

Measurements of Resonance Raman Spectra. The spinning cell was rotated at the rate of 1800 rpm.²⁶ The ferrous-gable porphyrin solution prepared as described above was excited by Ar laser irradiation at 4579 Å (80 mW) with a 458-nm pass filter. Resonance Raman spectra were recorded between 175 and 675 cm⁻¹ (scanning speed, 2.5 cm⁻¹ per min; time constant, 32 s; slit height, 10 mm; slit widths were kept at 400, 500, and 400 μm). Under the conditions, Raman spectra were satisfactory. However, at the low concentrations (ca. 10⁻³ M) of the ferrous porphyrins, intensities of the peaks in resonance Raman spectra were too weak to determine the band intensity of ν_{Fe-1m}.

CO Affinity Measurements. All procedures of sample preparation were carried out in a Vacuum Atmospheres drybox, the internal atmosphere of which was constantly circulated through a freshly prepared MnO column (20 × 40 mm) settled inside to remove traces of oxygen.

In a typical experiment, Fe^{II}-gable porphyrin dissolved in DMF (ca. 5 × 10⁻⁶ M, 2 mL) and a DMF solution of an axial ligand (0.5 × 10⁻³ M, 20 μL–0.2 mL) were placed in a 10-mm quartz cell equipped with a two-way high-vacuum stopcock.

The cell was then connected with a vacuum line, and the atmosphere in the cell was replaced by CO/Ar via repeated evacuation at 1 × 10⁻⁵

torr (with external cooling at -40 °C by use of a dry ice-acetone bath) followed by back-flushing of an Ar-CO gas mixture through the MnO column (8 × 100 mm). The stopcock was closed, and the solution was warmed up to 25 °C. Then, the electronic spectra of the solution were recorded.

The volume ratio of the Ar-CO gas mixture was determined by GC in the following conditions: 0.5 mL of gas mixture; molecular sieve 13X (1.5 m), He carrier (0.6 kg/cm²), column temperature 30 °C.

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Registry No. 3a-4a, 97467-44-2; 3a-4b, 104267-50-7; 3a-4c, 104241-86-3; 5 (i = 2), 104241-87-4; 5 (i = 4), 75529-04-3; 5-CO (i = 2), 104267-51-8; 5-CO (i = 4), 75529-00-9; TPP-Fe^{II}-DMI, 72186-60-8; TPP-Fe^{II}-(1MI)₂, 54032-54-1; CO, 630-08-0.

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Unusual Magnetic Properties of the Adduct of Copper Chloride with 2-Phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl 3-Oxide

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Abstract: A stable adduct was isolated from copper(II) chloride and the stable free radical 2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide. The stoichiometry of the adduct is 1:2, and a crystal structure analysis has shown the copper ion to be four planar coordinated by two chlorine atoms and two oxygen (nitroxyl) atoms. The nitroxyl ligands are bound with a short Cu-O distance of 1.988 (1) Å. Magnetic measurements show that this material is in a doublet state from 30 to 300 K. At lower temperature a spin pairing process became operative. Crystal data: monoclinic, *P*₂₁/*n*, *a* = 11.988 (4) Å, *b* = 10.878 (3) Å, *c* = 11.788 (4) Å, β = 106.14 (2)°, *Z* = 2.

Although a large number of relatively stable complexes of transition-metal ions with free radical have been described,² those classes which are sufficiently stable for isolation and characterization remain quite limited. Notable among these are the adducts of organometallic Lewis acid with dialkyl nitroxides.³⁻¹² Special

interest has been devoted to those in which the metal ion is paramagnetic and the nitroxide metal coordinated.⁴⁻¹³ These studies allow the opportunity of obtaining first hand information on metal-ligand interaction monitored by the magnetic coupling with the metal electrons.

Indeed several different behaviors have now been observed, ranging from a complete pairing of the unpaired electrons to an intermediate coupling, which can be either ferro-^{9,12,14} or anti-ferromagnetic^{5,7,10,13} depending on the nature of the metal ion and on the relative geometries of the magnetic orbitals on the radical and on the metal ion.

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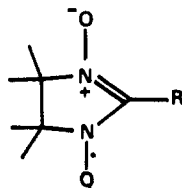


Figure 1. General formula of nitronyl nitroxides (NITPHEN: R = phenyl).

One of the most exciting opportunities given by systems like these is that of designing novel magnetic materials, a field which is now expanding for both theoretical reasons and for possible applications.

With these considerations in mind we decided to explore the ligand ability of nitronyl nitroxides, whose general formula is given in Figure 1.

The nitronyl nitroxides¹⁵⁻¹⁷ are more basic than the dialkyl homologues, and one can expect to obtain tighter binding in complexes with weak Lewis acids. Furthermore, the two nitrogen atoms of the ring are equivalent sites of coordination. As confirmed by EPR spectroscopy the electronic structure is delocalized, and one might expect to obtain compounds in which several metal ions are linked by an organic framework which possesses an unpaired electron leading to unprecedented magnetic properties.

Few reports of the coordination capabilities of the nitronyl nitroxides have appeared in the literature. In these studies the compounds with R = 2-, 3-, or 4-pyridyl^{6,17} were specially designed to avoid coordination by the *O*-nitroxyl oxygen atom. In one of these studies⁶ it is mentioned that R = phenyl derivative, 2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide, NITPHEN, does not coordinate readily with the copper atom of the strong Lewis acid copper hexafluoroacetylacetonate, Cu(hfac)₂.

In the study we report here we used NITPHEN (Figure 1) in which only the nitroxide group can coordinate to the metal ion. Although copper chloride is not as strong a Lewis acid as Cu(hfac)₂, we found that in the 2:1 adduct the nitroxyl group is coordinated to the copper atom with a short bond leading to unusual magnetic properties.

Experimental Section

Preparation of Dichlorobis(2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide)copper(II), CuCl₂(NITPHEN)₂. 2-Phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide, NITPHEN, was prepared by a previously reported procedure.¹⁵ The adduct was prepared by adding a solution of 400 mg (1.7 mmol) of NITPHEN in 5 mL of absolute ethanol to a solution of 300 mg (1.75 mmol) of copper(II) chloride dihydrate in 5 mL of absolute ethanol. The resulting deep red solution was cooled for 12 h at -4 °C, during which time the adduct crystallized as large brown crystals. Anal. Calcd for CuCl₂(C₁₃H₁₇N₂O₂): C, 51.93; H, 5.70; N, 9.32; O, 10.65; Cl, 11.78; Cu, 10.57. Found: C, 51.80; H, 5.65; N, 9.38; O, 10.73; Cl, 11.83; Cu, 10.35.

X-ray Data Collection and Reduction. Weissenberg photographs taken for a regularly shaped crystal of the title compound (0.18 × 0.20 × 0.23 mm) revealed Laue symmetry and exhibited systematic absences (*h*0*l*: *h* + *l* ≠ 2, 0*k*0 ≠ 2*n*) which were only consistent with the monoclinic space group *P*₂₁/*n*. The same crystal was mounted on an Enraf-Nonius CAD-4 four circle diffractometer with monochromatized Mo K α radiation. Accurate cell constants were derived from least-square refinement of the setting angles of 25 reflections and are reported in Table I with other crystal data.

The intensities of 3124 independent reflections were collected. Two standard reflections were periodically checked and showed no significant discrepancy. The data were corrected for the Lorentz polarization factor but not for the absorption or extinction. Among the independent reflections collected 2126 had *F*_o > 4 σ (*F*_c) and were used to refine the structural parameters.

Structure Solution and Refinement. The Harker section of the Patterson map allowed the determination of the position of the copper,

Table I. Crystallographic Data

formula	C ₂₆ H ₃₄ Cl ₂ CuN ₄ O ₄
mol wt	601.03
cryst syst	monoclinic
space group	<i>P</i> ₂ ₁ / <i>n</i>
<i>V</i> , Å ³	1476.6
<i>a</i> , Å	11.988 (4)
<i>b</i> , Å	10.878 (3)
<i>c</i> , Å	11.788 (4)
β , deg	106.14 (2)
<i>Z</i>	2
<i>d</i> (calcd), g/cm ³	1.352
radiant	Mo K α (λ = 0.7107 Å), graphite monochromtr
cryst. detctr dist, mm	368
detctr window width, mm	2.25 + 3.5 tg θ
take of angle, deg	6
scan mode	ω
max. Bragg angle, deg	1 < θ < 25
scan angle, deg	0.80 + 0.35 tg θ
scan speed, deg/min	variable 0.62-5
test reflctns	402, $\bar{2}$ 33

Table II. Atomic Coordinates (×10⁴) for CuCl₂(NITPHEN)₂

	<i>x</i>	<i>y</i>	<i>z</i>	<i>b</i> _{eq}
Cu	0 (0)	0 (0)	0 (0)	3.47
Cl	-1859 (1)	33 (1)	-886 (1)	4.79
O1	-397 (1)	859 (1)	1325 (1)	3.91
O2	1507 (2)	-399 (2)	5092 (2)	5.49
N2	1196 (2)	244 (2)	4158 (2)	4.11
N1	263 (2)	848 (2)	2411 (1)	3.77
C1	482 (2)	-116 (2)	3119 (2)	3.69
C2	739 (2)	2024 (2)	3008 (2)	4.14
C3	1675 (2)	1515 (2)	4093 (2)	4.12
C4	1794 (2)	2187 (3)	5247 (2)	5.27
C5	2863 (2)	1331 (3)	3894 (2)	5.05
C6	-268 (3)	2656 (3)	3324 (2)	5.23
C7	1189 (3)	2826 (2)	2172 (2)	5.51
C8	21 (2)	-1357 (2)	2823 (2)	4.10
C9	676 (2)	-2371 (2)	3336 (3)	4.95
C10	253 (3)	-3537 (3)	3045 (3)	6.16
C11	-812 (3)	-3697 (3)	2246 (3)	7.08
C12	-1468 (3)	-2713 (3)	1746 (3)	6.30
C13	-1059 (2)	-1529 (3)	2024 (2)	5.05

chlorine, and one of the oxygen atoms of the asymmetric unit. A first refinement with these three atoms resulted in a *R* value of 0.36. Then all the missing non-hydrogen atoms were located on a difference Fourier map. The structure was refined with the ORXFLS3 program¹⁸ with Cu (anomalous scattering factor included), C, N, and O atoms anisotropic using the 2126 selected reflections. At this stage of refinement the *R* values ($R = \sum |F_o - F_c| / \sum |F_o|$; $R_w = |\sum w(F_o - F_c)^2 / \sum w F_o^2|^{1/2}$) were *R* = 0.060 and *R*_w = 0.089. In the latter stages of refinement hydrogen atoms were included at idealized positions (C-H = 0.95 Å, tetrahedral or trigonal angles as appropriate, methyl group orientations defined by difference Fourier maps) but were not refined. Finally the *R* and *R*_w values were lowered to 0.034 and 0.043, respectively.

Magnetic Susceptibility Measurements. Magnetic susceptibilities were measured between 6 and 300 K by using an SHE superconducting SQUID susceptometer at a field strength of 0.5 T. Data were corrected for the magnetization of the sample holder and for diamagnetic contributions which were estimated for Pascal constants.

Electron Paramagnetic Measurements. EPR spectra of CuCl₂(NITPHEN)₂ were recorded with a Bruker ER200 and a Varian E9 Spectrometer at X- and Q-band, respectively. Low-temperature spectra were obtained with the use of an Oxford Instruments ESR9 continuous-flow cryostat. EPR suitable single crystals of the title compound were oriented with a Philips PW 1100 diffractometer and were found to have well developed (110) and ($\bar{1}$ 10) faces.

Results

Crystal Structure. Final values of the positional parameters are reported in Table II. Bond distances and angles are listed respectively in Tables III and IV. Tables of observed and cal-

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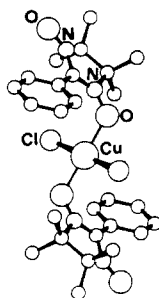
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Table III. Bond Distances (Å) for $\text{CuCl}_2(\text{NITPHEN})_2$

Cu	Cl	2.184 (0)
Cu	O1	1.989 (1)
O1	N1	1.305 (0)
O2	N2	1.270 (1)
N1	C1	1.321 (1)
N1	C2	1.495 (2)
N2	C1	1.343 (1)
N2	C3	1.507 (2)
C1	C8	1.464 (2)
C2	C7	1.523 (2)
C2	C6	1.524 (2)
C2	C3	1.550 (1)
C3	C4	1.516 (1)
C3	C5	1.520 (3)
C8	C13	1.387 (2)
C8	C9	1.391 (2)
C9	C10	1.374 (3)
C10	C11	1.372 (3)
C11	C12	1.362 (3)
C12	C13	1.385 (3)

Figure 2. View of the structure of dichlorobis(2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide)copper(II), $\text{CuCl}_2(\text{NITPHEN})_2$.

culated structure factors and anisotropic thermal parameters are deposited as supplementary material.

Structure Description. The crystal structure of dichlorobis(2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide)copper(II), $\text{CuCl}_2(\text{NITPHEN})_2$, consists of discrete four coordinate monomers. The molecule is centrosymmetric, the copper atoms being located at the centers of symmetry of the cell. A view of the molecule is shown in Figure 2. The copper ion is bound to two chlorine ions with a Cu–Cl distance of 2.185 Å and two nitroxyl oxygen atoms with a Cu–O bond distance of 1.988 Å. These values are well within the ranges previously observed for chlorine–copper¹⁹ and copper–oxygen^{8,10,13} (nitroxyl) bond lengths. The mean plane of the five-membered nitronyl ring is nearly perpendicular (80°) to the plane defined by the four-coordinated atoms. The angle between the CuO_1 and the O_1N_1 bonds is 123.6°, close to the value reported for some other metal–nitroxyl coordinated compounds.^{7,8,10,13} The five-membered nitronyl ring is thus bent toward the chlorine ion. In this location the chlorine atom has several intramolecular contacts with methyl hydrogen atoms (2.675 and 2.848 Å) which are smaller than or close to the sum of the van der Waals radii.

The overall features of the nitronyl nitroxide are almost identical with those previously described for the uncoordinated free radical.²⁰ The five-atom fragment $\text{O}_1\text{—N}_1\text{—C}_1\text{—N}_2\text{—O}_2$ is found to be very nearly planar; the least-squares plane defined by these atoms shows a maximum deviation of 0.03 Å. The bonds around the nitrogen atoms are also planar as shown by the sum of the bond angles (359.6° for N_1 , 359.9° for N_2). On the other hand the five-membered heterocyclic ring is not planar; the tetramethylethylene moiety is twisted out of the $\text{O}_1\text{—N}_1\text{—C}_1\text{—N}_2\text{—O}_2$ plane. The methyl groups are thus staggered relative to one another presumably in order to relieve steric repulsion.

The phenyl plane makes an angle of 32° with the $\text{O}_1\text{—N}_1\text{—C}_1\text{—N}_2\text{—O}_2$ plane suggesting some resonance interactions between

Table IV. Bond Angles (deg) for $\text{CuCl}_2(\text{NITPHEN})_2$

O1	Cu	O1	180.00 (1)
O1	Cu	Cl	86.13 (4)
O1	Cu	Cl	93.87 (4)
O1	Cu	Cl	93.87 (4)
O1	Cu	Cl	86.13 (4)
Cl	Cu	Cl	180.00 (1)
O1	N1	C1	125.93 (13)
O1	N1	C2	120.15 (11)
C1	N1	C2	113.56 (7)
O2	N2	C1	126.03 (14)
O2	N2	C3	121.71 (9)
C1	N2	C3	112.15 (8)
N1	C1	N2	107.95 (13)
N1	C1	C8	125.91 (7)
N2	C1	C8	126.14 (10)
N1	C2	C7	110.07 (7)
N1	C2	C6	106.04 (14)
N1	C2	C3	100.19 (11)
C7	C2	C6	110.32 (14)
C7	C2	C3	115.67 (15)
C6	C2	C3	113.63 (7)
N2	C3	C4	109.82 (9)
N2	C3	C5	105.88 (13)
N2	C3	C2	99.84 (11)
C4	C3	C5	110.09 (12)
C4	C3	C2	115.74 (14)
C5	C3	C2	114.47 (9)
C13	C8	C9	119.76 (16)
C13	C8	C1	120.40 (14)
C9	C8	C1	119.84 (14)
C10	C9	C8	119.93 (16)
C11	C10	C9	119.83 (23)
C12	C11	C10	120.89 (26)
C11	C12	C13	120.32 (20)
C12	C13	C8	119.27 (17)

the phenyl ring π -system and the N-oxide–N-oxyl system. This value of 32° brings the ortho hydrogen atoms on the phenyl ring to within 2.42 Å of O_2 and 2.37 Å of O_1 , distances which are smaller than the sum (2.6 Å) of the van der Waals radii of the oxygen and hydrogen atoms.

Most of the bond lengths and bond angles are normal and need no further comment. However a significant difference is found between the two nitrogen–oxygen bond lengths. The bond distance in the coordinated NO group is longer by 0.03 Å than the bond distance of the uncoordinated one.

Finally some short intermolecular contacts can be seen between the phenyl and the methyl groups of one molecule and the chlorine and O_2 (uncoordinated) oxygen atoms of another molecule. Of special interest are the short intermolecular distances observed between one meta hydrogen atom of the phenyl ring and a chlorine atom (2.844 Å) and between the second meta hydrogen atom and a nitronyl O_2 -oxygen atom (2.454 Å).

Also relevant to the discussion of the magnetic properties of $\text{CuCl}_2(\text{NITPHEN})_2$ are the distances between the individual paramagnetic centers. So the shortest copper–copper distance is that between the ion at the origin of the coordinates and that one reported by the axis, 5.76 Å. On the other hand, the shortest nitroxide–nitroxide contact is that between two oxygen atoms related by a translation along c , 3.94 Å.

Magnetic Susceptibility Data. Table SI of magnetic measurements is included with the supplementary material. In the temperature range investigated, 6–300 K, the molar magnetic susceptibility χ_M increases, reaches a maximum at 14 K, and then decreases as the temperature is lowered. As shown in Figure 3, the variation of $1/\chi_M$ vs. T follows a Curie law down to 30 K; therefore, from 30 to 300 K the magnetic moment is constant and equal to 1.76 μ_B , close to the value expected for a doublet state. Below 30 K the magnetic moment decreases showing that a spin pairing process becomes operative.

Electron Paramagnetic Resonance Spectra. Single crystal spectra at X-band frequency show at room temperature generally only one signal for a given crystal orientation in the static magnetic field. Only in a few cases did we observe evidence for two signals,

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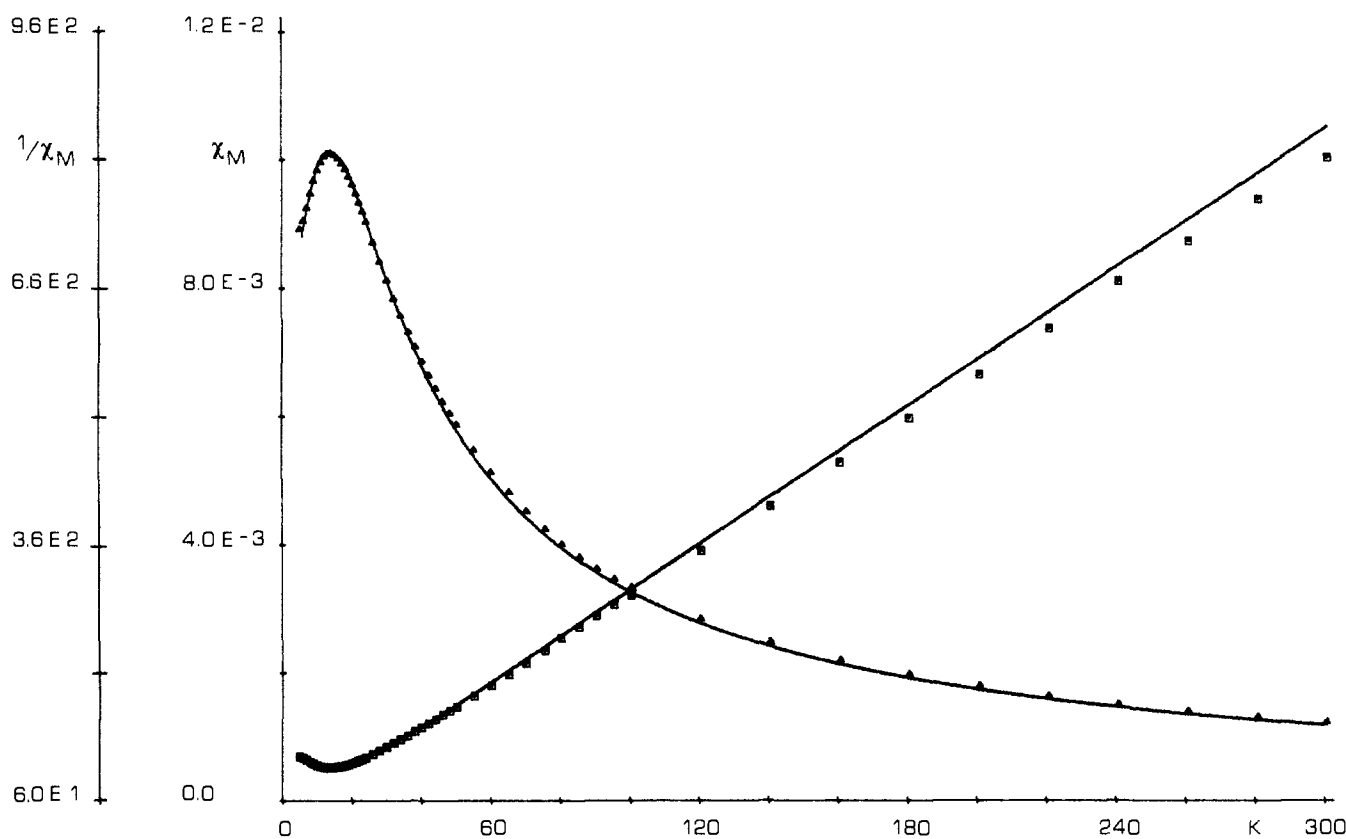


Figure 3. Temperature dependence of the magnetic susceptibility of dichlorobis(2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide)copper(II), $\text{CuCl}_2(\text{NITPHEN})_2$, in the form χ_M vs. T and $1/\chi_M$ vs. T . The curve represents the best fit of the experimental data obtained with $J' = 15.05$ (1) cm^{-1} , $g = 1.9957$ (4) (see text).

Table V. Principal g Values and Directions for $\text{CuCl}_2(\text{NITPHEN})_2$ at X-Band Frequency at 4.2 K^a

g_1	g_2	g_3
Site I		
1.997 (3) ^b	1.985 (2)	1.942 (4)
0.0205 (6)	0.7731 (1)	-0.6339 (3)
-0.5214 (5)	-0.5327 (9)	-0.6666 (1)
0.8530 (3)	-0.3442 (4)	-0.3922 (2)
Site II		
1.997 (2)	1.986 (4)	1.940 (3)
-0.6122 (4)	-0.3983 (7)	-0.6830 (1)
0.0909 (2)	0.8226 (3)	-0.5612 (6)
-0.7854 (5)	0.4057 (1)	0.4674 (2)

^a The directions are given by their direction cosines referred to the orthogonal crystal axes X , Y , and Z with Z parallel to c and X orthogonal to the (110) face. ^b The errors on g values and on direction cosines are reported in parentheses. They were calculated according to the method described by Schonland.³⁰

which however were never neatly resolved. On the other hand the Q-band spectra showed two signals for every crystal orientation as shown in Figure 4 as expected for a monoclinic cell.²¹ The transition fields were fit with a standard procedure to give the principal g values and the relative direction cosines shown in Table V. The resonances for the two inequivalent sites were fit independently. The agreement between the two sets of principal g values and directions can be considered as satisfactory, given the low accuracy with which the transition fields can be appreciated, since the lines are broad (30-60 G). According to one of the two possible sign choices in the monoclinic cell g_3 of site I makes an angle of 12° with the perpendicular to the $\text{Cu}-\text{O}_2-\text{Cl}_2$ plane, and for site II the angle is 6° . g_1 and g_2 values are very close to each other, so that their principal directions are obtained with less accuracy and are found to be fairly close to the bond directions.

Table VI. Principal g Values and Directions for $\text{CuCl}_2(\text{NITPHEN})_2$ at Q-Band Frequency at 300 K^a

g_1	g_2	g_3
Site I		
1.995 (5) ^b	1.990 (2)	1.954 (1)
-0.2129 (4)	0.6771 (2)	-0.7044 (1)
-0.2144 (2)	-0.7357 (7)	-0.6424 (8)
0.9532 (1)	-0.0143 (6)	-0.3018 (6)
Site II		
1.997 (8)	1.986 (4)	1.940 (3)
-0.4010 (4)	-0.6487 (1)	-0.6468 (4)
-0.2403 (1)	0.7558 (6)	-0.6090 (7)
-0.8840 (5)	0.0888 (2)	0.4590 (3)

^a The directions are given by their direction cosines referred to the orthogonal crystal axes X , Y , and Z with Z parallel to c and X orthogonal to the (110) face. ^b The errors on g values and on direction cosines are reported in parentheses. They were calculated according to the method described by Schonland.³⁰

We recorded also the single crystal spectra at X-band at liquid helium temperature. The signals are much narrower in this case, 2-3 G, and two resonances are resolved for every crystal orientation as shown in Figure 4. The same type of analysis outlined above yielded the principal g values and directions for the two sites given in Table VI. g_3 is calculated to make an angle of 5° with the perpendicular to the $\text{Cu}-\text{O}_2-\text{Cl}_2$ plane for site I and 2° for site II.

Comparing the room temperature Q-band and the liquid helium X-band data we see that the g tensor is not essentially changed. In the Q-band spectra at room temperature the signal of a nitroxide impurity is clearly resolved, with a hyperfine splitting into five lines, $A = 7.5$ G, corresponding to the hyperfine interaction of the unpaired electron with two equivalent ^{14}N .

Discussion

Dichlorobis(2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide)copper(II), $\text{CuCl}_2(\text{NITPHEN})_2$, is one of the few

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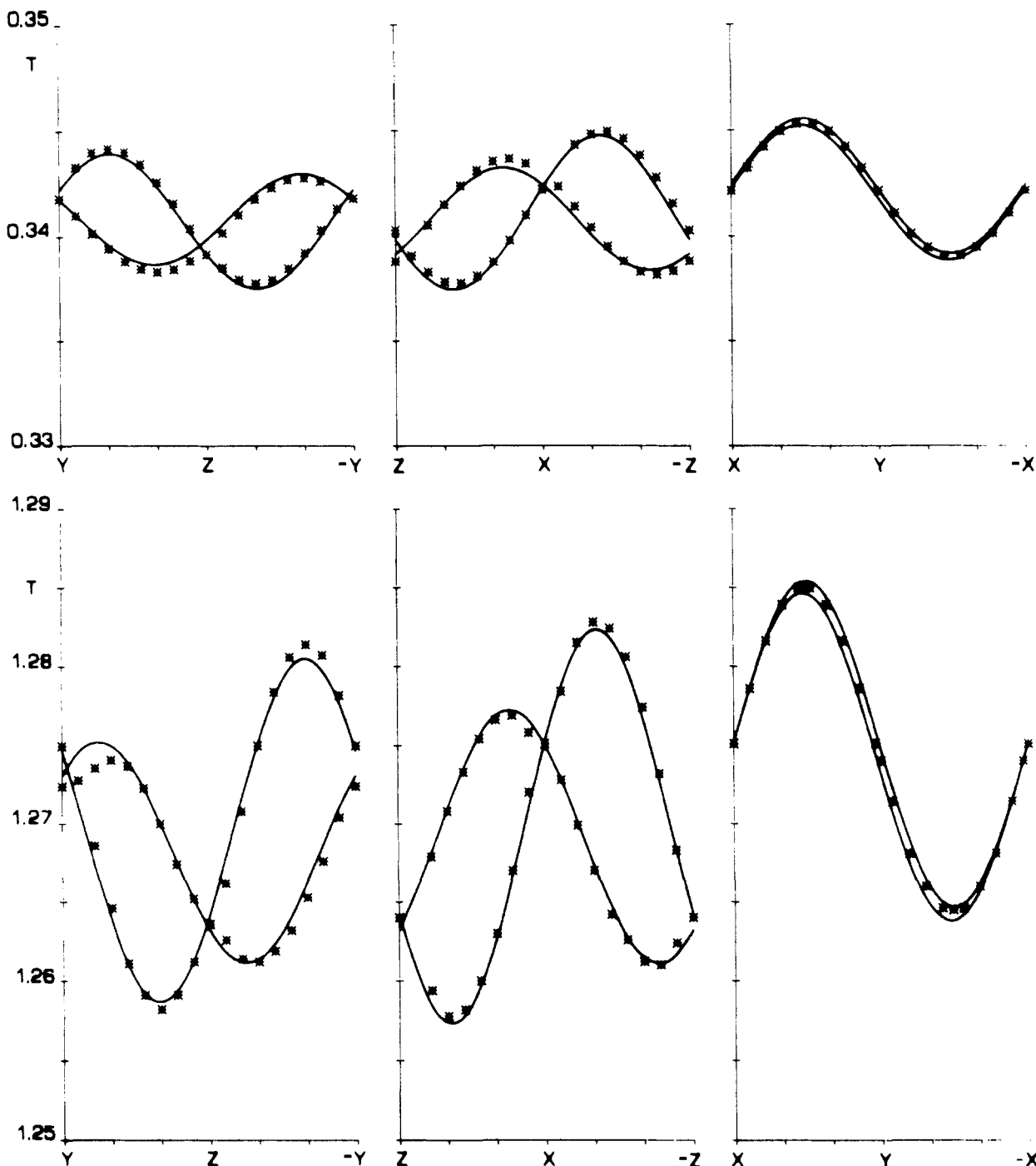


Figure 4. Angular dependence of the transition fields of dichlorobis(2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide)copper(II), $\text{CuCl}_2(\text{NIT-PHEN})_2$, at room temperature at Q-band frequency (bottom) and at 4.2 K at X-band frequency (top), in three orthogonal planes. X, Y, and Z are laboratory axes, with Z parallel to *c* and X orthogonal to the (110) face.

structurally characterized examples of molecules containing a covalent metal-nitroxyl bond. The coordinating ability of NIT-PHEN with the strong Lewis acid $\text{Cu}(\text{hfac})_2$ has been previously reported.^{6,21} We have not been able to obtain crystalline complexes or definite proof of complexation in solution by EPR spectroscopy. However the reaction with copper chloride proceeds readily in ethanol with the development of a brown-red color. We have investigated the UV-vis and EPR spectra of this solution. Dilute solutions gave the signals expected for the individual species. However the electronic spectrum of a concentrated solution showed a new band at 435 nm in addition to the lines from NIT-PHEN. The intensity of this new line is not proportional to the concentration and has been attributed to a LMCT transition. The same situation is observed for the EPR spectra. Dilute solutions showed only the nitroxide and the copper chloride signals while concentrated ones exhibited a new line ($g = 1.986$) the intensity of which

is also concentration dependent. The crystalline compound was only obtained from concentrated solutions (0.2 mol/L) at low temperatures ($-5/-10^\circ\text{C}$). The stoichiometry of the product was ascertained by elemental analysis and X-ray diffraction analysis.

Although the 435-nm transition in the electronic spectrum had sometimes been attributed to a Cu(III) species,⁶ the charge balance and symmetry require the two organic ligands to be neutral free radicals and the metal ion to be Cu(II) for the title compound. As mentioned above the O-coordinated NO bond (1.304 (2) Å) is longer by 0.03 Å than the uncoordinated one (1.270 (3) Å). As expected the two NO bonds are equal in the free radical (1.27 (2) Å)²⁰ and in the corresponding nitrosonium ion (1.225 (4) Å)²³.

(22) We have been able to isolate a 1:1 and 2:1 adducts of NIT-PHEN with $\text{Cu}(\text{hfac})_2$ (hfac = hexafluoroacetylacetonate).

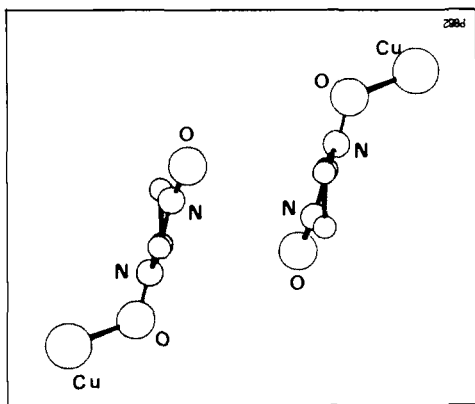


Figure 5. View of two interacting NITPHEN moieties responsible for the J' interaction.

The smaller bond length in the more oxidized compound is consistent with a higher bond order; therefore, in the copper complex the longer bond in the coordinated NO group must be related to a displacement of the spin density from the *N*-oxyl-*N*-oxide system toward the copper ion.

The rectangular bonding pattern of the metal ion with short Cu-O (nitroxyl) distances has not been observed before. In other short bonded nitroxyl-copper complexes that have been fully characterized^{8,10,13} the metal ion is unusually pentacoordinated, and only one is mononuclear.⁸ Therefore, the title compound is the simplest model for studying magnetic interactions between three paramagnetic centers.

Although the overall structure looks similar to some copper chloride adducts, and especially to one particular crystalline form of dichlorobis(pyridine *N*-oxide)copper(II),²⁴ it is unique among the class of the copper-nitroxyl bound complexes.

The nitronyl free radical has two equivalent sites of coordination, and the reason for obtaining discrete molecules is probably the result of steric hindrance and the geometry of binding of the nitroxyl group. Binding by a lone pair localized in a sp^2 hybrid orbital of the oxygen atom would be consistent with the Cu-O-N angle of 123.6° but is incompatible with the Cu-O₁-N₁, C₁-N₁-C₂ dihedral angle of 64.6° . This binding geometry which is qualitatively similar to that observed in other short bonded copper-nitroxyl complexes^{8,10,13} probably precludes the formation of chain by coordination of another metal ion to the second NO group. This geometry and the related electronic structure of the Cu-O (nitroxyl) bond is still poorly understood.

This complex contains three interacting paramagnetic centers arranged in a linear fashion. In each case examined so far where the metal-nitroxyl bond is short, substantial magnetic interaction between the metal ion and the nitroxyl radical has resulted. As expected on the basis of the short copper-nitroxide distance magnetic susceptibility shows a doublet state at room temperature consistent with a strong coupling between the metal ion and the organic free radicals. The linearity of the χ_M^{-1} vs. T plot is meaningful since it shows that the quartet state, the only other one available, is not populated. In terms of a spin Hamiltonian approach the interaction is antiferromagnetic.

Using the latter approach it is possible to express the g values of the ground doublet as²⁵

$$g = (-1/3)g_{Cu} + (4/3)g_r$$

and indeed the observed g values which are smaller than 2 agree with this equation. Assuming that g_r is isotropic and equal to 2 and using the experimental values, it is calculated that the g_{Cu}

tensor has $g_{\parallel,Cu} = 2.14 - 2.17$; $g_{\perp,Cu} = 2.03 - 2.00$. The parallel direction is roughly orthogonal to the Cu-O₂-Cl₂ plane, in good agreement with the expectations for the square planar copper(II) complex.

The other relevant information to be obtained from the room temperature EPR spectra is bound to the fact that the individual signals of the two magnetically inequivalent sites present in the monoclinic cell are neatly resolved at Q-band and practically resolved at X-band frequencies. This suggests that intermolecular coupling between these two sites is smaller than 0.01 cm^{-1} . Such a weak intermolecular coupling cannot be considered responsible for deviations of the magnetic susceptibility from Curie behavior, except at very low temperatures.

On the other hand, the magnetic data show a broad maximum in the susceptibility vs. T curve at 14 K, which is a clear indication of a moderate antiferromagnetic coupling between the $S = 1/2$ CuCl₂(NITPHEN)₂ species.

In order to fit these data it is necessary to develop a model for the possible exchange pathways leading to the coupling between the CuCl₂(NITPHEN)₂ complexes.

The simplest possible model is that of a variation of the structure of the complex leading to the formation of dimers. The low-temperature EPR data do not support this view, because the spectra are not those of a triplet but rather those of exchange narrowed species. Indeed it must be recalled that although the lines are 2-3 G broad, no hyperfine was resolved. Further it must be mentioned that the signals of the two magnetically inequivalent sites of the monoclinic cell are resolved even at low temperature, showing that the intermolecular exchange coupling does *not* involve the two sites. Finally the similarity of the g tensor at low temperature with that of room temperature suggests that no large structural variation has occurred on cooling the sample.

The only other possibility we see to reconcile the magnetic and EPR data is that chains are formed of magnetically equivalent sites. If this model is correct, the magnetic susceptibility curve should be obtained by a Bonner-Fischer^{26,27} treatment valid for antiferromagnetic chain of $S = 1/2$ spins, based on the Hamiltonian $\mathcal{H} = J\sum_i S_i S_{i+1}$. We performed these calculations, and we obtained the best fit shown in Figure 3 with $J' = 15.05 (1) \text{ cm}^{-1}$, $g = 1.9957 (4)$. The agreement with the experimental data can be considered to be good, the agreement factor R being 2.3×10^{-4} .

Now the problem remains open to identify these chains. Although the shortest intermolecular contacts involve the phenyl protons and the oxygen and chlorine atoms, they cannot be responsible for J' because they connect magnetically nonequivalent sites and therefore must be discarded for the reason mentioned above. We suggest that the relatively short contact between two NITPHEN units along the c axis can be responsible for the coupling. These units are centrosymmetrically related and arranged so that the oxygen and nitrogen atoms are located at the corners of a rectangle with O-N distances of 3.56 Å; the mean plane of the NITPHEN moiety is nearly orthogonal (84°) to the plane of the rectangle (Figure 2). This geometry brings the lobes of the π^* orbitals of the NO groups in coincidence with the O-N directions giving rise to the same overlap and magnetic coupling (Figure 5). Similar results^{28,29} have been reported for some nitroxides which are paired or even dimerized in the solid state.

Conclusion

The title compound is the first square planar coordinated copper-nitroxyl complex with short metal-oxygen (nitroxyl) bonds. Although two equivalent sites of coordination are available in the nitroxyl ligand, the 2:1 adduct consists of structurally discrete molecules which have a ground electronic doublet state. The CuCl₂(NITPHEN)₂ complexes are magnetically coupled through

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long NITPHEN-NITPHEN interactions, which open interesting new possibilities to obtain magnetic materials. We are currently attempting to isolate other similar compounds.

Registry No. $\text{CuCl}_2(\text{NIPHEN})_2$, 103816-75-7.

Supplementary Material Available: Tables of magnetic data and anisotropic thermal parameters for the non-hydrogen atoms for $\text{CuCl}_2(\text{NITPHEN})_2$ (3 pages); tables of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

Molecular Environment Effects on the Reactivity of Porphyrins. Influence of Basket-Handle Superstructures on the Formation of Five-Coordinated Complexes of Iron(II) with Neutral Nitrogen Bases

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Abstract: The association constants of two nitrogen bases, 1,2-dimethylimidazole and 2-methylpyridine, giving rise to five-coordinated iron(II) complexes, have been determined in a series of six iron porphyrins, involving besides tetraphenylporphyrin and orthotetraanisylporphyrin, two ether-linked $(\text{C}12)_2$ basket-handle porphyrins, protected on one face and on both faces, respectively, and the corresponding two $(\text{C}12)_2$ secondary amide linked basket-handle porphyrins. Comparison between the unprotected and superstructured complexes shows that the presence of the chains has two effects. One derives from the steric hindrance to axial ligation in porphyrins that are protected on both faces. The other and more remarkable effect is the significant enhancement of the affinity of iron(II) toward the nitrogen base resulting from the presence of the secondary amide groups borne by the chains.

It has been shown recently that the grafting of protecting basket-handle carbon chains² onto the ortho position of the phenyl rings of tetraphenylporphyrin complexes produces remarkable microenvironment effects on the reactivity of the central metal complex,³ in a manner reminiscent of the functions of the protein chains toward the reactivity of the prosthetic groups in metallo proteins. Of particular relevance to the following discussion is the observation that the presence of ether-linked and secondary amide-linked basket-handle superstructures strongly influences the reactivity of iron porphyrins in reactions that involve the creation of a negative charge on the porphyrin complex.^{3a,c,e,f}

Three main effects were identified and estimated.⁴ Steric protection by the chains of the negatively charged complexes from external solvation renders the reaction more difficult in the eth-

er-linked series. Steric protection against solvation also exists in the amide-linked series. It is however largely overcompensated by a "local solvation" effect resulting from the interaction of the negative charge with the CONH dipoles which, on the overall, facilitates the reaction. These effects have been demonstrated to significantly influence the thermodynamics of several reactions: $(\text{Fe}^1)^- + e^- \rightleftharpoons \text{Fe}(\text{"O"})^{2-}$, $(\text{S})\text{Fe}^{\text{II}} + e^- \rightleftharpoons (\text{Fe}^1)^- + \text{S}$, (where S is a coordinating solvent molecule), $(\text{S})\text{Fe}^{\text{II}} + \text{Cl}^- \rightleftharpoons \text{Fe}^{\text{II}}\text{Cl}^- + (\text{S})$,^{3a,f} $(\text{S})\text{Fe}^{\text{II}} + \text{OH}^- \rightleftharpoons \text{Fe}(\text{OH})^- + (\text{S})$,^{3c} $\text{Fe}^{\text{II}}\text{Cl}^- + e^- \rightleftharpoons \text{Fe}^{\text{II}}\text{Cl}^-$,^{3f} $\text{Fe}^{\text{III}}\text{R} + e^- \rightleftharpoons \text{Fe}^{\text{II}}\text{R}^-$, $\text{Fe}^{\text{II}}\text{R}^- + e^- \rightleftharpoons \text{Fe}^{\text{I}}\text{R}^{2-}$ (where R is an alkyl group).^{3e} In those of these reactions which involve the cleavage of an axial ligand or the exchange between two axial ligands, steric hindrance of ligation by the chains has also been shown to influence the thermodynamics of the reaction leading to ligand discrimination effects in the latter case.^{3a,f} The kinetics of the $(\text{S})\text{Fe}^{\text{II}} + \text{Cl}^- \rightleftharpoons \text{Fe}^{\text{II}}\text{Cl}^- + \text{S}$ reaction has also been shown to be similarly influenced by the presence of the chains.^{3f} This is also the case for the nucleophilic reactivity of the $(\text{Fe}^1)^-$ and $\text{Fe}(\text{"O"})^{2-}$ complexes toward alkyl halides.^{3e}

Another point of interest, along the same lines, is the question of the possible influence of basket-handle chains upon the coordination of iron(II) porphyrins by neutral ligands. There is, a priori, little doubt that the chains should influence these reactions by steric hindrance to axial coordination. The actually interesting question is whether dipolar interactions with the CONH groups contained in the amide-linked basket-handle chains are able to significantly influence not only the coordination of negatively charged ligands as already demonstrated but also the axial coordination of neutral ligands. Answering this question was the aim of the work described hereafter.⁵ In this purpose, we investigated the coordination of iron(II) with 1,2-dimethylimidazole (1,2-Me₂Im) and 2-methylpyridine (2-MePy) in the series of

(5) Indirect evidence that such an effect could exist has been obtained^{3f} in the investigation of the $\text{SFe}^{\text{II}} + e^- \rightleftharpoons (\text{Fe}^1)^- + \text{S}$ reaction (where S is a coordinating solvent molecule) as a function of the nature of the solvent and of the porphyrin superstructure in the same ether-linked and amide-linked basket-handle series as investigated here.

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