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Structure of Bis(hexafluoroacetylacetonato)(2,2,6,6-tetramethylpiperidinyl-1-oxy)copper(II), a Copper(II)–Nitroxyl Radical Complex with Substantial Magnetic Coupling

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The crystal and molecular structures of Cu(hfac)$_2$TMPO (hfac = hexafluoroacetylacetonato; TMPO = 2,2,6,6-tetramethylpiperidinyl-1-oxy) have been determined by a single-crystal X-ray analysis. Crystals of Cu(hfac)$_2$TMPO are triclinic, space group $P\bar{1}$, with two molecules in a unit cell of dimensions a = 9.900 (1) Å, b = 11.862 (2) Å, c = 13.416 (3) Å, α = 87.34 (1)°, β = 99.72 (1)°, γ = 122.95 (1)°. Blocked full-matrix least-squares refinement, based upon 2998 nonzero intensity data, converged to a conventional R factor of 0.083. The Cu(hfac)$_2$TMPO molecule is a discrete five-coordinate monomer, with a pair of chelating hfac ligands and a monodentate O-bonded nitroxyl radical. The coordination about the copper ion is best described as distorted square pyramidal, with the nitroxyl oxygen atom occupying a basal coordination site. Significant parameters of the coordinated nitroxide include Cu–O = 1.920 (5) Å, O–N = 1.267 (7) Å, and Cu–O–N = 123.9 (4)°. The structural results are of use in rationalizing the magnetic properties of this and related molecules.

Introduction

Nitroxyl radicals are one of the largest and best characterized groups of stable organic free radicals.[1-3] Much of the interest in these molecules stems from their utility as spin labels in the study of biological systems.[4-9] In such applications, the nitroxyl functional group normally serves only as the carrier of the unpaired spin and does not enter into covalent bonding interactions beyond the confines of the spin label molecule. The nitroxyl group can, however, act as a Lewis base,[8-10] and a limited number of compounds have been isolated in which the nitroxyl function itself is believed to be bound to a Lewis acid center, usually a transition-metal ion.[8,10-14] In cases where the metal ion is paramagnetic, such complexes provide the interesting possibility of studying the interaction between the inequivalent unpaired spins of the metal and the ligand. Owing to the proximity of the paramagnetic centers in such molecules, it might be expected that this interaction could be large, in contrast to the small couplings observed in cases where the nitroxyl moiety is remote from the metal ion.[7] In known complexes believed to contain nitroxyl groups bound to paramagnetic metal ions, interactions have been found of greatly varying magnitudes, ranging from strong antiferromagnetic coupling to relatively weak interactions.[14]

An early example of a metal complex containing a coordinated nitroxyl group was Cu(hfac)$_2$TMPO,[15] first reported by Lim and Drago in 1972.[10] This compound was characterized by elemental analysis, calorimetric studies, NMR spectra, and variable-temperature magnetic susceptibility measurements. It was formulated as a Cu(II) complex of the TMPO radical rather than as the product of a metal–ligand redox process. Its near diamagnetism was interpreted as resulting from strong antiferromagnetic coupling (estimated $|2J|$ > 450 cm^{-1}) of the metal and ligand free spins.[10] Further understanding of the properties of this complex was hampered by the absence of definitive structural information; in fact, until very recently[14] there have been no crystal structure data available for any complex containing a metal-coordinated nitroxyl moiety. This provided the motivation for our crystal structure analysis of the title compound.

Table I. Crystal Data and Experimental Parameters

	A. Crystal Data		
formula	CuC$_{19}$H$_{20}$NO$_5$	fw	405.91
a, Å	9.900 (1)	V, Å^3	1301.0 (4)
b, Å	11.862 (2)	Z	2
c, Å	13.416 (3)	d(obsd), g cm^{-3}	1.61 (2)
α, deg	87.34 (1)	d(calcd), g cm^{-3}	1.61
β, deg	99.72 (1)	space group	$P\bar{1}$
γ, deg	122.95 (1)	μ(Mo Kα), cm^{-1}	9.9
	B. Experimental Parameters		
radiation	Mo Kα; λ(Kα) = 0.71073 Å; graphite monochromator	scan range	−1.1° from Kα_1 to +1.1° from Kα_2
temp, °C	24	bkgd counting	stationary counts for $^1/_2$ of scan time at each end of scan
receiving aperture	circular, 4-mm diam, 20 cm from crystal		
scan rate, deg min^{-1}	variable, 2 to 12	2θ(max), deg	50
		data collected	4609
		data with $F_o^2 > 3\sigma(F_o^2)$	2998

Experimental Section

Preparation of Cu(hfac)$_2$TMPO. Solvents were dried over molecular sieves prior to use. Cu(hfac)$_2$,[16] TMPO,[17] and the adduct[10] were prepared by the reported procedures. Crystals were grown by slow evaporation of dichloromethane–heptane or pentane–heptane solutions.

Data Collection and Reduction. Dark green crystals of the adduct were mounted in sealed glass capillaries or coated with epoxy cement after mounting on glass fibers. The quality of these crystals was marginal, as indicated by asymmetric, broad, and/or split peak profiles of ω scans of many low-angle reflections. All of the approximately 30 crystals examined showed these problems to some degree. Complete data sets were collected from two of these crystals which were judged best. Refinement based upon both of these data sets yielded comparable results. The structural results reported here are derived from an irregularly shaped crystal of dimensions 0.3 × 0.4 × 0.5 mm.

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Typical low-angle reflections of this crystal had ω-scan half-widths of 0.26° with high-angle shoulders which were sometimes partially resolved into a second maximum of about half the height of the main peak and 0.17° above it in ω. Initial centering of reflections, generation of unit cell vectors, and assignment of indices were performed on a Syntex $P2_1$ automated diffractometer by published procedures.[18] Triclinic symmetry was indicated by interaxial angles and confirmed by axial photographs and a Delaunay reduction.[19] Refined cell parameters were obtained from the settings of 15 reflections with $30° \leq 2\theta \leq 35°$. The tabulated values are the three shortest noncoplanar lattice translations. The density was measured by flotation in aqueous zinc bromide with detergent added. Part A of Table I contains a summary of crystal data. The 2θ–θ scan technique in bisecting geometry was used to collect intensity data. Other experimental parameters are listed in part B of Table I. No reflections were strong enough to exceed the valid range of the coincidence correction. Four standard reflections were monitored after every 50 data. These showed a decline of approximately 15% during the data collection and the intensities were corrected accordingly. Data processing was accomplished as previously described.[20] The *p* factor in the expression for the standard deviation of the observed intensities[21] was given a value of 0.05. No absorption correction was made.

Structure Solution and Refinement. Intensity statistics indicated a centrosymmetric structure. The MULTAN system of direct-method programs[22] successfully located the copper atom, its inner coordination sphere, and the carbon skeleton of one hfac ring. The remaining nonhydrogen atoms were located by difference Fourier syntheses.[23] In the final least-squares refinement, anisotropic thermal parameters were employed for all nonhydrogen atoms. Because of the large number of variable parameters, refinement was carried out in three blocks, with each hfac ligand and the TMPO refined separately. The copper atom and the scale factor were refined with each block. 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 not refined. In the course of refinement, difference Fourier maps were carefully examined for evidence of disorder of the CF_3 groups. Although peaks were found in the vicinity of these groups, no plausible overall disorder model could be constructed for any CF_3 group. As a final check, structure factors were calculated for a model from which the fluorine atoms had been omitted. A difference map based upon these structure factors showed only the fluorine atoms which had been used in the refinement, with no chemically reasonable alternative peaks of significant height. Consequently, the fluorine atoms were represented by an ordered model with anisotropic thermal parameters. Final refinement converged to conventional *R* factors of $R_1 = 0.083$ and $R_2 = 0.116$.[24] These higher than usual final values are presumably a consequence of the marginal crystal quality and/or the large thermal motion of the CF_3 groups. In the final cycle, the maximum parameter shift was 1.1 standard deviations for a fluorine atom and 0.75 σ for all other atoms. A final difference map contained no peaks higher than 0.2 e/A^3.

In all structure factor calculations, atomic scattering factors (including anomalous terms for Cu) were taken from ref 25. The final standard deviation of an observation of unit weight was 3.10. Calculation of structure factors for the data with $F_o^2 \leq 3\sigma(F_o^2)$ showed 51 reflections with $F_c^2 \leq 3\sigma(F_o^2)$; of these, 13 had $\Delta F/\sigma$ values greater than 5.

Final atomic positional and thermal parameters are listed in Tables II and III, respectively. Intramolecular distances are given in Table IV, and bond angles are tabulated in Table V. Data relating to selected molecular planes are presented in Table VI. Tables of observed and calculated structure factors and of calculated hydrogen atom parameters are available.[26]

Table II. Atomic Positional Parameters

atom	*x*	*y*	*z*
Cu	0.07987 (12)[a]	0.04415 (9)	0.22763 (9)
O(1)	0.3077 (6)	0.1810 (5)	0.2353 (4)
O(2)	0.1277 (6)	−0.0915 (5)	0.2519 (4)
O(3)	−0.1556 (7)	−0.0907 (6)	0.2211 (6)
O(4)	0.0305 (6)	0.1546 (5)	0.1304 (4)
O(5)	0.0834 (7)	0.1634 (6)	0.3463 (4)
N	0.4179 (7)	0.1565 (6)	0.2369 (5)
C(1)	0.4637 (11)	0.1526 (9)	0.1374 (7)
C(2)	0.5525 (13)	0.0768 (11)	0.1472 (9)
C(3)	0.6805 (13)	0.1239 (12)	0.2375 (10)
C(4)	0.6045 (12)	0.1016 (10)	0.3326 (9)
C(5)	0.5524 (10)	0.1763 (8)	0.3371 (6)
C(6)	0.3033 (12)	0.0763 (11)	0.0579 (7)
C(7)	0.5693 (14)	0.2983 (10)	0.1051 (8)
C(8)	0.6482 (13)	0.3310 (10)	0.3583 (9)
C(9)	0.4185 (12)	0.1236 (10)	0.4175 (7)
C(10)	0.0283 (10)	−0.2152 (8)	0.2631 (6)
C(11)	−0.1375 (10)	−0.2784 (8)	0.2585 (7)
C(12)	−0.2158 (10)	−0.2083 (9)	0.2377 (7)
C(13)	0.1022 (12)	−0.2950 (9)	0.2811 (10)
C(14)	−0.4012 (14)	−0.2917 (16)	0.2320 (14)
C(15)	0.0797 (9)	0.2739 (8)	0.1499 (6)
C(16)	0.1310 (10)	0.3401 (8)	0.2439 (7)
C(17)	0.1240 (10)	0.2821 (9)	0.3316 (7)
C(18)	0.0879 (17)	0.3547 (11)	0.0580 (9)
C(19)	0.1698 (21)	0.3672 (16)	0.4234 (11)
F(13-1)[b]	0.2075 (10)	−0.2669 (8)	0.2242 (7)
F(13-2)	0.0023 (9)	−0.4212 (6)	0.2719 (10)
F(13-3)	0.1974 (12)	−0.2596 (9)	0.3748 (6)
F(14-1)	−0.4751 (8)	−0.2515 (10)	0.1719 (8)
F(14-2)	−0.4679 (9)	−0.4099 (9)	0.2569 (11)
F(14-3)	−0.4309 (13)	−0.2549 (16)	0.3189 (10)
F(18-1)	0.1460 (12)	0.4780 (7)	0.0724 (6)
F(18-2)	−0.0585 (14)	0.2992 (10)	0.0057 (8)
F(18-3)	0.1694 (18)	0.3488 (12)	−0.0048 (7)
F(19-1)	0.2473 (19)	0.4994 (12)	0.4126 (7)
F(19-2)	0.0600 (14)	0.3585 (16)	0.4563 (9)
F(19-3)	0.2646 (15)	0.3516 (12)	0.4973 (7)

[a] Throughout this paper, numbers in parentheses are estimated standard deviations in the least significant figures. [b] Numbering of fluorine and hydrogen atoms includes specification of the carbon atom to which they are bound.

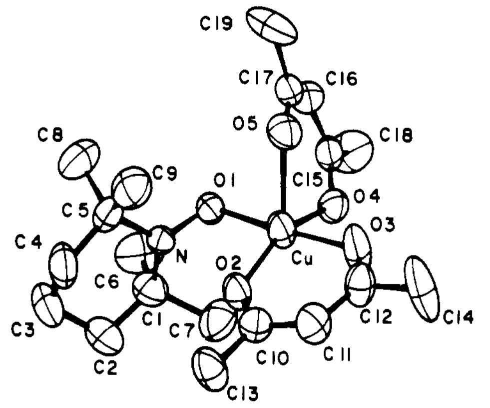

Figure 1. View of the molecular structure of Cu(hfac)$_2$TMPO. Thermal ellipsoids are drawn at the 50% probability level. Fluorine and hydrogen atoms have been omitted for clarity.

Description of the Structure

Views of the molecular structure of bis(hexafluoroacetylacetonato)(2,2,6,6-tetramethylpiperidinyl-1-oxy)copper(II) are shown in Figures 1 and 2. As proposed,[9] the molecule is a

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(26) Supplementary material.

Table III. Atomic Thermal Parameters, Å^2

atom	B_{11}[a]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	3.39 (4)	3.58 (4)	7.00 (6)	2.06 (4)	0.82 (4)	0.81 (4)
O(1)	3.3 (2)	3.4 (2)	4.8 (3)	1.9 (2)	0.6 (2)	−0.1 (2)
O(2)	3.6 (2)	3.7 (2)	6.7 (3)	2.1 (2)	0.8 (2)	0.9 (2)
O(3)	3.4 (3)	4.9 (3)	11.7 (5)	2.5 (2)	1.2 (3)	2.2 (3)
O(4)	4.4 (3)	4.0 (2)	4.3 (3)	2.5 (2)	−0.6 (2)	0.0 (2)
O(5)	5.5 (3)	6.9 (4)	4.3 (3)	4.0 (3)	1.2 (2)	0.3 (2)
N	3.3 (3)	3.3 (3)	4.0 (3)	1.7 (2)	0.3 (2)	0.2 (2)
C(1)	4.9 (4)	5.2 (4)	5.5 (5)	2.6 (4)	1.3 (4)	−0.3 (4)
C(2)	6.3 (5)	8.2 (6)	8.1 (6)	4.8 (5)	2.1 (5)	−0.9 (5)
C(3)	5.3 (5)	8.9 (7)	11.3 (9)	5.2 (5)	0.9 (6)	−0.2 (6)
C(4)	4.3 (4)	6.8 (5)	8.8 (7)	3.4 (4)	−0.5 (4)	0.5 (5)
C(5)	4.1 (4)	4.4 (4)	4.7 (4)	1.9 (3)	−0.3 (3)	−0.2 (3)
C(6)	5.8 (5)	8.2 (6)	4.8 (5)	3.3 (5)	0.3 (4)	−1.1 (4)
C(7)	7.7 (6)	5.6 (5)	7.5 (6)	2.1 (5)	3.7 (5)	1.4 (5)
C(8)	6.2 (6)	5.5 (5)	8.3 (7)	1.9 (5)	−1.3 (5)	−2.3 (5)
C(9)	6.4 (5)	7.8 (6)	4.4 (5)	4.0 (5)	0.1 (4)	−0.2 (4)
C(10)	4.1 (4)	3.8 (4)	4.4 (4)	2.0 (3)	0.7 (3)	0.6 (3)
C(11)	4.1 (4)	4.1 (4)	6.7 (5)	1.6 (3)	2.0 (4)	1.2 (3)
C(12)	3.5 (4)	4.6 (4)	6.1 (5)	1.7 (3)	0.6 (3)	1.7 (4)
C(13)	4.9 (5)	4.2 (4)	10.4 (8)	2.8 (4)	2.4 (5)	1.7 (4)
C(14)	4.8 (5)	10.2 (4)	14.6 (11)	5.0 (6)	4.1 (7)	6.3 (8)
C(15)	3.4 (3)	4.2 (4)	5.3 (5)	2.2 (3)	0.5 (3)	0.4 (3)
C(16)	4.5 (4)	4.0 (4)	5.6 (5)	2.3 (3)	0.2 (3)	−0.5 (4)
C(17)	4.6 (4)	5.8 (5)	4.6 (5)	3.6 (4)	−0.1 (3)	−0.7 (4)
C(18)	9.3 (8)	6.1 (6)	6.2 (6)	5.1 (6)	−1.2 (6)	0.4 (5)
C(19)	12.5 (10)	10.2 (9)	9.1 (9)	8.9 (9)	3.4 (8)	0.2 (7)
F(13-1)	10.0 (5)	10.0 (4)	15.6 (6)	8.0 (4)	4.7 (5)	2.7 (4)
F(13-2)	6.7 (4)	4.1 (3)	37.3 (15)	3.1 (3)	4.9 (6)	3.1 (5)
F(13-3)	16.3 (7)	14.7 (6)	10.2 (5)	12.9 (6)	−0.8 (5)	1.6 (4)
F(14-1)	3.9 (3)	15.9 (7)	17.4 (8)	4.0 (4)	1.1 (4)	6.3 (6)
F(14-2)	4.7 (3)	9.1 (5)	31.4 (13)	2.5 (4)	4.6 (5)	8.3 (8)
F(14-3)	8.0 (6)	24.6 (13)	17.7 (10)	7.4 (7)	4.7 (6)	3.8 (9)
F(18-1)	16.0 (7)	6.1 (4)	10.9 (5)	5.3 (4)	0.3 (5)	2.7 (3)
F(18-2)	15.7 (8)	12.1 (6)	12.5 (7)	4.2 (6)	−6.3 (6)	4.2 (5)
F(18-3)	28.8 (14)	20.5 (10)	10.1 (6)	19.5 (11)	10.7 (8)	9.1 (6)
F(19-1)	28.2 (14)	14.7 (8)	9.3 (6)	15.2 (9)	−3.4 (7)	−4.4 (5)
F(19-2)	13.3 (8)	25.3 (13)	13.8 (8)	9.2 (9)	2.5 (6)	−10.1 (8)
F(19-3)	22.5 (11)	22.5 (10)	9.5 (6)	17.6 (10)	−8.6 (6)	−8.6 (6)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

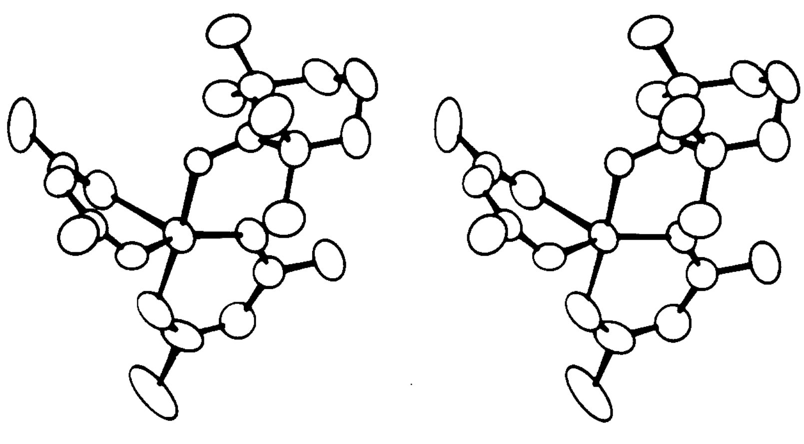

Figure 2. Stereoscopic view of the molecular structure.

discrete five-coordinate monomer, with a pair of chelating hfac ligands and a monodentate O-bonded nitroxyl radical. On the basis of bond angles at the copper atom, the coordination geometry is intermediate between square pyramidal and trigonal bipyramidal. The pattern of one long and four short Cu–O distances suggests that the configuration is best described as distorted square pyramidal. The nitroxyl oxygen atom O(1) then occupies a basal coordination site and is nearly coplanar with Cu, O(3), and O(4); these four atoms hence can be taken to define the basal plane of the square pyramid. The principal distortion from C_{4v} local symmetry about Cu is then a displacement of O(2) by 1.01 Å below the basal plane. This distortion is reflected in the bond angles O(2)–Cu–O(4) = 149.4 (2)° and O(2)–Cu–O(5) = 123.9 (2)°. All other O–Cu–O angles are within a few degrees of 90 or 180°.

The TMPO ligand is bound to Cu via a short Cu–O(1) bond of length 1.920 (5) Å. In contrast to the near-linear Cu–O–N angle of 170.1 (5)° found in the only other structurally characterized system containing a metal-coordinated nitroxyl function,[14] the Cu–O(1)–N angle in this molecule is 123.9 (4)°. The N–O(1) distance of 1.269 (7) Å and the C(1)–N–C(5) angle of 124.3 (7)° are close to the comparable values of 1.283 (9) Åand 123.6 (3)° found in free TMPO.[27] The

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[27] Capiomont, A.; Lajzerowicz-Bonneteau, J. *Acta Crystallogr., Sect. B* **1974**, *B30*, 2160.

Table IV. Bond Distances (Å)

(a) Copper Coordination Sphere			
Cu–O(1)	1.920 (5)	Cu–O(4)	1.995 (5)
Cu–O(2)	1.910 (5)	Cu–O(5)	2.162 (6)
Cu–O(3)	1.971 (6)		
(b) TMPO Ligand			
N–O(1)	1.269 (7)	C(2)–C(3)	1.470 (15)
N–C(1)	1.491 (11)	C(3)–C(4)	1.529 (16)
N–C(5)	1.493 (10)	C(4)–C(5)	1.502 (12)
C(1)–C(2)	1.552 (12)	C(5)–C(8)	1.563 (12)
C(1)–C(6)	1.559 (13)	C(5)–C(9)	1.491 (13)
C(1)–C(7)	1.544 (12)		
(c) Chelate Rings			
O(2)–C(10)	1.265 (9)	O(4)–C(15)	1.244 (9)
C(10)–C(11)	1.375 (11)	C(15)–C(16)	1.381 (11)
C(11)–C(12)	1.407 (12)	C(16)–C(17)	1.328 (12)
C(12)–O(3)	1.209 (9)	C(17)–O(5)	1.252 (10)
(d) Trifluoromethyl Groups			
C(10)–C(13)	1.471 (12)	C(15)–C(18)	1.512 (13)
C(13)–F(13-1)	1.284 (12)	C(18)–F(18-1)	1.258 (11)
C(13)–F(13-2)	1.265 (11)	C(18)–F(18-2)	1.299 (14)
C(13)–F(13-3)	1.364 (13)	C(18)–F(18-3)	1.289 (14)
C(12)–C(14)	1.528 (13)	C(17)–C(19)	1.474 (15)
C(14)–F(14-1)	1.248 (13)	C(19)–F(19-1)	1.332 (17)
C(14)–F(14-2)	1.240 (14)	C(19)–F(19-2)	1.192 (15)
C(14)–F(14-3)	1.392 (19)	C(19)–F(19-3)	1.325 (15)

nitrogen atom coordination is significantly nonplanar, with N displaced by 0.14 Å from the O(1)–C(1)–C(5) plane. A similar degree of nonplanarity is observed both in free TMPO[27] and in its 4-hydroxy derivative.[28] The O(1)–C(1)–C(5) and Cu–O(1)–N planes are nearly perpendicular, forming a dihedral angle of 85.1°.

The two inequivalent six-membered chelate rings have distinctly different conformations. In both rings, the oxygen and carbon atoms are nearly coplanar. However, in the ring containing two basal oxygen atoms, O(2) and O(3), the displacement of the metal ion from the ligand plane is only 0.09 Å. In the apical to basal ring, which contains O(4) and O(5), the copper atom is out of the ligand plane by 0.69 Å. This sort of "tilted" ring has been observed previously in other copper(II) hfac complexes.[29,30] The bond distances and angles within the chelate rings are generally within ranges of previously observed values; some apparent variations between chemically equivalent distances are found, but in view of the limitations in this structure analysis, their significance is dubious.

As is frequently found in molecules containing CF_3 groups, the thermal parameters of many of the fluorine atoms are very large, indicative of large torsional motions and/or rotational disordering of these groups. Since no convincing disorder model could be constructed for any of the CF_3 groups, refinement was based on a single set of fluorine atoms with anisotropic thermal paramters. Because of the imperfection of this model and the large magnitude of the thermal motion, no significance should be ascribed to the variations in distances or angles within the CF_3 groups.

Discussion

The results of this structure analysis are consistent with the conclusion of Lim and Drago,[10] based upon thermochemical data, that $\mathrm{Cu(hfac)_2TMPO}$ is best formulated as a complex containing copper(II) and a neutral TMPO radical rather than as the product of an internal oxidation–reduction process. The latter possibility requires explicit consideration because of the relative ease of oxidation and reduction of nitroxyl radicals.[31] However, in the present case the distorted tetragonal-pyramidal coordination is consistent with the presence of Cu(II) and the structure of the coordinated TMPO radical closely resembles that of free TMPO in all significant respects. These observations support the view that the $\mathrm{Cu^I}$–$\mathrm{TMPO^+}$ and $\mathrm{Cu^{III}}$–$\mathrm{TMPO^-}$ formulations need not be seriously considered.

The presence of an axial-to-basal hfac ligand and a basal TMPO is not without precedent in other square-pyramidal or tetragonally elongated octahedral copper(II) complexes $\mathrm{Cu(AA)_2L}$ or $\mathrm{Cu(AA)_2L_2}$ (AA = a chelating β-ketoenolate or related ligand, L = a monodentate addend). Structurally characterized examples of such systems include six-coordinate adducts of pyridine[30] and bipyridine[32] with $\mathrm{Cu(hfac)_2}$, a 4-aminopyridine adduct of $\mathrm{Cu(acac)_2}$,[33] and 2-picolinebis(2-nitroacetophenonato)copper(II).[34] The latter two structures most closely resemble that found in the present case, though in each of them the distortions from normal square-pyramidal geometry are smaller. In the triphenylphosphine adduct of $\mathrm{Cu(hfac)_2}$, electronic and EPR spectra have been interpreted as indicating the existence of isomers with basal or axial $\mathrm{PPh_3}$ ligands, depending upon the medium in which observations were made.[35]

The only other structurally characterized complex containing a metal-coordinated nitroxyl function is $\mathrm{Cu(hfac)_2}$-(TMPO–OH) (TMPO–OH = 4-hydroxy derivative of TMPO), whose crystal structure was reported very recently by Anderson and Kuechler.[14] Although the $\mathrm{Cu(hfac)_2}$ adducts of TMPO and TMPO–OH are formally analogous, their structures differ in several important respects. The configuration about the copper ion in the TMPO–OH adduct is that of a tetragonally elongated octahedron, with the hfac ligands occupying basal coordination sites. The nitroxyl ligand is bidentate, linking the $\mathrm{Cu(hfac)_2}$ units into a chain structure. Both of the axial Cu–O distances are relatively long—2.439 (6) Å to the nitroxyl oxygen atom and 2.414 (4) Å to the hydroxyl oxygen atom. A surprising feature is the near-linear Cu–O–N bond angle of 170.1 (5)°, very different from the value expected for an sp^2-hybridized oxygen atom and from the value of 123.9 (4)° which we find in the TMPO adduct. Also unusual are the relative flatness of the chair conformation of the TMPO–OH ring and the near planarity of the nitroxyl nitrogen atom. Free TMPO,[27] free TMPO–OH,[28] and coordinated TMPO in $\mathrm{Cu(hfac)_2TMPO}$ all have distinctly less planar six-membered rings and more pyramidal nitrogen atoms.

As noted by Anderson and Kuechler,[14] the thermal parameters of the atoms of the TMPO–OH ligand provide a partial explanation for the anomalies noted above. The pattern of thermal motion is consistent with the presence of a "chair–chair" disorder, either static or dynamic, between two conformations of the TMPO–OH ring. A similar disorder was found in the tetragonal form of free TMPO.[27] The averaging of the coordinates of the TMPO atoms over those of the two disordered conformers could account, at least in part, for the unusual flatness of the six-membered ring and the planarity of the nitrogen atom. The Cu–O–N angle could also be affected somewhat, but estimates based upon the principal root-mean-square thermal displacements of O(1) indicated that the actual angle in a single conformer could not differ by more than 20° from the reported value of 170.1 (5)°. Hence it can be stated with confidence that the Cu–O–N angle we observe is substantially smaller than that in the TMPO–OH adduct. This observation, together with the longer Cu–O distance in

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Table V. Bond Angles (Deg)

(a) Copper Coordination Sphere

O(1)–Cu–O(2)	91.1 (2)	O(1)–Cu–O(5)	86.0 (2)	O(2)–Cu–O(5)	123.9 (2)	O(3)–Cu–O(5)	92.1 (2)
O(1)–Cu–O(3)	177.7 (2)	O(2)–Cu–O(3)	91.1 (2)	O(3)–Cu–O(4)	90.5 (2)	O(4)–Cu–O(5)	86.5 (2)
O(1)–Cu–O(4)	88.1 (2)	O(2)–Cu–O(4)	149.4 (2)				

(b) TMPO Ligand

Cu–O(1)–N	123.9 (4)	N–C(1)–C(6)	107.8 (7)	C(1)–C(2)–C(3)	112.4 (8)	C(4)–C(5)–C(9)	110.0 (8)
O(1)–N–C(1)	116.4 (6)	N–C(1)–C(7)	108.6 (7)	C(2)–C(3)–C(4)	109.6 (8)	C(8)–C(5)–C(9)	109.2 (8)
O(1)–N–C(5)	116.4 (6)	C(2)–C(1)–C(6)	110.2 (8)	C(3)–C(4)–C(5)	114.0 (8)	N–C(5)–C(8)	107.3 (7)
C(1)–N–C(5)	124.3 (6)	C(2)–C(10)–C(7)	113.0 (9)	C(4)–C(5)–N	108.6 (7)	N–C(5)–C(9)	109.4 (7)
N–C(1)–C(2)	109.0 (7)	C(6)–C(1)–C(7)	108.2 (8)	C(4)–C(5)–C(8)	112.1 (8)		

(c) Chelate Rings

Cu–O(2)–C(10)	127.4 (5)	Cu–O(4)–C(15)	123.3 (5)	O(2)–C(10)–C(11)	126.1 (7)	O(4)–C(15)–C(16)	127.9 (8)
Cu–O(3)–C(12)	125.5 (6)	Cu–O(5)–C(17)	119.7 (5)	C(10)–C(11)–C(12)	121.6 (7)	C(15)–C(16)–C(17)	124.8 (8)
				O(3)–C(12)–C(11)	128.1 (8)	O(5)–C(17)–C(16)	128.0 (8)

(d) Trifluoromethyl Groups

O(2)–C(10)–C(13)	114.8 (7)	C(12)–C(14)–F(14-2)	118.5 (10)	C(15)–C(18)–F(18-3)	113.1 (9)
C(11)–C(10)–C(13)	119.1 (7)	C(12)–C(14)–F(14-3)	106.3 (13)	F(18-1)–C(18)–F(18-2)	108.2 (10)
O(3)–C(12)–C(14)	115.7 (9)	F(14-1)–C(14)–F(14-2)	122.4 (13)	F(18-1)–C(18)–F(18-3)	105.1 (13)
C(11)–C(12)–C(14)	116.2 (8)	F(14-1)–C(14)–F(14-3)	95.1 (12)	F(18-2)–C(18)–F(18-3)	103.2 (12)
C(10)–C(13)–F(13-1)	113.6 (9)	F(14-2)–C(14)–F(14-3)	90.6 (13)	C(17)–C(19)–F(19-1)	116.5 (12)
C(10)–C(13)–F(13-2)	115.3 (9)	O(4)–C(15)–C(18)	114.7 (8)	C(17)–C(19)–F(19-2)	116.2 (14)
C(10)–C(13)–F(13-3)	109.4 (9)	C(16)–C(15)–C(18)	117.4 (8)	C(17)–C(19)–F(19-3)	112.7 (9)
F(13-1)–C(13)–F(13-2)	106.5 (10)	O(5)–C(17)–C(19)	115.5 (9)	F(19-1)–C(19)–F(19-2)	95.2 (12)
F(13-1)–C(13)–F(13-3)	101.3 (9)	C(16)–C(17)–C(19)	116.5 (10)	F(19-1)–C(19)–F(19-3)	105.4 (15)
F(13-2)–C(13)–F(13-3)	109.7 (10)	C(15)–C(18)–F(18-1)	117.9 (10)	F(19-2)–C(19)–F(19-3)	109.1 (15)
C(12)–C(14)–F(14-1)	114.5 (10)	C(15)–C(18)–F(18-2)	108.3 (11)		

Table VI. Molecular Planes (Deg)

1. $0.4793X - 0.4457Y - 0.7561Z = -11.1088$

O(1)	0.011	Cu	−0.021
O(3)	0.010	O(2)*	−1.009
O(4)	0.000		

2. $0.1379X - 0.1550Y - 0.9782Z = -11.2853$

O(2)	0.008	O(3)	−0.007
C(10)	−0.010	Cu*	0.086
C(11)	0.002	C(13)*	−0.069
C(12)	0.008	C(14)*	0.018

3. $-0.9682X - 0.2498Y - 0.0143Z = -4.2182$

O(4)	0.004	O(5)	0.007
C(15)	−0.015	Cu*	0.680
C(16)	0.022	C(18)*	−0.040
C(17)	−0.019	C(19)*	−0.101

4. $0.0835X + 0.9960Y - 0.0308Z = 7.2430$

O(1)	0.000	C(5)	0.000
C(1)	0.000	N*	0.140

5. $0.5073X + 0.8616Y - 0.0154Z = 5.4445$

C(1)	−0.012	C(5)	0.012
C(2)	0.013	C(3)*	−0.701
C(4)	−0.013	N*	0.444

[a] Tabulated values are distances in Å to the plane. Atoms marked with an asterisk were not used in the definition of the plane, while all others were given unit weights. [b] Equations of planes are expressed with respect to coordinates (*X*, *Y*, *Z*) referred to an orthogonal system (*A*, *B*, *C*) with *A* parallel to *a*, *B* parallel to $c^* \times a$, and *C* parallel to $A \times B$.

the TMPO–OH adduct, indicates a qualitative difference in the nature of the Cu–O bonds in these two molecules. At this point it is unclear whether this difference has its origin in some electronic property of the nitroxide ligands or if it is a consequence of the bidentate bridging geometry of the TMPO–OH ligand.

The near perpendicularity of the Cu–O–N and C(1)–N–C(5) planes (dihedral angle 85.1°) is somewhat surprising. The simplest bonding picture for the nitroxide ligand would involve coordination via an oxygen lone pair localized in an sp^2-hybrid orbital lying approximately in the C(1)–N–C(5) plane. This picture is consistent with the Cu–O(1)–N angle of 123.9 (4)° but not with the observed dihedral angle. An alternative bonding picture, in which the unpaired ligand and metal electrons form the Cu–O(1) bond is inconsistent with the residual paramagnetism of the adduct,[10] with the similarity of the configurations of free and coordinated TMPO, and with the enthalpy data of Lim and Drago.[10] It should be noted that the near-linear Cu–O–N angle in the TMPO–OH adduct is also difficult to rationalize on the basis of simple bonding models.

On the other hand, the large magnetic interaction observed in $Cu(hfac)_2TMPO$[10] may readily be rationalized on the basis of these structural results. Since the bond angles about the copper atom are approximately midway between those expected for a square pyramid and for a trigonal bipyramid, it is not possible to specify unequivocally the identity of the metal orbital containing the odd electron; in the square-pyramidal limit it would be expected to be the $d_{x^2-y^2}$ orbital, while for a trigonal bipyramid the d_{z^2} orbital would be most likely. For the observed bent metal–ligand bonding configuration, both of these orbitals are of appropriate symmetry for overlap with the nitroxyl π^* orbital, in which the free electron of the TMPO ligand is expected to reside. In the analogous TMPO–OH complex, for which a much smaller magnetic interaction has been observed, the orbital overlap would be expected to be smaller owing to the larger Cu–O–N angle and the longer Cu–O distance in that molecule.[14]

We can thus conclude that the structural differences between the TMPO and TMPO–OH adducts of $Cu(hfac)_2$ are qualitatively in accord with the magnetic properties of these two adducts. More detailed analysis of the interrelationships between structure and magnetic interactions in metal–nitroxyl complexes will require studies of these and related systems. Such studies are currently under way in our laboratory.

Registry No. $Cu(hfac)_2TMPO$, 37768-27-7.

Supplementary Material Available: Listings of structure factors and H atomic parameters (22 pages). Ordering information is given on any current masthead page.