Published in final edited form as:

Inorganica Chim Acta. 2008 March 3; 361(4): 1142–1148. doi:10.1016/j.ica.2007.09.016.

Synthesis, Characterization and Copper Chemistry of a Non-symmetric Ligand: 2-Methyl-9-(3,5-dimethyl-N-pyrazolylmethyl)-1,10-phenanthroline

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Abstract

The synthesis of an unsymmetrical phenanthroline based ligand, 2-methyl-9-(3,5-dimethylpyrazolylmethyl)-1,10-phenanthroline (**L**), and its cupric [Cu(II)] (**1**) and cuprous [Cu(I)] (**2**) complexes, are reported. The X-ray structures of each of these Cu complexes show distinct changes in coordination environments consistent with the geometrical preferences of the two oxidation states. In the solid state the Cu(II) complex (**1**) adopts a geometry best described as trigonal bipyramidal, while the Cu(I) complex (**2**) consists of a single dicationic dimer in which the ligand bridges between two copper ions, separated by 4.26 Å. The two Cu(I) coordination sites differ in **2** with one copper center complexed in a trigonal planar geometry and the other copper in a distorted tetrahedral environment; the latter coordination results from an additional CH₃CN ligand. Complex **1** exhibits a reversible redox process at −0.34 V vs. Fc/Fc⁺ in CH₃CN, attributable to the Cu²⁺/Cu⁺ couple, while the dimeric Cu(I) complex (**2**) is resistant to oxidation on the CV timescale. Over minutes however, complex **1** does oxidize in the presence of dioxygen to **2** in CH₃CN.

Keywords

Copper; crystal structure; phenanthroline; pyrazole

1. Introduction

Studies of the interaction of small-molecule Cu(I) complexes with dioxygen, and the subsequent oxidative processes of the resulting Cu-O₂ complexes, provide insights into the mechanism of action of Cu-containing metalloenzymes as well as aid in the development of bio-inspired Cu-oxidation catalysts.[1–4] In biochemical systems, Cu-containing metalloenzymes exist in mononuclear[5] as well as coupled multinuclear configurations,[1] that have evolved to carry out essential redox processes. The development of functional models of O₂-activating Cu enzymes is a multifaceted endeavor as there are many design features that need consideration. Ligands that are able to accommodate multiple metal oxidation states, and thus are conformationally flexible, while also allowing for binding and subsequent activation of O₂, are required. In addition, the ligands must limit undesired side-reactions and unintended oligomerization processes in homogenous solution. Significant effort has been devoted to the

development of such ligands, and important insights have been made as a result of these studies. [6]

This work investigates the copper chemistry of a non-symmetric tridentate phenanthroline-based (phen) ligand, 2-methyl-9-(3,5-dimethyl-N-pyrazolyl)methyl-1,10-phenanthroline (**L**). Metal complexes of phen generally take on the form of $[M(\text{phen})_2]^{n+}$ or $[M(\text{phen})_3]^{n+}$ depending upon the geometric preferences of the metal ions. The presence of bulky substituents *ortho* to the nitrogen donor atoms of phen biases the metal stereochemistry towards a four-coordinate tetrahedral-like coordination. In the case of copper, a tetrahedral biasing through sterically demanding phen ligands clearly stabilizes Cu(I) over Cu(II). [7,8]

The reactivity of Cu-phen complexes with dioxygen, which was investigated initially over 30 years ago, [9] reported that the bis-chelated copper(I) complex of phen, $\text{Cu}(\text{phen})_2^+$, reacts with dioxygen in polar solvents, while the 2,9-dimethyl-phen analogue was found to be inert. [9] Subsequent work by Anson and colleagues [10] has shown that ligand dissociation to form a $\text{Cu}(\text{phen})^+$ species in solution is required for efficient O_2 activation by either phen or 2,9-dimethyl-phen. Adsorption of such species onto graphite electrodes has aided in the study of their electrocatalytic dioxygen reactivity. [11]

As found in biochemical systems, the reaction of Cu(I) with O_2 most often proceeds through either a three-coordinate (T or Y shape). In model systems, four-coordinate mono-pyramidal complexes also react with O_2 . [3,12] Thus, if dioxygen activity by Cu-phen complexes is to occur, then ligand design should preclude bis-phen chelation of a Cu(I) center. The non-symmetric tridentate phenanthroline ligand **L** reported here was designed to bind the Cu(I) ion in a trigonal geometry, yet would allow facile inter-conversion to a facially capped ligating mode once bound to dioxygen. [13] Non-symmetric phenanthroline-based ligands are limited in number [14,15] due primarily to the synthetic effort needed to unsymmetrically derivatize phen. In this paper we describe the synthesis of a new non-symmetric phenanthroline ligand **L**, as well as the isolation and characterization of its Cu(I) and Cu(II) complexes.

2. Experimental Section

2.1 General Information

All chemicals were of reagent grade and were used without further purification. Infrared spectra were recorded as KBr pellets on a Mattson Research Series RSI FTIR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Varian XL 400 spectrometer. Mass spectra were recorded by liquid secondary ion mass spectrometry (+LSIMS) method at the University of California San Francisco. Electronic spectra were obtained in CH_3CN solutions with a fiber optic diode array Polytec X-dap spectrometer. For water or dioxygen sensitive studies, a 1 cm Hellman quartz dip probe in a custom designed cell was used. EPR spectra were recorded at 77 K in a CH_3CN glass on a Bruker ER 220D-SRC spectrometer. Cyclic voltammograms were obtained on a PAR electrochemistry system consisting of a 174 A polarographic analyzer and a single compartment cell with a Pt working electrode, a Pt auxiliary electrode, and a Ag/Ag^+ reference electrode prepared from a $1 \times 10^{-3} \text{ mol dm}^{-3}$ AgNO_3 solution in CH_3CN . The Fc/Fc^+ couple was measured to be +0.47 V relative to the reference electrode; all potentials will be reported relative to Fc/Fc^+ . The supporting electrolyte was 0.1 mol dm^{-3} tetraethylammonium perchlorate (TEAP). All electrochemical experiments and dioxygen sensitive reactions were performed in a Braun LabMaster 130 dry box with dioxygen levels below 1 ppm.

2.2 Preparations

2.2.1. Synthesis of 2-methyl-9-(3,5-dimethylpyrazolylmethyl)-1,10-phenanthroline (**L**)—2-methyl-9-chloromethyl-1,10-phenanthroline [16] (0.120 g, 0.05

mmol) was dissolved in 50 ml of benzene/CH₂Cl₂ solution (1/1 v/v) with 3,5-dimethylpyrazole (0.096 g, 1.0 mmol). To this solution were added 20 mL of a 40% solution of NaOH and 0.25 mL of a 40% tetrabutylammonium hydroxide solution. The mixture was heated at reflux for 24 h. After cooling, the organic fraction was collected, and the aqueous layer was extracted with three 25 mL portions of CH₂Cl₂. The organic fractions were combined, dried over MgSO₄, filtered, and the solvent was removed *in vacuo*. Chromatography on neutral alumina with CH₂Cl₂ as the eluent afforded **L** as a white solid (0.105 g, 70%; 20% yield from 2,9-dimethyl-1,10-phenanthroline), mp 188–190 °C, (R_f: 0.40, neutral alumina, 5/1 v/v CH₂Cl₂/CH₃CN). ¹H NMR (CDCl₃): δ 2.15 (3H, s, pyrazolyl CH₃); 2.30 (3H, s, pyrazolyl CH₃); 2.95 (3H, s, phen CH₃); 2.80 (2H, s, CH₂); 5.95 (1H, s, pyrazolyl H); 6.90 (1H, d); 7.55 (1H, d); 7.70 (2H); 8.15 (2H). ¹³C NMR (CDCl₃): δ 11.3, 13.6, 26.0, 55.3, 106.0, 120.0, 124.0, 125.4, 126.3, 127.0, 128.0, 136.4, 137.4, 140.0, 143.0, 148.2, 151.0, 158.4, 160.0 ppm. IR (KBr pellet): 3413, 3186, 2917, 1680, 1623, 1590, 1553, 1499, 1460, 1423, 1367, 1143, 1029, 852, 783 cm⁻¹.

2.2.2. Synthesis of [Cu(L)(CH₃CN)(CF₃SO₃)]CF₃SO₃ (1**)**—A 2 mL CH₃OH solution containing Cu(CF₃SO₃)₂ [17] (0.036g, 0.1 mmol) was added dropwise to a stirred solution containing **L** (0.033g, 0.11 mmol) dissolved in CH₂Cl₂ / CH₃CN (3 mL, 1:1 v/v). The resulting dark green solution was stirred for few min, and the solvent was removed *in vacuo* to afford a dark green solid. Recrystallization by diffusion of Et₂O into a CH₃CN solution of the complex afforded dark green solvent-loss sensitive crystals of **1** in 80% yield. IR (KBr pellet): 3352, 1510, 1429, 1289, 1238, 1163, 1029, 639, 787, 517 cm⁻¹. Mass spectrum (+LSIMS): m/z = 514.1 [CuL(CF₃SO₃)]⁺.

2.2.3. [Cu₂(L)₂(CH₃CN)](CF₃SO₃)₂·(CH₃)₂CO (2**)**—Under an inert atmosphere, a solution of [Cu(CH₃CN)₄](CF₃SO₃) [18] (0.037 g, 0.1 mmol) in CH₃CN (2 mL) was added to a stirred solution of **L** (0.033 g, 0.11 mmol) dissolved in CH₃CN / acetone (5 mL, 9:1 v/v). The red solution which formed was stirred briefly, and the volume was reduced under a constant flow of dinitrogen to *ca.* 2 mL. Slow diffusion of Et₂O into the reaction solution afforded red crystals of **2** in 80% yield. ¹H NMR (CD₃CN): δ 2.20 (s, pyrazolyl-CH₃); 2.90 (s, phen-CH₃); 5.12 (s); 5.55 (s); 5.80 (s); 6.15 (s); 7.35 (m); 7.65 (s); 7.80 (d); 8.15(d); 8.35 (m); 8.60 (m). IR (KBr pellet): 3502, 1632, 1603, 1500, 1428, 1256, 1224, 1147, 1028, 860, 783, 638, 517 cm⁻¹. Mass spectrum (+LSIMS): 1032.1 [Cu₂L₂(CF₃SO₃)₂]⁺, 881.1 [(Cu₂L₂(CF₃SO₃)]⁺, 730.1 [Cu₂L₂]⁺, 667.2 [CuL²]⁺.

2.3. X-ray Crystallography

Green X-ray quality crystals of **1** (0.30 × 0.20 × 0.15 mm) were obtained by Et₂O diffusion into a CH₃CN solution of the complex. Orange-red crystals of **2** (0.70 × 0.30 × 0.40 mm) were grown from a CH₃CN-acetone solution by slow diffusion of Et₂O. These solvent-loss sensitive crystals were mounted in paratone oil on a glass fiber and placed in a cold stream of dinitrogen (198 K), on an Enraf-Nonius CAD-4 diffractometer equipped with a molybdenum tube [λ(Mo Kα) = 0.71073 Å] and a highly oriented graphite monochromator for data collection. The structures were solved by direct methods [19] and refined with the teXsan software. [20] Both data sets were corrected for Lorentz and polarization, absorption and decay effects. Crystal data and refinement details of complexes **1** and **2** are detailed in Table 1.

3. Results

3.1. Synthesis

The ligand **L** was prepared in moderate yield as outlined in Scheme 1. The starting material (2,9-dimethyl-1,10-phenanthroline) was converted to its mono-chlorinated form in four-steps, [16] followed by phase transfer coupling to 3,5-dimethylpyrazole to afford **L**. The Cu(II) (**1**)

and Cu(I) (**2**) complexes were synthesized by equimolar addition of either $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ [17] or $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{CF}_3\text{SO}_3$ [18], respectively, to a solution of **L**. While the red Cu(I) complex (**2**) is stable as a solid in air, the complex is air-sensitive in a CH_3CN solution, and undergoes complete oxidation to a green Cu(II) species in *ca.* 60 min at RT.

3.2. Description of the X-ray structures

3.2.1. Complex 1—The copper(II) structure (**1**) consists of a discrete $[\text{Cu}(\text{L})(\text{CH}_3\text{CN})(\text{CF}_3\text{SO}_3)]^+$ cation (**1**⁺) and an independent triflate anion. A view **1**⁺ is presented in Figure 1 and selected metrical parameters of the structure are listed in Table 2. The copper center adopts a five-coordinate distorted trigonal bipyramidal geometry. The coordination environment comprises two nitrogen atoms [N(1) and N(2)] from the phen portion of the ligand, one nitrogen atom [N(4)] from the pyrazolyl moiety, an CH_3CN nitrogen atom [N(5)], and a triflate oxygen atom [O(1)]. A τ value of 0.55⁵² and analysis of dihedral angles suggests that the observed geometry is best described as distorted trigonal bipyramidal.[21] As expected for trigonal bipyramidal complexes, the equatorial phen nitrogen to copper bond length (Cu(1)-N(2)) of 1.986 Å is significantly shorter than the corresponding axial Cu(1)-N(1) bond length of 2.029 Å. The N(2)-C(10)-C(14)-N(3) and N(3)-N(4)-C(10)-C(14) torsion angles around the nominally single C-C bonds linking the phen and pyrazolyl ring, also defined as the tilt and cant angles,[22] are -47.8° and 40.6° respectively, while the dihedral angle between the pyrazolyl and phen rings is 27.2°.

3.2.2. Complex 2—In contrast to the Cu(II) complex (**1**), the Cu(I) complex $[\text{Cu}_2(\text{L})_2(\text{CH}_3\text{CN})](\text{CF}_3\text{SO}_3)_2(\text{CH}_3)_2\text{CO}$ (**2**) crystallizes as an unsymmetrical 2:2 dimer (Figure 2, Table 2) with a Cu(1)-Cu(2) distance of 4.26 Å. The structure consists of a single dicationic dimer, two discrete triflate anions, an acetone of solvation, and one coordinated CH_3CN molecule. The non-symmetric nature of this dimer results from the differential coordination at each Cu(I) center; one copper atom is coordinated in a trigonal planar environment while the other copper atom is bound in a pseudo-tetrahedral environment. Both copper atoms derive two nitrogen atoms from a phen unit and one nitrogen atom from a pyrazolyl unit of the opposite ligand. The pseudo-tetrahedral geometry at one center results from additional coordination of an CH_3CN molecule. For complex **2** the two phen planes are nearly parallel to each other, however, the pyrazoles and phen moieties within a single ligand are not coplanar. The dihedral angles between the phen containing the N(1) and N(2) atoms and pyrazole moieties containing the N(3) and N(7) atoms are 79.5° and 91.0° respectively. The analogous angles for the second phen are 80.4° and 94.7° respectively, consistent with their nearly perpendicular appearance. The two pyrazoles are inclined at an angle of 91°. The 4-coordinate copper exists in a pseudo-tetrahedral/trigonal-pyramidal environment due to the constraints of the ligand. Analysis of the bond angles clearly demonstrates a substantial distortion either from an ideal tetrahedral or ideal trigonal planar geometry. The average Cu-N (phen) distances are consistent with the most notable change observed in the Cu-N(pyrazole) distances, which significantly lengthen from 1.907 Å to 2.05 Å with increased coordination number. The Cu-acetonitrile bond (Cu(1)-N(9)) length of 2.050 Å is longer than similar interactions observed in mononuclear[23] and dinuclear[24] Cu(I) complexes.

3.3. Spectroscopy

Complex **1** exhibits a broad low-energy absorption band in CH_3CN solution with a maximum at 760 nm ($\epsilon = 140 \text{ M}^{-1} \text{ cm}^{-1}$) consistent with a ligand field $d \rightarrow d$ transition of a Cu(II) complex in either a square pyramidal or trigonal-bipyramidal geometry (Figure 3).[25,26] The X-ray structure of **1** indicates a trigonal-bipyramidal geometry in the solid-state, however, in solution the complex could be in equilibrium between trigonal bipyramidal and square pyramidal geometries. The EPR spectrum of **1** in a frozen CH_3CN solution does not provide much information as the signal is isotropic ($g_{\text{av}} = 2.13$). Absorption features for **1** at higher energy

are assigned to ligand transitions as similar features are present in the spectrum of **2** (*vide infra*), and the free ligand.

The absorption spectrum of the Cu(I) complex (**2**) exhibits an intense band at 440 nm ($\epsilon = 3480 \text{ M}^{-1} \text{ cm}^{-1}$), [8] which is presumably a metal to ligand charge transfer band (MLCT) similar to that reported for the Cu(I) complex of 2,9-bis(N-pyrazolylmethyl)-1,10-phen (Figure 3). [25] On exposure to air over one hr, solutions of **2** change color from red to green. During this time, the 440 nm band diminishes and is replaced by a d→d transition 760 nm, presumably due to reaction of the Cu(I) complex with dioxygen to form **1**.

3.4. Electrochemistry

The ligand **L** is electrochemically inert in the range investigated (1.3 V to -1.0 V), therefore all electrochemical processes can be attributed to the Cu center(s). At slow scan rates (20 mV/s), the Cu(II) complex (**1**) exhibits a reversible wave at $E_{1/2} = -0.34 \text{ V vs. Fc/Fc}^+$ attributable to the $\text{Cu}^{2+/+}$ couple. This assignment is consistent with the observation of approximately equal cathodic and anodic currents, and a plot of the (sweep rate)^{1/2} vs. ΔE_p , which has an intercept of 85 mV comparable to the value observed for the Fc/Fc^+ couple. On repeated scans no alteration in cyclic voltammetric profiles occurred, while increasing scan rates reduced the Nernstian behavior with peak separation increasing to 130 mV at a scan rate of 100 mV/s. Interestingly, the Cu(I) complex (**2**) was found to be redox inactive on the electrochemical timescale.

4. Discussion

In an effort to further understand the interaction of small-molecule Cu complexes with dioxygen, a sterically-hindered non-symmetric phenanthroline ligand **L** has been synthesized (Scheme 1) and its Cu complexes studied. The present results show that the ligand, **L**, containing a sterically hindered phenanthroline with an appended pyrazolyl group, is able to adopt different coordination geometries, thus stabilizing both Cu(I) and Cu(II) oxidation states. The solid state structures are of interest as only a small number of X-ray structures of metal complexes containing non-symmetric phenanthroline ligands exist. [15] While the Cu(II) complex (**1**) adopts a trigonal bipyramidal geometry (Figure 1), a non-symmetric dinuclear complex **2** (Figure 2) is formed upon reaction of Cu(I) with **L**. A similar dimeric structural motif has been reported for a dinuclear Cu(I) complex with two tridentate timm ligands (timm = tris[2-(1-methylimidazolyl)]methoxymethane), in which each copper(I) ion is ligated by three imidazole groups with two donors coming from one tridentate ligand and the third donor from the opposite ligand acting as a bridge. [27] Related dinuclear Cu(I) complexes have been recently reported with timm derivatives. [28] Reactions of **L** with the Cu(I) and Cu(II) precursors afforded 1:1 ligand:metal complexes even with addition of excess ligand. Bis-phen copper complexes of very sterically demanding 2,9-disubstituted phens have been reported, [29] and thus in the case of **L** it is likely that an unfavorable change in free energy, as opposed to ligand steric bulk, prevents the formation of 2:1 ligand:metal complexes with Cu. Interestingly, the Cu(I) complex **2** was found to be redox inactive, indicating that on the electrochemical timescale the Cu(I) species formed via reduction of **1** is different from the isolated and characterized dinuclear Cu(I) species **2**. However, upon exposure to air over one hr, **2** reacted with dioxygen to form the Cu(II) complex **1** highlighting the difference between simple electrochemical processes with only weakly coordinating anions and inner sphere processes whereby electron transfer creates a strong binding ligand such as superoxide. [3,4] The redox reactivity of **2** is more facile than that reported for timm analogs [28] suggesting that the increased flexibility of **L** is better able to stabilize the resulting Cu(II) species. Site-isolation of ligands such as **L** on suitable solid supports would prevent dimerization, and could permit

access to metal coordination environments and reactivity not easily accessible in a homogeneous medium.[30]

Supplementary data

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC); CCDC-648450 (complex **1**), and CCDC-648449 (complex **2**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

This work was supported by an NIH grant (grant GM-50730), and an NSERC post-doctoral fellowship (TS).

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Figure 1.
ORTEP diagram of $\mathbf{1}^+$ with 50 % thermal ellipsoid probability.

Figure 2.
ORTEP diagram of 2^{2+} with 50 % thermal ellipsoid probability.

Figure 3. Electronic spectra of **1** (0.004 M, solid line) and **2** (0.0005 M, dashed line) in CH₃CN. Extinction coefficients calculated on a per mole Cu basis.

Scheme 1.

Synthesis of 2-methyl-9-(3,5-dimethyl-N-pyrazolylmethyl)-1,10-phenanthroline (**L**); (a) CH_3COOH , H_2O_2 ; (b) acetic anhydride; (c) K_2CO_3 , EtOH ; (d) PCl_3 ; (e) 3,5-dimethylpyrazole, NBu_4OH , NaOH , CH_2Cl_2 , benzene.

Table 1

Crystal data and refinement details.

Crystal Data	1	2
Formula	$C_{23}H_{21}CuF_6N_5O_6S_2$	$C_{45}H_{45}Cu_2F_6N_9O_7S_2$
Formula weight	705.11	1129.11
Crystal system, space group	monoclinic, $P2_1/c$ (#14)	triclinic, $P1$ (#2)
a (Å)	14.479 (1)	13.306 (3)
b (Å)	8.523 (2)	13.5392 (10)
c (Å)	24.131 (3)	16.046 (3)
α (deg)	90.000 (14)	89.377 (12)
β (deg)	104.414 (8)	73.394 (17)
γ (deg)	90.000 (13)	61.438 (14)
Volume [Å ³]	2884.1 (8)	2405.7 (1)
Z, D_{calc} [g/cm ³]	4, 1.624	2, 1.559
μ (MoK α) [cm ⁻¹]	9.88	10.54
$F(000)$	1428	1156
Temperature (K)	198 (2)	198 (2)
$\theta_{min-max}$	2.53, 24.97°	2.43, 24.97°
reflens collcd/unique	5566/5460 ($R_{int}=0.066$)	8798/8410 ($R_{int}=0.044$)
Residuals (F2, all data)	$wR_2 = 0.140$	$wR_2 = 0.128$
Residuals (F, $I > 2\sigma(I)$)	$R_1 = 0.041$	$R_1 = 0.023$

Table 2Selected Intramolecular Distances (Å) and Bond Angles (°) for complex **1**.^a

Cu(1)-O(1)	2.002(6)	O(1)-Cu(1)-N(1)	83.1(2)
Cu(1)-N(1)	2.042(7)	O(1)-Cu(1)-N(2)	119.1(2)
Cu(1)-N(2)	1.893(5)	O(1)-Cu(1)-N(4)	92.2(2)
Cu(1)-N(4)	1.906(5)	O(1)-Cu(1)-N(5)	104.8(2)
Cu(1)-N(5)	1.430(8)	N(1)-Cu(1)-N(2)	82.6(2)
		N(1)-Cu(1)-N(4)	169.0(2)
		N(1)-Cu(1)-N(5)	99.5(2)
		N(2)-Cu(1)-N(4)	91.1(2)
		N(2)-Cu(1)-N(5)	136.0(2)
		N(4)-Cu(1)-N(5)	91.3(2)

^a Estimated standard deviations in parentheses.

Table 3Selected Intramolecular Distances (Å) and Bond Angles (°) for complex **2^a**.

Cu(1)-N(1)	2.090(4)	N(1)-Cu(1)-N(2)	79.9(2)
Cu(1)-N(2)	2.098(4)	N(1)-Cu(1)-N(8)	121.1(2)
Cu(1)-N(8)	1.980(4)	N(1)-Cu(1)-N(9)	108.0(2)
Cu(1)-N(9)	2.050(5)	N(2)-Cu(1)-N(8)	135.6(2)
Cu(2)-N(4)	1.907(4)	N(2)-Cu(1)-N(9)	93.7(2)
Cu(2)-N(5)	2.044(4)	N(8)-Cu(1)-N(9)	112.4(2)
Cu(2)-N(6)	2.030(4)	N(4)-Cu(2)-N(5)	133.9(2)
		N(4)-Cu(2)-N(6)	143.6(2)
		N(5)-Cu(2)-N(6)	82.1(2)

^aEstimated standard deviations in parentheses.