

Synthesis, Structure, and Spectroscopic and Electrochemical Properties of Copper(II/I) Complexes with Symmetrical and Unsymmetrical 2,9-Diaryl-1,10-phenanthroline Ligands

Peiju Yang,^[a] Xiao-Juan Yang,^{*,[a,b]} and Biao Wu^{*,[a,b]}

Keywords: Copper / Structure elucidation / Electrochemistry / N ligands

A series of copper(II) and copper(I) complexes, $[\text{CuX}_2\text{L}]$ (**1–6**) and $[\text{CuL}_2][\text{CuX}_2]$ (**7–12**) ($\text{X} = \text{Cl}, \text{Br}$; $\text{L} = 2\text{-R-R}'\text{-1,10-phenanthroline}$, dpp: $\text{R} = \text{R}' = \text{Ph}$; npp: $\text{R} = \text{naphthyl}$, $\text{R}' = \text{Ph}$; dnp: $\text{R} = \text{R}' = \text{naphthyl}$) were synthesized and characterized by elemental analysis, UV/Vis and IR spectroscopy, and X-ray crystal diffraction (for **1**, **3**, **6**, and **12**). The copper(II) complexes are four-coordinate with one phenanthroline ligand and two halogen atoms, whereas the copper(I) complexes are

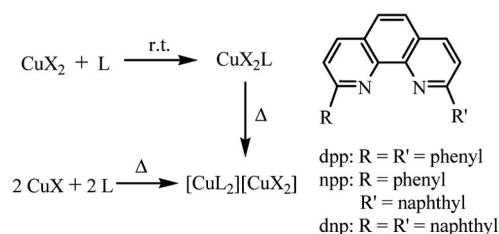
tetrahedrally coordinated by two bidentate phenanthroline ligands. Cyclic voltammetry studies of the Cu^{I} complexes in CH_2Cl_2 reveal that bulky groups in the 2,9-positions have significant effects on the redox potential of the $\text{Cu}^{\text{II/I}}$ couple, which is more positive for the complexes with the dnp ligand than those with the dpp and npp ligands.

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Introduction

The chelating N-donor system 1,10-phenanthroline and its derivatives represent a widely studied family of ligands in transition-metal coordination chemistry as a result of the rigidity of the phenanthroline backbone and the ease of modifying their properties by appending various substituents at different positions of the phenanthroline moiety.^[1,2] A large number of metal complexes with phenanthroline ligands have been synthesized, and they display promising properties in a variety of fields such as photochemistry, electron-transfer processes, biological systems, and self-assembly of supramolecular architectures.^[3–6] In particular, copper complexes of phenanthroline ligands are of great interest because of their photoluminescent behavior and DNA and RNA binding properties.^[7–14] Furthermore, it has been shown that the substituents on the phenanthroline ring can have significant effects on the structure and properties of the copper complexes. Among the 1,10-phenanthroline derivatives, the 2,9-disubstituted agents are probably the most studied, as these sterically demanding ligands can provide a highly protected coordination environment for metal ions.

We recently synthesized a series of symmetrical and unsymmetrical 2,9-diaryl-1,10-phenanthroline ligands and their transition-metal complexes.^[15,16] In the preparation of the copper complexes, a novel four-coordinate Cu^{II} species $[\text{CuBr}_2(\text{dpp})]$ was obtained, which could be converted into the Cu^{I} complex $[\text{Cu}(\text{dpp})_2](\text{CuBr}_2)$ under certain conditions.^[16] It is known that the Cu^{II} complexes usually have a five- or six-coordinate, Jahn–Teller-distorted geometry with 1,10-phenanthrolines, whereas non-square-planar, four-coordinate Cu^{II} complexes are very rare.^[17–19] To gain more insight into the structural features of such Cu^{II} complexes and the steric effects of the substituents on their properties, we prepared a series of Cu^{II} and Cu^{I} complexes of three 2,9-diaryl-1,10-phenanthroline ligands, dpp (2,9-diphenyl-1,10-phenanthroline), npp (2-naphthyl-9-phenyl-1,10-phenan-



$[\text{CuX}_2\text{L}]$	1	2	3	4	5	6
$[\text{CuL}_2][\text{CuX}_2]$	7	8	9	10	11	12
L	dpp	npp	dnp	dpp	npp	dnp
X	Cl	Cl	Cl	Br	Br	Br

Scheme 1. Synthesis of complexes **1–12**.

[a] State Key Laboratory for Oxo Synthesis & Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China
E-mail: yangxj@lzb.ac.cn
wubiao@lzb.ac.cn

[b] State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, China

throline), and dnp (2,9-dinaphthyl-1,10-phenanthroline) (Scheme 1). The conversion of the $[\text{CuX}_2\text{L}]$ complexes into the Cu^{I} species, $[\text{CuL}_2](\text{CuX}_2)$, was also studied. Herein we report the syntheses, structures, and spectroscopic and electrochemical properties of the complexes $[\text{Cu}^{\text{II}}\text{X}_2\text{L}]$ and $[\text{Cu}^{\text{I}}\text{L}_2](\text{CuX}_2)$ (**1–12**, $\text{X} = \text{Cl}, \text{Br}$; $\text{L} = \text{dpp}, \text{npp}$, or dnp).

Results and Discussion

Synthesis

The dpp, npp, and dnp ligands were synthesized as previously reported.^[15] Copper(II) complexes **1–6** were prepared by the reaction of an equimolar amount of CuX_2 ($\text{X} = \text{Cl}, \text{Br}$) and the ligand in THF as brick-red solids (for **1–3**), or in dichloromethane as brown powders (for **4–6**). Dark-red copper(I) complexes **7–12** were prepared by the reaction of anhydrous CuX with the corresponding ligand in a 1:1 ratio. Because conversion of (dibromido)copper(II) complex **4** into the corresponding Cu^{I} complex **10** was observed previously,^[16] we examined Cu^{II} species **1–6** under different conditions and found that the ligand steric bulk, the halide ligand (Cl or Br), and the solvent could affect this process significantly. The complexes with the smallest ligand (dpp), **1** and **4**, can readily undergo this conversion to form the corresponding Cu^{I} species, **7** and **10**, in acetone or CH_2Cl_2 at room temperature (or by heating to speed up the process), and the conversion of dibromido analogue **4** is much faster than that of dichlorido **1**. The dibromido complexes with the other two bulkier ligands (npp and dnp), **5** and **6**, can also be partially converted into the corresponding monovalent Cu^{I} complexes (**11**, **12**) by heating their CH_2Cl_2 or acetone solution, whereas their dichlorido analogues (**2**, **3**) do not show detectable change under the same conditions. Moreover, the conversion in acetone is easier than in CH_2Cl_2 . These results reveal that bulky groups in the 2,9-positions of phenanthroline can provide efficient protection for the metal center to prevent ligand redistribution, and the more labile bromido ligand can promote the process. Such processes were also supported by MS (ESI) studies. In the MS (ESI) spectrum of complex **1**, both $[\text{CuCl}(\text{dpp})]^+$ [m/z (%) = 430.6 (20.2)] and $[\text{Cu}(\text{dpp})_2]^+$ [m/z (%) = 727.8 (100)] can be found, whereas complex **4** shows almost complete conversion to the $[\text{CuL}_2]^+$ species [m/z (%) = 727.8 (100)] for $[\text{Cu}(\text{dpp})_2]^+$ with only a trace amount of $[\text{CuBr}(\text{dpp})]^+$ (<5%).

X-ray Crystal Structures

The crystal structures of complexes **4** and **10** were reported previously by this group.^[16] The Cu^{I} complex $[\text{Cu}(\text{dpp})_2](\text{CuCl}_2) \cdot 2/3\text{CH}_3\text{CN}$ was also structurally characterized.^[20] Here we present the structures of three Cu^{II} complexes (**1**, **3**, and **6**) and one Cu^{I} complex (**12**). Single crystals suitable for X-ray diffraction were obtained from $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (50:50 for **1**, **3**, and **6**) or acetone (for **12**). Notably, it is very difficult to obtain crystals of either Cu^{II} or Cu^{I}

complexes bearing the unsymmetrical ligand npp, as many attempts to crystallize the complexes failed. The molecular structures of **1**, **3**, **6**, and **12** are depicted in Figures 1, 2, 3, and 4, respectively, and selected bond lengths and angles are given in Table 1.

Table 1. Selected bond lengths [$\text{\AA}$] and bond angles [$^\circ$] for complexes **1**, **3**, **6**, and **12**.

Complex 1			
Cu–N1	2.023(2)	Cu–Cl1	2.200(1)
Cu–N2	2.012(2)	Cu–Cl2	2.217(1)
N1–Cu–N2	83.33(8)	N2–Cu–Cl1	104.90(6)
N1–Cu–Cl1	135.55(6)	N2–Cu–Cl2	127.90(6)
N1–Cu–Cl2	100.67(6)	Cl1–Cu–Cl2	107.00(4)
Complex 3			
Cu1–N1	2.014(4)	Cu1–Cl1	2.210(1)
Cu2–N2	2.019(4)	Cu2–Cl2	2.201(1)
N1–Cu1–N1A ^[a]	82.9(2)	N1–Cu1–Cl1A ^[a]	131.2(1)
N1–Cu1–Cl1	102.3(1)	Cl1–Cu1–Cl1A ^[a]	108.8(1)
N2–Cu2–N2A ^[b]	83.2(2)	N2–Cu2–Cl2A ^[b]	130.8(1)
N2–Cu2–Cl2	102.2(1)	Cl2–Cu2–Cl2A ^[b]	109.4(1)
Complex 6			
Cu–N1	1.99(1)	Cu–Br1	2.343(3)
N1–Cu–N1A ^[c]	82.5(6)	N1–Cu–Br1	102.7(3)
N1–Cu–Br1A ^[c]	129.6(3)	Br1–Cu–Br1A ^[c]	110.5(1)
Complex 12			
Cu1–N1	2.017(4)	Cu1–N2	2.120(5)
Cu1–N3	2.022(4)	Cu1–N4	2.109(4)
Cu2–Br1	2.205(2)	Cu2–Br2	2.205(2)
N1–Cu1–N3	139.1(2)	N1–Cu1–N4	124.6(2)
N3–Cu1–N4	81.6(2)	N1–Cu1–N2	82.4(2)
N3–Cu1–N2	127.4(2)	N4–Cu1–N2	99.9(2)
Br1–Cu2–Br2	177.22(6)		

[a] Symmetry code: $1 - x, y, z$. [b] $-x, -y, z$. [c] $1 - x, 1 - y, z$.

Copper(II) Complexes 1, 3, and 6

The structures of three non-square-planar, four-coordinate copper(II) complexes $[\text{CuX}_2\text{L}]$ (**1**, **3**, **6**) were determined, and they all display a metal-to-ligand ratio of 1:1 similar to **4**. Complex **1** contains a $[\text{CuCl}_2(\text{dpp})]$ molecule in an asymmetrical unit, whereas complex **3** contains two independent halves of the $[\text{CuCl}_2(\text{dnp})]$ molecule ($Z'' = 2$),^[21] and **6** consists of a half $[\text{CuBr}_2(\text{dnp})]$ molecule per asymmetrical unit, because there is a crystallographic C_2 axis bisecting the N–Cu–N and X–Cu–X angles in the latter two complexes (**3** and **6**). The Cu^{II} centers of the complexes are coordinated by one bidentate ligand and two halide ions (Figures 1, 2, and 3). According to a new four-coordinate geometry index (τ_4) established by Houser et al.,^[22] the coordination geometry about the Cu^{I} center in complexes **1**, **3**, and **6** is best described as seesaw with τ_4 values of 0.68, 0.69, and 0.71, respectively (the value of τ_4 ranges from 1.00 for a perfect tetrahedral geometry to zero for a perfect square-planar geometry, whereas intermediate structures, including trigonal-pyramidal and seesaw, fall within the range of 0 to 1.00). The dihedral angle between the N–Cu–N and X–Cu–X planes is 65.7 (for **1**), 65.5/65.8 (for **3**), 67.4 (for **6**), and 59.2° (for **4**), which is smaller than that for the

analogous compound $[\text{CuCl}_2(\text{phen})]$ (80.3°).^[18] There are no significant intermolecular or intramolecular π -stacking interactions in these complexes.

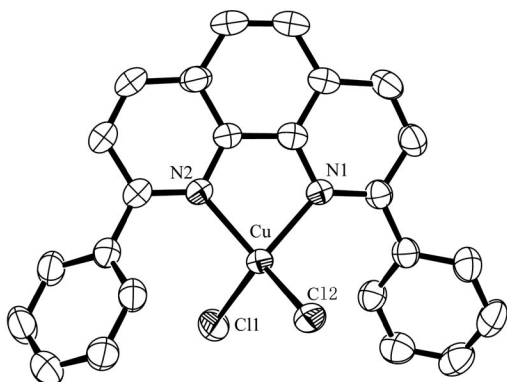


Figure 1. The molecular structure of complex **1** with 50% probability ellipsoids.

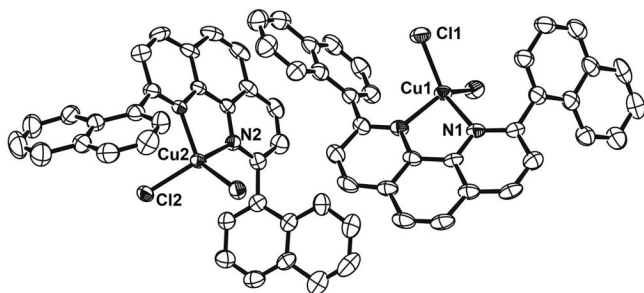


Figure 2. The molecular structure of complex **3**, showing the two independent molecules. Hydrogen atoms are omitted for clarity.

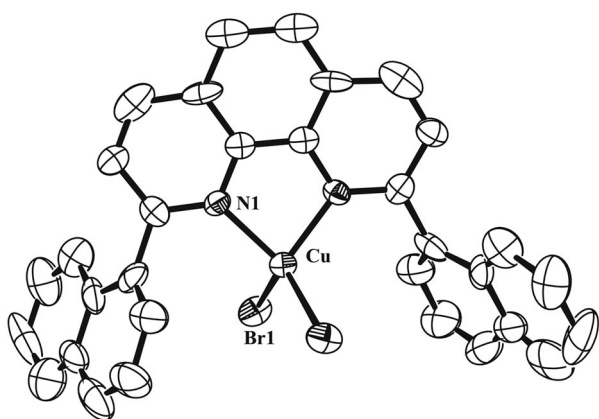


Figure 3. The molecular structure of complex **6**. Hydrogen atoms are omitted for clarity.

It is noteworthy that four-coordinate copper(II) complexes with 1,10-phenanthroline ligands are not typical. In the few known examples, $[\text{Cu}(\text{dpp})_2](\text{ClO}_4)_2$, $[\text{Cu}(\text{phen})_2](\text{PF}_6)_2$,^[23] and $[\text{Cu}^{\text{II}}(\text{dpq})_2](\text{ClO}_4)_2$ (dpq = dipyrdo[3,2-f:2',3'-h]quinoxaline)^[19] have a 1:2 metal-to-ligand molar ra-

tio. In complex $[\text{Cu}(\text{phen})_2](\text{PF}_6)_2$, however, the Cu^{II} coordination sphere is enhanced by a secondary Cu–F interaction ($2.75 \text{ \AA}$) with the PF_6^- ion. The 1:1 complexes, $[\text{CuBr}_2\text{L}]$ [$\text{L} = 2,9\text{-bis}(2,6\text{-dimethoxyphenyl})\text{-}1,10\text{-phenanthroline}$] and $[\text{CuCl}_2(\text{phen})]$, which are similar to Cu^{II} complexes **1–6** presented in this work, have also been reported.^[24]

The Cu–N bond lengths ($1.978\text{--}2.023 \text{ \AA}$) in complexes **1**, **3**, and **6** are comparable to those in **4** ($2.03 \text{ \AA}$)^[16] and in other phenanthroline or bipyridine copper(II) complexes, for example, $[\text{CuBr}_2\text{L}]$ [$2.05 \text{ \AA}$, $\text{L} = 2,9\text{-bis}(2,6\text{-dimethoxyphenyl})\text{-}1,10\text{-phenanthroline}$], $[\text{Cu}(\text{dpp})_2](\text{ClO}_4)_2$ ($1.98\text{--}2.00 \text{ \AA}$),^[17] and $[\text{Cu}^{\text{II}}(\text{dpq})_2](\text{ClO}_4)_2$ ($1.987\text{--}2.026 \text{ \AA}$).^[19] The Cu–Cl distances in **1** and **3** (mean value ca. $2.21 \text{ \AA}$) are similar to that in $[\text{CuCl}_2(\text{phen})]$ ($\approx 2.21 \text{ \AA}$)^[18] and slightly shorter than that in $[\text{Cu}^{\text{II}}\text{Cl}(\text{tet})]^+$ ($2.30 \text{ \AA}$, $\text{tet} = 2,2'\text{-bis}[6\text{-(}2,2'\text{-bipyridyl)}\text{]biphenyl}$).^[25] The Cu–Br distance in **6** [$2.346(3) \text{ \AA}$] is close to that ($2.35 \text{ \AA}$) in $[\text{CuBr}_2(\text{dpp})]$ (**4**),^[16] but it is longer than that in the $[\text{CuBr}_2\text{L}]$ compound [$\text{L} = 2,9\text{-bis}(2,6\text{-dimethoxyphenyl})\text{-}1,10\text{-phenanthroline}$] ($2.01 \text{ \AA}$). There are only minor differences in the N–Cu–N bite angle ($82.9\text{--}83.7^\circ$) and the Cl–Cu–Cl angle ($107.0\text{--}109.4^\circ$ for **1** and **3**) in the complexes. However, the Br–Cu–Br angle of complex **6** (110.5°) is wider than that in complex **4** (104.6°), indicating larger steric hindrance in the complex with the dinaphthyl ligand dnp (**6**) than with the diphenyl derivative dpp (**4**). The dihedral angle between the phenanthroline moiety and the attached phenyl or naphthyl substituent [34.7 and 47.4° for **1**, $64.0/53.4^\circ$ (two independent molecules) for **3**, and 58.2° for **6**] also reflects the steric effects of the ligands.

Copper(I) Complex $[\text{Cu}(\text{dnp})_2](\text{CuBr}_2)$ (**12**)

Similar to the analogous compound $[\text{Cu}(\text{dpp})_2](\text{CuBr}_2)$ (**10**) reported by this laboratory, Cu^{I} complex **12** consists of a $[\text{Cu}(\text{dnp})_2]^+$ cation and a CuBr_2^- anion. In the complex cation the Cu atom is coordinated by two dnp ligands in a seesaw geometry ($\tau_4 = 0.66$, Figure 4)^[22] with a dihedral angle of 77.4° between the two chelating N–Cu–N planes, which is smaller than that in **10** (84.3°). As in other bis(phenanthroline)copper(I) complexes,^[17,26,27] there are two long Cu–N bonds (to N2 and N4) and two short Cu–N bonds (to N1 and N3) in complex **12** (Table 2). The inclusion of CuBr_2^- as the counteranion in **12** is similar to that in the cases of $[\text{Cu}(\text{dpp})_2](\text{CuBr}_2)$ (**10**),^[16] $[\text{Cu}(\text{phen})_2](\text{CuBr}_2)$,^[28] and the chloride analog $[\text{Cu}(\text{dpp})_2](\text{CuCl}_2)$.^[20] The CuBr_2^- ion is slightly bent with a Br–Cu–Br angle of 177.2° in **12**, which is comparable to the Cl–Cu–Cl angle of 177.3° in $[\text{Cu}(\text{dpp})_2](\text{CuCl}_2)$. In contrast, the same CuBr_2^- anion is linear in **10** and in $[\text{Cu}(\text{phen})_2](\text{CuBr}_2)$, and the Cu–Br distance of $2.205(2) \text{ \AA}$ is close to that in these compounds.

Bis(phenanthroline)copper(I) complexes generally display distorted tetrahedral geometries, and the distortion from D_{2d} symmetry can be described by a set of angles θ_x , θ_y , and θ_z , which represent the interligand angles based on the CuN_4 core of the complexes.^[29] The θ_z value is a measure of the dihedral angle relating two opposing phenan-

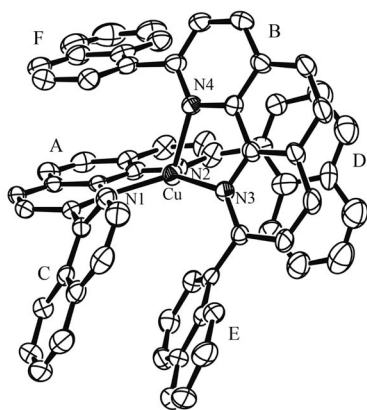


Figure 4. The molecular structure of complex **12**. Hydrogen atoms are omitted for clarity.

Table 2. Room-temperature spectroscopic and electrochemical data of **1–12**.

	λ_{max} [nm] (ϵ , $\text{M}^{-1} \text{cm}^{-1}$)	E_{pa} (E_{pc})		E_{pa}	E_{pc}
		$\text{Cu}^{\text{III}} ([\text{CuL}_2]^+)$	$\text{Cu}^{\text{III}} (\text{CuX}_2^-)$		
1	445 (750)	0.89 (0.85)		0.70	0.25
2	444 (730)			0.70	0.19
3	452 (760) 540 (410)			0.70	0.14
4	445 (1400) 592 (690)	0.90 (0.83)	0.75 (0.64)		0.32
5	466 (1500) 591 (910)	0.95 (0.87)	0.75 (0.64)		0.28
6	468 (1400) 582 (720)	1.04 (0.94)	0.76		0.25
7	441 (2200) 569 (970)	0.90 (0.85)			0.28
8	457 (2400)	1.00 (0.90), 0.91 (0.81)	≈ 0.74		0.28
9	461 (2400)	1.05 (0.98), 0.96 (0.87)	≈ 0.74		0.20
10	441 (2700) 563 (1300)	0.92 (0.85)			
11	453 (3300)	0.99 (0.91)	≈ 0.81		
12	460 (2800)	1.06 (0.98)	≈ 0.81 (0.6)		

throline ligands, and θ_x and θ_y indicate the degree of a “rocking” distortion. In D_{2d} symmetry, $\theta_x = \theta_y = \theta_z = 90^\circ$, and deviation of θ_z from 90° indicates a flattening of the molecule. In complex **12**, these angles are $\theta_x = 105.7^\circ$, $\theta_y = 105.8^\circ$, and $\theta_z = 77.4^\circ$. Similar to a related copper(I) compound $[\text{Cu}(\text{dpp})_2](\text{CuCl}_2) \cdot \text{CH}_3\text{CN}$ ($\theta_z = 71.8^\circ$),^[20] the large deviation of the θ_z value from 90° is due to intramolecular π -stacking interactions, which cause considerable distortion of the coordination geometry. The θ_z value of $[\text{Cu}(\text{dpp})_2](\text{PF}_6)$ (100.2°)^[17] and $[\text{Cu}(\text{dpp})_2](\text{CuBr}_2)$ (95.7°) is larger than that in complex **12**.

There are three important intramolecular π -stacking interactions in complex **12** involving all the six conjugation systems (four naphthyl and two phenanthroline groups).^[30] Two of the interactions are between the naphthyl and the phenanthroline moieties and the third one is between the two remaining naphthyl planes (Figure 4). The two sets of naphthyl–phen stacking interactions are different, with the

one between naphthyl (F) and the phenanthroline (A) (dihedral angle 1.9° , centroid–centroid distance $3.56 \text{ \AA}$, and the vertical displacements between ring centroids 0.70 and $0.81 \text{ \AA}$) being stronger than that between the naphthyl D and the phenanthroline B (dihedral angle 3.0° , centroid–centroid distance $3.84 \text{ \AA}$, the vertical displacements between ring centroids 1.23 and $1.41 \text{ \AA}$). Moreover, the π -stacking interactions are stronger than those between the phenyl and the phenanthroline planes in analogous complex **10** (the centroid–centroid distances are 3.94 and $4.09 \text{ \AA}$).^[16] These two interactions between the phenanthroline planes and the aryl substituents have also been reported in similar $[\text{Cu}(\text{NN})_2]^+$ complexes.^[17,20]

Most interestingly, a third intramolecular π -stacking interaction occurs in **12** between two naphthyl planes (C and E) of the dnp ligands (Figure 4). Although the orientations of the two naphthyl groups are not the same, there is sufficient stacking between them (dihedral angle 6.9° , centroid–centroid distance $3.56 \text{ \AA}$, the vertical displacements between ring centroids 0.17 and $0.59 \text{ \AA}$). In contrast, there is no such interaction between two phenyl planes in the complexes with the diphenyl-substituted phenanthroline ligand. In fact, an edge-to-face interaction of two phenyl groups was observed in the compound $[\text{Cu}(\text{dpp})_2](\text{PF}_6)$.^[17] This difference could be ascribed to the stronger π -conjugation effect of the naphthyl group than the phenyl group.

The dihedral angles between the phenanthroline systems and the naphthyl groups are 69.8 (A/D), 56.0 (A/C), 47.1 (B/E), and 65.3° (B/F; Figure 4). There are several factors that affect the conformation of the ligands, for example, steric hindrance, intramolecular π -stacking interactions, and π -conjugation properties. It is noteworthy that the dihedral angles involving the naphthyl–naphthyl interaction (B/E and A/C) is smaller than those involving the phen–naphthyl interactions, implying the importance of both π -conjugation and stacking effects of the ligands.

UV/Vis Spectra

The electronic spectra of the ligands and complexes were recorded in CH_2Cl_2 . The ligands show absorptions at 260 and 308 nm for dpp and at 230 and 290 nm for npp and dnp. The complexes display very intense bands in the UV region and much weaker bands in the visible region (400 – 650 nm). The intense UV absorptions can be assigned to the corresponding ligand-centered $\pi \rightarrow \pi^*$ transitions, whereas the visible bands are characteristic metal-to-ligand or ligand-to-metal charge transfer (MLCT or LMCT) processes.^[4,13,31] The absorption spectra of the copper(II) complexes are similar, and those of dibromido complexes **4–6** are shown in Figure 5a. The band at 430 – 460 nm is assigned to MLCT, and the lower-energy band at 550 – 600 nm is due to the LMCT transition. Such LMCT transitions of four-coordinate Cu^{II} complexes are also observed in the complex $[\text{Cu}(\text{dpp})_2](\text{ClO}_4)_2$.^[17] Furthermore, the complexes with the more sterically demanding ligands (npp and dnp) exhibit a significant redshift relative to those with dpp, especially for the dibromido complexes (Table 2).

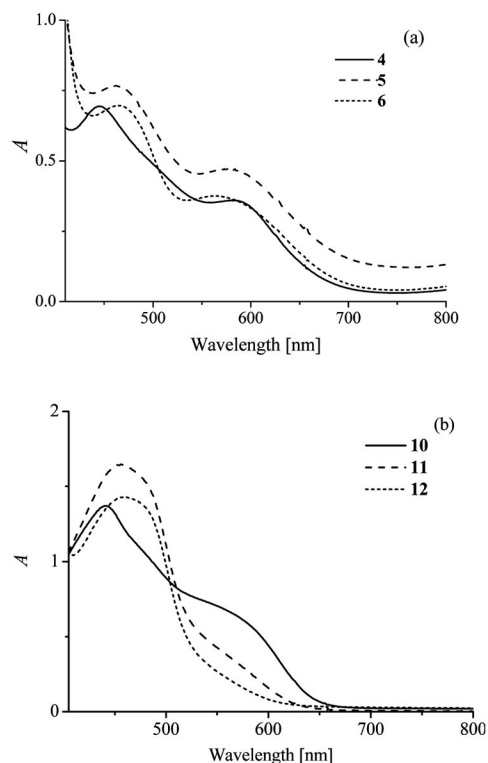


Figure 5. The UV/Vis spectra of complexes (a) **4–6** and (b) **10–12** (5×10^{-4} M in CH_2Cl_2).

For copper(I) complexes **7–12** the MLCT band occurs as a broad peak with a maximum absorption at 430–460 nm (Table 2 and Figure 5b). This is similar to most of the known bis(phenanthroline)copper(I) complexes with aryl substituents in the 2,9-positions of the phenanthroline backbone (maximum absorption in the range 440–470 nm).^[32–35] For **7** and **10**, there is a shoulder in the 550–600 nm range, which can be attributed to the distortion of the complex molecule from D_{2d} symmetry caused by intramolecular π -stacking interactions, as in some known Cu^{I} complexes, for example, $[\text{Cu}(\text{phen})_2]\text{ClO}_4$ (580 nm)^[28] and $[\text{Cu}(\text{tmp})_2]\text{PF}_6$ (595 nm).^[36] This lower-energy shoulder decreases with increasing steric bulk of the ligands (well resolved for **10**, much weaker for **11**, and disappeared for **12**; see Figure 5b), as more sterically demanding ligands may enforce the D_{2d} symmetry.

Electrochemical Properties

The redox behavior of Cu^{I} and Cu^{II} complexes **1–12** was studied by cyclic voltammetry in dichloromethane. Cu^{I} complexes **7–12** undergo a reversible (for **7** and **10**) or quasi-reversible (for **8**, **9**, **11**, and **12**) one-electron oxidation process at 0.90–1.06 V as a result of the $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ couple (Figure 6a,b), which is similar to many (phenanthroline)copper complexes.^[4,31,34,37] The peaks for complexes **8** and **9** show a slight split with a shoulder. It has been reported that the $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ couple of $[\text{Cu}(\text{NN})_2]^{n+}$ complexes depends largely on the nature of the substituents on the phenanthroline. In

particular, the redox potential becomes more positive when the steric constraint in the 2- and 9-positions increases, as this can prevent the rearrangement of the coordination sphere to the favored square-planar for the oxidized Cu^{II} species and thus stabilize the Cu^{I} state.^[14,33,34] A comparison of the complexes studied here revealed a complete agreement with this trend: increasing the 2,9-substituents on 1,10-phenanthroline from diphenyl (complexes **7**, **10**) to phenyl/naphthyl (**8**, **11**), and then to dinaphthyl (**9**, **12**) shifted the $[\text{CuL}_2]^{2+/+}$ couple to more positive potentials (Figure 6a,b; Table 2).

Notably, Cu^{I} complexes **8**, **9**, **11**, and **12** show another (quasi)reversible or irreversible redox process, occurring as a shoulder for **8** (≈ 0.74 V) and **11** (≈ 0.81 V) and well-resolved for **9** (≈ 0.74 V) and **12** (≈ 0.81 V), in a less-positive potential ($< [\text{CuL}_2]^{2+/+}$), which could be attributed to the $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ couple of the CuX_2^- anion in the complex $[\text{CuL}_2](\text{CuX}_2)$. Complexes **7** and **10** display only one reversible process, probably due to the overlapping of the two $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ couples of $[\text{CuL}_2]^+$ and CuX_2^- (Table 2). For the complexes with the CuCl_2^- anion, **7–9**, there is also an irreversible reduction peak at 0.2–0.3 V, which might be caused by the dissociation or ligand exchange during the redox process.^[14,38]

For the Cu^{II} complexes $[\text{CuX}_2\text{L}]$ there are significant differences between the dichlorido (**1–3**) and dibromido (**4–6**) analogues. An irreversible reduction occurs at the 0.14–0.32 V range for all complexes, which can be assigned to the reduction of the Cu^{II} center to the Cu^{I} state. These processes are often related to the dissociation of halide species that are adsorbed on the electrode surface and rebound in the return course,^[18,25,38,39] leading to a corresponding irreversible oxidation at around 0.7 V. There is a reversible shoulder at 0.8–0.9 V for complex **1** as a result of the reoxidation and reduction of the $[\text{CuL}_2]^{2+/+}$ couple as in the Cu^{I} complexes, but no redox signal in this region is found for complexes **2** and **3** (Figure 6c). This agrees well with the aforementioned observations that the (dichlorido)copper(II) complex $[\text{CuCl}_2(\text{dpp})]$ (**1**) can undergo partial ligand redistribution and reduction of Cu^{II} to give the Cu^{I} species $[\text{Cu}(\text{dpp})_2](\text{CuCl}_2)$ (**7**), whereas the more sterically crowded **2** and **3** cannot be converted into the corresponding Cu^{I} compounds.

The cyclic voltammograms of (dibromido)copper(II) complexes **4–6** also confirm the conversion of the Cu^{II} complexes into the Cu^{I} species. As shown in Figure 6d, two (quasi)reversible redox processes appear in the 0.8–1.0 V range, which are similar to those of Cu^{I} complexes **10–12** (Figure 6b). The peak at the more-positive potential can be assigned to the reoxidation/reduction of the $[\text{CuL}_2]^{2+/+}$ couple, whereas the other less-positive process should be the redox of the CuBr_2^- anion. The potential of the $[\text{CuL}_2]^{2+/+}$ couple increases in the order $4 < 5 < 6$ ($\text{dpp} < \text{npp} < \text{dnp}$) as observed for **10–12**. Moreover, the potential of the $[\text{CuL}_2]^{2+/+}$ couple for the complexes with the same ligand is very close, for example, 0.89 V (for **1**), 0.90 V (for **4**), 0.90 V (for **7**), and 0.92 V (for **10**) for the complexes with the dpp ligand. The $(\text{Cu}^{\text{II}}\text{X}_2)/(\text{Cu}^{\text{I}}\text{X}_2^-)$ couple is also comparable for the complexes (Table 2).

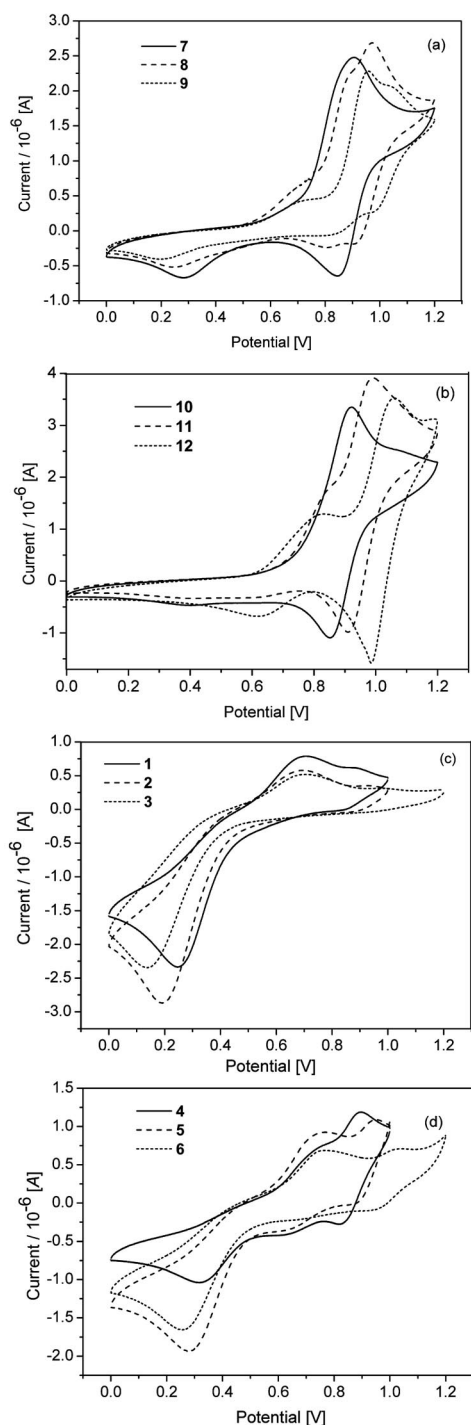


Figure 6. Cyclic voltammograms of the Cu^{I} and Cu^{II} complexes in dichloromethane (conc. 5×10^{-4} M): (a) 7–9; (b) 10–12; (c) 1–3; and (d) 4–6.

Conclusions

The synthesis, structure, and spectroscopic and electrochemical properties of a series of copper(II) and copper(I) complexes with 2,9-diaryl-1,10-phenanthroline ligands are reported. The conversion of the Cu^{II} complexes into the corresponding Cu^{I} species was studied, and it was found that the ligand steric bulk and the auxiliary ligand (Cl or

Br) can affect the ligand redistribution reaction. The smaller dpp and dibromido ligands can promote the process, as proved by MS (ESI) and electrochemical studies. Cyclic voltammetry of the complexes also revealed that bulkier groups in the 2,9-positions lead to a more-positive $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ couple than that for the less-bulky complexes.

Experimental Section

General Considerations: All manipulations were carried out under an atmosphere of nitrogen by using standard Schlenk vacuum line techniques. Solvents were heated at reflux over an appropriate drying agent and distilled under an atmosphere of nitrogen prior to use. 1,10-Phenanthroline, 1-bromonaphthalene, bromobenzene, the copper(II) and copper(I) salts, and other chemicals were commercially available and used without further purification. ^1H NMR spectra were obtained with a Mercury plus-400 spectrometer with TMS as the internal standard. IR spectra were recorded as KBr pellets with an HP5890 II GC/NEXUS-870 spectrometer. Element analyses were performed with an Elementar VarioEL instrument. Electronic spectra were recorded with an HP 8453 spectrometer. MS (ESI) spectra were measured with a Waters ZQ 4000 instrument.

Synthesis of Complexes 1–12

Complexes $[\text{CuBr}_2(\text{dpp})]$ (4) and $[\text{Cu}(\text{dpp})_2](\text{CuBr}_2)$ (10): Synthesized as previously reported.^[16]

General Procedure for the Synthesis of Dichlorido- or Dibromido-(2,9-diaryl-1,10-phenanthroline)copper(II) Complexes $[\text{CuX}_2(\text{L})]$, 1–6: The ligand (0.30 mmol) and $\text{CuX}_2 \cdot 2\text{H}_2\text{O}$ (0.30 mmol) were stirred in THF (10 mL) for 8 h, followed by filtration of the reaction mixture.

General Procedure for the Synthesis of [Bis(2,9-diaryl-1,10-phenanthroline)copper(I)]dichlorocuprate or -dibromocuprate $\{[\text{CuL}_2](\text{CuX}_2)\}$, 7–12: Ligand (0.30 mmol) and anhydrous CuX (0.30 mmol) were stirred in CH_2Cl_2 (10 mL) for 8 h. The reaction mixture was filtered and the product was obtained as a red powder.

$[\text{CuCl}_2(\text{dpp})]$ (1): Yield: 104 mg (74.9%). M.p. 232–234 °C. MS (ESI): m/z (%) = 430.6 (20.2) $[\text{CuCl}(\text{dpp})]^+$, 727.8 (100) $[\text{Cu}(\text{dpp})_2]^+$. IR (KBr): $\tilde{\nu}$ = 3432, 3050, 1622, 1587, 1549, 1509, 1487, 1446, 1423, 1360, 1278, 1155, 1122, 1078, 907, 867, 776, 762, 742, 656 cm^{-1} . $\text{C}_{24}\text{H}_{16}\text{Cl}_2\text{CuN}_2$ (466.85): calcd. C 61.94, H 3.44, N 6.02; found C 61.78, H 3.52, N 5.75.

$[\text{CuCl}_2(\text{npp})]$ (2): Yield: 110 mg (79.4%). M.p. 243–245 °C. MS (ESI): m/z (%) = 480.6 (100) $[\text{CuCl}(\text{npp})]^+$. IR (KBr): $\tilde{\nu}$ = 3446, 3056, 1623, 1586, 1553, 1512, 1486, 1427, 1363, 1296, 1243, 1188, 1149, 1024, 985, 908, 878, 802, 780, 744, 704 cm^{-1} . $\text{C}_{28}\text{H}_{18}\text{Cl}_2\text{CuN}_2$ (516.91): calcd. C 65.24, H 3.50, N 5.44; found C 64.89, H 3.64, N 5.12.

$[\text{CuCl}_2(\text{dnp})]$ (3): Yield: 128 mg (75.6%). M.p. 264–266 °C. MS (ESI): m/z (%) = 530.6 (100) $[\text{CuCl}(\text{dnp})]^+$. IR (KBr): $\tilde{\nu}$ = 3432, 3052, 1623, 1586, 1554, 1514, 1492, 1429, 1393, 1364, 1245, 1188, 1152, 972, 908, 878, 799, 778, 612 cm^{-1} . $\text{C}_{32}\text{H}_{20}\text{Cl}_2\text{CuN}_2$ (566.97): calcd. C 67.96, H 3.54, N 4.96; found C 67.52, H 3.69, N 4.62.

$[\text{CuBr}_2(\text{npp})]$ (5): Yield: 113 mg (64.3%). M.p. 236–238 °C. MS (ESI): m/z (%) = 526.6 (100) $[\text{CuBr}(\text{npp})]^+$. IR (KBr): $\tilde{\nu}$ = 3443, 3053, 1621, 1584, 1550, 1509, 1489, 1423, 1360, 1149, 865, 780, 778, 745, 700 cm^{-1} . $\text{C}_{28}\text{H}_{18}\text{Br}_2\text{CuN}_2$ (605.81): calcd. C 55.72, H 2.99, N 4.64; found C 55.75, H 3.21, N 4.30.

Table 3. Crystallographic data for compounds **1**, **3**, **6**, **12**.

Complex	1	3	6	12
Formula	C ₂₄ H ₁₆ Cl ₂ N ₂ Cu	C ₃₂ H ₂₀ Cl ₂ N ₂ Cu	C ₃₂ H ₂₀ Br ₂ N ₂ Cu	C ₆₄ H ₄₀ Br ₂ Cu ₂ N ₄
<i>F</i> _w	466.83	566.94	655.86	1151.90
Crystal system	monoclinic	orthorhombic	orthorhombic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> ba2	<i>P</i> 2 ₁ 2 ₁ 2	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> [Å]	8.832(2)	15.411(1)	15.837(3)	8.5372(4)
<i>b</i> [Å]	13.269(3)	17.183(2)	8.493(2)	24.504(1)
<i>c</i> [Å]	18.097(4)	9.670(1)	9.733(2)	23.581(1)
<i>α</i> [°]	90	90	90	90
<i>β</i> [°]	100.76(3)	90	90	95.472(2)
<i>γ</i> [°]	90	90	90	90
<i>V</i> [Å ³]	2083.4(7)	2560.7(4)	1309.2(4)	4910.5(4)
<i>Z</i>	4	4	2	4
<i>D</i> _{calcd.} [g cm ^{−3}]	1.488	1.471	1.664	1.558
<i>F</i> (000)	948	1156	650	2320
<i>μ</i> [mm ^{−1}]	1.32	1.09	3.91	2.54
<i>θ</i> range [°]	1.92–28.30	1.77–25.34	2.09–26.86	1.74–26.83
Reflections collected (<i>R</i> _{int})	13043 (0.036)	12722 (0.050)	7274 (0.135)	28932 (0.088)
Independent reflections	5022	4499	2803	10418
Observed reflns [<i>I</i> > 2σ(<i>I</i>)]	3414	2856	1356	3755
<i>R</i> ₁ ; <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0395; 0.0926	0.0427; 0.0810	0.0777; 0.2073	0.0607; 0.1346
<i>R</i> ₁ ; <i>wR</i> ₂ (all data)	0.0661; 0.1012	0.0821; 0.0945	0.1662; 0.2444	0.2002; 0.1827
GOF (<i>F</i> ²)	1.057	1.041	1.050	0.940

[CuBr₂(dnp)] (6): Yield: 134 mg (65.3%). M.p. 263–264 °C. MS (ESI): *m/z* (%) = 576.5 (100) [CuBr(dnp)]⁺. IR (KBr): $\tilde{\nu}$ = 3440, 3053, 1623, 1586, 1554, 1514, 1493, 1430, 1364, 1245, 1188, 1152, 973, 908, 797, 777, 663, 611 cm^{−1}. C₃₂H₂₀Br₂CuN₂ (655.87): calcd. C 58.81, H 3.06, N 4.29; found C 58.93, H 3.38, N 3.97.

[Cu(dpp)₂](CuCl₂) (7): Yield: 93 mg (73.5%). M.p. 128–130 °C. MS (ESI): *m/z* (%) = 727.8 (100) [Cu(dpp)₂]⁺. IR (KBr): $\tilde{\nu}$ = 3444, 3051, 1620, 1579, 1547, 1507, 1445, 1418, 1356, 1149, 1111, 1021, 861, 775, 742, 698 cm^{−1}. C₄₈H₃₂Cl₂Cu₂N₄ (862.79): calcd. C 66.98, H 3.72, N 6.51; found C 67.21, H 3.89, N 6.23.

[Cu(npp)₂](CuCl₂) (8): Yield: 94 mg (73.4%). M.p. 134–135 °C. MS (ESI): *m/z* (%) = 827.8 (100) [Cu(npp)₂]⁺. IR (KBr): $\tilde{\nu}$ = 3407, 3045, 1729, 1620, 1578, 1548, 1509, 1496, 1486, 1420, 1392, 1357, 1239, 1185, 1146, 1022, 863, 801, 777, 740, 699 cm^{−1}. C₅₆H₃₆Cl₂Cu₂N₄ (962.91): calcd. C 70.00, H 3.75, N 5.83; found C 70.23, H 4.10, N 5.66.

[Cu(dnp)₂](CuCl₂) (9): Yield: 110 mg (69.3%). M.p. 159–160 °C. MS (ESI): *m/z* (%) = 927.8 (100) [Cu(dnp)₂]⁺. IR (KBr): $\tilde{\nu}$ = 3440, 3050, 1621, 1581, 1548, 1511, 1495, 1392, 1358, 1185, 1148, 1130, 972, 865, 788, 774, 664, 611 cm^{−1}. C₆₄H₄₀Cl₂Cu₂N₄ (1063.03): calcd. C 72.45, H 3.77, N 5.28; found C 72.06, H 4.09, N 5.09.

[Cu(npp)₂](CuBr₂) (11): Yield: 96 mg (68.3%). M.p. 219–220 °C. MS (ESI): *m/z* (%) = 827.8 (100) [Cu(npp)₂]⁺. IR (KBr): $\tilde{\nu}$ = 3393, 3043, 1729, 1620, 1578, 1548, 1509, 1496, 1486, 1420, 1392, 1357, 1239, 1185, 1146, 1076, 1022, 864, 801, 792, 777, 740, 700 cm^{−1}. C₅₆H₃₆Br₂Cu₂N₄ (1051.81): calcd. C 64.12, H 3.44, N 5.34; found C 64.33, H 3.72, N 5.50.

[Cu(dnp)₂](CuBr₂) (12): Yield: 112 mg (64.9%). M.p. 293–295 °C. MS (ESI): *m/z* (%) = 927.8 (100) [Cu(dnp)₂]⁺. IR (KBr): $\tilde{\nu}$ = 3445, 3048, 1621, 1581, 1548, 1511, 1494, 1392, 1358, 1240, 1146, 1130, 973, 864, 788, 774, 663, 611 cm^{−1}. C₆₄H₄₀Br₂Cu₂N₄ (1151.93): calcd. C 66.90, H 3.48, N 4.88; found C 67.38, H 3.52, N 4.60.

X-ray Crystal Structure Determination: Diffraction data for the complexes were collected with a Bruker SMART CCD area detector (**1**, **3**, **6**, **12**) at room temperature (293 K) with graphite-monochromated Mo-*K*_α radiation (λ = 0.71073 Å). An empirical absorption correction with the use of SADABS^[40] was applied for all data.

The structures were solved by direct methods by using the SHELXS program. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on *F*² by the use of the program SHELXL.^[41] The hydrogen atoms were included in idealized geometric positions with thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Crystallographic data for **1**, **3**, **6**, and **12** are listed in Table 3.

CCDC-715827 (for **1**), -715828 (for **3**), 715829 (for **6**), and 715830 (for **12**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Electrochemical Measurements: Cyclic voltammetry was performed with a CHI660B electrochemistry workstation by using a one-compartment cell with a Pt button working electrode, a Pt thread counter electrode, and a Ag/AgCl reference electrode. The working electrode was polished to mirror finish with 0.05 μmol alumina and sonicated in pure water for 2 min. Typical solutions of 0.5 mM of the copper compounds with 0.1 M TBAH in CH₂Cl₂ were scanned at room temperature at 50 mV s^{−1}.

Acknowledgments

This work was supported by the “Bairen Jihua” project of the Chinese Academy of Sciences.

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Received: January 10, 2009
Published Online: June 5, 2009