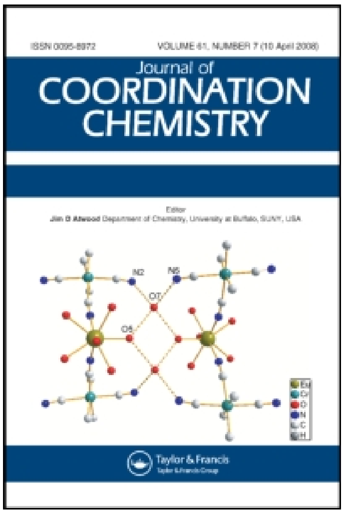

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Synthesis and crystal structure of a new copper(II) binuclear complex bridged by the reduced derivative of a nitronyl nitroxide biradical

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SYNTHESIS AND CRYSTAL STRUCTURE OF A NEW COPPER(II) BINUCLEAR COMPLEX BRIDGED BY THE REDUCED DERIVATIVE OF A NITRONYL NITROXIDE BIRADICAL

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A new copper(II) binuclear complex, $[Cu(hfac)_2]_2(IMH)_2Ph(OMe)_2$ ($(IMH)_2Ph(OMe)_2$ = 2,5-dimethoxyl-1,4-bis(4′,4′,5′,5′-tetramethylimidazoline-3′-oxide)benzene, hfac = hexafluoroacetonate), bridged by a reduced derivative of a nitronyl nitroxide biradical has been synthesized and characterized by X-ray crystallography. The complex crystallizes in the monoclinic space group $P2_1/n$, with $a = 10.002(14)$, $b = 19.950(3)$, $c = 14.504(2)$ Å, $\beta = 108.842(3)°$ and $Z = 2$. The structure refined to a final R value of 0.0644. The complex contains two copper(II) ions bridged by a reduced derivative of a nitronyl nitroxide biradical with a Cu⋯Cu separation of 8.430(2) Å.

Keywords: Biradical; Copper(II) complex; Crystal structure

INTRODUCTION

Nitronyl nitroxide radicals have been central to the development of molecular-based magnetic materials [1–6], especially in recent years, because of their exceptional stability and ease of chemical modification. Beyond binding to the metal and keeping their radical nature, it is known that nitroxides can undergo redox reactions with transition metal ions under certain conditions [7,8]. In fact, nitronyl free radicals are in an oxidation state intermediate between those of the hydroxylamino anion and the nitrosonium cation. Up to now, relatively little work has been devoted to the study of the redox properties of metal–nitroxyl systems. Oxidation of a nitroxide by some metal ions in a high oxidation state has been known for some time, but only a few complexes containing metal ions bound to the reduced monoradical have been reported [9–11].

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Nevertheless, no reduced derivative of a nitronyl nitroxide biradical has been reported. To the best of our knowledge, the complex $[Cu(hfac)_2]_2(IMH)_2Ph(OMe)_2$ ($(IMH)_2Ph(OMe)_2$ = 2,5-dimethoxyl-1,4-bis(4′,4′,5′,5′-tetramethylimidazoline-3′-oxide)benzene, hfac = hexafluoroacetonate) is the first example of a derivative of copper(II) with a reduced form of a nitroxide biradical. We report herein the synthesis, characterization and crystal structure of this new complex.

EXPERIMENTAL

Physical Measurements

Elemental analyses for C, H and N were performed with a Perkin Elmer 240 instrument. IR spectra were recorded in the range 400–4000 cm^{-1} on a Nicolet 560 E.S.P. FTIR spectrophotometer using KBr pellets and electronic spectra (in *n*-heptane) were measured on a Hitachi-240 spectrophotometer. ESR spectra were measured with a JES-FEIXG ESR instrument using X-band frequencies.

Synthesis

The biradical $(NIT)_2Ph(OMe)_2$ (2,5-dimethoxyl-1,4-bis(4′,4′,5′,5′-tetramethylimidazoline-1′-oxyl-3′-oxide)benzene) was prepared according to a published method [12], starting from 2,5-dimethoxyl-*p*-phthaldehyde instead of 2,5-dimethyl-*p*-phthaldehyde. Yield: 21%; mp 146–148°C. Anal. Calcd. for $C_{22}H_{32}N_4O_6$(%): C, 58.91; H, 7.19; N, 12.49. Found: C, 58.62; H, 7.52; N, 12.75. ESR spectra in CH_2Cl_2 solution at room temperature show five well-separated lines due to an unpaired electron localized on the NO groups and hyperfine coupling with the nitrogen nuclei, overlapped with one broad signal at $g = 2.0080$. The complex was prepared by adding 1 mmol of $(NIT)_2Ph(OMe)_2$ to 15 cm^3 of boiling, dry *n*-heptane containing 2 mmol of $Cu(hfac)_2 \cdot 2H_2O$. The solution was refluxed for 5 min and then filtered; the filtrate was allowed to cool. After 2 weeks red crystals suitable for X-ray structure determination were collected. Yield: 38%. Anal. Calcd. for $C_{42}H_{38}Cu_2F_{24}N_4O_{12}$(%): C, 36.72; H, 2.97; N, 40.78. Found: C, 36.85; H, 2.53; N, 41.01.

X-ray Crystal Structure Analysis

Crystallographic data were collected on a Bruker SMART 1000 diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 298(2) K. Intensity data were collected in the range $1.80 < \theta < 26.38°$. Unit cell parameters were determined by least-squares calculations based on the setting angles of 25 reflections. The structure was solved by direct methods using SHELXS-97 [13] and refined (on F^2) by full-matrix least-squares analysis with SHELXL-97 [14]. H-atoms were added geometrically and refined by mixed methods. All other atoms were refined anisotropically. Crystallographic data and refinement parameters are listed in Table I. Positional parameters are given in Table II, and selected bond lengths and angles in Table III. Full lists of crystallographic data are available from the authors upon request.

TABLE I Crystallographic data and data collection details for the complex

Formula	$C_{42}H_{38}F_{24}N_4O_{12}Cu_2$
Formula weight	1373.84
Temperature/K	298(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	10.002(14)
b/Å	19.950(3)
c/Å	14.504(2)
β/°	108.842(3)
V/Å^3	2739.0(6)
Z	2
μ/mm^{-1}	9.18
F(000)	1376
Measured/independent reflections	12 613/5546 [$R_{\text{int}} = 0.0493$]
R	0.0655
R_w	0.1634

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for the complex

Atom	*x/a*	*y/b*	*z/c*	*U(eq)*
Cu(1)	10 818(1)	5656(1)	2472(1)	62(1)
O(1)	11 314(4)	4857(2)	1889(3)	69(1)
O(2)	11 423(4)	6263(2)	1468(2)	66(1)
C(11)	11 833(4)	4841(2)	1213(3)	54(1)
C(12)	12 145(7)	5353(3)	709(4)	74(2)
C(13)	11 954(5)	6019(2)	881(4)	64(1)
C(14)	12 144(6)	4143(3)	959(4)	76(2)
C(15)	12 478(9)	6535(3)	329(6)	107(3)
O(3)	10 241(4)	6427(2)	3055(3)	74(1)
O(4)	8858(4)	5307(2)	2015(2)	72(1)
C(21)	9005(6)	6545(3)	3052(4)	69(1)
C(22)	7825(7)	6146(4)	2691(5)	88(2)
C(23)	7848(6)	5557(3)	2215(3)	73(1)
C(24)	8854(7)	7178(3)	3553(5)	97(2)
C(25)	6522(7)	5133(4)	1892(5)	103(3)
N(1)	13 142(5)	6201(3)	5804(3)	81(1)
N(2)	12 917(4)	5868(2)	4335(3)	54(1)
O(5)	12 591(3)	5501(2)	3525(2)	60(1)
C(31)	12 399(5)	5819(2)	5041(3)	57(1)
C(32)	14 174(5)	6323(3)	4571(4)	66(1)
C(33)	14 114(5)	6648(3)	5531(4)	68(1)
C(34)	13 995(9)	6791(4)	3722(5)	116(3)
C(35)	15 494(7)	5864(4)	4722(7)	110(2)
C(36)	13 392(11)	7321(4)	5347(7)	126(3)
C(37)	15 503(8)	6721(6)	6330(6)	138(4)
C(41)	11 171(5)	5399(2)	5030(3)	55(1)
C(42)	10 853(5)	4826(2)	4458(3)	56(1)
C(43)	9687(5)	4423(2)	4407(3)	56(1)
O(6)	9343(4)	3858(2)	3851(3)	74(1)
C(44)	10 172(7)	3667(3)	3268(5)	89(2)
F(1)	10 925(19)	3770(10)	860(20)	122(8)
F(2)	13 290(30)	3894(17)	1672(16)	153(14)
F(3)	12 480(30)	4053(14)	127(14)	105(7)
F(4)	13 270(30)	7025(11)	940(13)	131(7)
F(5)	13 390(20)	6344(11)	−118(17)	96(6)

(*continued*)

TABLE II Continued

Atom	*x/a*	*y/b*	*z/c*	*U(eq)*
F(6)	11 344(17)	6849(12)	−306(19)	117(7)
F(7)	9900(30)	7279(18)	4430(20)	118(9)
F(8)	7630(30)	7215(15)	3790(30)	100(6)
F(9)	8800(60)	7718(11)	2950(20)	141(11)
F(10)	5930(40)	4956(14)	937(9)	81(6)
F(11)	6620(40)	4562(15)	2440(30)	168(18)
F(12)	5430(30)	5562(17)	1890(30)	163(16)
F(1′)	11 570(20)	3656(8)	1345(17)	85(6)
F(2′)	13 540(12)	4008(9)	1310(13)	85(5)
F(3′)	11 755(18)	4015(11)	−4(8)	74(5)
F(4′)	13 750(30)	6745(15)	989(19)	178(17)
F(5′)	12 670(40)	6308(15)	−508(18)	119(12)
F(6′)	11 620(30)	7079(9)	60(20)	96(8)
F(7′)	9260(40)	7097(10)	4534(8)	113(7)
F(8′)	7507(17)	7430(13)	3240(20)	117(7)
F(9′)	9720(30)	7668(9)	3390(20)	115(8)
F(10′)	5900(30)	5205(11)	904(9)	75(7)
F(11′)	6830(20)	4464(6)	2090(14)	70(4)
F(12′)	5470(30)	5374(15)	2220(20)	100(10)
F(1″)	12 160(40)	3662(16)	1640(20)	99(9)
F(2″)	13 455(16)	4082(12)	860(20)	85(5)
F(3″)	11 190(20)	3990(17)	70(12)	88(8)
F(4″)	12 380(50)	7199(6)	500(40)	128(13)
F(5″)	13 906(18)	6490(30)	500(40)	200(20)
F(6″)	11 800(50)	6420(20)	−660(10)	170(11)
F(7″)	8340(50)	7030(12)	4310(20)	112(7)
F(8″)	7940(30)	7607(14)	2910(20)	118(9)
F(9″)	10 020(20)	7583(16)	3880(30)	109(9)
F(10″)	5850(30)	5433(12)	1003(13)	209(18)
F(11″)	6730(30)	4486(8)	1650(20)	183(16)
F(12″)	5690(30)	5115(12)	2480(20)	108(7)

TABLE III Selected bond lengths (Å) and angles (deg) for the complex

Cu(1)–O(3)	1.931(3)	O(3)–Cu(1)–O(1)	177.08(15)
Cu(1)–O(1)	1.942(3)	O(3)–Cu(1)–O(5)	96.17(15)
Cu(1)–O(5)	1.955(3)	O(1)–Cu(1)–O(5)	85.15(15)
Cu(1)–O(4)	1.982(4)	O(3)–Cu(1)–O(4)	91.30(15)
Cu(1)–O(2)	2.126(3)	O(1)–Cu(1)–O(4)	86.01(15)
N(2)–O(5)	1.331(5)	O(5)–Cu(1)–O(4)	139.04(15)
N(2)–C(31)	1.292(6)	O(3)–Cu(1)–O(2)	92.16(15)
N(2)–C(32)	1.498(5)	O(1)–Cu(1)–O(2)	90.04(13)
N(1)–C(31)	1.351(6)	O(5)–Cu(1)–O(2)	103.78(14)
N(1)–C(33)	1.464(6)	O(4)–Cu(1)–O(2)	116.14(15)
		N(2)–O(5)–Cu(1)	120.3(3)

RESULTS AND DISCUSSION

An ORTEP [15] drawing of the complex is shown in Fig. 1. The molecular structure of the complex shows that the molecule is centrosymmetric. The coordination geometry of the Cu(II) ion can be approximated to a distorted trigonal bipyramid with amidino-oxide bound in the basal plane by an oxygen atom with a Cu(1)–O(5) distance of 1.955(3) Å. Other basal coordination sites are occupied by two oxygen atoms (O(2), O(4)) of hfac ligands (2.126(3) and 1.982(4) Å for Cu(1)–O(2) and Cu(1)–O(4), respectively).

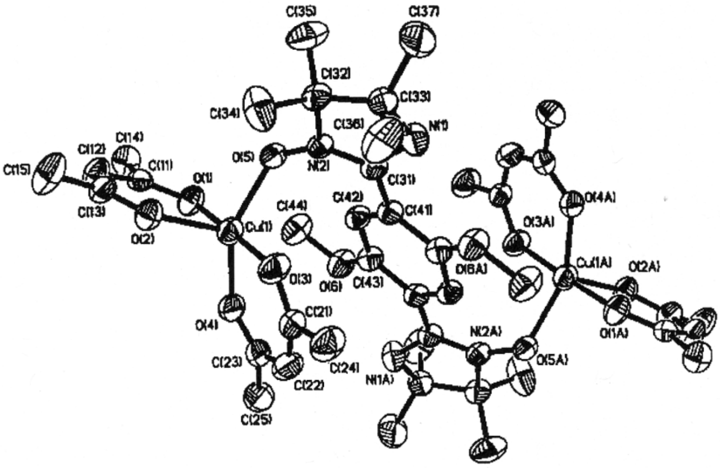

FIGURE 1 ORTEP drawing of the complex (30% probability ellipsoids). Fluorine and hydrogen atoms are omitted for clarity.

The axial positions are filled by the remaining oxygen atoms (O(1), O(3)) of hfac ligands with Cu–O bond lengths of 1.942(3) and 1.931(3) Å for Cu(1)–O(1) and Cu(1)–O(3), respectively. The CuO_5 trigonal bipyramid is severely distorted, which is also reflected in the deviation of the bond angles from 120 or 90°. The N–O bond distance is 1.331(5) Å, clearly indicative of the reduced form of the radical, while the corresponding distance in the nitroxide ranges from 1.25 to 1.32 Å [16–19]. The copper–copper separation is 8.430(2) Å.

In the complex, two NIT groups of $(NIT)_2Ph(OMe)_2$ were reduced by reaction of the nitroxide biradical with $Cu(hfac)_2$ and each N–O group of $(IMH)_2Ph(OMe)_2$ is bound to a Cu(II) ion to obtain a binuclear complex bridged by the reduced derivative of nitronyl nitroxide. Although the mechanistic details of the reaction are not well understood, it has been established that $Mn(hfac)_2$ is able to convert the NITR radical into IMHR [9–11]. To our knowledge, no example in which $Cu(hfac)_2$ converts the NITR biradical into IMHR has been reported.

The absorption attributed to π–π^* of the conjugated ONCNO group of the free radical at 358 nm disappears in electronic spectra of the complex, indicating that NO groups are reduced. Evidence for the presence of the IMHR amidino-oxide tautomeric form in the complex is provided by the IR spectra, which show the characteristic N–H stretching absorption at *ca* 3400 cm^{-1}, and by the X-ray structure analysis.

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