Synthesis, Crystal Structure and Magnetic Properties of A New Thiazolyl-Substituted Nitronyl Nitroxide and Its Copper(II) Complexes

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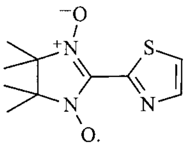
Keywords: Thiazole radicals / Nitronyl nitroxide / Copper / Magnetic properties

A new building block for molecule-based magnetic materials — thiazole-substituted nitronyl nitroxide NIT2-thz [**1**, NIT2-thz = 4,4,5,5-tetramethyl-2-(2′- thiazolyl)imidazolin-1-oxyl 3-oxide] and its copper(II) complexes [Cu(NIT2-thz)$_2$(N$_3$)$_2$] (**2**) and [CuCl$_2$(NIT2-thz)$_2$] (**3**) — have been synthesized and characterized structurally and magnetically. Compound **1** is found to contain two crystallographically independent molecules; the shortest contact between nitroxide groups is 4.900 Å. Both **2** and **3** are mononuclear complexes, in which the copper(II) centers are hexacoordinate. In complex **2**, the copper(II) ion has an elongated octahedral geometry, but complex **3** has a rare compressed-octahedral coordination sphere. Magnetic susceptibility data for compounds **1**–**3** have been measured in the range 5–300 K. There are ferromagnetic interactions (J = 10.13 cm^{-1}) between the Cu^{II} ions and the radicals of **2**, and antiferromagnetic interactions (J = –8.17 cm^{-1}) between the Cu^{II} ions and the radicals of **3**. The magnetic properties of complexes **2** and **3** are discussed in connection with their crystal structures.

Introduction

In the preparation of molecular magnetic materials, transition metal complexes with organic nitronyl nitroxide radical ligands have attracted widespread interest in recent years.[1−5] However, the weakly basic character of nitronyl nitroxide strongly limits their coordination ability. This has led to the development of functionalized nitronyl nitroxide radicals, in which a strong co-ligand is incorporated. Research has focused on nitronyl nitroxide radicals with electron-donating substituents such as 2-pyridyl,[6,7] imidazolyl,[8,9] 2,2′-bipyridinyl,[10] and 1,2,4-triazolyl.[11] Among them, the 2-pyridyl- and imidazolyl-substituted nitroxides have the advantage of forming stable chelated complexes with the support of the auxiliary substituent groups. The thiazolyl substituent too has a strong chelating ability for complexes with metal ions. This prompted us to synthesize a new thiazole-substituted nitronyl nitroxide radical and a group of metal compounds containing this radical ligand. In this contribution, we wish to report the synthesis, crystal structure and magnetic properties of the radical NIT2-thz [**1**, NIT2-thz = 4,4,5,5-tetramethyl-2-(2′- thiazolyl)imidazolin-1-oxyl 3-oxide] (Scheme 1) and its complexes [Cu(NIT2-thz)$_2$(N$_3$)$_2$] (**2**) and [CuCl$_2$(NIT2-thz)$_2$] (**3**).



Scheme 1

Results and Discussion

Crystal Structure of 1

Compound **1** (Figure 1) is found to contain two crystallographically independent molecules, but these two structures are not significantly different from each other. The N−O bond lengths of 1.284(4) Å [O(1)−N(3)] and 1.278(4) Å [O(2)−N(2)], respectively, are in agreement with those in radicals synthesized by other groups.[12,13] The two S−C bond lengths of 1.729(4) Å [S(1)−C(3)] and 1.692(5) Å [S(1)−C(1)], respectively, are longer than other three bond lengths of 1.305(5) Å [N(1)−C(3)], 1.366(5) Å [N(1)−C(2)] and 1.319(6) Å [C(1)−C(2)] in the thiazole ring. The dihedral angles between the nitronyl nitroxide fragment and the thiazole ring are 7.1(5)° and 3.6(4)°, respectively. The shortest contact between nitroxide groups is 4.900 Å [O(4)···O(4), (x, 1 − y, 1/2 + z)].

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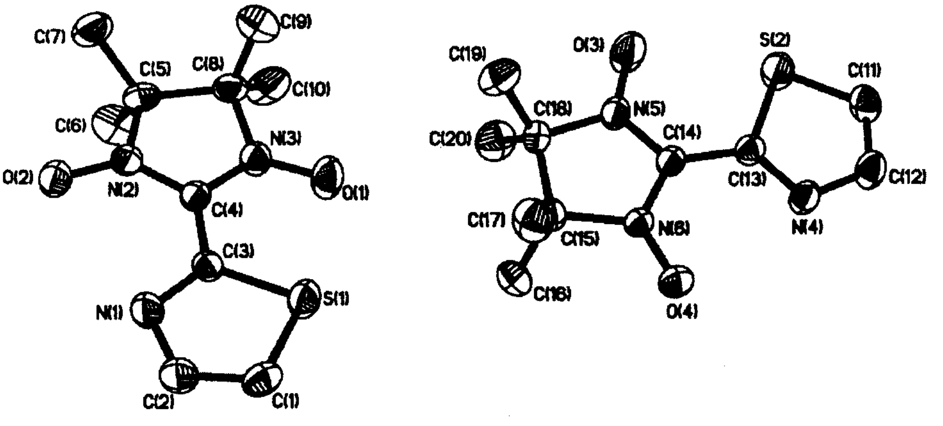

(a) (b)

Figure 1. ORTEP drawing of compound **1**

Crystal Structures of 2 and 3

The structures of **2** (Figure 2) and **3** (Figure 3) are centrosymmetric, and the copper(II) ions have a distorted octahedral environment. In both complexes, two NIT2-thz radicals, acting as bidentate chelating ligands, coordinate the copper(II) ion through the N−O unit and the nitrogen atom of the thiazole ring. However, the geometries of complexes **2** and **3** are different.

In complex **2**, the two nitrogen atoms [N(4), N(4A)) of the azide groups and the two nitrogen atoms [N(1), N(1A)) of the radical ligands are coordinated at the equatorial positions. The Cu−N bond lengths are 1.995(3) Å [Cu(1)−N(4)] and 2.024(2) Å [Cu(1)−N(1)], respectively. The two oxygen atoms [O(2), O(2A)] on the NO groups of the radical ligands are bonded at the axial positions, with a Cu−O distance of 2.364(2) Å, which is longer than for those coordinated at the equatorial positions. The copper(II) ion has, as expected, an elongated octahedral geometry.

In complex **3**, the basal plane is formed by the two oxygen atoms [O(1), O(1A)] of the NO groups [with a Cu−O bond length of 2.370(5) Å], and two chloride anions [with a Cu−Cl bond length of 2.348(2) Å]. The axial positions are occupied by the two nitrogen atoms [N(1), N(1A)) of the thiazole rings, with a Cu−N distance 2.001(6) Å, which is significantly shorter than for those coordinated at the equatorial positions. Thus the copper(II) ion has a rare compressed-octahedral coordination sphere.

The uncoordinated N−O bond lengths of 1.278(3) Å (for **2**) and 1.280(7) Å (for **3**), and the coordinated N−O bond lengths of 1.276(3) Å (for **2**) and 1.293(7) Å (for **3**), are close to those of the free radical NIT2-thz [corresponding N−O bond lengths 1.284(4) Å and 1.278(4) Å]. The dihedral angle between the nitronyl nitroxide fragment and the thiazole ring is 5.4(4)° (for **2**) and 16.7(11)° (for **3**). The shortest distances between the nitroxide groups are 4.728 Å (for **2**) and 4.521 Å (for **3**).

Magnetic Properties

The magnetic susceptibilities of compounds **1**, **2** and **3** were measured in the range 5−300 K at a magnetic field of 1 T.

For compound **1**, the variation of $\chi_M T$ vs. T is plotted in Figure 4. The $\chi_M T$ value is close to 0.357 cm^3·K·mol^{-1} in the range 30−300 K, and corresponds to the expected value

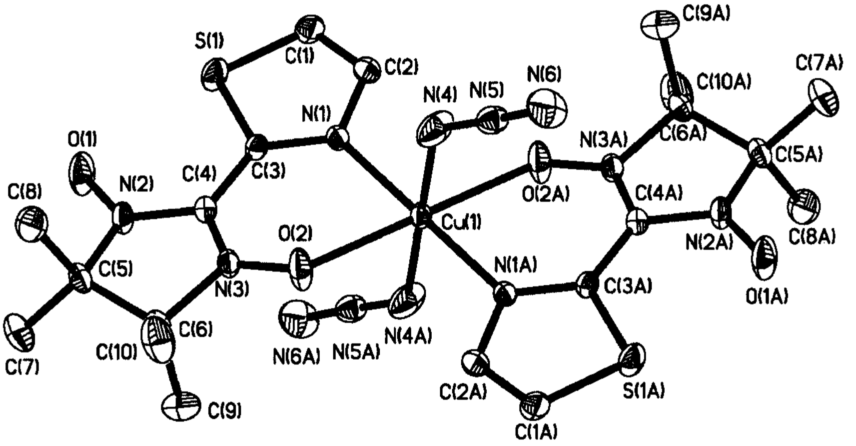

Figure 2. ORTEP drawing of complex **2**

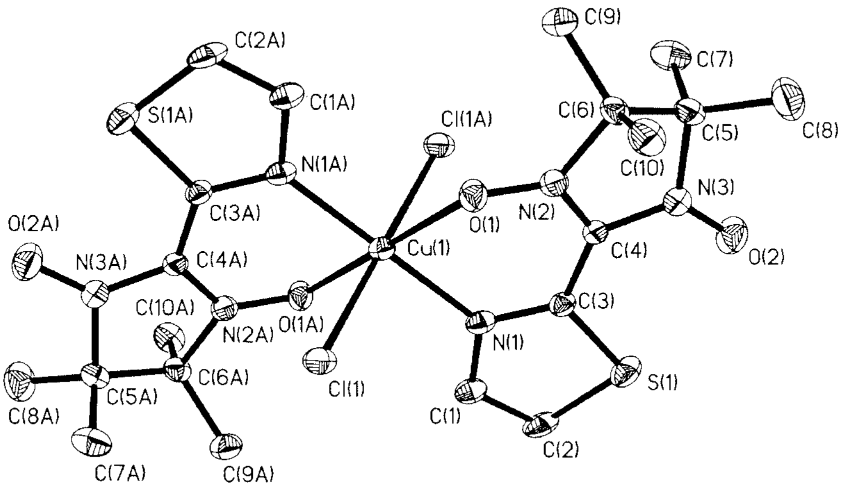

Figure 3. ORTEP drawing of complex **3**

(0.374 $cm^3 \cdot K \cdot mol^{-1}$) for a non-correlated $S = 1/2$ spin. As the temperature is lowered from about 30 K to 5 K, $\chi_M T$ decreases rapidly. Below 30 K, the magnetic susceptibility data obeys a Curie−Weiss law $\chi = C/(T - \theta)$, with the Weiss constant $\theta = -1.46$ K and $C = 0.364$ (inset in Figure 4). This behaviour is characteristic of weak intermolecular antiferromagnetic interactions.

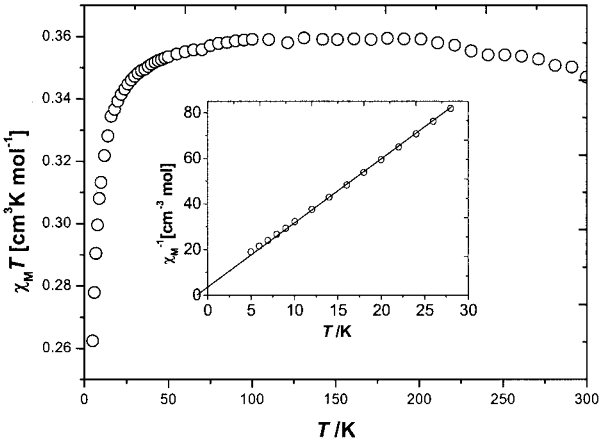

Figure 4. Plot of $\chi_M T$ vs. T for compound **1**. Inset: plot of $\chi_M{}^{-1}$ vs. T

For complex **2**, the plots of $\chi_M T$ and χ_M vs. T are shown in Figure 5. At 300 K, the $\chi_M T$ value is equal to 1.17 $cm^3 \cdot K \cdot mol^{-1}$, which is slightly higher than that expected for a non-interacting $S = 1/2$ spin for Cu^{II} and two $S = 1/2$ spins for the radicals (spin-only value 1.13 $cm^3 \cdot K \cdot mol^{-1}$). As the temperature decreases from about 300 to 5 K, $\chi_M T$ gradually increases and reaches a maximum of 1.475 $cm^3 \cdot K \cdot mol^{-1}$ at 7.0 K, from where it decreases down to a temperature of 4.91 K. This indicates that there are ferromagnetic interactions between the nitroxide radical and the copper(II) ion.

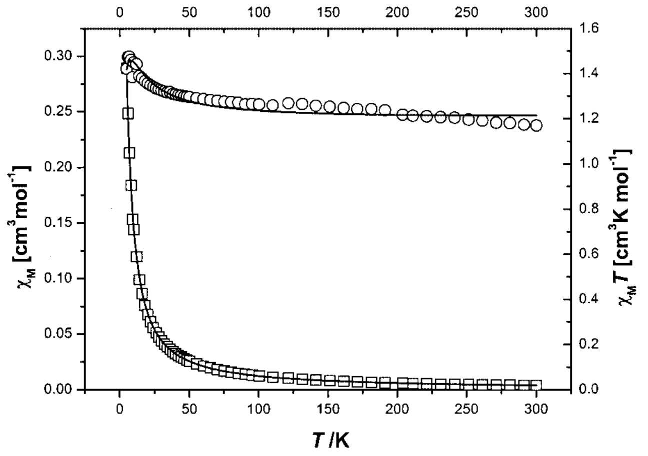

Figure 5. Plots of $\chi_M T$ vs. T and χ_M vs. T of complex **2**. *T*he solid line represents the fitting values

The magnetic data for **2** were treated by the theoretical expression[14] derived through the spin Hamiltonian $H = -J(S_{R1}S_{Cu} + S_{R2}S_{Cu})$, where J represents the exchange interaction between the Cu^{II} ion and the thiazole radical. Considering the magnetic coupling between the molecules, we used the mean-field approximation (zJ').[15] The best fitting for the data gives $J = 10.13 cm^{-1}$, $zJ' = -0.46\ cm^{-1}$, $g_{cu} = 2.13$, $g_{rad} = 2.0$ (fixed), and an agreement factor [defined as $R = (\chi_M)_{obsd.} - (\chi_M)^2_{calcd.}/(\chi_M)^2_{obsd.}$] of 3.34×10^{-4}. These results indicate a weak ferromagnetic exchange interaction between the Cu^{II} ion and the radical.

The plots of $\chi_M T$ and χ_M vs. T for **3** are shown in Figure 6. At 300 K, $\chi_M T$ is 1.12 $cm^3 \cdot K \cdot mol^{-1}$, which is consistent with that expected for one non-interacting $S_{Cu} = 1/2$ spin and two $S_{rad} = 1/2$ spins (1.13 $cm^3 \cdot K \cdot mol^{-1}$). Starting from a temperature of 300 K, $\chi_M T$ decreases smoothly down to 50 K, then rapidly decreases to 0.43 $cm^3 \cdot K \cdot mol^{-1}$ at 5 K. This magnetic behavior is clearly indicative of antiferromagnetic interactions.

The magnetic data for **3** were treated with a similar theoretical expression to that used for **2**; J characterizes the exchange interaction between the Cu^{II} ion and the thiazole radical.

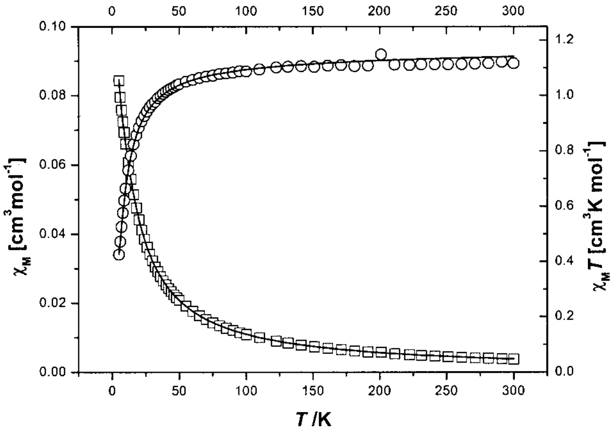

Figure 6. Plots of $\chi_M T$ vs. T and χ_M vs. T for complex **3**. The solid line represents the fitting values

The best fitting for the data gives $J = -8.17\text{cm}^{-1}$, $zJ' = -0.36\ \text{cm}^{-1}$, $g_{\text{cu}} = 2.04$, $g_{\text{rad}} = 2.0$ (fixed), with an agreement factor [defined as $R = [(\chi_M)_{\text{obsd.}} - (\chi_M)_{\text{calcd.}}]^2/[(\chi_M)_{\text{obsd.}}]^2]$ of 5.41×10^{-6}. The results indicate a weak antiferromagnetic exchange interaction between the Cu^{II} ion and the radical.[11]

The geometrical parameters of the binding of the radical to the metal are of great importance for the understanding of the magnetic properties of the complexes **2** and **3**. In our two complexes, the magnetic orbital of the nitronyl nitroxide radical is a π* orbital, with its axis lying perpendicular to the O−*N*−C−*N*−O plane.[16] The magnetic orbital of the copper(II) ion with an octahedral coordination environment is $d_{z^2-y^2}$ or d_{z^2}. Following the Kahn−Briat rules,[17] the extent of overlap between metal and radical magnetic orbitals is responsible for the appearance of antiferromagnetic interactions, whereas orthogonality of the same orbitals induces ferromagnetic contributions. With these ideas in mind, it is possible to correlate the metal-radical coupling to the crystal structures of the complexes. Complex **2** has an elongated-octahedral geometry, with the two nitroxide groups bound in an axial position. It is generally accepted that the interaction between a copper(II) centers and an axially bound nitroxide radical is ferromagnetic because, in this geometry, the π* radical orbital is strictly orthogonal to the $d_{x^2-y^2}$ orbital of the copper(II) ion.[18] Thus, the positive value of the copper(II) nitroxide coupling constant ($J_{\text{Cu,rad}} = 10.13\ \text{cm}^{-1}$) has been ascribed to the interaction between the copper(II) ion and the radicals located in axial positions. The relatively low value observed arises from the fact that the Cu−O distances are fairly long [Cu(1)−O(2) = 2.364(2) Å].

For compound **3**, two nitroxide groups coordinate in equatorial positions. In general, this results in a strong antiferromagnetic coupling between copper and radical.[19] However, in this case, a weak antiferromagnetic interaction is observed ($J_{\text{Cu,rad}} = -8.17\ \text{cm}^{-1}$). In complex **3**, the copper(II) ion has a compressed octahedral coordination geometry and the magnetic orbital of the copper(II) ion is d_{z^2}. This geometry will induce a weak antiferromagnetic coupling between the copper(II) ion and the radical due to the poor magnetic orbital overlap.

Conclusions

In summary, the novel thiazole-substituted nitronyl nitroxide radical **1** and the complexes **2** and **3** (the first examples of a new family of complexes) have been synthesized. In complex **3**, the copper(II) ion has a rare compressed-octahedral coordination sphere. This geometry results in a weak antiferromagnetic interaction between the copper(II) ion and the radical, even though the radical is coordinated in the equatorial plane.

Experimental Section

General: All reagents were purchased from commercial sources and used as received. Solvents were purified and dried by standard methods. Elemental analyses for C, H, and N were carried out with a Perkin−Elmer 240 elemental analyzer. The infrared spectra were recorded in KBr pellets in the range 4000−600 cm^{-1} with a SHIMADZU-408 IR spectrometer. EPR spectra were recorded as a solution of the compound in CH_2Cl_2 with a JESFEIXG EPR spectrometer. Variable-temperature magnetic susceptibilities were measured with a MPMS-7 SQUID magnetometer. Diamagnetic corrections were made using Pascal's constants for all the constituent atoms.

X-ray diffractions were measured with a RAXIS-IV area detector for **2** and **3** and with a Bruker−Smart 1000 diffractometer for **1**. The structures were solved by direct methods using the SHELXS-97[20] program. H atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restraints. A full-matrix least-squares refinement on F^2 was carried out using SHELXL 97.[21] Crystal data are summarized in Table 1, selected structural parameters in Table 2−4.

Preparation of Nitronyl Nitroxide Radical NIT2-thz: Prepared from 2-thiazolecarboxaldehyde by the literature method.[22,23] The dark green crystals of **1** were recrystallized from cyclohexane/ethyl acetate (5:1) in 55% yield. $C_{10}H_{14}N_3O_2S$: calcd. C 49.94, H 5.87, N 17.48; found C 49.89, H 5.85, N 17.40. IR: $\tilde{\nu}_{\text{thz}} = 1418, 1185, 1140$ cm^{-1}; $\tilde{\nu}_{\text{N-O}} = 1375$ cm^{-1}. ESR (299 K, CH_2Cl_2): five lines; $g = 2.00$; $a_N = 7.8$ G.

Preparation of [Cu(NIT2-thz)$_2$(N$_3$)$_2$] (2): $Cu(ClO_4)_2{\cdot}6H_2O$ (0.093 g, 0.25 mmol) and NaN_3 (0.033 g, 0.5 mmol) were added with stirring to a solution of **1** (0.120 g, 0.5 mmol) in dry methanol (30 mL), and the mixture was then filtered to remove a small amount of precipitate. The dark brown solution was allowed to stand at room temperature in the dark for two weeks. Black crystals were obtained in 43% yield. $C_{20}H_{28}CuN_{12}O_4S_2$: calcd. C 38.24, H 4.49, N 26.74; found C 38.30, H 4.44, N 26.76. IR: $\tilde{\nu}_{\text{thz}} = 1420, 1190, 1136$ cm^{-1}; $\tilde{\nu}_{\text{N-O}} = 1375$ cm^{-1}.

Preparation of [CuCl$_2$(NIT2-thz)$_2$] (3): $CuCl_2{\cdot}2H_2O$ (0.086 g, 0.5 mmol) was added with stirring to a solution of **1** (0.120 g, 0.5 mmol) in dry ethanol (30 mL), and the mixture was then filtered to remove a small amount of precipitate. The dark brown solution was allowed to stand at room temperature in the dark for three weeks. Dark blue crystals were obtained in 45% yield. $C_{20}H_{28}Cl_2CuN_6O_4S_2$: calcd. C 39.06, H 4.59, N 13.66; found C

Table 1. Crystallographic data for **1**, **2** and **3**

	1	**2**	**3**
Empirical formula	$C_{10}H_{14}N_3O_2S$	$C_{20}H_{28}CuN_{12}O_4S_2$	$C_{20}H_{28}Cl_2CuN_6O_4S_2$
Molecular mass	240.30	628.20	615.04
Temperature (K)	293 (2)	291(2)	291(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	triclinic
Space group	$C2/c$	$P2_1/c$	$P\bar{1}$
a (Å)	23.257(11)	10.171(2)	9.061(2)
b (Å)	23.447(10)	12.018(2)	9.856(2)
c (Å)	9.136(4)	11.180(2)	7.6988(15)
α (°)	90	90	97.25(3)
β (°)	96.458(9)	103.91(3)	94.89(3)
γ (°)	90	90	75.43(3)
V (Å^3)	4950(4)	1326.5(5)	659.1(2)
Z, calculated density (g·cm^{-3})	16, 1.290	2, 1.573	1, 1.550
Absorption coefficient (mm^{-1})	0.252	1.034	1.341
F(000)	2032	650	317
Crystal size/mm	0.25×0.20×0.10	0.26×0.20×0.20	0.25×0.21×0.20
θ range for data collection (°)	1.24 to 23.24	2.06 to 27.55	2.15 to 24
Reflections collected/unique	8365/3543 [R(int) = 0.0417]	4167/2279 [R(int) = 0.0209]	1714/1714 [R(int) = 0.0000]
Data/restraints/parameters	3543/2/297	3543/2/297	1709/ 0/161
Goodness-of-fit on F^2	1.052	1.096	1.038
R 1 [$I>2\sigma(I)$]	0.0536	0.0360	0.0776
wR	0.1461	0.0844	0.1923
R 1 (all data)	0.0931	0.0465	0.0886
wR	0.1701	0.0869	0.2098

Table 2. Selected bond lengths (Å) and angles (°) for **1**

S(1)−C(1)	1.692(5)	N(1)−C(2)	1.366(5)
S(1)−C(3)	1.729(4)	N(2)−C(4)	1.348(5)
S(2)−C(11)	1.676(5)	N(2)−C(5)	1.515(5)
S(2)−C(13)	1.735(4)	N(3)−C(4)	1.341(5)
O(1)−N(3)	1.284(4)	N(3)−C(8)	1.505(5)
O(2)−N(2)	1.278(4)	N(4)−C(13)	1.290(5)
O(3)−N(5)	1.285(5)	N(4)−C(12)	1.367(5)
O(4)−N(6)	1.278(4)	N(5)−C(14)	1.329(5)
N(1)−C(3)	1.305(5)	N(5)−C(18)	1.489(5)
N(6)−C(15)	1.509(4)	N(6)−C(14)	1.363(5)
C(1)−C(2)	1.319(6)	C(11)−C(12)	1.335(6)
C(1)−S(1)−C(3)	89.4(2)	C(13)−N(4)−C(12)	110.4(3)
C(11)−S(2)−C(13)	89.5(2)	O(3)−N(5)−C(14)	122.8(3)
C(3)−N(1)−C(2)	109.4(3)	O(3)−N(5)−C(18)	122.0(3)
O(2)−N(2)−C(4)	126.2(3)	C(14)−N(5)−C(18)	115.2(3)
O(2)−N(2)−C(5)	122.1(3)	O(4)−N(6)−C(14)	126.2(3)
C(4)−N(2)−C(5)	111.6(3)	O(4)−N(6)−C(15)	121.4(3)
O(1)−N(3)−C(4)	125.1(3)	C(14)−N(6)−C(15)	112.4(3)
O(1)−N(3)−C(8)	122.0(3)	C(4)−N(3)−C(8)	112.7(3)

Table 3. Selected bond lengths (Å) and angles (°) for **2**

Cu(1)−N(4)	1.995(3)	N(2)−O(1)	1.278(3)
Cu(1)−N(1)	2.024(2)	N(2)−C(4)	1.343(3)
Cu(1)−O(2)	2.364(2)	N(2)−C(5)	1.503(4)
N(3)−O(2)	1.276(3)	N(3)−C(4)	1.340(4)
S(1)−C(1)	1.699(3)	N(4)−N(5)	1.180(4)
S(1)−C(3)	1.721(3)	N(5)−N(6)	1.144(4)
N(1)−C(3)	1.325(3)	N(3)−C(6	1.508(3)
N(1)−C(2)	1.364(3)	C(1)−C(2)	1.346(4)
N(4)#1−Cu(1)−N(1)	91.92(10)	N(4)#1−Cu(1)−O(2)	89.87(13)
N(4)−Cu(1)−N(1)	88.08(10)	N(4)−Cu(1)−O(2)	90.13(13)
N(4)#1−Cu(1)−N(4)	180.0	N(1)#1−Cu(1)−O(2)	96.23(8)
N(1)−Cu(1)−O(2)	83.77(8)	O(2) #1−Cu(1)−O(2)	180.0
C(3)−N(1)−C(2)	111.2(2)	N(5)−N(4)−Cu(1)	128.6(2)
C(3)−N(1)−Cu(1)	129.69(18)	N(6)−N(5)−N(4)	177.6(3)
C(2)−N(1)−Cu(1)	118.49(17)	N(3)−O(2)−Cu(1)	120.38(17)

Symmetry transformations used to generate equivalent atoms (#1): $-x+1, -y+1, -z$

Table 4. Selected bond lengths (Å) and angles (°) for **3**

Cu (1)−N(1)	2.001(6)	N(1)−C(3)	1.328(9)
Cu (1)−Cl(1)	2.348(2)	N(1)−C(1)	1.363(9)
Cu (1)−Ol(1)	2.370(5)	N(2)−O(1)	1.293(7)
S(1)−C(2)	1.710(9)	N(2)−C(4)	1.330(8)
S(1)−C(3)	1.715(7)	N(2)−C(6)	1.498(8)
N(3)−C(5)	1.512(9)	N(3)−O(2)	1.280(7)
N(1)−Cu(1)−Cl(1)	89.0(2)	N(1)−Cu(1)−N(1)#1	180.0
N(1)#1−Cu(1)−Cl(1)	91.0(2)	Cl(1)#1−Cu(1)−O(1)#1	93.22(13)
Cl(1)−Cu(1)−Cl(1)#1	180.0	O(1)−Cu(1)−O(1)#1	180.0
N(1)−Cu(1)−O(1)	84.1(2)	C(2) −S(1)−C(3)	90.1(3)
N(1)#1−Cu(1)−O(1)	95.9(2)	C(3)−N(1)−C(1)	111.0(6)
Cl(1)−Cu(1)−O(1)	93.22(13)	C(3)−N(1)−Cu(1)	126.2(5)
Cl(1)#1−Cu(1)−O(1)	86.78(13)	C(1)−N(1)−Cu(1)	122.1(5)

Symmetry transformations used to generate equivalent atoms (#1): -x, $-y+1, -z+1$

38.97, H 4.56, N 13.59. IR: $\tilde{\nu}_{thz}$ = 1418, 1189, 1137 cm^{-1}; $\tilde{\nu}_{N\text{-}O}$ = 1380 cm^{-1}.

CCDC-209220, -210729 and -210736 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This work was supported by the Natural Science Foundation of China (Nos. 20171025, 20331010, and 90101028) and Tianji Natural Science Foundation (No. 033602011).

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Received December 1, 2003