Contribution from the Department of Chemistry,
University of California, Irvine, California 92717

An Adduct with a One-Dimensional Chain Structure from Bis(hexafluoroacetylacetonato)copper(II) and an Aliphatic Nitroxyl Diradical

Phillip T. Matsunaga, Dialne T. McCall, Michael D. Carducci, and Robert J. Doedens*

Received August 22, 1989

Reaction of the new nitroxyl diradical bis(1-oxy-2,5,5-trimethyl-2-pyrrolidinyl)methane (diprox) with bis(hexafluoroacetylacetonato)copper(II) (Cu(F$_6$acac)$_2$) yields a green-brown dichroic product, Cu(F$_6$acac)$_2$(diprox). A crystal structure analysis has shown this material to have a one-dimensional chain structure, with planar Cu(F$_6$acac)$_2$ units bridged by the nitroxyl diradicals. The coordination geometry about copper is tetragonal, with nitroxyl oxygen atoms occupying axial sites at a mean Cu–O distance of 2.419(7) Å. The four crystallographically independent metal–nitroxyl linkages show significant structural differences. Magnetic susceptibility measurements have been carried out for $T = 2.5$–300 K. The high-temperature susceptibilities are consistent with expectations for three uncorrelated spins per formula unit. Antiferromagnetic coupling that extends beyond a single copper coordination sphere is evident at lower temperatures. Crystal data for Cu(F$_6$acac)$_2$(diprox): monoclinic, space group $P2_1/c$, $Z = 8$, $a = 19.230$ (4) Å, $b = 21.211$ (5) Å, $c = 16.851$ (4) Å, $\beta = 108.48$ (2)°.

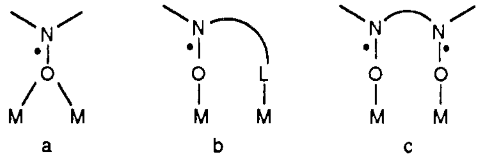
Introduction

In the last several years, a considerable number of compounds in which a stable nitroxyl radical is directly bound to a paramagnetic transition-metal ion have been prepared and characterized.[1-22] Much has been learned about the conditions under which such systems are stable and the factors that determine their magnetic properties. The metal–ligand spin coupling can be either ferromagnetic or antiferromagnetic and can vary greatly in magnitude. Factors influencing this coupling include the electronic structures of metal and ligand as well as the geometry of metal–ligand binding. Particularly critical are the nature and magnitude of the overlap between the "magnetic orbitals"—the orbitals that contain the metal and ligand unpaired electrons.

Table I. Crystallographic Data for Cu(F$_6$acac)$_2$(diprox)

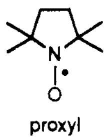
$CuC_{25}H_{30}F_{12}N_2O_6$	fw = 746.045
space group: $P2_1/c$	$T = 23$ °C
$a = 19.230$ (4) Å	$\rho_{calcd} = 1.520$ g cm^{-3}
$b = 21.211$ (5) Å	λ(Mo Kα) = 0.71073 Å
$c = 16.851$ (4) Å	$\mu = 7.74$ cm^{-1}
$\beta = 108.48$ (2)°	$R(F_o^2) = 0.094$
$V = 6518$ (3) Å^3	$R_w(F_o^2) = 0.116$
$Z = 8$	

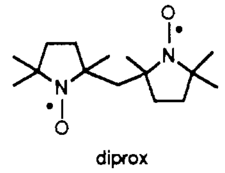
A challenge to workers in this area is to apply the generalizations derived from studies of isolated molecules to the preparation of systems with extended magnetic interactions. Prediction and control of such extended interactions would most readily be achieved if there were modifiable covalent linkages between the metal centers. Three general types of metal–nitroxyl interactions that could lead to extended structures are illustrated:



Monatomically bridging nitroxyls (a) are known[18] but rare. Linkages of type b are exemplified by the nitronyl nitroxyls, from which a number of compounds with linear chain structures and one-dimensional magnetic properties have been prepared.[13,18,19] The use of di- or polynitroxyl radicals (c) is potentially very interesting because of the possibility of controlling the magnetic coupling by systematically varying the linkage between the two radical centers. Unfortunately, very few stable radicals are known that would be appropriate for forming linkages of type c.

We now wish to report the preparation of a linear chain complex of bis(hexafluoroacetylacetonato)copper(II) with the new nitroxyl diradical diprox.[23] To our knowledge, this is the first well-characterized example of a type c system.


proxyl


diprox

Experimental Section

Synthesis and Characterization. General Data. Bis(hexafluoroacetylacetonato)copper(II) was prepared by a standard procedure.[24] Solvents were dried over anhydrous magnesium sulfate prior to use. Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, TN. Mass spectra were obtained by the chemical ionization

---

(1) (a) Anderson, O. P.; Kuechler, T. C. *Inorg. Chem.* **1980**, *19*, 1417–1422. (b) Bencini, A.; Benelli, C.; Gatteschi, D.; Zanchini, C. *J. Am. Chem. Soc.* **1984**, *106*, 5813–5818. (c) Benelli, C.; Gatteschi, D.; Carnegie, D. W., Jr.; Carlin, R. L. *J. Am. Chem. Soc.* **1985**, *107*, 2560–2561.

(2) Dickman, M. H.; Doedens, R. J. *Inorg. Chem.* **1981**, *20*, 2677–2681.

(3) (a) Espie, J. C.; Ramasseul, R.; Rassat, A.; Rey, P. *Bull. Soc. Chim. Fr., II* **1981**, 33–39. (b) Laugier, J.; Ramasseul, R.; Rey, P.; Espie, J. C.; Rassat, A. *Nouv. J. Chem.* **1983**, *7*, 11–14.

(4) Grand, A.; Rey, P.; Subra, R. *Inorg. Chem.* **1983**, *22*, 391–394.

(5) Porter, L. C.; Dickman, M. H.; Doedens, R. J. (a) *Inorg. Chem.* **1983**, *22*, 1962–1964. (b) *Inorg. Chem.* **1986**, *25*, 678–684.

(6) Benelli, C.; Gatteschi, D.; Zanchini, C. *Inorg. Chem.* **1984**, *23*, 798–800.

(7) Porter, L. C.; Doedens, R. J. *Inorg. Chem.* **1985**, *24*, 1006–1010.

(8) Dickman, M. H.; Porter, L. C.; Doedens, R. J. *Inorg. Chem.* **1986**, *25*, 2595–2599.

(9) Benelli, C.; Gatteschi, D.; Zanchini, C.; Doedens, R. J.; Dickman, M. H.; Porter, L. C. *Inorg. Chem.* **1986**, *25*, 3453–3457.

(10) Laugier, J.; Rey, P.; Benelli, C.; Gatteschi, D.; Zanchini, C. *J. Am. Chem. Soc.* **1986**, *108*, 6931–6937.

(11) Benelli, C.; Gatteschi, D.; Zanchini, C.; Latour, J. M.; Rey, P. *Inorg. Chem.* **1986**, *25*, 4242–4244.

(12) Gatteschi, D.; Laugier, J.; Rey, P.; Zanchini, C. *Inorg. Chem.* **1987**, *26*, 938–943.

(13) Caneschi, A.; Gatteschi, D.; Laugier, J.; Rey, P. *J. Am. Chem. Soc.* **1987**, *109*, 2191–2192.

(14) Caneschi, A.; Gatteschi, D.; Grand, A.; Laugier, J.; Pardi, L.; Rey, P. *Inorg. Chem.* **1988**, *27*, 1031–1035.

(15) Caneschi, A.; Grand, A.; Laugier, J.; Rey, P.; Subra, R. *J. Am. Chem. Soc.* **1988**, *110*, 2307–2309.

(16) Caneschi, A.; Gatteschi, D.; Laugier, J.; Rey, P.; Sessoli, R.; Zanchini, C. *J. Am. Chem. Soc.* **1988**, *110*, 2795–2799.

(17) Porter, L. C.; Dickman, M. H.; Doedens, R. J. *Inorg. Chem.* **1988**, *27*, 1548–1552.

(18) Caneschi, A.; Gatteschi, D.; Laugier, J.; Rey, P.; Sessoli, R. *Inorg. Chem.* **1988**, *27*, 1553–1557.

(19) (a) Caneschi, A.; Gatteschi, D.; Rey, P.; Sessoli, R. *Inorg. Chem.* **1988**, *27*, 1756–1761. (b) Caneschi, A.; Gatteschi, D.; Renard, J. P.; Rey, P.; Sessoli, R. *Inorg. Chem.* **1989**, *28*, 1976–1980.

(20) Caneschi, A.; Gatteschi, D.; Laugier, J.; Pardi, L.; Rey, P.; Zanchini, C. *Inorg. Chem.* **1988**, *27*, 2027–2032.

(21) Caneschi, A.; Gatteschi, D.; Sessoli, R.; Hoffmann, S.; Laugier, J.; Rey, P. *Inorg. Chem.* **1988**, *27*, 2390–2392.

(22) Caneschi, A.; Gatteschi, D.; Laugier, J.; Rey, P.; Zanchini, C. *Inorg. Chem.* **1989**, *28*, 1969–1975.

(23) Abbreviations used in this paper: proxyl = 2,2,5,5-tetramethylpyrrolidinyl-1-oxy; diprox = bis(1-oxy-2,5,5-trimethyl-2-pyrrolidinyl)methane; tempo = 2,2,6,6-tetramethylpiperidinyl-1-oxy; F$_6$acac = hexafluoroacetylacetonato.

(24) Funck, L. L.; Ortolano, T. R. *Inorg. Chem.* **1968**, *7*, 567–573.

0020-1669/90/1329-1655$02.50/0

Table II. Atomic Coordinates and Equivalent Isotropic Temperature Factors

atom	*x*	*y*	*z*	U(eq),[a] Å^2	atom	*x*	*y*	*z*	U(eq),[a] Å^2
Cu(1)	0.3629 (0.7)	0.1369 (0.5)	0.2468 (0.7)	0.046 (1)	C(31)	0.6345 (6)	0.0555 (6)	0.0840 (8)	0.074 (11)
Cu(2)	0.8538 (0.7)	0.1198 (0.5)	0.2361 (0.7)	0.054 (1)	C(32)	0.5575 (8)	0.0575 (9)	0.0770 (9)	0.140 (17)
O(1)	0.3418 (4)	0.2246 (3)	0.2592 (4)	0.063 (6)	C(33)	0.5461 (6)	0.1006 (7)	0.1409 (8)	0.107 (12)
O(2)	0.3611 (3)	0.1493 (3)	0.1323 (4)	0.048 (5)	C(34)	0.6160 (6)	0.0984 (5)	0.2142 (6)	0.067 (9)
O(3)	0.3860 (3)	0.0491 (3)	0.2339 (4)	0.051 (5)	C(35)	0.6571 (10)	0.0996 (7)	0.0264 (8)	0.125 (16)
O(4)	0.3655 (3)	0.1239 (3)	0.3623 (4)	0.049 (5)	C(36)	0.6596 (9)	−0.0109 (6)	0.0733 (10)	0.123 (17)
O(11)	0.8195 (4)	0.2056 (3)	0.2385 (4)	0.062 (6)	C(37)	0.6141 (7)	0.0493 (5)	0.2807 (8)	0.088 (12)
O(12)	0.8549 (4)	0.1284 (3)	0.1209 (4)	0.060 (6)	C(38)	0.6446 (6)	0.1631 (5)	0.2536 (6)	0.065 (9)
O(13)	0.8884 (4)	0.0342 (3)	0.2325 (4)	0.065 (6)	C(41)	0.0612 (7)	0.2020 (8)	0.3915 (9)	0.104 (14)
O(14)	0.8549 (4)	0.1107 (3)	0.3514 (4)	0.063 (6)	C(42)	0.1397 (7)	0.2152 (8)	0.4031 (10)	0.126 (15)
O(21)	0.2332 (4)	0.1164 (4)	0.2024 (5)	0.080 (7)	C(43)	0.1618 (7)	0.1613 (8)	0.3545 (9)	0.113 (15)
O(31)	0.7346 (4)	0.0725 (4)	0.2102 (5)	0.089 (8)	C(44)	0.0984 (6)	0.1540 (5)	0.2776 (7)	0.067 (9)
O(41)	−0.0261 (4)	0.1649 (4)	0.2639 (6)	0.102 (9)	C(45)	0.0130 (9)	0.2639 (9)	0.3800 (12)	0.163 (21)
O(51)	0.4966 (4)	0.1477 (4)	0.3035 (5)	0.077 (7)	C(46)	0.0463 (14)	0.1543 (14)	0.4539 (10)	0.236 (30)
N(2)	0.1774 (4)	0.0815 (4)	0.1674 (5)	0.056 (7)	C(47)	0.1008 (7)	0.2025 (6)	0.2089 (10)	0.102 (14)
N(3)	0.6674 (4)	0.0782 (4)	0.1692 (5)	0.058 (7)	C(51)	0.5843 (6)	0.1921 (6)	0.4261 (7)	0.077 (10)
N(4)	0.0393 (5)	0.1704 (4)	0.3100 (6)	0.070 (8)	C(52)	0.6582 (6)	0.2219 (6)	0.4307 (7)	0.079 (10)
N(5)	0.5569 (5)	0.1779 (4)	0.3335 (5)	0.060 (7)	C(53)	0.6448 (7)	0.2541 (5)	0.3496 (8)	0.078 (11)
C(1)	0.3279 (6)	0.2651 (5)	0.2022 (7)	0.065 (10)	C(54)	0.5944 (6)	0.2102 (5)	0.2849 (6)	0.061 (9)
C(2)	0.3264 (6)	0.2567 (5)	0.1201 (6)	0.062 (9)	C(55)	0.5940 (8)	0.1293 (6)	0.4774 (8)	0.103 (13)
C(3)	0.3437 (5)	0.1993 (5)	0.0932 (5)	0.050 (8)	C(56)	0.5304 (8)	0.2392 (6)	0.4459 (9)	0.109 (15)
C(4)	0.3063 (14)	0.3279 (7)	0.2247 (10)	0.121 (19)	C(57)	0.5367 (7)	0.2468 (6)	0.2120 (8)	0.090 (11)
C(5)	0.3430 (6)	0.1951 (5)	0.0025 (6)	0.057 (9)	F(1)	0.2920 (10)	0.3698 (4)	0.1749 (6)	0.238 (18)
C(6)	0.3990 (5)	0.0084 (4)	0.2912 (6)	0.052 (8)	F(2)	0.2771 (10)	0.3317 (5)	0.2756 (10)	0.211 (20)
C(7)	0.3994 (6)	0.0172 (5)	0.3724 (6)	0.065 (9)	F(3)	0.3689 (11)	0.3524 (6)	0.2828 (13)	0.249 (23)
C(8)	0.3815 (5)	0.0731 (5)	0.4011 (6)	0.053 (8)	F(4)	0.3280 (5)	0.2481 (3)	−0.0389 (4)	0.121 (8)
C(9)	0.4116 (8)	−0.0555 (5)	0.2620 (8)	0.070 (11)	F(5)	0.2905 (5)	0.1566 (4)	−0.0409 (4)	0.109 (7)
C(10)	0.3838 (8)	0.0769 (6)	0.4886 (8)	0.077 (12)	F(6)	0.4023 (4)	0.1705 (4)	−0.0045 (4)	0.118 (8)
C(11)	0.8200 (6)	0.2469 (5)	0.1868 (7)	0.063 (9)	F(7)	0.4317 (7)	−0.0972 (4)	0.3182 (5)	0.180 (12)
C(12)	0.8370 (6)	0.2381 (5)	0.1128 (6)	0.063 (9)	F(8)	0.3559 (6)	−0.0801 (4)	0.2088 (7)	0.170 (12)
C(13)	0.8529 (5)	0.1795 (5)	0.0844 (6)	0.057 (8)	F(9)	0.4529 (7)	−0.0583 (4)	0.2227 (10)	0.214 (19)
C(14)	0.8039 (12)	0.3120 (7)	0.2068 (11)	0.106 (16)	F(10)	0.3191 (6)	0.0915 (6	0.4960 (5)	0.173 (12)
C(15)	0.8636 (8)	0.1762 (8)	0.0018 (8)	0.075 (12)	F(11)	0.4216 (6)	0.1252 (5)	0.5311 (4)	0.133 (9)
C(16)	0.8935 (6)	−0.0065 (5)	0.2881 (7)	0.068 (10)	F(12)	0.4127 (7)	0.0314 (4)	0.5354 (5)	0.179 (12)
C(17)	0.8821 (7)	0.0020 (6)	0.3638 (7)	0.084 (11)	F(21)	0.8049 (8)	0.3545 (4)	0.1600 (7)	0.199 (16)
C(18)	0.8628 (6)	0.0607 (6)	0.3906 (7)	0.063 (9)	F(22)	0.8258 (11)	0.3272 (5)	0.2794 (7)	0.225 (17)
C(19)	0.9170 (10)	−0.0703 (6)	0.2675 (9)	0.090 (14)	F(23)	0.7308 (10)	0.3134 (6)	0.1976 (13)	0.268 (27)
C(20)	0.8588 (13)	0.0635 (10)	0.4733 (11)	0.114 (19)	F(24)	0.8601 (6)	0.2277 (4)	−0.0376 (5)	0.137 (10)
C(21)	0.1577 (6)	0.0643 (6)	0.0771 (7)	0.077 (10)	F(25)	0.8111 (6)	0.1423 (5)	−0.0514 (5)	0.151 (11)
C(22)	0.0867 (8)	0.0286 (7)	0.0661 (8)	0.096 (13)	F(26)	0.9202 (6)	0.1446 (5)	0.0028 (5)	0.156 (11)
C(23)	0.1001 (8)	−0.0022 (6)	0.1490 (12)	0.124 (17)	F(27)	0.9765 (8)	−0.0711 (4)	0.2550 (12)	0.240 (21)
C(24)	0.1398 (7)	0.0462 (6)	0.2170 (8)	0.081 (11)	F(28)	0.9183 (7)	−0.1144 (4)	0.3185 (6)	0.176 (13)
C(25)	0.1451 (9)	0.1262 (7)	0.0261 (8)	0.113 (15)	F(29)	0.8720 (8)	−0.0910 (5)	0.1974 (7)	0.187 (14)
C(26)	0.2183 (7)	0.0240 (6)	0.0661 (8)	0.093 (12)	F(30)	0.7957 (9)	0.0810 (12)	0.4738 (7)	0.274 (22)
C(27)	0.1969 (8)	0.0161 (7)	0.2958 (9)	0.123 (15)	F(31)	0.8731 (13)	0.0204 (7)	0.5195 (8)	0.286 (23)
C(28)	0.0819 (7)	0.0872 (5)	0.2388 (7)	0.079 (11)	F(32)	0.8931 (12)	0.1069 (9)	0.5203 (8)	0.248 (23)

[a] U(eq) = one-third of the trace of the orthogonalized **U** tensor.

technique on a Finnigan 4000 instrument with isobutane as the reagent gas.

Preparation of Diprox. The diprox diradical was first observed as a side product in the synthesis of proxyl by previously described methods.[8] Mass spectra of crude product samples showed varying proportions of proxyl and diprox. The coupling occurs during the preparation of 2,2,5,5-tetramethylpyrrolinyl-1-hydroxy, the immediate precursor of proxyl, by the Grignard methylation of 2,2,5-trimethylpyrroline 1-oxide. Mixtures of monomeric and coupled products were obtained from this step, with longer reaction times (ca. 24 h) increasing the proportion of dimer. After oxidation to the corresponding nitroxyls, the products could be separated by column chromatography (silica gel, dichloromethane eluent). Typical yields were 10–15%, depending on purity. Diprox is a viscous orange liquid that melts at approximately −35 °C. Major peaks in its mass spectrum include a parent ion $M^+ + H$ ($m/e = 269$, 54% of base peak), two fragments from cleavage of a ring-CH_2 bond ($m/e =$ 142, base peak; $m/e = 128$, 34%) and fragment 2 − O ($m/e = 112$, 10%). For comparison, the proxyl mass spectrum included a parent ion $M^+ +$ H ($m/e = 143$, base peak) and fragments corresponding to successive loss of methyl groups $m/e = 128$, 7%; $m/e = 113$, 5%; $m/e = 98$, 2%).

Preparation of Cu(F$_6$acac)$_2$(diprox). To a solution of 0.03 g of crude diprox in 30 mL of 3:1 heptane/dichloromethane was added 0.10 g of anhydrous Cu(F$_6$acac)$_2$. Concentration and cooling to −15 °C yielded air-stable green–brown dichroic crystals, which were recrystallized from heptane/pentane. Mp (uncor): 118–120° °C dec. Anal. Calcd for $CuC_{25}H_{30}F_{12}N_2O_6$: C, 40.25; H, 4.05; N, 3.76; F, 30.55. Found: C, 40.40; H, 4.08; N, 3.75; F, 30.44.

Crystal Structure. All crystallographic data were collected on a Nicolet P2$_1$ diffractometer from a crystal of dimensions 0.55 × 0.50 × 0.40 mm. General procedures used in the structure analysis have been described.[25,26] Crystallographic data are given in Table I; further details are included with the supplementary material. Refined unit cell parameters were based upon the setting angles of 15 reflections with $30° \leq 2\theta \leq 35°$. A total of 9580 intensity data with $2\theta \leq 45°$ were collected; of these, 6033 reflections with $F_o^2 > 1.5\sigma(F_o^2)$ were used in the structure refinement. Solution of the structure was accomplished by a combination of direct and heavy-atom methods. Final least-squares refinement included anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms of CH and CH_2 groups were included in fixed, idealized positions; methyl hydrogen atoms were not included. As is frequently found in crystal structures of compounds containing CF_3 groups, the fluorine thermal ellipsoids are large and highly anisotropic. This problem, together with the rather weak diffraction pattern, accounts for the somewhat high R factors. The crystal used was the best of many that were examined from a number of batches. In any event, the chemicaly significant features of the structure are well established. Computer programs utilized included a local version of the UCLA Crystallographic Computing Package,[27] MITHRIL,[28] and the graphics portions of the SHELXTL package.[29]

---

(25) Sams, D. B.; Doedens, R. J. *Inorg. Chem.* **1979**, *18*, 153–156.

(26) *R3m/V Crystallographic Systems Users Guide*; Nicolet Instrument Corp.: Madison, WI, 1988.

(27) Strouse, C. E. Personal communication.

(28) Gilmore, C. J. MITHRIL: A Computer Program for the Automatic Solution of Crystal Structures from X-ray Data. University of Glasgow, 1983.

(29) *SHELXTL Plus*; Nicolet Instrument Corp.: Madison, WI, 1988.

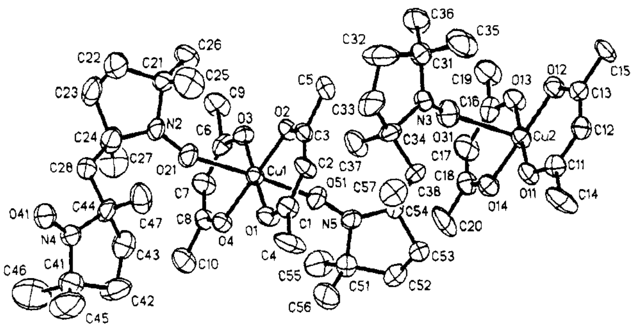


Figure 1. View of the asymmetric unit of the chain structure. Thermal ellipsoids are drawn at the 35% probability level. Fluorine atoms have been omitted for clarity.

Final atomic parameters for the non-hydrogen atoms are listed in Table II and selected bond distances and angles are tabulated in Table III. Full tables of all crystallographic results are included with the supplementary material.

Magnetic Susceptibility Measurements. Magnetic data were obtained for T = 2.5–300 K at 10 T by use of an SHE Corp. SQUID magnetometer located at the University of Southern California. Data were corrected for magnetization of the sample holder and for ligand diamagnetism, estimated from Pascal's constants. A table of observed susceptibility values is included with the supplementary material.

Results

Synthesis. The adduct $\mathrm{Cu(F_6acac)_2}$ diprox is readily obtained from the reaction of anhydrous copper(II) hexafluoroacetylacetonate with the diradical ligand in heptane/dichloromethane. Because it is considerably less soluble than the corresponding proxyl complex, it can be isolated even if the initial ligand sample contains significant amounts of proxyl as an impurity. Its characteristic green–brown dichroism makes it easily recognizable. To our knowledge, this is the first metal complex of a nitroxyl diradical in which both radical centers are metal-coordinated.

Structure. The diprox adduct has a one-dimensional chain structure, with each diradical bridging two $\mathrm{Cu(F_6acac)_2}$ units. The chain direction is approximately parallel to the crystallographic a axis, and the closest interchain Cu-Cu contact is 9.58 Å. The crystallographic asymmetric unit, shown in Figure 1, contains two independent and structurally different (*vide infra*) formula units. Figure 2 is a stereoscopic view of the unit cell contents.

The coordination geometry about each copper is tetragonal, with the oxygen atoms of the chelating $\mathrm{F_6acac}$ ligands occupying equatorial sites (mean Cu–O = 1.943 Å) and axially bound nitroxyl oxygens (mean Cu–O = 2.419 Å). All of the O–Cu–O bond angles are within 10° of their ideal values of 90° or 180°. The intra-chain Cu(1)–Cu(2) distance is 9.51 A.

Table III. Selected Bond Distances and Angles

(a) Distances (Å)			
Cu(1)–O(1)	1.929 (6)	Cu(2)–O(11)	1.941 (7)
Cu(1)–O(2)	1.937 (6)	Cu(2)–O(12)	1.957 (6)
Cu(1)–O(3)	1.943 (6)	Cu(2)–O(13)	1.941 (7)
Cu(1)–O(4)	1.951 (6)	Cu(2)–O(14)	1.946 (6)
Cu(1)–O(21)	2.405 (7)	Cu(2)–O(31)	2.412 (8)
Cu(1)–O(51)	2.453 (7)	Cu(2)–O(41)	2.405 (8)
O(21)–N(2)	1.283 (9)	O(31)–N(3)	1.263 (10)
O(51)–N(5)	1.280 (10)	O(41)–N(4)	1.257 (10)
(b) Angles (deg)			
O(1)–Cu(1)–O(2)	92.2 (3)	O(11)–Cu(2)–O(12)	92.5 (3)
O(1)–Cu(1)–O(3)	178.8 (3)	O(11)–Cu(2)–O(13)	179.3 (3)
O(1)–Cu(1)–O(4)	88.2 (3)	O(11)–Cu(2)–O(14)	88.2 (3)
O(1)–Cu(1)–O(21)	88.6 (3)	O(11)–Cu(2)–O(41)	86.3 (3)
O(1)–Cu(1)–O(51)	95.6 (3)	O(11)–Cu(2)–O(31)	94.8 (3)
O(2)–Cu(1)–O(3)	87.2 (3)	O(12)–Cu(2)–O(13)	86.8 (3)
O(2)–Cu(1)–O(4)	179.5 (3)	O(12)–Cu(2)–O(14)	178.8 (3)
O(2)–Cu(1)–O(21)	91.5 (3)	O(12)–Cu(2)–O(31)	99.7 (3)
O(2)–Cu(1)–O(51)	93.5 (3)	O(12)–Cu(2)–O(41)	81.0 (3)
O(3)–Cu(1)–O(4)	92.4 (3)	O(13)–Cu(2)–O(14)	92.5 (3)
O(3)–Cu(1)–O(21)	92.5 (3)	O(13)–Cu(2)–O(31)	85.5 (3)
O(3)–Cu(1)–O(51)	83.4 (3)	O(13)–Cu(2)–O(41)	93.5 (3)
O(4)–Cu(1)–O(21)	88.9 (3)	O(14)–Cu(2)–O(31)	81.3 (3)
O(4)–Cu(1)–O(51)	86.1 (2)	O(14)–Cu(2)–O(41)	98.0 (3)
O(21)–Cu(1)–O(51)	173.4 (3)	O(31)–Cu(2)–O(41)	178.7 (3)
Cu(1)–O(21)–N(2)	151.8 (6)	Cu(2)–O(31)–N(3)	143.9 (7)
Cu(1)–O(51)–N(5)	155.1 (6)	Cu(2)–O(41)–N(4)	150.3 (8)
O(21)–N(2)–C(21)	121.0 (8)	O(31)–N(3)–C(31)	123.9 (8)
O(21)–N(2)–C(24)	121.5 (9)	O(31)–N(3)–C(34)	118.6 (8)
C(21)–N(2)–C(24)	116.3 (9)	C(31)–N(3)–C(34)	116.6 (8)
O(51)–N(5)–C(51)	118.9 (8)	O(41)–N(4)–C(41)	123.8 (9)
O(51)–N(5)–C(54)	125.0 (9)	O(41)–N(4)–C(44)	119.7 (9)
C(51)–N(5)–C(54)	115.0 (8)	C(41)–N(4)–C(44)	115.8 (9)

Structural parameters of the nitroxyl groups are consistent with the formulation of these ligands as metal-coordinated free radicals. Specifically, the N–O distances (mean value = 1.271 Å) indicate that no ligand-centered redox process has taken place. The conformations of the two crystallographically independent diradicals are virtually identical. This is most readily seen by comparison of the torsion angles about the bonds to the bridging methylene groups: N(2)–C(24)–C(28)–C(44) = 50.0°; N(5)–C(54)–C(38)–C(34) = 46.6°; N(3)–C(34)–C(38)–C(54) = 162.2°; N(4)–C(44)–C(28)–C(24) = 164.7°. The N–N and O–O distances within the two diradicals provide another measure of the similarity of their conformations: N(2)–N(4) = 4.52 Å; N(3)–N(5) = 4.52 Å; O(21)–O(41) = 5.50 Å; O(31)–O(51) = 5.53 Å. Other structural details of the nitroxyl groups are much as expected.

The four crystallographically independent copper–nitroxyl linkages differ significantly in their structural details. This is best seen by considering the three angles φ, θ, and ϕ, defined as follows: φ = dihedral angle between Cu-O-N and C-N-C planes; θ = 180° – (Cu-O-N bond angle); ϕ = smallest angle from a Cu–O

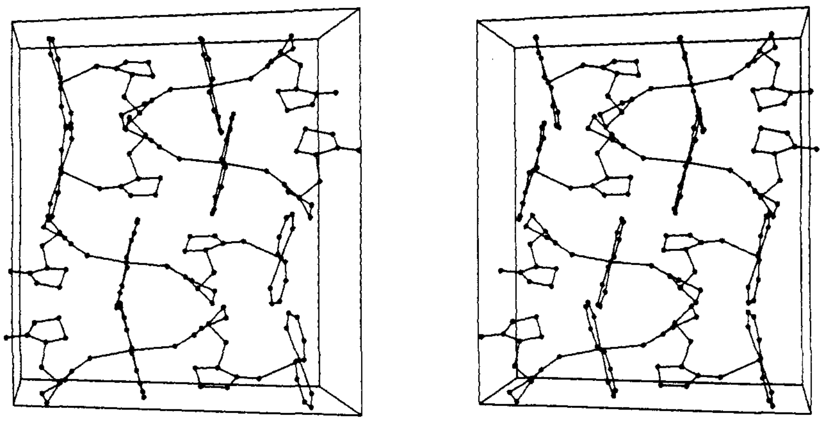


Figure 2. Stereoscopic view of the unit cell contents, projected down the c axis. The $+a$ direction is to the left, and $+b$ points downward. For clarity, $\mathrm{CF_3}$ and $\mathrm{CH_3}$ groups have been omitted.

Table IV. Copper–Nitroxyl Orientation Angles[a] (deg)

group	θ	φ	ϕ
Cu(1)-O(21)-N(2)	28.2	69.1	15.7
Cu(1)-O(51)-N(5)	24.9	90.4	2.8
Cu(2)-O(31)-N(3)	36.1	77.5	42.4
Cu(2)-O(41)-N(4)	29.7	64.4	30.9

[a] The angles are defined in the text.

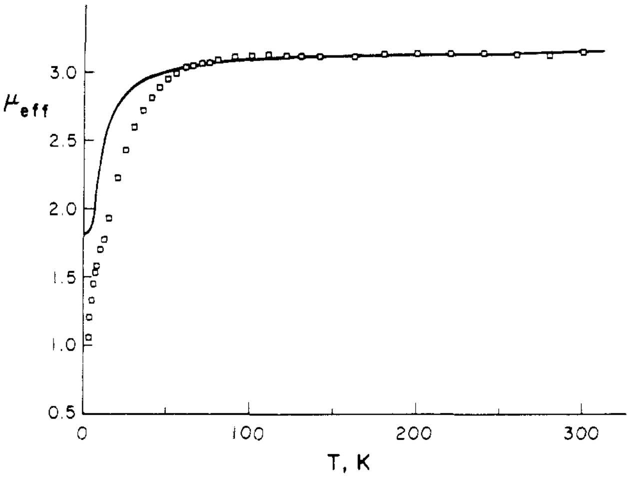


Figure 3. Magnetic susceptibility data, represented as a plot of μ_{eff} vs T. The solid line represents the "best" fit of data for $T \geq 55$ K to a three-spin ($^1/_2$–$^1/_2$–$^1/_2$) coupling model. See text for details.

bond to the projection of the O–N bond on the equatorial plane.[30] Values of these angles for the four independent copper–nitroxyl linkages are given in Table IV. All three angles show significant variations, with those in ϕ being particularly large.

Magnetic Susceptibility. The magnetic susceptibility data are represented in Figure 3 by a plot of $\mu_{eff} = 2.828(\chi_m T)^{1/2}$ vs T. From 90 to 300 K, the μ values are essentially constant, with a mean value of 3.130 (12) μ_B. At lower temperatures, the effective moment decreases, reaching a minimum value of 1.055 μ_B at 2.5 K, the lowest temperature investigated.

Discussion

The diprox adduct of bis(hexafluoroacetylacetonato)copper(II) is the first documented example of a metal–nitroxyl complex with an extended structure derived from a bridging nitroxyl diradical. Previously reported metal–nitroxyl chain structures[1,13,19] have all employed bidentate monoradicals as bridging groups. The axial bis(nitroxyl) configuration about copper in the diprox adduct is in contrast to the five-coordinate adducts formed by the closely related monoradicals tempo and proxyl.[2,31] Six-coordinate bis adducts of $Cu(F_6acac)_2$ have previously been observed with a number of cyclic nitronyl nitroxyls.[12,13,21]

The high-temperature μ_{eff} of 3.13 μ_B is a reasonable value for three uncorrelated spins per nitroxyl–copper–nitroxyl unit. The declining moments below 90 K are indicative of antiferromagnetic coupling, with the low-temperature (≤10 K) values showing that this coupling must extend beyond a single copper coordination sphere. The presence of four crystallographically independent and structurally different copper–nitroxyl linkages makes problematical any attempt to fit the magnetic susceptibility curve to a theoretical expression. The portion of the curve above T = 55 K can be fit moderately well (mean discrepancy = 1.4%) to the spin-only expression[32] for a three spin ($^1/_2$–$^1/_2$–$^1/_2$) system with best-fit values of $g = 2.10$ and $J = -4.6$ cm^{-1}. This fit to a featureless portion of the curve should only be taken to provide a rough estimate of an upper bound for the mean Cu–nitroxyl coupling constant.

Previously reported copper(II) complexes with axially bound nitroxyls have all had ferromagnetic metal–nitroxyl interactions.[4,12–14,21] In systems like these, the net magnetic behavior is normally considered to be a sum of ferromagnetic and antiferromagnetic contributions. Net ferromagnetic behavior may be observed when the antiferromagnetic component is small or zero. Antiferromagnetic interaction in systems like these is a consequence of overlap of metal and ligand magnetic orbitals and so will be rigorously zero if these orbitals are orthogonal. In axial copper(II)–nitroxyl complexes, the magnetic orbitals are ligand π^* and metal $d_{x^2-y^2}$ orbitals, and the conditions for strict orthogonality of these orbitals may be expressed in terms of the previously defined angles θ, φ, and ϕ. The two conditions for orthogonality are (1) $\theta = 0°$ (linear Cu–O–N bond) and (2) $\varphi = 90°$ and $\phi = 45°$ (π^* orbital directed between lobes of $d_{x^2-y^2}$). None of the four independent metal–nitroxyl linkages in the diprox adduct meet these criteria. Neither, however, do the corresponding linkages in any of the ferromagnetically coupled systems. Overlap will also depend on the Cu–O bond distance, but here again no clear correlation is observed. By elimination, the remaining variable is the electronic nature of the nitroxyl ligand. Indeed, previously experimental and theoretical results[14,20] suggest that saturated cyclic nitroxyls should have a larger antiferromagnetic interaction component than nitronyl nitroxyls.

For $T \leq 10$ K, the magnetic susceptibilities are lower than those expected for a single unpaired electron per formula unit. Clearly then, there must be additional intrachain or interchain interactions. As mentioned above, the individual chains are well separated with no obvious superexchange pathway between them. The closest direct interchain contact involving copper atoms or nitroxyl groups is an N(3)···N(5) separation of 7.46 Å, and the closest copper–copper distance between chains is 9.58 Å. Closer separations are observed within the chains, with the shortest being 4.52 Å in length between nitrogen atoms in the same diprox ligand. These results suggest a predominantly intrachain pathway for the additional interactions.

The chain contains four crystallographically independent and structurally different copper–nitroxyl linkages and also two independent but structurally similar nitroxyl–nitroxyl linkages. Hence, a detailed magnetic model would include at least five independent coupling constants. It is unlikely that meaningful values for this many independent parameters could be obtained by fitting the susceptibility curve. One possible simplification would occur if the copper–nitroxyl coupling constants were all significantly greater in magnitude than the nitroxyl–nitroxyl J values. At low temperatures, the system would then behave like a chain of $S = {}^1/_2$ centers. The low-temperature data could not, however, be fit by such a model; qualitatively, they do not show the broad maximum that is characteristic of one-dimensional Heisenberg chains.[33,34] It is possible that this maximum occurs at a temperature below the limit of our measurement or that it is masked by an analytically undetectable amount of paramagnetic impurity. In any event, we are forced to settle for a qualitative interpretation of the magnetic data.

The small magnetic coupling between copper coordination spheres could occur by either a dipolar or a superexchange mechanism. The nitrogen and oxygen atoms of each diprox ligand are separated by 4.52 and 5.52 Å, respectively and the nitrogen atoms are also linked by a three-carbon aliphatic bridge. Whatever the mechanism of the interaction, these results suggest a strategy for the rational design of new extended systems by use of different di- or polyradical ligands. For preparation of materials with extended interactions of larger magnitude, it would be desirable to employ ligands in which the radical centers either are in close proximity or are linked by a set of atoms that provides a good superexchange pathway. Unfortunately, the number of known nitroxyl species that satisfy these criteria is very small.

Acknowledgment. The X-ray diffractometer and the MicroVAX II computer were purchased with the assistance of NSF

---

(30) These are essentially the same angles previously defined by Gatteschi, Rey, et al.[14]

(31) Odenkirk, W.; Ziller, J. W.; Doedens, R. J. Unpublished work.

(32) Sinn, E. *Coord. Chem. Rev.* **1970**, *5*, 313–347.

(33) Bonner, J. C.; Fisher, M. E. *Phys. Rev.* **1964**, *135*, A640–A658.

(34) Carlin, R. L. *Magnetochemistry*; Springer-Verlag: Berlin, 1986.

Grant CHE-85-14495. The SQUID magnetometer at the University of Southern California was also purchased with the aid of an NSF grant.

Supplementary Material Available: Tables listing experimental details of the crystallographic study, hydrogen atomic positional parameters, anisotropic thermal parameters, bond distances, bond angles, and observed magnetic susceptibilities (13 pages); a listing of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, D-006,
University of California at San Diego, La Jolla, California 92093-0506

Insertion of a Copper Nitrene into a C–H Bond To Form Bis(2-(phenylamino)-1,10-phenanthrolinato)dicopper(I): A Short Cu–Cu Distance with No Bond?

Soon W. Lee and William C. Trogler*

Received October 3, 1989

The complex $Cu(phen)Cl_2$ (phen = 1,10-phenanthroline) reacts with $[Li(THF)_x]_2[PhNN{=}NNPh]$ (I) to yield the copper(I) dimer $[Cu(2\text{-}NPh\text{-}phen)]_2$ (II), formed by insertion of NPh into the ortho C–H bond of phenanthroline. Complex II crystallizes in the monoclinic crystal system at 294 K with space group $P2_1/n$ and lattice constants $a = 5.551$ (2) Å, $b = 13.700$ (5) Å, $c = 17.865$ (6) Å, $\beta = 97.85$ (3)°, and $Z = 2$. Refinement of the structure led to an R factor of 0.055 for 1399 reflections with $I > 3\sigma(I)$ and 82 least-squares parameters. In the structure of II, the coordination sphere of Cu approximates a square plane with a Cu–Cu separation of 2.600 (2) Å. Each square plane shares a common vertex. Complex II is inert to unsaturated ($PhN{=}NPh$, $PhC{\equiv}CPh$, $CH_2{=}CHCH_2Cl$) and amine (CH_3NH_2) ligands. Electrochemical studies show that II undergoes one chemically reversible oxidation, forming the mixed-valence complex, and a second chemically irreversible oxidation. SCF–Xα–DV calculations of model complexes for II and for a monomeric fragment suggest a repulsive interaction between the d^{10} Cu(I) centers. The dinuclear configuration appears to be dictated by the 2-(phenylamino)-1,10-phenanthroline(1–) ligand.

Introduction

Since 1967, several transition-metal tetrazene complexes have been reported, including derivatives of Ni, Pt, Co, Rh, Ir, and Fe.[1] We recently prepared[2,3] several transition-metal tetrazene complexes from the readily available tetrazenido dianion of I (eq 1).[3]

$$PhNHLi + PhN_3 \xrightarrow[THF]{} Ph(H)NN{=}NN(Ph)Li \xrightarrow[THF]{^nBuLi} \underset{\text{I}}{[Li(THF)_x]_2[PhNN{=}NNPh]} \quad (1)$$

This reagent has permitted the synthesis of tetrazene complexes of Ni, Pd, and Pt, which allows a comparison of metal–tetrazene bonding within a triad. This reagent has also been applied to the preparation of main-group tetrazene compounds[4] and the first early-transition-metal tetraazabutadienes.[5] The results of the above studies prompted us to investigate the possibility of forming a Cu–tetrazene complex with I, since they are unknown for this metal. Herein we report the unexpected results from the reactions between I and a dihalo Cu(II) complex.

Experimental Section

Reactions were performed with standard Schlenk and cannula filtration techniques under a nitrogen atmosphere. Solids were manipulated in a Vacuum Atmospheres glovebox equipped with an HE-493 dry chain. Glassware was either oven-dried or flame-dried before use. Benzene, diethyl ether, toluene, THF, and hydrocarbon solvents were refluxed over sodium or potassium benzophenone ketyl and distilled under nitrogen or by vacuum transfer. Dichloromethane and pyridine were distilled over CaH_2 and BaO, respectively. $CDCl_3$ was freeze–pump–thaw degassed before use and stored under nitrogen. The dianion of I, $[Li(THF)_x]_2[PhNN{=}NNPh]$,[3] and $Cu(phen)Cl_2$[6] were prepared by literature methods.

Table I. Crystallographic Data and Summary of Data Collection and Structure Refinement for II

chemical formula	$C_{36}H_{24}N_6Cu_2$	β, deg	97.85 (3)
fw	698.51	V, Å^3	1346 (1)
cryst syst	monoclinic	ρ_{calc}, g cm^{-3}	1.65
space group	$P2_1/n$	μ, cm^{-1}	16.2
a, Å	5.551 (2)	Z	2
b, Å	13.700 (5)	$R(F_o)$	0.055
c, Å	17.865 (6)	$R_w(F_o)$	0.061

Cyclic voltammetric studies were carried out by using a BAS 100 electrochemical analyzer equipped with a Houston Instruments DMP-40 plotter. Solutions (CH_2Cl_2) were ca. 1 mM in the metal complex and contained 0.1 M $[^nBu_4N][PF_6]$ as supporting electrolyte. For these measurements, a conventional three-electrode cell (Pt-disk working electrode, Pt-wire auxiliary electrode, Ag-wire pseudoreference electrode) was employed. Instrumental IR compensation was applied in all measurements. The $E°'$ value for the Cp_2Fe/Cp_2Fe^+ couple was 0.59 V at 300 mV/s in the cell. ^1H NMR were obtained with either a Varian EM-390 or a General Electric-QE 300-MHz spectrometer. IR spectra were recorded with an IBM IR/32 spectrometer. UV spectra were recorded with an IBM UV 9420 spectrometer. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory.

Synthesis of Bis(2-(phenylamino)-1,10-phenanthrolinato)dicopper(I) (II). Addition of 0.5 g of I in 30 mL of pyridine to a stirred green slurry of 0.5 g (1.59 mmol) of $Cu(phen)Cl_2$ in 30 mL of pyridine gave a dark red solution. After 8 h the solution was filtered, concentrated under vacuum, and layered with diethyl ether to yield purple crystals. These crystals were washed with THF (20 mL × 3) and Et_2O (20 mL × 2) and dried under vacuum to yield 0.31 g (30%) of II. ^1H NMR ($CDCl_3$): δ 7–8 (m, phen). Anal. Calcd for $C_{36}H_{26}N_6Cu_2$: C, 64.58; H, 3.89; N, 12.55. Found: C, 64.12; H, 3.25; N, 12.89. Mp: 264–266 °C. UV (THF): 310 nm (38 000 M^{-1} cm^{-1}), 404 (23 600), 460 (5500).

X-ray Structure Determination. X-ray data were collected with use of a Nicolet R3m/V automated diffractometer equipped with a Mo X-ray tube and a graphite-crystal monochromator. Crystal and intensity data are given in Table I. The orientation matrix and unit cell parameters were determined from 20 machine-centered reflections with $15 < 2\theta < 30°$. Intensities of three check reflections were monitored after every 100 reflections during data collection. The ω–2θ scan procedure was used to collect 2506 unique data. The scan range was 0.6° below K_{α_1} to 0.6° above K_{α_2}. Intensities were corrected for Lorentz and polarization effects. No absorption correction was applied.

---

(1) Moore, D. S.; Robinson, S. D. *Adv. Inorg. Radiochem.* **1986**, *30*, 1.
(2) Lee, S. W.; Miller, G. A.; Campana, C. F.; Maciejewski, M. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1987**, *109*, 5050.
(3) Lee, S. W.; Miller, G. A.; Campana, C. F.; Trogler, W. C. *Inorg. Chem.* **1988**, *27*, 1215.
(4) Miller, G. A.; Lee, S. W.; Trogler, W. C. *Organometallics* **1989**, *8*, 738.
(5) Lee, S. W.; Trogler, W. C. *Organometallics*, in press.
(6) Kwick, W. L.; Ang, K. P. *Inorg. Synth.* **1982**, *21*, 114.

0020-1669/90/1329-1659$02.50/0