the $P2_1/c$ space group with $Z = 4$, $a = 16.418$ (7) Å, $b = 9.727$ (4) Å, $c = 18.632$ (6) Å, and $\beta = 94.59$ (3)°. The stereochemistry is rhombically compressed with the unique axis defined by the metal isoindole nitrogen atoms, which are 1.97 Å from the nickel ion. The other two Ni–N distances are 2.18 and 2.22 Å, for the macrocyclic and adduct pyridine nitrogen atoms, respectively. In agreement with this, the EPR spectrum of the Cu-doped nickel complex is typical of a predominant $|z^2\rangle$ ground state with a strong rhombic component. Other related complexes were investigated by EPR spectroscopy and found to have a qualitatively similar geometry due to the "elliptical" coordination hole of the hemiporphyrazinato ligand.

Hemiporphrazine, hpH_2 (I), is a highly conjugated, although nonaromatic (20π), N_4 macrocycle with several structural features in common with porphyrins and phthalocyanines. In spite of this, recent work[1] has shown that the hemiporphyrazinato dianion (hp) exhibits a rather peculiar coordination chemistry partly due to the weakness and asymmetry of its ligand field. Its metal complexes display a marked tendency toward six-coordination. Various adducts with protic donors such as water or hydrohalic acids were investigated and found to be strongly stabilized by proton interaction with the aza groups of the hp ligand.



I

The EPR spectra of Cu(hp), magnetically diluted in six-coordinated hosts such as $Zn(hp)(HCl)_2$, were typical of a rhombically compressed symmetry, with an essentially $|z^2\rangle$ ground state. This was ascribed to the pronounced ellipticity of the hp coordination hole.[2-4] Apparently, upon axial coordination the unique axis shifts from the normal to the macrocyclic plane to the direction of the strongest metal–ligand bond, i.e. to the metal isoindole nitrogen direction with a simultaneous change of the stereochemistry from rhombically elongated to rhombically compressed.

This behavior, which is induced by the unique geometry of the macrocycle, depends of course on the nature of the central metal ion and on the strength of the axial donors. However, detailed information could not be obtained due to the lack of single crystals suitable for X-ray analysis. For this reason we investigated the interaction of some M(hp) complexes with different N bases and now report the crystal and molecular structure of $Ni(hp)(py)_2$ together with some spectroscopic information concerning this compound and some related Ni(II) and Cu(II) complexes.

Experimental Section

The complexes $Ni(hp)(py)_2$ and $Ni(hp)(4\text{-}Mepy)_2$ were obtained by simple crystallization of Ni(hp)[1] from the neat bases. Slow evaporation of a concentrated pyridine solution (100 mg, 4 mL) gave green, prismatic crystals of $Ni(hp)(py)_2$ suitable for X-ray work.

$Ni(hp)(4\text{-}Mepy)_2$ is a stable compound, whereas $Ni(hp)(py)_2$ slowly loses the coordinated base converting to the dihydrate derivative in a few weeks. Anal. Calcd for $C_{36}H_{24}N_{10}Ni$ (py derivative): C, 65.98; H, 3.69; N, 21.37. Found: C, 66.3; H, 3.84; N, 21.6. Calcd for $C_{38}H_{28}N_{10}Ni$ (4-Mepy derivative): C, 66.78; H, 4.13; N, 20.50. Found: C, 66.6; H, 4.2; N, 20.3.

Preparation of the Cu(II) and Zn(II) analogues was attempted in a similar way, but the starting materials Cu(hp) and $Zn(hp)H_2O$ were recovered unchanged after crystallization. The Cu-doped Ni(II) complexes were prepared by cocrystallization using ca. 2% of $^{63}Cu(hp)$ (^{63}Cu obtained from Oak Ridge National Laboratories in the form of ^{63}CuO). The EPR spectra were measured on freshly crystallized samples. After 1 or 2 days, $Cu/Ni(hp)(py)_2$ gives a drastically different spectrum, presumably due to loss of the coordinated base.

Elemental analyses and physical measurements were performed as previously reported.[1]

Crystal Data. $C_{36}H_{24}N_{10}Ni$: mol wt. 655.368, monoclinic, $a = 16.418$ (7) Å, $b = 9.727$ (4) Å, $c = 18.632$ (6) Å, $\beta = 94.59$ (3)°, $V = 2966$ (2) Å^3, $\rho_{obsd} = 1.47$ (2) g·cm^{-3} (by flotation), $Z = 4$, $\rho_{calcd} = 1.468$ g·cm^{-3}, $F(000) = 338$, space group $P2_1/c$ (No. 14), systematic presences $h0l$ ($l = 2n$), $0k0$ ($k = 2n$), Mo Kα radiation $\lambda = 0.71069$ Å, μ(Mo Kα) = 7.19 cm^{-1}.

Structure Solution and Refinement. Diffraction data were collected from a crystal of approximate dimensions 0.1 × 0.1 × 0.5 mm on a Syntex $P2_1$ diffractometer with graphite-monochromated Mo Kα radiation by the θ–2θ scan technique ($2\theta_{max} \le 50$).

Intensity data were corrected for Lorentz and polarization effects. Given the low value of μ and the crystal dimensions, no absorption correction was applied. A set of 1726 independent reflections ($I > 3\sigma(I)$) was used for solution by standard heavy-atom techniques. The structure was refined by a full-matrix least-squares method based on minimization of the function $w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F_o)$ and

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Table I. Fractional Atomic Coordinates ($\times 10^4$) for Bis(pyridine)(hemiporphyrazinato)nickel(II)

atom	*x/a*	*y/b*	*z/c*
Ni	2511 (2)	1344 (2)	4478 (1)
N(1)	3317 (8)	436 (14)	3916 (7)
N(2)	1521 (9)	304 (15)	3828 (7)
N(3)	1690 (8)	2266 (14)	5031 (7)
N(4)	3480 (8)	2311 (13)	5149 (7)
N(5)	4558 (8)	1499 (14)	4430 (8)
N(6)	2469 (8)	−1006 (14)	3132 (7)
N(7)	431 (8)	1552 (15)	4373 (7)
N(8)	2544 (9)	3422 (15)	5942 (7)
N(9)	2527 (9)	−446 (13)	5200 (7)
N(10)	2469 (9)	3093 (15)	3693 (8)
C(1)	4141 (10)	715 (16)	3970 (9)
C(2)	4539 (11)	−88 (16)	3410 (9)
C(3)	5341 (11)	−177 (20)	3243 (11)
C(4)	5467 (13)	−1039 (19)	2672 (11)
C(5)	4874 (12)	−1764 (18)	2295 (11)
C(6)	4070 (11)	−1701 (17)	2499 (9)
C(7)	3918 (11)	−858 (17)	3052 (9)
C(8)	3144 (11)	−472 (17)	3380 (8)
C(9)	1686 (10)	−727 (16)	3356 (8)
C(10)	1065 (10)	−1566 (17)	3037 (8)
C(11)	259 (11)	−1338 (21)	3159 (9)
C(12)	93 (12)	−281 (21)	3585 (9)
C(13)	696 (11)	529 (17)	3928 (9)
C(14)	854 (10)	2258 (18)	4860 (9)
C(15)	458 (11)	3167 (16)	5367 (8)
C(20)	1090 (10)	3633 (20)	5842 (8)
C(16)	−345 (11)	3564 (20)	5407 (9)
C(17)	−498 (11)	4460 (19)	5955 (10)
C(18)	146 (12)	4936 (20)	6436 (10)
C(19)	945 (13)	4560 (20)	6376 (10)
C(21)	1863 (12)	3094 (18)	5605 (8)
C(22)	3320 (10)	3113 (17)	5741 (9)
C(23)	3953 (10)	3793 (20)	6145 (10)
C(24)	4752 (11)	3691 (23)	5984 (11)
C(25)	4939 (12)	2902 (19)	5384 (10)
C(26)	4278 (10)	2273 (17)	5000 (9)
C(27)	3189 (11)	−1233 (19)	5326 (8)
C(28)	3193 (11)	−2432 (20)	5691 (10)
C(29)	2504 (12)	−2901 (18)	5985 (10)
C(30)	1838 (11)	−2076 (19)	5898 (9)
C(31)	1851 (11)	−899 (19)	5488 (9)
C(32)	2266 (11)	2908 (22)	2998 (9)
C(33)	2229 (12)	4031 (22)	2509 (11)
C(34)	2435 (11)	5268 (21)	2746 (11)
C(35)	2672 (12)	5513 (19)	3462 (12)
C(36)	2678 (12)	4400 (20)	3909 (10)

Table II. Some Relevant Bond Distances (Å) and Angles (deg) in Bis(pyridine)(hemiporphyrazinato)nickel(II)

Ni-N(1)	1.96 (1)	N(1)-Ni-N(2)	90.0 (5)
Ni-N(2)	2.19 (2)	N(2)-Ni-N(3)	89.5 (6)
Ni-N(3)	1.98 (1)	N(3)-Ni-N(4)	90.1 (5)
Ni-N(4)	2.16 (1)	N(4)-Ni-N(1)	90.4 (5)
Ni-N(9)	2.20 (2)	N(2)-Ni-N(9)	86.8 (5)
Ni-N(10)	2.24 (2)	N(4)-Ni-N(10)	91.7 (5)
N(5)-C(1)	1.30 (2)	C(1)-N(5)-C(26)	129 (1)
N(5)-C(26)	1.41 (2)	C(8)-N(6)-C(9)	127 (1)
N(6)-C(8)	1.28 (2)	C(13)-N(7)-C(14)	129 (1)
N(6)-C(9)	1.41 (2)	C(21)-N(8)-C(22)	127 (1)
N(7)-C(13)	1.39 (2)		
N(7)-C(14)	1.29 (2)		
N(8)-C(21)	1.28 (2)		
N(8)-C(22)	1.39 (2)		

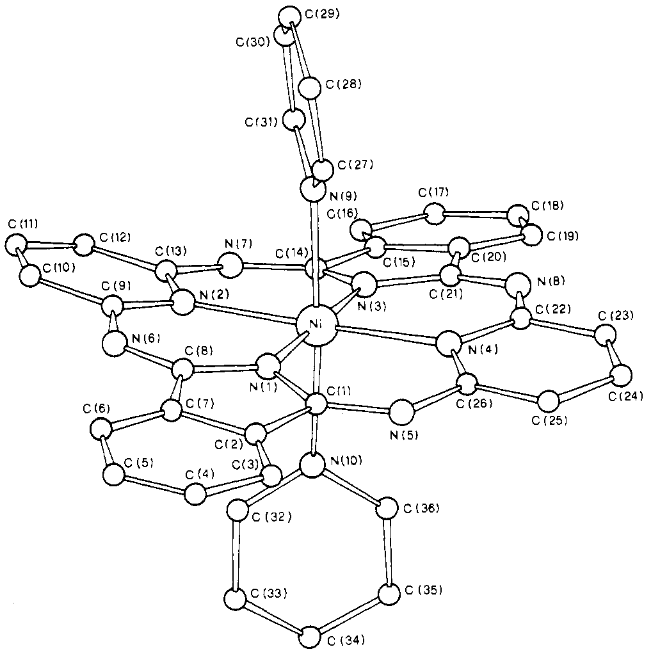

Figure 1. Stereoscopic view of the molecular structure of bis(pyridine)(hemiporphyrazinato)nickel(II).

F_o and F_c are the observed and calculated structure factor amplitudes, respectively. Anisotropic temperature factors were included in the refinement for all non-hydrogen atoms. Hydrogen atoms were included in the refinment in their geometrically calculated positions (C–H = 0.95 Å). The final R is $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.0534$, and the ratio of data to parameters is 4.07:1. Atomic coordinates for all non-hydrogen atoms are listed in Table I. Important bond distances and angles are given in Table II.

Results and Discussion

Description of the Structure. The molecular structure of Ni(hp)(py)$_2$ is displayed in Figure 1. Its essential feature is the rhombically compressed stereochemistry around nickel. The two metal–isoindole nitrogen distances are 1.97 Å and locate the compression axis of the molecule. The other Ni–N bond distances are 2.18 and 2.22 Å, respectively, with the macrocyclic and adduct pyridine nitrogens.

Comparison with the molecular structure of the diamagnetic four-coordinate Ni(hp)[2] shows that transition to the paramagnetic six-coordinate configuration, and hence transfer of one electron from the $|z^2\rangle$ to the $|x^2 - y^2\rangle$ orbital, causes radial expansion of the macrocycle. In Ni(hp) the metal–nitrogen bond distances are respectively 1.90 (isoindole N's) and 1.985 Å (pyridine N's), this latter value being possible because of severe distortion of the ligand from planarity. Would the macrocycle be perfectly planar, the nickel pyridine nitrogens distance would rise to ca. 2.3–2.4 Å.[2]

Turning to Ni(hp)(py)$_2$, we note that the hp ligand expands in an asymmetric fashion, the Ni–N bonds stretching being three times larger for the pyridine than for the isoindole nitrogens, 0.20 vs. 0.07 Å. Furthermore, the lengthening of the macrocyclic pyridine bonds allows the hp ligand to assume a less strained conformation. The deviations from planarity are qualitatively similar in the two compounds but much less pronounced in the pyridine adduct. The Ni atom and the four coordinated hp nitrogens are closely coplanar. The macrocyclic pyridine rings are tilted out of this plane by 12 and 7° in the same direction. The two isoindole rings, which are also tilted of about 8°, are rotated around the N(1)–Ni–N(3) axis in opposite direction so as to be 16° from one another.

The deviation of hp from planarity can be described as a quasi-D_{2d} ruffling, the extent of the distortion being reflected in the displacement of the aza nitrogens above and below the Ni–N(4) plane.[5] The average value of this displacement is 0.2 ± 0.04 Å.

The two axial pyridine rings form angles respectively of 30 and 60° with the Ni–N(1) direction and are rotated by 90° from one another. Within the ligand the bond distances of the bridging nitrogen atoms to the pyridine and isoindole ring

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Table III. 35-GHz EPR Parameters of Pyridine and 4-Methylpyridine Adducts of ^{63}Cu(hp) in Nonoriented Matrices[a]

compd	K	g_1	g_2	g_3	A^{Cu}_1	A^{Cu}_2	A^{Cu}_3	b	r,[d] %
Cu/Ni(hp)(py)$_2$	300	2.225	2.131	2.017	71	45	133	0.250	25
Cu/Ni(hp)(py)$_2$	110	2.222	2.143	2.011	62	43	141	0.195	15
Cu(hp)(py)$_2$[b]	300		2.116[c]			20			
Cu(hp)(py)$_2$	110	2.225	2.135	2.030	90	50	123	0.326	42
Cu/Ni(hp)(4-Mepy)$_2$	300	2.228	2.133	2.017	76	42	129	0.261	27
Cu/Ni(hp)(4-Mepy)$_2$	110	2.229	2.140	2.014	71	42	136	0.223	20
Cu(hp)(4-Mepy)$_2$[b]	300		2.117[c]			20			
Cu(hp)(4-Mepy)$_2$	110	2.217	2.100	2.035	97	42	109	0.405	66

[a] Hyperfine components in units of 10^{-4} cm^{-1}. [b] N base/toluene 5:1 solutions. [c] Isotropic parameters. [d] $r = b^2/0.5^2$; see text.

systems are largely different. Average values are 1.39 and 1.29 Å, respectively. In agreement with previous spectroscopic[6] and structural[3,4] findings this shows that the major contribution to the actual structure is given by the incompletely conjugated formula illustrated in I and that the hp ligand is essentially nonaromatic.

EPR Results. The optical spectra of hemiporphyrazinato complexes are invariably dominated by ligand- and charge-transfer transitions down to ca. 16 000 cm^{-1}. Both as solids or in solution of the neat base, Ni(hp)(py)$_2$ and Ni(hp)(4-Mepy)$_2$ exhibit a single d–d absorption centered at ca. 10 200 cm^{-1}. This band, which is assigned as the $^3B_{1g} \rightarrow {}^3B_{2g}$ transition, is not expected to be diagnostic of the compressed stereochemistry present.[7] Similar considerations hold for Cu(hp), which upon dissolution in pyridine or 4-methylpyridine, gives a single, broad, uninformative band at ca. 12 500 cm^{-1}.

With the aim of comparing the stereochemistries of these and other six-coordinated hp derivatives for which structural information is not available, we recorded the EPR spectra of ^{63}Cu(hp) in frozen solutions of the bases and diluted in Ni(hp)(py)$_2$ and Ni(hp)(4-Mepy)$_2$.

Dilution into paramagnetic hosts, although seldom used, has long been known to be possible, provided that the paramagnetic host relaxes much faster than the resonating ion at the temperature of the measurements.[8,9] Experimentally, no guest–host interaction could be detected in the spectra recorded at room temperature, whereas cooling down to ca. 110 K gave somewhat less resolved signals.

At the X- and Q-band frequencies both frozen-solution and solid-state samples gave strongly rhombic signals, with one g value close to g_e and an unusually small A^{Cu} anisotropy, suggesting extensive d-orbital mixing.

From a procedure outlined before[10] and by assigning the magnetic axes 123 as xyz, the experimental parameters reported in Table III have been used to calculate the mixing coefficients in a ground-state orbital of the type $a|z^2\rangle + b|x^2 - y^2\rangle$. Contributions from other d orbitals have also been taken into account, but they are usually negligible.

Referring to the coordinate system of I, the two limiting situations, i.e. tetragonally compressed octahedron along z and tetragonally elongated octahedron along x, are described by the two sets of coefficients $a = 1$, $b = 0$ and $a = 3^{1/2}/2$, $b = 1/2$. The corresponding ground states are $|z^2\rangle$ and $|z^2 - y^2\rangle$ (or the familiar $|x^2 - y^2\rangle$, after interchanging the z and x axes). In our case, due to the rhombic symmetry of the hp ligand, the latter geometry cannot be achieved and the actual limit is given by the rhombically elongated symmetry of Cu(hp).[1]

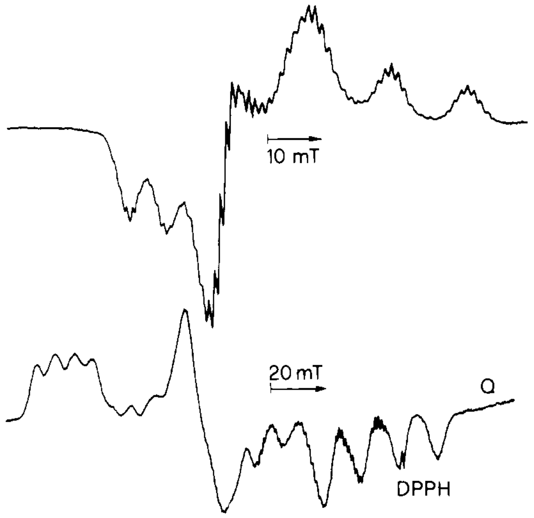

Figure 2. X- and Q-band room-temperature EPR powder spectra of ^{63}Cu/Ni(hp)(py)$_2$. Additional low-intensity signals are present in the Q-band spectrum. Their origin has not been identified.

The frozen-solution spectra were recorded in various N base/toluene mixtures, the lowest N-base concentration being 50% by volume. In this range the spectra were independent from the concentration of base and qualitatively similar to the solid-state ones, showing that, in these conditions, Cu(hp) is stable as a bisadduct derivative.

At 110 K ^{63}Cu(hp)(py)$_2$ gives $b = 0.326$. The ratio $r = b^2/0.5^2$ indicates that the $|x^2 - y^2\rangle$ mixing is 42% of that required by a purely elongated geometry and provides a quantitative estimate of the rhombic distortion present. The extent of the d mixing is even larger in the 4-Mepy derivative ($r = 66\%$), showing that these are purely rhombic compounds with the $|z^2\rangle$ and $|x^2 - y^2\rangle$ orbitals giving similar contributions to the actual ground state.

Dilution of ^{63}Cu(hp) into Ni(hp)(py)$_2$ or Ni(hp)(4-Mepy)$_2$ gives spin-Hamiltonian parameters much closer to the axially compressed limit. Sample spectra are given in Figure 2. The room-temperature calculated b and r values for ^{63}Cu/Ni(hp)(py)$_2$ are 0.250 and 25%, respectively. Moreover the spectrum is temperature dependent, and the above parameters lower to 0.195 and 15% at 110 K.

These results imply that the structures of the Ni and Cu complexes are somewhat different and that the dilution process forces the copper ion to assume a less rhombic geometry. As expected low temperatures promote a more efficient deformation of this geometry.

The difference in rhombicity can be reasonably ascribed to a variation of the bond distance between the metal and the nitrogens of the adduct pyridine molecules. This is in line with the different tendency of Ni(hp) and Cu(hp) toward six-coordination and with their different orbital populations. With respect to nickel, the doubly occupied out-of-plane copper orbital allows approach of axial ligands to a very limited extent and gives rise to more rhombic six-coordinated geometries.

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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.

Registry No. Ni(hp)(py)$_2$, 88904-93-2; Ni(hp)(4-Mepy)$_2$, 88904-94-3; Cu, 7440-50-8.

Supplementary Material Available: Listings of crystallographic data, anisotropic thermal parameters, bond lengths and angles, and observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, University of Denver, Denver, Colorado 80208,
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Metal–Nitroxyl Interactions. 35. Conformational Effects on Spin–Spin Interaction in Spin-Labeled Copper Salicylaldimines

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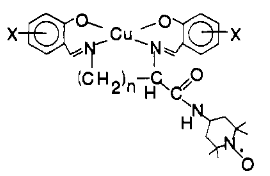
Received June 14, 1983

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

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

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