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Preparation and Crystal Structure of Aqua(3-cyano-2,2,5,5-tetramethylpyrrolinyl-1-oxy)bis(hexafluoroacetylacetonato)copper(II), a Metal Complex of a Nitroxide Radical Having a Hydrogen-Bonded One-Dimensional Chain Structure

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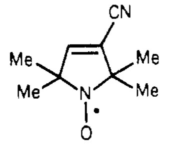
A hydrated 1:1 adduct of bis(hexafluoroacetylacetonato)copper(II) with the stable nitroxyl radical 3-cyano-2,2,5,5-tetramethylpyrrolinyl-1-oxy (tmpCN) has been prepared and characterized by a single-crystal X-ray analysis. Crystals of this compound are triclinic, space group $P\bar{1}$, with two molecules in a unit cell of dimensions $a = 11.835$ (2) Å, $b = 11.942$ (2) Å, $c = 11.988$ (2) Å, $\alpha = 111.21$ (1)°, $\beta = 95.31$ (1)°, and $\gamma = 118.65$ (1)°. Full-matrix least-squares refinement, based upon 3366 nonzero intensity data, converged to a final conventional R factor of 0.054. The crystal structure consists of $Cu(hfac)_2(tmpCN)H_2O$ molecules linked by O–H···O hydrogen bonds into a one-dimensional chain structure. The monomer unit has a tetragonally distorted octahedral structure, with chelating hfac ligands in the equatorial plane. The axial sites are occupied by a water molecule and by the nitrile nitrogen atom of the tmpCN ligand. The equatorial bond distances range from 1.945 (3) to 1.956 (3) Å, while the axial bond distances are as follows: Cu–O, 2.255 (4) Å; Cu–N, 2.616 (5) Å. The nitroxyl group does not form a bond to the copper atom; rather, its oxygen atom participates in the chain-forming hydrogen bond to the water molecule of an adjacent monomer. Magnetic susceptibility measurements over the temperature range 81–294 K show no evidence for interaction between the metal and ligand unpaired spins.

Introduction

Two recent reports provided the first crystal structure data for transition-metal complexes derived from stable nitroxyl radicals in which the radical is bound to the metal ion directly through the nitroxyl oxygen atom.[1,2] Although the two complexes have analogous stoichiometries, $Cu(hfac)_2L$ (L = tmpo, tmpoOH),[3] their structures and magnetic properties are quite different. The tmpo adduct is a discrete pentacoordinate monomer with a short Cu–O (nitroxyl) bond of 1.920 (5) Å.[2] Magnetic susceptibility data are indicative of substantial coupling between the unpaired spins of the metal and the radical.[4] The tmpoOH complex, in contrast, has a linear-chain structure with hexacoordinate Cu^{2+} ions, bridging tmpoOH ligands, and a long Cu–O(nitroxyl) bond of 2.439 (6) Å. This adduct is reported not to have a large magnetic exchange interaction between the metal and ligand free spins.[1] On the basis of the structural differences between these two compounds, a qualitative rationale for their differences in magnetic behavior has been formulated.[2] Both of the structures, however, have features that are not readily rationalized on the basis of simple localized electronic structure models.

The number of stable transition-metal complexes containing a metal-bound nitroxyl group is limited,[5] both because the nitroxyl function is a relatively poor ligand and because nitroxides frequently undergo facile redox reactions in the presence of transition-metal species.[6] Because of the interesting structural and magnetic results obtained to date for these systems and because they provide one of the few opportunities to study a metal-bound free-radical center, we have begun exploratory studies directed toward the preparation and characterization of metal–nitroxyl complexes derived from various types of nitroxyl ligands and transition-metal systems. The title compound was prepared from $Cu(hfac)_2$ and 3-cyano-2,2,5,5-tetramethylpyrrolinyl-1-oxy (tmpCN), a ligand that was felt to have the potential of forming a one-dimensional chain structure similar to that of $Cu(hfac)_2$tmpoOH. In fact, a quite different type of one-dimensional chain structure has been found and is reported herein.



tmpCN

Experimental Section

Synthesis. Anhydrous $Cu(hfac)_2$ and its monohydrate were prepared by literature methods.[7] The ligand 3-cyano-2,2,5,5-tetramethylpyrrolinyl-1-oxy (tmpCN) was made by a standard method.[8] Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

When dichloromethane solutions of tmpCN and either $Cu(hfac)_2$ or $Cu(hfac)_2 \cdot H_2O$ were mixed, a change from the blue color of the copper hfac complex to lime green occurred. However, the nature of the products isolated upon evaporation of the solvent was highly dependent on the amount of water present. With use of anhydrous $Cu(hfac)_2$ and dry solvents, this procedure yielded a mixture containing, among other components, starting materials and a compound exhibiting green–blue dichroism tentatively identified as $Cu(hfac)_2(tmpCN)_2$.[9] If undried solvents, or dry solvents and $Cu(hfac)_2 \cdot H_2O$, were used, the main product was $Cu(hfac)_2(H_2O)(tmpCN)$. The following procedure was found to provide a relatively pure sample of this latter compound. A solution of 0.10 g of $Cu(hfac)_2 \cdot H_2O$ (0.2 mmol) and 0.035 g of tmpCN (0.2 mmol) in 5 mL of dichloromethane and 20 mL of heptane (both dried over $CaCl_2$) was allowed to stand about a week at −10 °C in a 50-mL erlenmeyer flask covered with commercial plastic food wrap. Dichroic green–yellow prismatic crystals formed, which were filtered and washed with heptane. The crystals were stable if kept in a sealed container but

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(1) Anderson, O. P.; Kuechler, T. C. *Inorg. Chem.* **1980**, *19*, 1417.
(2) Dickman, M. H.; Doedens, R. J. *Inorg. Chem.* **1981**, *20*, 2677.
(3) Abbreviations: hfac = hexafluoroacetylacetonato; tmpo = 2,2,6,6-tetramethylpiperidinyl-1-oxy; tmpoOH = the 4-hydroxy derivative of tmpo.
(4) Lim, Y. Y.; Drago, R. S. *Inorg. Chem.* **1972**, *11*, 1334.
(5) A representative listing of nitroxyl complexes is given in ref 2.
(6) Gaffney, B. J. In "Spin Labeling: Theory and Applications"; Berliner, L. J., Ed.; Academic Press: New York, 1976; pp 184–187.
(7) Funck, L. L.; Ortolano, T. R. *Inorg. Chem.* **1968**, *7*, 567.
(8) Rozantsev, E. G. "Free Nitroxyl Radicals"; Plenum Press: New York, 1970; pp 203–207.
(9) This identification is based upon the following preliminary data for a triclinic unit cell: $a = 11.84$ Å, $b = 12.02$ Å, $c = 12.27$ Å, $\alpha = 96.4°$, $\beta = 104.0°$, $\gamma = 82.7°$ (esd's of these crude measurements were approximately 0.01 Å for cell edges and 0.04° for cell angles). Under the reasonable assumptions of $Z = 2$ formula units/cell and a crystal density of 1.6 g cm^{-3}, the calculated formula weight is 806 g mol^{-1} compared to 808 g mol^{-1} calculated for $Cu(hfac)_2(tmpCN)_2$. A pure bulk sample of this material was not obtained.

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Table I. Crystal Data and Experimental Parameters

A. Crystal Data

formula	$CuC_{19}H_{17}F_{12}N_2O_6$	fw	660.88
a, Å	11.835 (2)	V, Å^3	1311.0 (3)
b, Å	11.942 (2)	*Z*	2
c, Å	11.988 (2)	*d*(obsd), g cm^{-3}	1.66 (2)
α, deg	111.21 (1)	*d*(calcd), g cm^{-3}	1.67
β, deg	95.31 (1)	space group	$P\bar{1}$
γ, deg	118.65 (1)	μ(Mo Kα), cm^{-1}	9.5

B. Experimental Parameters

radiation	Mo Kα, λ(Kα) = 0.710 73 Å, graphite monochromator
temp, °C	21
receiving aperture	circular, 4-mm diam, 20 cm from cryst
scan rate, deg min^{-1}	variable, 2-12
scan range	−1.1° from Kα_1 to +1.2° from Kα_2
bkgd counting	stationary counts for $^1/_2$ of scan time at each end of scan
2θ(max), deg	50
data collected	4641
data with $F_o^2 > 3\sigma(F_o^2)$	3366

decomposed if exposed continuously to air or if heated under vacuum: yield 0.10 g (74%); mp 117–119 °C. Anal. Calcd for $CuC_{19}H_{19}F_{12}N_2O_6$: C, 34.53; H, 2.59; N, 4.24; Cu, 9.61. Found: C, 35.07; H, 2.68; N, 4.30; Cu, 9.81.

Collection and Reduction of X-ray Data. An irregularly shaped crystal of dimensions 0.4 × 0.5 × 0.6 mm was mounted in a random orientation on a glass fiber with epoxy glue and coated with a thin lacquer film to retard decomposition. Fifteen reflections taken from a φ rotation photograph were centered and used to generate unit cell vectors; indexing was based on the three shortest noncoplanar lattice translations.[10] Interaxial angles, axial photos, and a Delaunay reduction all indicated triclinic symmetry. Refined cell parameters were obtained from the settings of 15 reflections with $30° \leq 2\theta \leq 35°$. 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. 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 less than 10% during the course of data collections, and the intensities were corrected accordingly. Data processing was accomplished as previously described.[11] The *p* factor in the expression for the standard deviations of the observed intensities[12] was given a value of 0.05. No absorption correction was made.

Structure Solution and Refinement. The MULTAN system of direct-methods programs[13] was used to solve the structure. Intensity statistics were consistent with a centrosymmetric space group. Initial phasing was carried out for 390 reflections with $|E| \geq 1.70$. An *E* map calculated from one of three solutions with high figures of merit clearly showed an image of the Cu atom, skeletons of both hfac rings, and parts of three CF_3 groups. The remaining non-hydrogen atoms were located by difference Fourier techniques. It was at this stage that the presence of a coordinated water molecule was recognized. Final refinement was carried out by blocked full-matrix least-squares methods with anisotropic temperature factors for all non-hydrogen atoms.[14] Three blocks were used, consisting of the parameters of each hfac chelate ring and the tmpCN + H_2O ligands. The blocks were refined in sequence, and the scale factor and copper atom parameters were included in each block. A difference Fourier map in the latter stages of refinement (R_1 = 0.068) showed peaks in reasonable positions for all hydrogen atoms. These were included at fixed, idealized positions in the final refinement. One of the hydrogen atoms of the water molecule appeared to be disordered. Two peaks of approximately equal height were found on either side of the plane defined by the Cu atom, O(2), and H1O2 (which is hydrogen bonded to the nitroxide oxygen in a neighboring molecule). The

Table II. Positional Parameters of Non-Hydrogen Atoms

atom	*x*	*y*	*z*
Cu	0.51655 (4)[a]	0.49899 (4)	0.22181 (5)
O(1)	−0.0936 (3)	0.5682 (4)	0.1888 (4)
O(2)	0.6314 (3)	0.4633 (4)	0.0875 (3)
O(3)	0.6789 (3)	0.6247 (2)	0.3710 (3)
O(4)	0.5317 (3)	0.6616 (3)	0.2045 (3)
O(5)	0.3451 (3)	0.3742 (3)	0.0812 (3)
O(6)	0.4912 (3)	0.3403 (3)	0.2520 (3)
N(1)	−0.0347 (3)	0.5166 (4)	0.2250 (4)
N(2)	0.3656 (4)	0.5320 (6)	0.3599 (5)
C(1)	0.1153 (4)	0.5901 (5)	0.2597 (4)
C(2)	0.1274 (4)	0.4863 (5)	0.2956 (4)
C(3)	0.0102 (5)	0.3774 (5)	0.2831 (4)
C(4)	−0.1080 (4)	0.3859 (5)	0.2412 (4)
C(5)	−0.2114 (5)	0.2548 (6)	0.1143 (5)
C(6)	−0.1760 (5)	0.4080 (6)	0.3420 (5)
C(7)	0.1854 (6)	0.7409 (6)	0.3706 (6)
C(8)	0.1614 (5)	0.5958 (2)	0.1457 (5)
C(9)	0.2591 (5)	0.5100 (6)	0.3325 (4)
C(10)	0.7413 (4)	0.7574 (4)	0.4260 (4)
C(11)	0.7180 (4)	0.8457 (4)	0.3927 (4)
C(12)	0.6152 (4)	0.7902 (4)	0.2839 (4)
C(13)	0.8592 (5)	0.8284 (5)	0.5473 (5)
C(14)	0.6001 (5)	0.8972 (5)	0.2542 (5)
C(15)	0.2631 (4)	0.2440 (4)	0.0491 (4)
C(16)	0.2747 (4)	0.1595 (4)	0.0963 (4)
C(17)	0.3901 (4)	0.2154 (4)	0.1945 (4)
C(18)	0.1329 (5)	0.1719 (5)	−0.0599 (5)
C(19)	0.3989 (6)	0.1131 (5)	0.2365 (6)
F(1)	0.9230 (4)	0.9686 (3)	0.6074 (3)
F(2)	0.9528 (3)	0.8026 (4)	0.5189 (4)
F(3)	0.8183 (4)	0.7767 (4)	0.6237 (3)
F(4)	0.7077 (4)	1.0234 (4)	0.3025 (5)
F(5)	0.5498 (7)	0.8554 (4)	0.1419 (4)
F(6)	0.5194 (6)	0.9211 (6)	0.3066 (7)
F(7)	0.0485 (3)	0.2026 (5)	−0.0172 (4)
F(8)	0.1566 (3)	0.2124 (4)	−0.1465 (3)
F(9)	0.0632 (3)	0.0304 (3)	−0.1163 (3)
F(10)	0.2816 (4)	−0.0080 (4)	0.2006 (4)
F(11)	0.4704 (5)	0.0708 (5)	0.1806 (6)
F(12)	0.4556 (6)	0.1692 (4)	0.3533 (4)

[a] Throughout this paper, numbers in parentheses are standard deviations in the least significant figures.

Table III. Bond Distances (Å)[a]

(a) Copper Coordination Sphere			
Cu–O(2)	2.255 (4)	Cu–O(5)	1.956 (3)
Cu–O(3)	1.949 (3)	Cu–O(6)	1.945 (3)
Cu–O(4)	1.952 (2)	Cu–N(2)	2.616 (5)
(b) Nitrile-Nitroxide Ligand			
N(1)–O(1)	1.266 (4)	C(3)–C(4)	1.504 (6)
N(1)–C(1)	1.484 (5)	C(4)–C(5)	1.536 (7)
N(1)–C(4)	1.476 (6)	C(4)–C(6)	1.527 (7)
C(1)–C(2)	1.512 (6)	C(1)–C(7)	1.526 (7)
C(2)–C(3)	1.315 (6)	C(1)–C(8)	1.529 (7)
C(9)–N(2)	1.144 (6)	C(2)–C(9)	1.436 (6)
O(1)···O(2)[b]	2.810 (4)		
(c) hfac Rings			
C(10)–O(3)	1.234 (4)	C(15)–O(5)	1.248 (4)
C(10)–C(13)	1.542 (5)	C(15)–C(18)	1.538 (5)
C(10)–C(11)	1.384 (5)	C(15)–C(16)	1.374 (6)
C(11)–C(12)	1.388 (5)	C(16)–C(17)	1.399 (6)
C(12)–C(14)	1.526 (5)	C(17)–C(19)	1.522 (6)
C(12)–O(4)	1.247 (4)	C(17)–O(6)	1.235 (4)

[a] The C–F distances of the CF_3 groups are included with the supplementary material. [b] This is the presumed intermolecular hydrogen-bonding contact.

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[10] All work was performed on a Syntex $P2_1$ automated diffractometer by use of published procedures: Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265.

[11] Sams, D. B.; Doedens, R. J. *Inorg. Chem.* **1979**, *18*, 153.

[12] Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197.

[13] Main, P.; Lessinger, L.; Woolfson, M. M.; Germain, G.; Declercq, J. P. "MULTAN 77"; Universities of York, England, and Louvain, Belgium, 1977.

[14] Programs used for least-squares refinement, difference Fourier maps, and calculation of derived results have been listed: Little, R. G.; Doedens, R. J. *Inorg. Chem.* **1973**, *12*, 844.

Table IV. Bond Angles (deg)[a]

(a) Copper Coordination Sphere			
O(2)-Cu-O(3)	93.70 (8)	O(3)-Cu-N(2)	91.22 (10)
O(2)-Cu-O(4)	94.25 (9)	O(4)-Cu-O(5)	87.45 (8)
O(2)-Cu-O(5)	90.92 (8)	O(4)-Cu-O(6)	173.84 (10)
O(2)-Cu-O(6)	91.91 (8)	O(4)-Cu-N(2)	83.97 (11)
O(2)-Cu-N(2)	174.84 (11)	O(5)-Cu-N(2)	84.17 (10)
O(3)-Cu-O(4)	92.51 (11)	O(5)-Cu-O(6)	92.62 (11)
O(3)-Cu-O(5)	175.37 (10)	O(6)-Cu-N(2)	89.90 (10)
O(3)-Cu-O(6)	86.92 (8)		
(b) Nitrile-Nitroxide Ligand			
O(1)-N(1)-C(1)	120.9 (4)	C(1)-C(2)-C(9)	119.1 (4)
O(1)-N(1)-C(4)	123.0 (4)	C(3)-C(2)-C(9)	126.9 (4)
C(1)-N(1)-C(4)	116.0 (3)	C(2)-C(3)-C(4)	112.7 (4)
Cu-N(2)-C(9)	130.9 (4)	C(3)-C(4)-N(1)	99.2 (3)
N(1)-C(1)-C(2)	98.0 (3)	N(1)-C(4)-C(5)	110.5 (4)
N(1)-C(1)-C(7)	110.2 (4)	N(1)-C(4)-C(6)	110.8 (4)
N(1)-C(1)-C(8)	110.7 (4)	C(3)-C(4)-C(5)	111.5 (4)
C(2)-C(1)-C(7)	113.1 (4)	C(3)-C(4)-C(6)	112.6 (4)
C(2)-C(1)-C(8)	112.9 (4)	C(5)-C(4)-C(6)	111.6 (4)
C(7)-C(1)-C(8)	111.2 (4)	N(2)-C(9)-C(2)	177.6 (6)
C(1)-C(2)-C(3)	114.0 (4)		
(c) hfac Rings			
Cu-O(3)-C(10)	124.5 (2)	Cu-O(5)-C(15)	123.6 (2)
Cu-O(4)-C(12)	124.0 (2)	Cu-O(6)-C(17)	125.0 (2)
O(3)-C(10)-C(13)	113.3 (4)	O(5)-C(15)-C(18)	113.4 (4)
O(3)-C(10)-C(11)	128.5 (4)	O(5)-C(15)-C(16)	129.2 (4)
C(11)-C(10)-C(13)	118.2 (4)	C(16)-C(15)-C(18)	117.4 (4)
C(10)-C(11)-C(12)	121.7 (4)	C(15)-C(16)-C(17)	121.4 (4)
O(4)-C(12)-C(11)	128.3 (4)	O(6)-C(17)-C(16)	128.0 (4)
O(4)-C(12)-C(14)	114.2 (3)	O(6)-C(17)-C(19)	113.6 (4)
C(11)-C(12)-C(14)	117.5 (4)	C(16)-C(17)-C(19)	118.3 (4)
(d) Hydrogen Bond Angles			
Cu-O(2)···O(1)	118.6 (2)	O(2)···O(1)-N(1)	133.1 (3)

[a] The C-C-F and F-C-F angles of the CF_3 groups are tabulated with the supplementary material.

disordered hydrogen atoms (H2O2 and H3O2) were each assigned a 50% occupancy factor. The final refinement converged to R factors of $R_1 = 0.054$ and $R_2 = 0.067$,[15] with a maximum parameter shift of 0.16 standard deviation in the last cycle. The highest peaks in a final difference map were no higher than 0.9 e Å^{-3}.

In all structure factor calculations, atomic scattering factors (including anomalous terms for Cu) were taken from ref 16. The final standard deviation of an observation of unit weight was 1.88. Calculation of structure factors for the data with $F_o^2 \leq 3\sigma(F_o^2)$ showed 24 reflections with $F_c^2 \leq 3\sigma(F_o^2)$; of these, none had $\Delta F/\sigma$ values greater than 5.

Final positional parameters for non-hydrogen atoms are listed in Table II. Bond distances and angles (excluding those within the CF_3 groups) are tabulated in Tables III and IV, respectively. Tables of structure factors, anisotropic thermal parameters, hydrogen atomic parameters, distances and angles within the CF_3 groups, and molecular planes are available as supplementary material.

Magnetic Susceptibility Measurements. Magnetic susceptibility data were obtained for $T = 81-294$ K by Professor A. B. P. Lever of York University (Canada). The Faraday apparatus employed for these measurements has been described.[17] Data were corrected for ligand diamagnetism and for the temperature-independent paramagnetism of the Cu^{2+} ion. A complete table of magnetic data is available as supplementary material.

Results

Description of the Structure. The crystal structure of aqua(3-cyano-2,2,5,5-tetramethylpyrrolinyl-1-oxy)bis(hexafluoroacetylacetonato)copper(II) consists of one-dimensional chains of $Cu(hfac)_2(tmpCN)H_2O$ monomers linked by O–H···O hydrogen bonds. A view of the monomer is shown in Figure 1, and a stereoscopic drawing of a portion of the linear-chain structure is presented as Figure 2, which is included with the supplementary material. The most significant feature of the structure is the absence of a covalent metal–nitroxyl bond. The substituted pyrroline ligand is coordinated solely through its nitrile group, and the nitroxyl oxygen atom participates in the hydrogen bond, which gives rise to the chain structure.

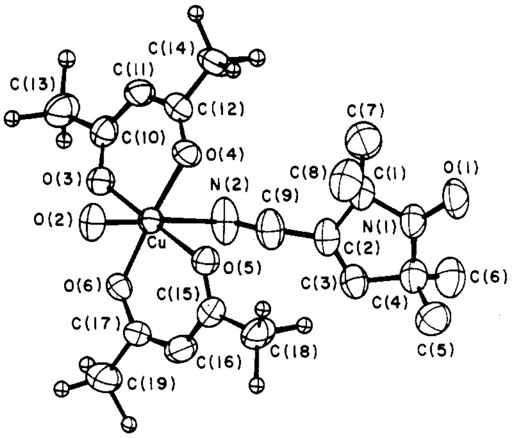

Figure 1. View of the molecular structure, with hydrogen atoms omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level, with the exception that the fluorine atoms are represented by artificially small isotropic temperature factors.

The coordination geometry about the copper(II) ion closely approximates that of a tetragonally distorted octahedron, with four short equatorial bonds to the hfac oxygen atoms ranging in length from 1.945 (3) to 1.956 (3) Å. One axial position is occupied by the water molecule at a distance of 2.255 (4) Å, and the other axial bond is a long one of 2.616 (5) Å to the nitrile nitrogen atom. All angles about the metal ion are within about 6° of their ideal values of 90 or 180°. An unexpected feature is the Cu–N(2)–C(9) bond angle of 130.9 (4)°, far different from the linear value predicted by the conventional model for metal coordination of an sp-hybridized nitrogen atom.

The hfac ligands have a planar O–C–C–C–O grouping and equivalent C–C and C–O bond distances with mean values of 1.386 and 1.241 Å, respectively. The Cu^{2+} ion is only slightly (0.08 and 0.15 Å) displaced from the planes of the two chelating ligands, in contrast to the large displacements that are sometimes found in copper(II) hfac complexes.[2,18] Some fluorine atomic thermal parameters are large, indicative of large torsional vibrations and/or some degree of disorder.

The five atoms of the pyrroline ring are coplanar, with a maximum deviation of 0.019 Å from the least-squares ring plane. Structural details of the tmpCN radical are closely similar to those of analogous nitroxyl radicals based on 3-carboxy- and 3-carbamidopyrrolines.[19,20] The nitroxyl nitrogen atom is within 0.02 Å of the plane defined by the three atoms to which it is bound. Such planar C_2NO groupings are typically found in nitroxides in which the nitrogen atoms is part of a five-membered ring. In six-membered ring systems, on the other hand, nitroxyl nitrogen atoms are normally pyramidal.[21,22]

The O–H···O hydrogen bond which links the $Cu(hfac)_2tmpCN$ monomers into linear chains involves the coordinated water molecule and the oxygen atom of the nitroxyl

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(15) $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

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group. The O(2)···O(1) distance is 2.810 (4) Å, and the angles at O(1) and O(2) are 133.1 (3) and 118.6 (2)°, respectively. The water hydrogen atom not involved in hydrogen bonding appears to be disordered, being situated with approximately equal probabilities on either side of the Cu–O(2)–O(1) plane. Aside from the hydrogen bond, there are no unusual intermolecular interactions; the shortest contact between non-hydrogen atoms is a F···F separation of 2.933 Å.

Magnetic Results. Over the temperature range 81–294 K, the reciprocal molar paramagnetic susceptibility is a linear function of temperature. The equation of the least-squares line for these data is $1/\chi_M = 1.20T - 4.68$ or, in standard Curie–Weiss form, $\chi_M = 0.833/(T - 3.90)$.

Discussion

Because $Cu(hfac)_2$ readily forms bonds to the nitroxyl oxygen atoms of tmpo and tmpoOH, it was anticipated that other nitroxides would interact in a similar fashion. This expectation has not been realized for tmpCN, a ligand that was chosen because it is stable, easily prepared, and potentially capable of forming an adduct with a chain structure like that of $Cu(hfac)_2(tmpoOH)$. In preference to forming a bond to the nitroxyl group, the $Cu(hfac)_2$ completes its coordination sphere with bonds to the water molecule and the nitrile nitrogen atom. Once it became clear from the crystal structure analysis that we were dealing with a hydrate, the preparation was repeated with rigorous exclusion of water. No pure product could be isolated under these conditions. Along with substantial amounts of unreacted starting materials, crystals of a new Cu(II) complex tentatively formulated as $Cu(hfac)_2(tmpCN)_2$ were obtained.

A very recent report by Cotton and Felthouse of the structures of two nitroxide derivatives of $Rh_2(O_2CCF_3)_4$ describes several structural features analogous to those we observe.[23] Motivated in part by the results of earlier solution studies of Drago et al.,[24] these workers sought to prepare 2:1 adducts of the rhodium dimer in which nitroxyl groups occupied the axial coordination sites. The specific nitroxides investigated were tmpoOH and di-*tert*-butyl nitroxide (Bu_2NO). Crystalline products of 2:1 stoichiometry were isolated in each case, but in neither of them was the nitroxyl group metal coordinated. In the tmpoOH adduct, the Rh atom binds to the hydroxyl oxygen atom in preference to the nitroxyl group and hydrogen bonds link the dimers into a one-dimensional chain structure. The Bu_2NO derivative was shown to be a hydrate, with water molecules occupying the axial sites and the nitroxide bound in the crystal solely by an O–H···O hydrogen bond. Thus, both of the devices by which formation of a metal–nitroxyl bond in $Cu(hfac)_2(tmpCN)(H_2O)$ is avoided are also found in this pair of rhodium trifluoroacetate dimers.

Distances and angles involving the hydrogen bond are representative of those found in other hydrogen-bonded systems involving nitroxyl groups. The O(1)···O(2) distance of 2.810 (4) Å is normal, and the angle of 133.1 (3)° at O(1) is close to the mean value of 134° obtained for a series of free nitroxides in which intermolecular hydrogen bonding occurs.[22] The Cu–O(2)···O(1) angle of 118.6 (2)° is within the expected range of values for an angle at a sp^3 oxygen atom. The strong tendency of nitroxyl groups to engage in hydrogen bonding in the free crystalline nitroxides has been pointed out;[22] clearly this tendency is frequently an important factor in metal–nitroxyl complexes as well.

The magnetic susceptibility measurements over the range 81–294 K show no evidence for interaction between the metal and ligand free spins. This is not surprising given the structural results, although there is precedent for substantial exchange coupling through a hydrogen-bond linkage.[25] The room-temperature molar susceptibility is comparable to that which can be inferred for $Cu(hfac)_2(tmpoOH)$ from published data.[1]

Registry No. $Cu(hfac)_2(H_2O)(tmpCN)$, 85134-97-0; $Cu(hfac)_2(tmpCN)_2$, 85116-32-1; $Cu(hfac)_2$, 14781-45-4.

Supplementary Material Available: Figure 2, a stereoscopic drawing of a portion of the linear chain structure, and Supplementary Tables 1–6 containing, respectively, observed and calculated structure amplitudes, anisotropic thermal parameters, hydrogen atom parameters, distances and angles within the CF_3 groups, molecular planes, and magnetic susceptibility data (30 pages). Ordering information is given on any current masthead page.

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