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Crystal and Molecular Structure and Magnetic Properties of the Adducts of Copper(II) Hexafluoroacetylacetonate with the Nitroxide Ligand 2-Phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl 3-Oxide

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Stable 1:1 and 1:2 adducts were isolated from the reaction of copper(II) hexafluoroacetylacetonate and the free radical 2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide (NITPh), namely $Cu(hfac)_2(NITPh)$ and $Cu(hfac)_2(NITPh)_2$. The striking feature of the structure of the diamagnetic $Cu(hfac)_2(NITPh)$ is the presence of two molecules in different conformations in the asymmetric unit with the copper ion in a distorted square-pyramidal environment and a trigonal-bipyramidal environment, respectively. The nitroxyl group is equatorially bound in both molecules. Crystal data for $Cu(hfac)_2(NITPh)$: triclinic, $P\bar{1}$, $a = 11.346$ (5) Å, $b = 14.115$ (6) Å, $c = 20.129$ (9) Å, $\alpha = 70.12$ (3)°, $\beta = 76.68$ (4)°, $\gamma = 75.20$ (3)°, $Z = 4$. In $Cu(hfac)_2(NITPh)_2$ the copper ion is in a tetragonally distorted octahedral environment with the axial coordination sites occupied by the oxygen atoms of the two nitroxyl ligands at bonding distances of 2.362 (5) and 2.393 (5) Å. Crystal data for $Cu(hfac)_2(NITPh)_2$: monoclinic, $P2_1/c$, $a = 12.358$ (6) Å, $b = 15.428$ (7) Å, $c = 22.61$ (1) Å, $\beta = 102.33$ (3)°, $Z = 4$. Magnetic measurements show a weak ferromagnetic interaction. EPR spectra of $Cu(hfac)_2(NITPh)_2$ show a g shift on varying the energy of the microwave quantum and nonparallelism of the two **g** tensors at X- and Q-band frequencies.

Introduction

The mechanism of the magnetic coupling between paramagnetic transition-metal ions and stable nitroxides is under investigation,[2–7] due to the possibility of synthesizing novel magnetic materials and studying the nature of the bonding between metal ions and paramagnetic ligands.

Several different coordination geometries have been observed, and the coupling between the metal ions and the nitroxides has been found to range from antiferromagnetic,[8,9] implying a complete pairing of the spins and no thermally accessible excited state, to weak ferromagnetic,[10–12] passing through systems in which spin pairing occurs only at low temperature.[13–15]

Special interest has been devoted to the adducts formed by $Cu(hfac)_2$ since the metal center is a strong Lewis acid making it relatively easy to obtain complexes with the nitroxides. Adducts of $Cu(hfac)_2$ have been obtained with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) and the 4-hydroxylated derivative (TEMPOL). Distinctly different structures and magnetic properties have been observed for these two adducts. The $Cu(hfac)_2$TEMPO adduct is a diamagnetic,[16] equatorially short-bonded complex[17] while in $Cu(hfac)_2$TEMPOL the nitroxyl group is axially coordinated through a long bond and a ferromagnetic behavior has been observed.[11,18]

Table I. Crystallographic Data and Experimental Parameters

	$Cu(hfac)_2(NITPh)$	$Cu(hfac)_2(NITPh)_2$
formula	$C_{23}H_{19}CuF_{12}N_2O_6$	$C_{36}H_{36}CuF_{12}N_4O_8$
M_r	710.94	944.23
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
V, Å^3	2894.1	4211.7
a, Å	11.346 (5)	12.358 (6)
b, Å	14.115 (6)	15.428 (7)
c, Å	20.129 (9)	22.61 (1)
α, deg	70.12 (3)	90
β, deg	76.68 (4)	102.33 (3)
γ, deg	75.20 (3)	90
Z	4	4
d(calcd), g/cm^3	1.72	1.69
Experimental Parameters for Both Compounds		
radiation	Mo Kα (λ = 0.7107 Å), graphite monochromator	
cryst detector dist, mm	368	
detector window width, mm	$2.25 + 3.5 \tan \vartheta$	
detector window height, mm	4	
takeoff angle, deg	6	
scan mode	ω	
max Bragg angle, deg	$2 < \vartheta < 25$	
scan angle, deg	$0.80 + 0.35 \tan \vartheta$	
scan speed, deg/min	variable from 0.42 to 3	

We recently reported[9] the synthesis of the adduct of copper chloride with 2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide (NITPh) (Figure 1), a nitronyl nitroxide in which, as in TEMPOL, two sites of coordination are available. Although it has been reported[19] that NITPh does not give any adduct with $Cu(hfac)_2$, we decided to reinvestigate this reaction since the nitronyl nitroxides are known to be stronger Lewis bases than their dialkyl analogues.[20,21] In this paper we report the results of our study on the 1:1 and the 2:1 adducts of NITPh with $Cu(hfac)_2$.

Experimental Section

Synthesis of the Adducts. Anhydrous $Cu(hfac)_2$ (956 mg, 2×10^{-3} mol) was dissolved in 100 mL of hot pentane. To this solution 466 mg (2×10^{-3} mol) of NITPh[19] were added. The dark blue solution turned brown as it was refluxed for 20 min. When the solution was cooled to

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(1) (a) University of Florence. (b) Centre d'Etudes Nucléaires de Grenoble.
(2) Dong, T. Y.; Hendrickson, D. N.; Felthouse, T. R.; Shieh, H. S. *J. Am. Chem. Soc.* **1984**, *106*, 5373.
(3) Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1982**, *21*, 2667.
(4) Richman, R. M.; Kuechler, T. C.; Tanner, S. P.; Drago, R. S. *J. Am. Chem. Soc.* **1977**, *99*, 1055.
(5) Brown, D. G.; Maier, T.; Drago, R. S. *Inorg. Chem.* **1971**, *10*, 2804.
(6) Eaton, S. S.; Eaton, G. R. *Coord. Chem. Rev.* **1978**, *26*, 207.
(7) Damoder, R.; Kundalika, M. M.; Eaton, G. R.; Eaton, S. S. *J. Am. Chem. Soc.* **1983**, *105*, 2147.
(8) Porter, L. C.; Dickman, M. H.; Doedens, R. J. *Inorg. Chem.* **1986**, *25*, 678.
(9) Laugier, J.; Rey, P.; Benelli, C.; Gatteschi, D.; Zanchini, C. *J. Am. Chem. Soc.* **1986**, *108*, 6931.
(10) Grand, A.; Rey, P.; Subra, R. *Inorg. Chem.* **1983**, *22*, 391.
(11) Bencini, A.; Benelli, C.; Gatteschi, D.; Zanchini, C. *J. Am. Chem. Soc.* **1984**, *106*, 5813.
(12) Benelli, C.; Gatteschi, D.; Zanchini, C.; Latour, J. M.; Rey, P. *Inorg. Chem.* **1986**, *25*, 4242.
(13) Dickman, M. H.; Porter, L. C.; Doedens, R. J. *Inorg. Chem.* **1986**, *25*, 2595.
(14) Benelli, C.; Gatteschi, D.; Zanchini, C. *Inorg. Chem.* **1984**, *23*, 798.
(15) Beck, W.; Schmidter, K.; Keller, H. S. *Chem. Ber.* **1967**, *100*, 503.
(16) Lim, Y. Y.; Drago, R. S. *Inorg. Chem.* **1972**, *11*, 1334.
(17) Dickman, H. M.; Doedens, R. J. *Inorg. Chem.* **1981**, *20*, 2677.
(18) Anderson, O. P.; Kuechler, T. C. *Inorg. Chem.* **1980**, *19*, 1417.
(19) Richardson, P. F.; Kreilick, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 8183.
(20) Osiecki, J. H.; Ullman, F. E. *J. Am. Chem. Soc.* **1968**, *90*, 1678.
(21) Helbert, J. N.; Kopf, P. W.; Poindexter, E. H.; Wagner, E. B. *J. Chem. Soc., Dalton Trans.* **1975**, 998.

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Table II. Atomic Positional Parameters (×10^4) for $Cu(hfac)_2(NITPh)$

	x	*y*	*z*	B_{eq}, Å^2		*x*	*y*	*z*	B_{eq}, Å^2
Cu	1241 (1)	8832 (1)	9115 (1)	5.92	Cu′	−3610 (1)	5986 (1)	6066 (1)	6.92
O1	2469 (7)	8721 (5)	9691 (3)	7.37	O1′	−4763 (6)	6500 (5)	5407 (4)	7.60
O2	2178 (6)	9549 (5)	8261 (3)	6.21	O2′	−2465 (6)	5186 (5)	5455 (4)	8.06
O3	−5 (5)	8594 (5)	9954 (3)	6.60	O3′	−4732 (6)	5036 (6)	6794 (4)	7.38
O4	1786 (6)	7188 (5)	9299 (4)	7.36	O4′	−2437 (7)	5580 (6)	6699 (5)	8.00
F1	3967 (8)	9127 (10)	10434 (5)	18.57	F1′	−6642 (10)	7024 (9)	4715 (6)	15.61
F2	5482 (8)	8655 (9)	9743 (5)	16.30	F2′	−5575 (10)	8003 (7)	4194 (6)	14.12
F3	4348 (11)	7642 (10)	10387 (6)	16.99	F3′	−5578 (11)	6832 (9)	3830 (6)	21.49
F4	4993 (8)	10169 (7)	7353 (4)	14.57	F4′	−591 (11)	5274 (14)	4219 (8)	23.92
F5	3609 (11)	9985 (10)	6973 (4)	19.93	F5′	−1695 (8)	4513 (11)	3948 (6)	23.39
F6	3401 (9)	11193 (7)	7332 (5)	16.95	F6′	−976 (11)	3897 (11)	4864 (8)	21.96
F7	−1586 (8)	8409 (11)	11173 (6)	23.53	F7′	−5017 (11)	2922 (8)	8024 (6)	16.84
F8	−1790 (15)	7106 (9)	11232 (9)	27.96	F8′	−5826 (13)	4058 (10)	8447 (7)	23.62
F9	−2416 (9)	8232 (17)	10539 (7)	27.25	F9′	−6381 (11)	4002 (11)	7574 (6)	19.53
F10	1606 (11)	5306 (6)	9205 (5)	15.94	F10′	−1025 (9)	5635 (8)	7524 (7)	15.33
F11	1211 (7)	4795 (5)	10325 (4)	11.08	F11′	−534 (9)	4175 (8)	7498 (7)	19.09
F12	2908 (8)	5239 (6)	9824 (7)	16.44	F12′	−1674 (11)	4526 (13)	8356 (6)	19.91
C1	3515 (10)	8925 (8)	9427 (6)	7.05	C1′	−4556 (10)	6408 (8)	4785 (6)	6.50
C2	4362 (15)	8577 (16)	9997 (9)	11.31	C2′	−5494 (15)	7062 (13)	4337 (9)	9.94
C3	3978 (9)	9346 (8)	8741 (7)	7.69	C3′	−3552 (11)	5861 (9)	4480 (6)	8.72
C4	3279 (10)	9667 (7)	8201 (6)	6.20	C4′	−2581 (11)	5308 (10)	4833 (7)	8.56
C5	3819 (13)	10213 (11)	7461 (8)	8.94	C5′	−1480 (19)	4808 (18)	4400 (12)	14.23
C6	−345 (9)	7780 (9)	10280 (5)	5.72	C6′	−4476 (12)	4519 (9)	7385 (7)	7.98
C7	−1491 (12)	7907 (12)	10792 (8)	9.36	C7′	−5391 (20)	3890 (17)	7859 (12)	12.27
C8	160 (9)	6795 (8)	10242 (5)	6.97	C8′	−3472 (14)	4428 (10)	7694 (7)	8.68
C9	1221 (10)	6596 (8)	9751 (6)	6.13	C9′	−2545 (12)	4962 (10)	7326 (7)	7.22
C10	1734 (14)	5470 (10)	9785 (9)	9.31	C10′	−1456 (16)	4785 (14)	7675 (10)	10.01
N1	−180 (6)	9615 (6)	7994 (4)	5.69	N1′	−3328 (6)	7818 (5)	6224 (4)	5.39
N2	−6 (7)	10425 (6)	6863 (4)	5.82	N2′	−2307 (7)	8545 (6)	6626 (4)	6.17
O5	−32 (5)	8909 (5)	8595 (3)	6.44	O5′	−4128 (5)	7346 (5)	6196 (3)	6.95
O6	279 (6)	10630 (5)	6196 (4)	7.42	O6′	−1948 (6)	8882 (5)	7041 (4)	8.45
C11	−1097 (9)	10582 (8)	7974 (5)	6.75	C11′	−2671 (9)	8434 (7)	5563 (5)	6.17
C12	−2350 (10)	10284 (9)	8139 (6)	10.25	C12′	−2112 (11)	7828 (10)	5065 (6)	10.93
C13	−974 (10)	11006 (8)	8559 (5)	8.84	C13′	−3669 (12)	9307 (10)	5248 (7)	10.13
C14	−733 (10)	11246 (8)	7195 (6)	7.66	C14′	−1755 (8)	8769 (7)	5848 (5)	6.19
C15	165 (13)	11909 (8)	7127 (6)	10.64	C15′	−1669 (11)	9884 (8)	5528 (6)	9.23
C16	−483 (10)	8085 (10)	5832 (6)	10.19	C16′	−1798 (11)	11845 (9)	6797 (7)	11.53
C17	339 (8)	9530 (7)	7341 (5)	5.14	C17′	−3145 (8)	7942 (7)	6818 (5)	5.43
C18	1121 (8)	8614 (8)	7181 (5)	5.66	C18′	−3751 (9)	7518 (7)	7546 (5)	6.25
C19	2029 (9)	8709 (8)	6601 (5)	6.99	C19′	−3149 (9)	7329 (8)	8114 (6)	7.35
C20	2732 (10)	7841 (12)	6426 (7)	9.22	C20′	−3716 (14)	6872 (10)	8798 (7)	9.51
C21	2545 (13)	6912 (11)	6808 (8)	9.44	C21′	−4850 (16)	6647 (10)	8916 (7)	11.22
C22	1618 (13)	6769 (9)	7427 (8)	8.41	C22′	−5459 (11)	6862 (10)	8351 (9)	10.90
C23	880 (9)	7655 (9)	7612 (12)	6.95	C23′	−4918 (10)	7291 (8)	7672 (6)	8.19

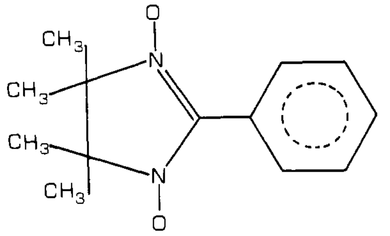

Figure 1. Formula of the nitronyl nitroxide 2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide, NITPh.

room temperature, crystallization occurred; the crystals were collected by filtration (878 mg) and dried under vacuum.

Examination of the crude crystalline compound showed that two kinds of crystals were present. A 50-mg sample of each of the two kinds could be easily obtained since they were large crystals different in shape and color. The dark brown platelike crystals analyzed satisfactorily for the 1:1 adduct, $Cu(hfac)_2(NITPh)$ (Anal. Calcd for $C_{23}H_{19}F_{12}N_2O_6Cu$: C, 38.85; H, 2.69; F, 32.06; N, 3.96; O, 13.50; Cu, 8.94. Found: C, 39.17; H, 2.91; F, 31.63; N, 4.28; Cu, 8.73), while the analysis of the blue parallelepipeds corresponded to the 2:1 adduct, $Cu(hfac)_2(NITPh)_2$ (Anal. Calcd for $C_{36}H_{36}F_{12}N_4O_8Cu$: C, 45.85; H, 3.85; F, 24.05; N, 5.94; O, 13.57; Cu, 6.74. Found: C, 46.11; H, 3.78; F, 23.20; N, 5.79; Cu, 6.61). The crystals of both compounds were suitable for a X-ray diffraction study.

X-ray Data Collection and Reduction. X-ray data for $Cu(hfac)_2(NITPh)$ and $Cu(hfac)_2(NITPh)_2$ were collected on an Enraf-Nonius CAD-4 four-circle diffractometer with Mo Kα radiation. Accurate unit cell parameters were derived from least-squares refinement of the setting angles of 25 reflections and are reported in Table I with other experimental parameters. Intensities of three standard reflections were measured after every 100 data and showed no decrease during the course of data collection. The data were corrected for Lorentz and polarization effects.

For both compounds the data were collected from regularly shaped crystals of approximate dimensions (0.2 × 0.2 × 0.2 mm) obtained by cleavage of larger crystals. The triclinic crystal symmetry for $Cu(hfac)_2(NITPh)$ and the monoclinic symmetry for $Cu(hfac)_2(NITPh)_2$ were confirmed by Weissenberg photographs.

Structure Solution and Refinement. Both crystal structures were solved by conventional Patterson and Fourier methods using the SHELX-76 package.[22] The copper positions were determined by means of sharpened Patterson functions, and the phases provided by these heavy atoms were used for successive difference syntheses that revealed the positions of the remaining non-hydrogen atoms. Structure refinements were carried out by full-matrix least-squares methods, with anisotropic thermal parameters for all non-hydrogen atoms.

For $Cu(hfac)_2(NITPh)$ the refinement with 4044 reflections ($|F_o| > 2\sigma|F_o|$) converged to final R values of $R = 0.064$ and $R_w = 0.063$. For $Cu(hfac)_2(NITPh)_2$ the refinement was carried out on 3593 reflections ($|F_o| > 4\sigma|F_o|$) and converged to $R = 0.056$ and $R_w = 0.075$. For both compounds the final refinement model included all hydrogen atoms in fixed and idealized positions.

Atomic positional parameters for $Cu(hfac)_2(NITPh)$ and $Cu(hfac)_2(NITPh)_2$ are listed in Tables II and Table III. Selected bond lengths and angles are listed in Table IV and Table V. Complete listings of bond lengths and angles, anisotropic thermal parameters, and observed and

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[22] (a) Sheldrick, G. *SHELX 76 System of Computing Programs*; University of Cambridge: Cambridge, England, 1976. (b) Busing, W. R.; Martin, K. O.; Levy, H. A. *Oak Ridge Natl. Lab.* [*Rep.*] *ORNL* (*U. S.*) **1971**, *ORNL-594-37*.

Table III. Atomic Positional Parameters ($\times 10^4$) for $Cu(hfac)_2(NITPh)_2$

	x	y	z	B_{eq}, Å^2		x	y	z	B_{eq}, Å^2
Cu	7263 (1)	719 (1)	2331 (0)	4.88	C11	7454 (7)	3042 (5)	1266 (4)	5.86
O1	6537 (4)	1595 (3)	2724 (2)	5.06	C12	6325 (7)	2953 (6)	1402 (4)	7.55
O2	8584 (4)	749 (3)	2966 (2)	5.35	C13	8045 (9)	3793 (6)	1647 (4)	8.70
O3	7990 (4)	−127 (3)	1912 (2)	5.35	C14	7498 (8)	3080 (6)	586 (4)	7.21
O4	5938 (4)	700 (3)	1698 (2)	5.26	C15	6561 (9)	2538 (8)	198 (4)	10.48
F1	6818 (6)	3285 (5)	3717 (4)	14.75	C16	7562 (10)	3967 (7)	314 (5)	11.42
F2	5560 (7)	2550 (5)	3527 (5)	19.18	C17	8811 (6)	2074 (5)	1069 (4)	5.32
F3	5972 (11)	3255 (6)	2879 (3)	20.80	C18	9670 (7)	1416 (5)	1168 (5)	6.50
F4	10255 (5)	1926 (4)	4101 (3)	10.22	C19	10065 (9)	1093 (7)	671 (5)	8.86
F5	10072 (6)	598 (5)	4089 (4)	15.40	C20	10893 (11)	458 (9)	769 (8)	11.82
F6	10681 (5)	1237 (6)	3409 (3)	14.52	C21	11274 (10)	146 (9)	1338 (9)	12.05
F7	9015 (9)	−1497 (7)	1670 (6)	17.98	C22	10902 (9)	465 (8)	1830 (7)	10.21
F8	7688 (7)	−1945 (5)	1083 (5)	16.46	C23	10096 (7)	1100 (6)	1755 (5)	7.53
F9	8590 (9)	−1050 (6)	822 (5)	19.76	N1′	6668 (4)	−812 (4)	3268 (2)	4.37
F10	4523 (5)	937 (4)	544 (3)	9.42	N2′	6358 (5)	−1008 (4)	4186 (3)	4.84
F11	4275 (5)	−410 (4)	515 (3)	9.51	O5′	6608 (4)	−543 (3)	2730 (2)	5.34
F12	3843 (5)	339 (5)	1214 (3)	11.21	O6′	5923 (5)	−989 (4)	4641 (2)	6.95
C1	7019 (7)	2040 (5)	3149 (4)	5.15	C11′	7418 (6)	−1564 (5)	3507 (3)	5.07
C2	6317 (10)	2782 (7)	3290 (4)	7.42	C12′	6810 (8)	−2370 (5)	3210 (4)	7.14
C3	8099 (8)	1985 (5)	3498 (4)	5.82	C13′	8515 (7)	−1454 (6)	3333 (4)	6.91
C4	8776 (7)	1329 (5)	3366 (3)	5.28	C14′	7428 (7)	−1490 (5)	4200 (3)	5.62
C5	9977 (9)	1249 (8)	3739 (5)	7.60	C15′	7431 (9)	−2329 (6)	4539 (4)	8.29
C6	7495 (8)	−553 (5)	1474 (4)	6.50	C16′	8340 (7)	−888 (6)	4536 (4)	7.67
C7	8213 (12)	−1258 (8)	1277 (6)	8.93	C17′	6025 (6)	−566 (4)	3661 (3)	4.28
C8	6405 (8)	−494 (6)	1138 (4)	6.27	C18′	5112 (6)	35 (4)	3521 (3)	4.54
C9	5752 (7)	147 (6)	1282 (3)	5.37	C19′	4574 (6)	189 (5)	2921 (3)	4.91
C10	4581 (8)	242 (7)	888 (4)	6.91	C20′	3705 (6)	745 (6)	2799 (4)	6.04
N1	8151 (5)	2256 (4)	1451 (3)	5.03	C21′	3340 (7)	1170 (6)	3260 (4)	6.88
N2	8545 (6)	2615 (5)	589 (3)	6.66	C22′	3863 (8)	1027 (6)	3857 (4)	6.90
O5	8167 (4)	1915 (3)	1966 (2)	6.23	C23′	4750 (7)	461 (5)	3986 (3)	5.51
O6	9030 (6)	2676 (5)	153 (3)	10.74					

Table IV. Selected Bond Lengths (Å) and Angles (deg) for $Cu(hfac)_2(NITPh)$

molecule A		molecule B	
Cu–O1	1.955 (8)	Cu′–O1′	1.912 (7)
Cu–O2	1.905 (5)	Cu′–O2′	1.983 (7)
Cu–O3	1.929(5)	Cu′–O3′	2.060 (7)
Cu–O4	2.167 (7)	Cu′–O4′	1.903 (9)
Cu–O5	1.932 (7)	Cu′–O5′	1.948 (7)
N1–O5	1.292 (9)	N1′–O5′	1.27 (1)
N2–O6	1.25 (1)	N2′–O6′	1.27 (1)
O1–Cu–O2	92.0 (3)	O1′–Cu′–O2′	91.4 (3)
O1–Cu–O3	91.2 (2)	O1′–Cu′–O3′	91.8 (3)
O1–Cu–O4	87.9 (3)	O1′–Cu′–O4′	175.5 (3)
O1–Cu–O5	176.8 (2)	O1′–Cu′–O5′	84.4 (3)
O2–Cu–O3	159.9 (2)	O2′–Cu′–O3′	107.4 (3)
O2–Cu–O4	110.8 (2)	O2′–Cu′–O4′	90.2 (3)
O2–Cu–O5	91.2 (2)	O2′–Cu′–O5′	143.5 (2)
O3–Cu–O4	89.2 (2)	O3′–Cu′–O4′	91.7 (3)
O3–Cu–O5	85.6 (2)	O3′–Cu′–O5′	108.9 (2)
O4–Cu–O5	91.3 (3)	O4′–Cu′–O5′	91.8 (3)
Cu–O5–N1	121.1 (6)	Cu′–O5′–N1′	120.2 (4)

Table V. Selected Bond Lengths (Å) and Angles (deg) for $Cu(hfac)_2(NITPh)_2$

Cu–O1	1.940 (5)	N1–O5	1.274 (8)
Cu–O2	1.931 (4)	N2–O6	1.26 (1)
Cu–O3	1.943 (5)	Cu–O5′	2.362 (5)
Cu–O4	1.931 (4)	N1′–O5′	1.273 (6)
Cu–O5	2.393 (5)	N2′–O6′	1.259 (9)
O1–Cu–O2	92.5 (1)	O3–Cu–O4	92.0 (1)
O1–Cu–O3	177.8 (2)	O3–Cu–O5	93.0 (1)
O1–Cu–O4	87.0 (2)	O3–Cu–O5′	82.1 (1)
O1–Cu–O5	85.2 (1)	O4–Cu–O5	98.1 (1)
O1–Cu–O5′	99.8 (1)	O4–Cu–O5′	88.0 (1)
O2–Cu–O3	88.5 (2)	O5–Cu–O5′	172.4 (1)
O2–Cu–O4	179.5 (2)	Cu–O5–N1	135.7 (3)
O2–Cu–O5	81.7 (1)	Cu–O5′–N1′	132.8 (3)
O2–Cu–O5′	92.3 (1)		

calculated structure factors are deposited as supplementary material (Tables SI–SVI).

Magnetic Susceptibility Measurements. The magnetic susceptibilities of both complexes were measured between 6 and 300 K by use of an SHE superconducting SQUID magnetometer operating at a field strength of 0.5 T. The data were corrected for the magnetization of the sample holder and for the diamagnetism of the compounds estimated by use of Pascal's constant.

Electron Paramagnetic Resonance. EPR spectra of $Cu(hfac)_2(NITPh)_2$ were recorded with Bruker ER200 and a Varian E9 spectrometers at X- and Q-bands, 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 (001) and (00$\bar{1}$) faces.

Results

Synthesis. A brief report of the reaction of NITPh with $Cu(hfac)_2$ in chloroform stated that no crystalline material could be obtained.[19] We, also, were unable to obtain any crystalline adduct in these conditions. Moreover, EPR spectra of dilute chloroform solutions of the two adducts—prepared in pentane—showed a superposition of the lines from $Cu(hfac)_2$ and the radical, indicating an extensive dissociation of the complexes in this solvent. Therefore it appears that the use of a nonpolar solvent, in which the adducts are sparingly soluble, is an essential condition for obtaining crystalline materials. The reaction in pentane afforded always a mixture of the two adducts, the relative yields of which probably depend on the relative molarity of the starting materials. Since the two adducts were quite easily obtained in the pure state by hand picking (see Experimental Section) no attempt was made to optimize the yield in one of the adducts.

Crystal Structure. Views of the structure of the two adducts are shown in Figures 2 and 3 ($Cu(hfac)_2(NITPh)$) and Figure 4 ($Cu(hfac)_2(NITPh)_2$). As expected, owing to the different stoichiometries the copper ion is octahedrally coordinated in the bis(nitroxyl) adduct and pentacoordinated in the mono(nitroxyl) one.

The striking feature of the structure of $Cu(hfac)_2(NITPh)$ is the presence of two molecules in different conformation in the asymmetric unit. In the first one, A, the copper atom has the same overall bonding pattern as the one described for the adduct of $Cu(hfac)_2$ with TEMPO.[17] It is surrounded by five oxygen atoms, four belonging to the two hfac ligands and the fifth one to the nitroxyl group. The nitroxyl group is equatorially bound with a

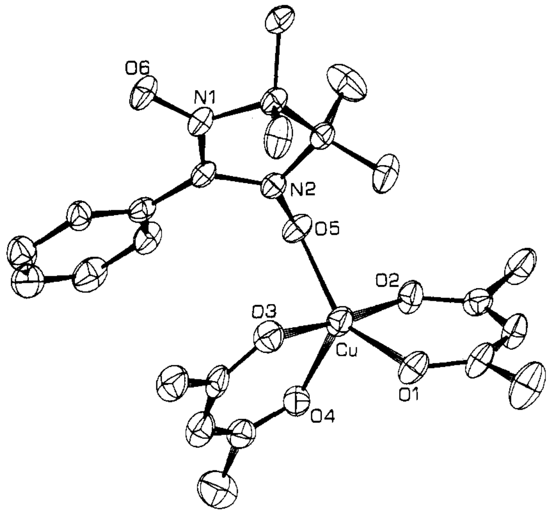

Figure 2. View of the structure of (2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide)bis(hexafluoroacetylacetonato)copper(II), Cu(hfac)$_2$(NITPh), molecule A (see text).

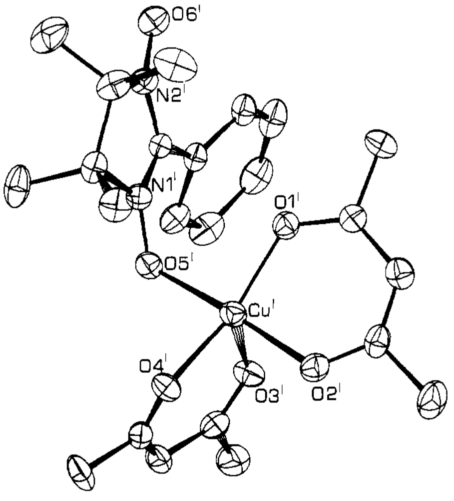

Figure 3. View of the structure of (2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide)bis(hexafluoroacetylacetonato)copper(II), Cu(hfac)$_2$(NITPh), molecule B (see text).

short Cu–O5 distance (1.932 (7) Å) so that one of the hfac oxygen atoms occupies the axial position of the square-pyramidal coordination polyhedron with a Cu–O4 distance of 2.167 (7) Å. However there are some significant deviations from this idealized bonding pattern. The four atoms (O1–O2–O5–Cu) are coplanar and have been used to define the basal plane of the pyramid. The principal distortion from a square pyramid is a displacement of the O3 atom below the plane (0.65 Å). At the same time the O4 atom is displaced from the axial site with the resultant deviation of the O2–Cu–O4 angle (110.8 (2)°) from the 90° value.

The nitronyl nitroxide moiety has the usual geometry.[9,23] The π-system (O5–N1–C17–N2–O6) containing the unpaired electron is perfectly planar and forms an angle of 34° with the phenyl ring. This value is close to that found for CuCl$_2$ (NITPh)$_2$,[9] and it seems to allow some conjugation between the two π-systems and to minimize the interactions between the phenyl ortho hydrogen atoms and the N–O oxygen atoms. The binding of the N1–O5 group to the copper atoms is such that the Cu–O5–N1 plane is perpendicular to the nitroxide π-system and forms an angle of 23.76° with the basal plane of the pyramid.

In the second molecule, B, of the 1:1 adduct the coordination geometry around the copper ion approximates a trigonal bipyramid. Each hfac bidentate ligand is coordinated through an axially and an equatorially bound oxygen atom; the last equatorial site of the trigonal bipyramid is occupied by the nitroxyl oxygen atom at a Cu–O distance of 1.903 (9) Å. Large deviations from this idealized geometry are observed in the basal plane: the O′–Cu′–O′ angles deviate from the 120° value, especially O2′–Cu′–O5′ (143.5 (2)°), probably releasing steric hindrance between the nitroxyl phenyl group and the hfac ligands. All the other angles are within a few degrees of either 90 or 180°.

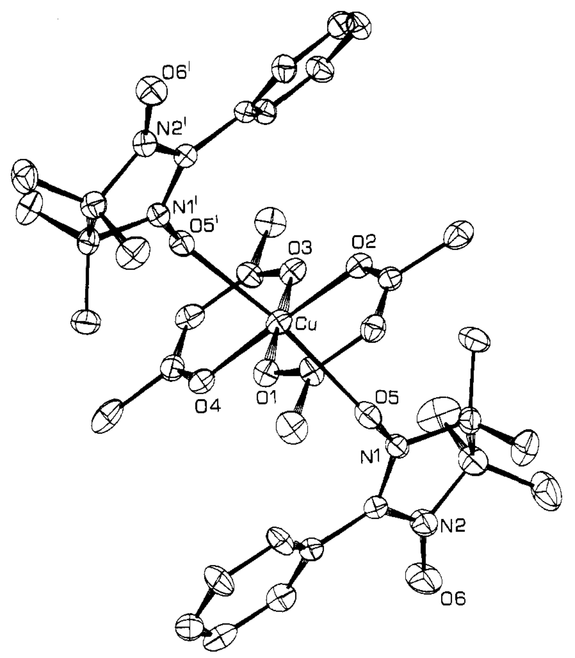

Figure 4. View of the structure of bis(2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide)bis(hexafluoroacetylacetonato)copper(II), Cu(hfac)$_2$(NITPh)$_2$.

All the geometrical features of the nitroxyl moiety are similar to those found in molecule A. However its binding to the copper(II) ions is different: the Cu′–O5′–N1′ plane forms an angle of 103.5° with the nitroxyl π-system (O5′–N1′–C17′–N2′–O6′) and an angle of 48.5° with the basal plane of the trigonal bipyramid.

All the bonding interactions for the copper atom in Cu(hfac)$_2$(NITPh)$_2$ are shown in Figure 4. It is surrounded by six oxygen atoms at the vertices of a tetragonally distorted octahedron. Four of these atoms belong to the two hfac ligands and occupy the equatorial coordination sites at short and normal (1.940 (5)–1.931 (4) Å) distances. The axial coordination sites are occupied by the oxygen atoms of the two nitroxyl ligands at larger bonding distances (2.362 (5) and 2.393 (5) Å). Although this binding geometry closely approximates that of an octahedron, the copper ion is not located on a center of symmetry and the two Cu–O(nitroxyl) distances are different; however, the Cu ion and the four equatorially bound oxygen atoms are coplanar. All the O–Cu–O angles are within a few degrees of 90 or 180°. The geometry of the two hfac ligands is similar to that found in the 1:1 adduct except the relative orientations of the phenyl and bis –N–O π-systems. The angle between these two planes was ca. 40° in the two molecules of the 1:1 adduct and only ca. 20° in the 2:1 adduct. Significantly different also are the binding of the two NITPh ligands to the copper ion as compared to that observed in the 1:1 adduct. The Cu–O5–N1 and Cu–O5′–N1′ planes are respectively almost orthogonal to the O5–N1–C17–N2–O6 and O5′–N1′–C17′–N2′–O6′ π-systems; they are also perpendicular to the basal plane of the octahedron (O1–O2–Cu–O3–O4).

Magnetic Data. The temperature dependence of the magnetic susceptibility of Cu(hfac)$_2$(NITPh)$_2$ in the form of a plot of χT vs. T is shown in Figure 5. χT is practically constant from room temperature, when its value of 1.091 emu mol^{-1} K is close to that expected for three noninteracting $S = {}^1/_2$ free spins, 1.125 emu mol^{-1} K, down to 7.0 K, where the value has increased to 1.54 emu mol^{-1} K, definitely smaller than the value expected for a free spin quartet ground state ($\sim$1.875 emu mol^{-1} K). Therefore it

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(23) Wong, W.; Watkins, S. F. *J. Chem. Soc. Chem. Commun.*, **1973**, 888.

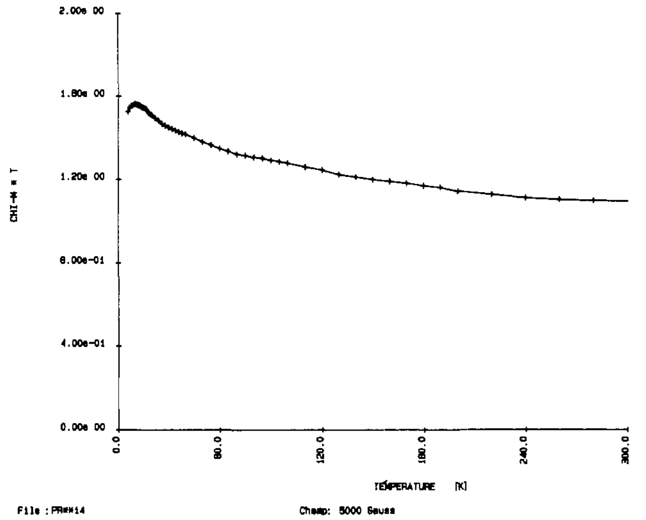

Figure 5. Temperature dependence of the magnetic susceptibility of bis(2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide)bis(hexafluoroacetylacetonato)copper(II), $Cu(hfac)_2(NITPh)_2$, in the form χT vs. T.

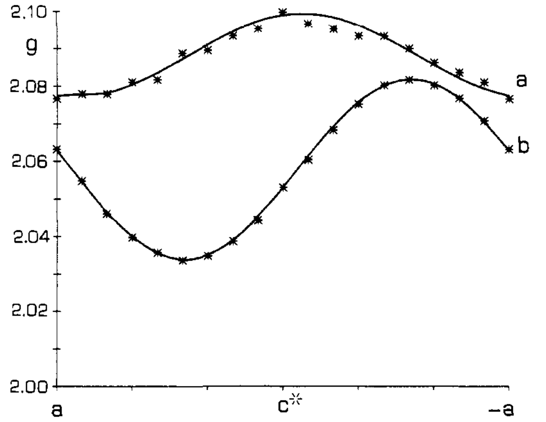

Figure 6. Angular dependence of the g values in the ac^* plane for bis(2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide) bis(hexafluoroacetylacetonato)copper(II), $Cu(hfac)_2(NITPh)_2$, at (a) X-band and (b) Q-band frequencies at 140 K.

seems safe to conclude that in this case the coupling among the three $S = {}^1/_2$ spins must be presumably ferromagnetic but small. Some attempts were made to fit the data, but due to the inherent difficulty in obtaining reliable J values in the limit of weak ferromagnetic coupling,[24,25] we could not obtain a very good agreement with the experiment. However the coupling constant between the metal ion and the nitroxide can be estimated to be smaller than 10 cm^{-1}. In contrast $Cu(hfac)_2(NITPh)$ is diamagnetic. The small paramagnetic susceptibilities observed at low temperature are presumably a consequence of a small amount of paramagnetic impurities.

Electron Paramagnetic Resonance. The single-crystal EPR spectra of $Cu(hfac)_2(NITPh)_2$ at both X- and Q-band frequencies show only one signal for each orientation of the static magnetic field. Since the unit cell is monoclinic, two magnetically nonequivalent sites are expected to be present,[26] and, indeed, if the bond directions of copper with the oxygen atoms of the NITPh ligand are used to locate the z molecular axes, it is easily checked that the z axes of the two molecules form an angle of 80° with each other. Since only one signal is observed in any case, it can be safely assumed that an intermolecular exchange interaction is operative to average the two different signals. Under these conditions one principal direction of **g** must be parallel to the crystal b axis while the other two are in the ac^* plane.

Table VI. Principal g Values and Directions for $Cu(hfac)_2(NITPh)_2$ at X- and Q-Band Frequencies at 140 K[a]

	X-Band	
g_{xx} = 2.0759 (5)	g_{yy} = 2.0574 (8)	g_{zz} = 2.0980 (5)
-0.990 (3)	0.000	0.13 (2)
0.000	1.000	0.000
-0.13 (2)	0.000	-0.990 (3)
	Q-Band	
g_{xx} = 2.0326 (2)	g_{yy} = 2.0783 (3)	g_{zz} = 2.0803 (2)
0.631 (3)	0.000	0.775 (2)
0.000	1.000	0.000
0.775 (2)	0.000	-0.631 (2)

[a] The directions are given by their direction cosines referred to the orthogonal crystal axes a, b, and c^*.

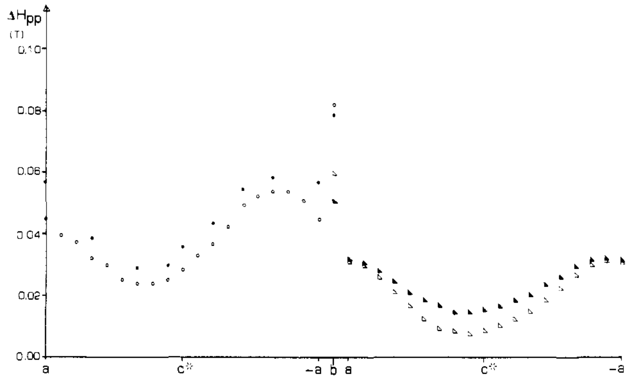

Figure 7. Angular dependence of ΔH_{pp} (T) for bis(2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide)bis(hexafluoroacetylacetonato)copper(II), $Cu(hfac)_2(NITPh)_2$, in the ac^* plane and along the b axis at X-band frequency, room temperature (•) and 140 K (∘), and at Q-band frequency, room temperature (▲) and 140 K (△).

The only signal that is observed can be followed by using an effective $S = {}^1/_2$ spin. The angular dependence of the g values in the ac^* plane at both X- and Q-band frequencies is plotted in Figure 6. It is apparent that the g values are strongly frequency dependent. On the other hand the g values do not depend on temperature, at least in the range 140-300 K. The analysis of these data was performed with a least-squares-fit procedure, yielding the principal g values and directions shown in Table VI. It is apparent that not only are the principal g values frequency dependent but so are also the principal directions. Indeed the **g** tensors at X- and Q-band frequencies have one principal axis in common, but different values (2.057 (1) vs. 2.074 (1)), while one set of the other two axes is rotated by 41° from the second set.

The X-band tensor is rhombic, the largest g value being observed along an axis forming a 55° angle with the perpendicular to the equatorial plane of the copper coordination polyhedron, while g_2 is roughly in the plane, close to a bisector of the O-Cu-O angles (Table VI).

The Q-band tensor is closer to the axial limit, with the smallest g value observed almost parallel to the Cu-O2 bond. The other two g values are rotated by 45° from the perpendicular to the equatorial plane.

Also the line widths of the EPR signals are angular, frequency, and temperature dependent, as shown in Figure 7 for the ac^* plane and the b direction. In particular the broadest line width is observed parallel to b. In the ac^* plane the line is broadest parallel to a at Q-band frequency, while it goes through a maximum at about 20° from this at X-band frequency. At both frequencies a decrease in the temperature determines a decrease in the line width.

Discussion

$Cu(hfac)_2(NITPh)$ is practically diamagnetic, showing that the metal and the nitroxide spins are paired. This behavior has already

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(24) Carlin, R. L.; Burriel, R.; Cornelisse, R. M.; Van Duyneveldt, A. J. *Inorg. Chem.* **1983**, *22*, 831.

(25) Hatfield, W. E. *Inorg. Chem.* **1983**, *22*, 833.

(26) Bencini, A.; Gatteschi, D. *Transition Met. Chem.* (*N. Y.*) **1982**, *8*, 9.

Table VII. Binding Geometry of the Nitroxyl Group in Axially Bound Copper(II) Nitroxyl Complexes

compound	Cu–O, Å	Cu–O–N, deg	β,[d] deg	γ,[e] deg	J, cm^{-1}	ref
$Cu(hfac)_2TEMPOL$[a]	2.439	170.1	5	85.88	13	11, 18
Cu(pacTEMPOL)[b] A	2.583	158.5	7.13	76.40	19	10
Cu(pacTEMPOL)[b] B	3.157	139.5	11.79	53.99	19	10
Cu(ProxFORMYL)[c]	2.606	133.6	11.94	55.36	21	28
$Cu(hfac)_2(NITPh)_2$	2.393	135.7	9.14	58.07		this work
	2.362	132.8	9.22	52.02		this work

[a] $Cu(hfac)_2TEMPOL$ = bis(hexafluoroacetylacetonato)(1-oxy-2,2,6,6-tetramethylpiperidin-4-yl)copper(II). [b] Cu(pacTEMPOL) = Bis[(1-oxy-2,2,6,6-tetramethylpiperidin-4-yl)pivaloylacetato]copper(II). [c] Cu(ProxFORMYL) = Bis[3-formyl-4-oxo-1-oxy-2,2,5,5-pyrrolidinyl]copper(II). [d] β = angle between the perpendicular to the equatorial coordination plane of the copper ion and the Cu–O (nitroxide) direction. [e] γ = angle between the equatorial coordination plane of the copper ion and the nitroxide plane.

been observed for $Cu(hfac)_2TEMPO$[16] and is a characteristic of copper(II) complexes that have nitroxide ligands in the equatorial plane. Since two different molecules are observed in the unit cell of $Cu(hfac)_2(NITPh)$, which can be described according to different distortion from a square pyramid to a trigonal bipyramid, it is apparent that both cases lead to full coupling of the spins, although the magnetic orbital on copper must be different in the two different molecules.

The magnetic properties of $Cu(hfac)_2(NITPh)_2$ are indicative of a very weak coupling between the three spins. In order to relate this difference to structural parameters, in Table VII we have collected the bond distances and angles that may be considered as relevant to the exchange interaction together with the coupling constants experimentally determined. From Table VII we learn that in $Cu(hfac)_2(NITPh)_2$ the shortest copper–axial oxygen distance of the series is observed, together with the smallest Cu–O–N angle. The coupling between copper and nitroxide is expected to be weakly ferromagnetic as long as the two magnetic orbitals, $x^2 - y^2$ on copper and x (π^*) on the oxygen and nitrogen atoms of the nitroxide, are orthogonal to each other. This condition is met for axially bound nitroxides when the Cu–O–N angle is 180°. When this angle decreases, the overlap between the two magnetic orbitals increases, thus yielding an increasingly larger antiferromagnetic coupling. Another factor must obviously be the metal–oxygen distance, a shorter distance giving a larger overlap and a stronger antiferromagnetic coupling. Therefore we tentatively attribute the small ferromagnetic coupling observed in $Cu(hfac)_2(NITPh)_2$ to the fact that the Cu–O–N angle is markedly different from 180°, and the copper–oxygen distance is short, thus giving a $x^2 - y^2$ to π^* overlap different from zero.

The most interesting result of the EPR spectra is the g shift observed on varying the energy of the microwave quantum and the nonparallelism of the two **g** tensors at the two different frequencies. This is totally new, because in all previous cases of clusters of three $S = {}^1/_2$ spins involving copper ions and nitroxides, we always observed frequency-independent **g** tensors.[9,12] The main difference of this cluster from the previous ones is that the intramolecular exchange in this case must be small; therefore, we suspect that an explanation of this strange behavior must rely on a model within a small exchange limit.

In a three-spin cluster, when the isotropic and anisotropic exchange terms are comparable, four Kramers doublets are obtained.[27] Transitions within the Kramers doublets and transitions involving different doublets can be induced, if the zero-field splittings are comparable to the microwave quanta. If intermolecular coupling averages these transitions, only one signal will be observed for each crystal orientation. Due to the mixing of the different doublets that are quasi-degenerate in the zero field, the average comprises both field-dependent and field-independent contributions. It is the latter that causes the resonance field to occur at different effective g values at various frequencies.

In principle it would be possible to calculate the apparent g values, but the number of parameters required, J, J', and the zero-field splitting tensors relative to the copper–nitroxyl and nitroxyl–nitroxyl interactions, make a quantitative analysis of the data impossible. Sample calculations however show that the above interpretation is feasible, yielding meaningful g shifts when the zero-field splitting parameters become of the order of 0.3–0.5J. For instance, for the external magnetic field parallel to z the g values are calculated to be 2.10 at both X- and Q-band frequencies for $J = -1\ cm^{-1}$, $J' = 0\ cm^{-1}$ and $D = 0\ cm^{-1}$. If D increases to 0.48 cm^{-1} the g value at X-band frequency shifts to 2.13 and that at Q-band frequency remains unchanged. The rotation of the principal axes of **g** on varying the frequency shows that the zero-field splitting tensors are not axial, a result in line with our finding of the **D** tensor in $Cu(hfac)_2TEMPOL$ (hfac = hexafluoroacetylacetonate; TEMPOL = 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl).[11]

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Registry No. $Cu(hfac)_2(NITPh)$, 106681-95-2; $Cu(hfac)_2(NITPh)_2$, 106681-96-3; $Cu(hfac)_2$, 14781-45-4.

Supplementary Material Available: Complete listing of bond lengths and angles (Tables SI and SIV) and anisotropic thermal parameters (Tables SII and SV) for $Cu(hfac)_2(NITPh)$ and $Cu(hfac)_2(NITPh)_2$ (11 pages); complete listing of observed and calculated structure factors for both compounds (Tables SIII and SVI) (36 pages). Ordering information is given on any current masthead page.

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(27) Gatteschi, D.; Bencini, A. In *Magneto-Structural Correlations in Exchange Coupled Systems*; Willett, R. I., Gatteschi, D., Kahn, O., Eds.; D. Reidel: Dordrecht, Holland, 1985; pp 241–268.

(28) Laugier, J.; Ramasseul, R.; Rey, P.; Espie, J. C.; Rassat, A. *Nouv. J. Chim.* **1983**, *7*, 11.