

Structural Characterization of Copper(I) Complexes Supported by β-Diketiminate Ligands with Different Substitution Patterns

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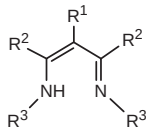
Copper(I) complexes generated by using a series of β-diketiminate ligands ($^{R1,R2}L^{R3-}$, $[(R^3)N–C(R^2)–C(R^1)–C(R^2)–N(R^3)]^-$, see Chart 1; "β-diketiminate" denotes enaminone imine analogs) have been structurally characterized by X-ray crystallographic analysis. In the α-nitro-ligand system ($R^1 = NO_2$ and $R^2 = H$), the structure of the resulting products were largely affected by the nitrogen substituent R^3, providing bis(β-diketiminato)copper(II) complex **1** [a product of the disproportionation reaction of copper(I)] (R^3 = Ph), head-to-tail linear coordination polymer copper(I) complex **2** (R^3 = Mes, (mesityl)), and mononuclear copper(I) complex **3** (R^3 = Dipp (2,6-diisopropylphenyl)). On the other hand, α-cyano-ligand (R^1 = CN and R^2 = H or Me) always gave head-to-tail coordination polymer copper(I) complexes (**4**–**8**) regardless of the aromatic substituent R^3. In both systems, β-diketiminate ligands exhibited a U-shaped closed conformation, forming a six-membered chelate ring with copper(I). Copper(I) complexes with a β-diketiminate ligand with a W-shaped open conformation were also obtained in the case of α-methyl and α-hydrogen derivatives (R^1 = Me or H, R^2 = H, and R^3 = Dipp). In these cases, the dinuclear and tetranuclear copper(I) macrocyclic complexes **9** and **10** were obtained.

A great deal of attention has recently been focused on coordination and/or organometallic chemistry of β-diketiminato complexes with various metal ions.[1] For copper, structure and physicochemical properties as well as the reactivity of mononuclear and dinuclear copper(II) complexes of β-diketiminate ligands have been studied in detail over many years.[2–21] Recently, considerable efforts have been made in modeling metallo-biosites such as those involved in type-1 blue copper proteins[11–13,17] and copper-containing redox enzymes using β-diketiminato copper(I) and copper(II) complexes.[14,15,18,20,22–25] In addition, β-diketiminatocopper(I) complexes have recently been applied to catalytic cyclopropanation and aziridation of olefins.[26,27] In most cases, however, the β-diketiminate ligands used in those studies are limited to simple acetylacetone derivatives, which can be easily prepared by the condensation reaction between acetylacetone and aniline derivatives.[28] In this context, we have recently reported a linear coordination polymer complex of copper(I) supported by a β-diketiminate ligand containing a nitro group at the α-position of the carbon framework ($^{NO_2,H}L^{Mes-}$, deprotonated form of $^{NO_2,H}L^{Mes}H$, see Chart 1), demonstrating a possible application of β-diketiminate derivatives to supramolecular chemistry.[29]

In this study, we have extended our research on β-diketiminatocopper(I) coordination chemistry using the series of ligands listed in Chart 1 to find that the structures of the complexes are significantly affected not only by the aromatic group R^3 attached to the ligand nitrogen, but also by the substituents R^1 and R^2 on the ligand carbon framework. The results provide further insights into coordination chemistry of β-diketiminate ligands.

Experimental

General. The reagents and solvents used in this study, except for the ligands and the complexes, were commercial products of the highest available purity and were further purified by standard methods, if necessary.[30] Ligands in the neutral form, $^{H,H}L^{Dipp}H$,[31] $^{H,Me}L^{Dipp}H$,[32] $^{NO_2,H}L^{Ph}H$,[19] $^{NO_2,H}L^{Mes}H$,[29] $^{CN,H}L^{Ph}H$,[19] $^{CN,H}L^{Mes}H$,[19] $^{CN,H}L^{Dep}H$,[19] $^{CN,H}L^{Dipp}H$,[19] and $^{CN,Me}L^{Dipp}H$,[33] were prepared according to the reported procedures. FT-IR spectra were recorded with a Shimadzu FTIR-8200PC. Mass spectra were recorded with a JEOL JMS-700T Tandem MS station. ^{1}H NMR spectra were recorded on a JEOL LMN-ECP300WB or a LMX-GX400. UV–vis spectra were measured using a Hewlett Packard HP8453 diode array spectrophotometer. Elemental analyses were recorded with a Perkin-Elmer or a Fisons Instruments EA1108 Elemental Analyzer.



$^{R1,R2}L^{R3}H$	R^1	R^2	R^3
$^{H,H}L^{Dipp}H$	H	H	2,6-Diisopropylphenyl
$^{Me,H}L^{Dipp}H$	Me	H	2,6-Diisopropylphenyl
$^{H,Me}L^{Dipp}H$	H	Me	2,6-Diisopropylphenyl
$^{NO_2,H}L^{Ph}H$	NO_2	H	Phenyl
$^{NO_2,H}L^{Mes}H$	NO_2	H	Mesityl
$^{NO_2,H}L^{Dipp}H$	NO_2	H	2,6-Diisopropylphenyl
$^{CN,H}L^{Ph}H$	CN	H	Phenyl
$^{CN,H}L^{Mes}H$	CN	H	Mesityl
$^{CN,H}L^{Dep}H$	CN	H	2,6-Diethylphenyl
$^{CN,H}L^{Dipp}H$	CN	H	2,6-Diisopropylphenyl
$^{CN,Me}L^{Dipp}H$	CN	Me	2,6-Diisopropylphenyl

Chart 1.

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X-ray Structure Determination. A single crystal was mounted on a glass-fiber. Data of X-ray diffraction were collected by a Rigaku RAXIS-RAPID imaging plate two-dimensional area detector and a Rigaku AFC7/CCD mercury area detector using graphite-monochromated Mo Kα radiation ($\lambda = 0.71070$ Å) to $2\theta_{max}$ of 55.0°. All the crystallographic calculations were performed using the Crystal Structure software package of the Molecular Structure Corporation (version 3.6 and 3.7). The crystal structures were solved by direct methods and refined by full-matrix least-squares using SIR-92 or SHELX97. All non-hydrogen atoms and hydrogen atoms were refined anisotropically and isotropically, respectively. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition numbers CCDC-283079 for $^{NO_2,H}L^{Dipp}H$, CCDC-283080 for $^{Me,H}L^{Dipp}H\cdot CH_3OH$, CCDC-283081 for $[Cu^I(^{NO_2,H}L^{Dipp})(CH_3CN)]$ (**3**), CCDC-283082 for $[\{Cu^I(^{CN,H}L^{Dep})\}_n]$ (**6**), CCDC-283083 for $[\{Cu^I(^{CN,H}L^{Dipp})\}_n]$ (**7**), and CCDC-283084 for $[\{Cu^I(^{H,H}L^{Dipp})\}_2]\cdot CH_2Cl_2$ (**9**). Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Theoretical Calculations. Heats of formation (ΔH_f) of $^{R1,R2}L^{Dipp}H$ were calculated using the PM3 semi-empirical molecular orbital method.[34] The calculations were performed using the CAChe program version 3.2. Final geometries and energetics were obtained by optimizing the total molecular energy with respect to all structural variables.

Synthesis. *N*-(2,6-Diisopropylphenyl)-3-(2,6-diisopropylphenyl)amino-2-methyl-2-propenimine ($^{Me,H}L^{Dipp}H$): This compound was prepared according to the reported procedure with a little modification herein after described.[35] To an ethanol solution (50 mL) of 2,6-diisopropylaniline (5.32 g, 30 mmol) and 1,1,3,3-tetraethoxy-2-methylpropane (3.52 g, 15 mmol) was added concentrated hydrochloric acid (1.25 mL, 15 mmol). The mixture was refluxed for 24 h and then concentrated to give a brown residue. The crude product of $^{Me,H}L^{Dipp}H\cdot HCl$ was neutralized with a saturated sodium carbonate aqueous solution and the neutral ligand $^{Me,H}L^{Dipp}H$ was extracted into dichloromethane (50 mL × 3). The combined organic layer was dried over $MgSO_4$. After removal of $MgSO_4$ by filtration, evaporation of the solvent gave a pale brown material, from which $^{Me,H}L^{Dipp}H$ was obtained as a white powder by recrystallization from methanol in a 51% isolated yield. Single crystals suitable for X-ray crystallographic analysis were obtained by slow diffusion of liquid methanol into a chloroform solution containing $^{Me,H}L^{Dipp}H$. IR (KBr): 3169 (NH), 1638 cm^{-1} (C=N); ^1H NMR (CD_3OD, 400 MHz): δ 1.19 (24H, d, J = 6.8 Hz, CH_3), 2.05 (3H, s, CH_3), 3.20 (4H, septet, J = 6.8 Hz, C*H*), 6.67–7.24 (8H, m, aromatic protons and C*H*); HRMS (EI^+): m/z 404.3195, calcd for $C_{28}H_{40}N_2$ 404.3191; Anal. Calcd for $C_{28}H_{40}N_2\cdot 1/6H_2O$: C, 82.50; H, 9.97; N, 6.87%. Found: C, 82.58; H, 10.00; N, 6.80%.

***N*-(2,6-Diisopropylphenyl)-3-(2,6-diisopropylphenyl)amino-2-nitro-2-propenimine ($^{NO_2,H}L^{Dipp}H$):** This compound was prepared by applying the following reported procedure.[36] 2,6-Diisopropylaniline (5.32 g, 30 mmol) was added to a methanol solution (100 mL) of 1-methyl-5-nitro-1*H*-pyrimidin-2-one (2.33 g, 15 mmol). The mixture was refluxed for 96 h. After the reaction, evaporation of the solvent gave a brown oily material, from which $^{NO_2,H}L^{Dipp}H$ was isolated in a 21% yield by flash SiO_2 column chromatography with chloroform as the eluent. Single crystals suitable for X-ray crystallographic analysis were obtained by slow diffusion of liquid methanol into a chloroform solution containing $^{NO_2,H}L^{Dipp}H$. IR (KBr): 3066 (NH), 1638 (C=N), 1573, 1304, 1279 cm^{-1} (NO_2); ^1H NMR ($CDCl_3$, 400 MHz): δ 1.22 (24H, d, J = 6.8 Hz, CH_3), 3.06 (4H, septet, J = 6.8 Hz, C*H*), 7.18–7.28 (6H, m, aromatic protons), 8.74 (2H, s, C*H*), 12.81 (1H, br, N*H*); HRMS (EI^+): m/z 435.2883, calcd for $C_{27}H_{37}N_3O_2$ 435.2886; Anal. Calcd for $C_{27}H_{37}N_3O_2$: C, 74.45; H, 8.56; N, 9.65%. Found: C, 74.72; H, 8.81; N, 9.41%.

$[Cu^I(^{NO_2,H}L^{Dipp})(MeCN)]$ (3): To a methanol solution (2 mL) containing $^{NO_2,H}L^{Dipp}H$ (43.7 mg, 0.1 mmol) and $[Cu^I(MeCN)_4]PF_6$ (37.3 mg, 0.1 mmol) was added triethylamine (10.1 mg, 0.1 mmol), and the mixture was stirred for 12 h at room temperature in a glovebox ($[O_2] < 1$ ppm and $[H_2O] < 1$ ppm). The resulting precipitates were collected by filtration and dried to give a yellow powder in a 56% yield. Single crystals suitable for X-ray crystallographic analysis were obtained by recrystallization from an acetonitrile solution containing the complex at −40 °C. IR (KBr): 1605 (C=N), 1531, 1458, 1277 cm^{-1} (NO_2); ^1H NMR (DMSO-d_6, 400 MHz): δ 1.15 (12H, d, J = 6.8 Hz, CH_3), 1.22 (12H, d, J = 6.8 Hz, CH_3), 2.08 (3H, s, CH_3), 3.24 (4H, septet, J = 6.8 Hz, C*H*), 7.19 (6H, m, aromatic protons), 8.61 (2H, s, C*H*); HRMS (FAB^+): m/z 498.2185, calcd for $C_{27}H_{37}CuN_3O_2$ 498.2282; Anal. Calcd for $C_{29}H_{39}CuN_4O_2$: C, 64.60; H, 7.29; N, 10.39%. Found: C, 64.38; H, 7.33; N, 10.25%.

$[\{Cu^I(^{CN,H}L^{Ph})\}_n]$ (4): Compound $^{CN,H}L^{Ph}H$ (24.7 mg, 0.1 mmol) in dichloromethane (1 mL) was added to a methanol solution (1 mL) of $[Cu^I(MeCN)_4]PF_6$ (37.3 mg, 0.1 mmol), and the mixture was stirred for 12 h at room temperature. The resulting precipitates were collected by filtration and dried to give a yellow powder in a 95% yield. IR (KBr): 2203 (C≡N), 1601 cm^{-1} (C=N); Anal. Calcd for $C_{16}H_{12}CuN_3\cdot 1/6H_2O$: C, 61.43; H, 3.97; N, 13.43%. Found: C, 61.66; H, 3.85; N, 13.36%.

$[\{Cu^I(^{CN,H}L^{Mes})\}_n]$ (5): This compound was prepared in a similar manner to that described for the synthesis of $[\{Cu^I(^{CN,H}L^{Ph})\}_n]$ by using $^{CN,H}L^{Mes}H$ (33.1 mg, 0.1 mmol) instead of $^{CN,H}L^{Ph}H$ in a 83% isolated yield. IR (KBr): 2189 (C≡N), 1647 cm^{-1} (C=N); HRMS (FAB^+): m/z 394.1347, calcd for $C_{22}H_{25}CuN_3$ 394.1344; Anal. Calcd for $C_{22}H_{24}CuN_3$: C, 67.07; H, 6.14; N, 10.67%. Found: C, 66.89; H, 6.16; N, 10.57%.

$[\{Cu^I(^{CN,H}L^{Dep})\}_n]$ (6): This compound was prepared in a similar manner to that described for the synthesis of $[\{Cu^I(^{CN,H}L^{Ph})\}_n]$ by using $^{CN,H}L^{Dep}H$ (36.0 mg, 0.1 mmol) instead of $^{CN,H}L^{Ph}H$ in a 73% isolated yield. Single crystals suitable for X-ray crystallographic analysis were obtained by slow diffusion at the interface between a methanol solution containing $[Cu^I(MeCN)_4]PF_6$ and a dichloromethane solution containing $^{CN,H}L^{Dep}H$. IR (KBr): 2197 (C≡N), 1647 cm^{-1} (C=N); HRMS (FAB^+): m/z 422.1666, calcd for $C_{24}H_{29}CuN_3$ 422.1757; Anal. Calcd for $C_{24}H_{28}CuN_3$: C, 68.30; H, 6.69; N, 9.96%. Found: C, 68.49; H, 6.77; N, 9.96%.

$[\{Cu^I(^{CN,H}L^{Dipp})\}_n]$ (7): This compound was prepared in a similar manner to that described for the synthesis of $[\{Cu^I(^{CN,H}L^{Ph})\}_n]$ by using $^{CN,H}L^{Dipp}H$ (41.6 mg, 0.1 mmol) instead of $^{CN,H}L^{Ph}H$ in a 66% isolated yield. Single crystals suitable for X-ray crystallographic analysis were obtained by slow diffusion at the interface between a methanol solution containing $[Cu^I(MeCN)_4]PF_6$ and a dichloromethane solution containing $^{CN,H}L^{Dipp}H$. IR (KBr): 2193 (C≡N), 1647 cm^{-1} (C=N); HRMS (FAB^+): m/z 478.2283, calcd for $C_{28}H_{37}CuN_3$ 478.2283; Anal. Calcd for $C_{28}H_{36}CuN_3$: C, 70.33; H, 7.59; N, 8.79%. Found: C, 70.03; H, 7.66; N, 8.73%.

$[\{Cu^I(^{CN,Me}L^{Dipp})\}_n]$ (8): To a methanol solution (2 mL) con-

taining $^{CN,Me}L^{Dipp}H$ (44.4 mg, 0.1 mmol) and $[Cu^{I}(MeCN)_4]PF_6$ (37.3 mg, 0.1 mmol) was added triethylamine (0.1 mmol), and the mixture was stirred for 24 h at room temperature in a glovebox ($[O_2] < 1$ ppm and $[H_2O] < 1$ ppm). The resulting precipitates were collected by filtration and dried to give a yellow powder in a 81% yield. IR (KBr): 2181 (C≡N), 1560 cm^{-1} (C=N); Anal. Calcd for $C_{30}H_{40}CuN_3 \cdot 1/2CH_3OH$: C, 70.15; H, 8.11; N, 8.05%. Found: C, 70.26; H, 7.98; N, 8.14%.

$[\{Cu^{I}(^{H,H}L^{Dipp})\}_2]$ (9): This compound was prepared by applying the following reported procedure.[23a] In an inert atmosphere, *n*-BuLi (0.7 mL, 1.1 equiv, 1.58 mol L^{-1} in hexane) was added dropwise to a stirred solution of $^{H,H}L^{Dipp}H$ (391 mg, 1.0 mmol) in THF (1 mL). The yellow solution was stirred for 30 min and added to a slurry of $[Cu^{I}(MeCN)_4]PF_6$ (373 mg, 1.0 mmol) in THF (1 mL) and stirred for 5 min. The solvent was removed under vacuum and the residue was extracted with hexane (20 mL) and filtered. The volume was reduced and the resulting precipitates were collected by filtration and dried to give a yellow powder in a 89% yield. Single crystals suitable for X-ray crystallographic analysis were obtained by slow diffusion of liquid methanol into a dichloromethane solution containing the complex. IR (KBr): 1605 cm^{-1} (C=N); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.16 (24H, d, J = 6.9 Hz, C*H*$_3$), 1.19 (24H, d, J = 6.9 Hz, C*H*$_3$), 3.45 (8H, septet, J = 6.9 Hz, C*H*), 7.04–7.09 (12H, m, aromatic protons), 7.11 (4H, d, J = 11.2 Hz, C*H*), 7.91 (2H, t, J = 11.2 Hz, C*H*); HRMS (FAB^+): m/z 904.4499, calcd for $C_{54}H_{74}Cu_2N_4$ 904.4506; Anal. Calcd for $C_{54}H_{74}Cu_2N_4 \cdot C_6H_{14} \cdot 2H_2O$: C, 70.07; H, 9.02; N, 5.45%. Found: C, 70.34; H, 8.80; N, 5.43%.

$[\{Cu^{I}(^{Me,H}L^{Dipp})\}_4]$ (10): This compound was prepared in a similar manner to that described for the synthesis of $[\{Cu^{I}(^{H,H}L^{Dipp})\}_2]$ by using $^{Me,H}L^{Dipp}H$ (40.4 mg, 0.1 mmol) instead of $^{H,H}L^{Ph}H$ in a 68% isolated yield. Single crystals suitable for X-ray crystallographic analysis were obtained by slow diffusion of liquid methanol into a dichloromethane solution containing the complex. IR (KBr): 1593 cm^{-1} (C=N); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.29 (6H, d, J = 7.2 Hz, C*H*$_3$), 0.83 (6H, d, J = 6.8 Hz, C*H*$_3$), 1.24 (6H, d, J = 7.2 Hz, C*H*$_3$), 1.35 (6H, d, J = 6.8 Hz, C*H*$_3$), 2.85 (2H, septet, J = 6.8 Hz, C*H*), 3.09 (3H, s, C*H*$_3$), 3.57 (2H, septet, J = 7.2 Hz, C*H*), 6.83 (2H, d, J = 7.6 Hz, aromatic protons), 6.89 (2H, s, C*H*), 6.99 (2H, t, J = 7.6 Hz, aromatic protons), 7.06 (2H, d, J = 7.6 Hz, aromatic protons); HRMS (FAB^+): m/z 1864.9629, calcd for $C_{112}H_{156}Cu_4N_8$ 1864.9637; Anal. Calcd for $C_{112}H_{156}Cu_4N_8 \cdot H_2O$: C, 71.30; H, 8.44; N, 5.94%. Found: C, 71.39; H, 8.48; N, 5.93%.

Results and Discussion

Structure of the Neutral Ligands. Many of the neutral ligands (precursors of the β-diketiminate ligands) so far reported exhibit the U-shaped closed conformation **A** in crystals (Scheme 1). X-ray structures of $^{H,Me}L^{Ph}H$, $^{H,Me}L^{Dipp}H$, $^{NO_2,H}L^{Mes}H$, $^{CN,H}L^{Mes}H$, and $^{CN,H}L^{Dep}H$ exhibiting the closed conformation **A** have been reported in the literatures.[19,37,38] Compound $^{NO_2,H}L^{Dipp}H$, the crystal structure of which has been newly determined in this study, also exhibits the closed conformation **A** as shown in Fig. 1. The overall structure of $^{NO_2,H}L^{Dipp}H$ is essentially the same as that of $^{NO_2,H}L^{Mes}H$ previously reported.[19] On the other hand, compound $^{Me,H}L^{Dipp}H$ shows the W-shaped open conformation **B** as indicated in Fig. 2. In this case, methanol molecules are involved in the crystal lattice to make an intermolecular hydrogen-bonding network, as indicated in Fig. 2b. This hydrogen-bonding interaction may stabilize the open conformation **B** discussed below. The crystallographic data and the selected bond lengths and angles of compounds $^{NO_2,H}L^{Dipp}H$ and $^{Me,H}L^{Dipp}H$ are presented in Tables 1 and 2, respectively.

In order to get insight into the structural difference between **A** and **B**, energetics of the neutral ligands $^{H,H}L^{Dipp}H$, $^{Me,H}L^{Dipp}H$, $^{CN,H}L^{Dipp}H$, $^{NO_2,H}L^{Dipp}H$, and $^{H,Me}L^{Dipp}H$ on both conformations have been examined using semiempirical molecular

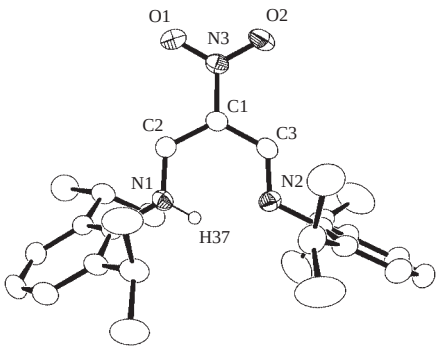


Fig. 1. ORTEP drawing of $^{NO_2,H}L^{Dipp}H$ with 50% probability thermal-ellipsoids. Hydrogen atoms except the one at the amino group [H(37)] are omitted for clarity.

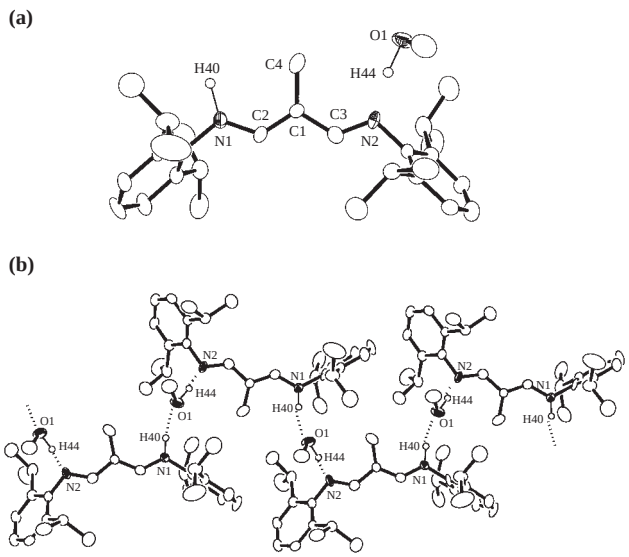
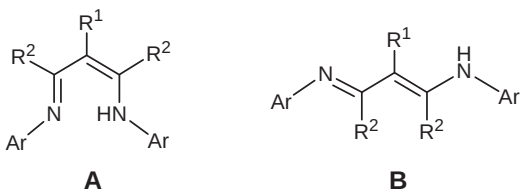


Fig. 2. ORTEP drawings of (a) $^{Me,H}L^{Dipp}H \cdot MeOH$ and (b) a side view of the hydrogen-bonding network in the crystal with 50% probability thermal-ellipsoids. Hydrogen atoms except the one on MeOH [H(44) of (a) and (b)] and the one at the amino group [H(40) of (a) and (b)] are omitted for clarity.



(Ar = 2,6-diisopropylphenyl)

Scheme 1.

Table 1. Summary of X-ray Crystallographic Data of $^{NO_2,H}L^{Dipp}H$, $^{Me,H}L^{Dipp}H\cdot CH_3OH$, $[Cu^I(^{NO_2,H}L^{Dipp})(CH_3CN)]$ (**3**), $[\{Cu^I(^{CN,H}L^{Dep})\}_n]$ (**6**), $[\{Cu^I(^{CN,H}L^{Dipp})\}_n]\cdot CH_2Cl_2$ (**7**), and $[\{Cu^I(^{H,H}L^{Dipp})\}_2]\cdot CH_2Cl_2$ (**9**)

	$^{NO_2,H}L^{Dipp}H$	$^{Me,H}L^{Dipp}H\cdot CH_3OH$	$[Cu^I(^{NO_2,H}L^{Dipp})(CH_3CN)]$ (**3**)	$[\{Cu^I(^{CN,H}L^{Dep})\}_n]$ (**6**)	$[\{Cu^I(^{CN,H}L^{Dipp})\}_n]\cdot CH_2Cl_2$ (**7**)	$[\{Cu^I(^{H,H}L^{Dipp})\}_2]\cdot CH_2Cl_2$ (**9**)
Empirical formula	$C_{27}H_{37}O_2N_3$	$C_{29}H_{44}N_2O$	$C_{29}H_{39}CuN_4O_2$	$C_{24}H_{28}CuN_3$	$C_{29}H_{38}Cl_2CuN_3$	$C_{55}H_{76}Cu_2N_4Cl_2$
Formula weight	434.60	436.68	539.20	422.05	563.09	991.23
Crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$ (#2)	$P2_1/n$ (#14)	$P2_1/n$ (#14)	$P2_1/n$ (#14)	$P2_1/n$ (#14)	$C2/c$ (#15)
a/Å	9.075(5)	9.166(6)	14.552(4)	8.836(2)	17.804(8)	29.786(20)
b/Å	10.793(3)	24.77(1)	11.989(3)	20.328(5)	14.864(5)	8.963(5)
c/Å	13.935(7)	12.720(5)	18.286(5)	11.854(3)	24.310(10)	22.193(13)
α/deg	107.09(1)					
β/deg	95.99(1)	108.37(2)	116.141(5)	92.331(6)	111.371(12)	118.15(2)
γ/deg	102.53(2)					
V/Å^3	1252(1)	2740(2)	2863.9(13)	2127.4(9)	5991.0(43)	5224.2(53)
Z	2	4	4	4	8	4
$F(000)$	470.00	960.00	1144.00	888.00	2368.00	2104.00
D_{calcd}/g cm^{-3}	1.152	1.058	1.250	1.318	1.248	1.260
T/°C	−115	−115	−115	−115	−115	−115
Crystal size/mm^3	0.20 × 0.20 × 0.20	0.10 × 0.20 × 0.30	0.10 × 0.10 × 0.30	0.10 × 0.10 × 0.10	0.20 × 0.20 × 0.30	0.10 × 0.10 × 0.10
μ (Mo Kα)/cm^{-1}	0.73	0.63	87.94	10.40	9.28	9.550
Radiation	Mo Kα (0.71075 Å)	Mo Kα (0.71075 Å)	Mo Kα (0.71070 Å)	Mo Kα (0.71070 Å)	Mo Kα (0.71070 Å)	Mo Kα (0.71075 Å)
$2\theta_{max}$/deg	54.9	55.0	55.0	55.0	55.0	55.0
No. of reflns measd	11739	26998	27939	20941	56772	3570
No. of reflns obsd	5599 [$I > 3.00\sigma(I)$]	5722 [$I > 3.00\sigma(I)$]	15783 [$I > 3.00\sigma(I)$]	11843 [$I > 3.00\sigma(I)$]	16260 [$I > 3.00\sigma(I)$]	5766 [$I > 2.00\sigma(I)$]
No. of variables	330	334	365	282	708	326
R[a]; Rw[b]	0.057; 0.058	0.057; 0.059	0.060; 0.061	0.069; 0.070	0.067; 0.076	0.062; 0.071
Goodness of fit indicator	1.05	1.02	1.00	1.03	0.95	1.03

a) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. b) $Rw = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of $^{NO_2,H}L^{Dipp}H$, $^{Me,H}L^{Dipp}H \cdot CH_3OH$, $[Cu^I(^{NO_2,H}L^{Dipp})(CH_3CN)]$ (**3**), $[\{Cu^I(^{NO_2,H}L^{Dipp})\}_n]$ (**6**), $[\{Cu^I(^{CN,H}L^{Dep})\}_n]$ (**7**), and $[\{Cu^I(^{H,H}L^{Dipp})\}_2] \cdot CH_2Cl_2$ (**9**)[a]

$^{NO_2,H}L^{Dipp}H$		$^{Me,H}L^{Dipp}H \cdot CH_3OH$		$[Cu^I(^{NO_2,H}L^{Dipp})(CH_3CN)]$ (**3**)		$[\{Cu^I(^{CN,H}L^{Dep})\}_n]$ (**6**)		$[\{Cu^I(^{CN,H}L^{Dipp})\}_n]$ (**7**)		$[\{Cu^I(^{H,H}L^{Dipp})\}_2] \cdot CH_2Cl_2$ (**9**)	
O(1)–N(3)	1.238(2)	N(1)–C(29)	1.424(5)	Cu(1)–N(1)	1.934(2)	Cu(1)–N(1)	1.901(3)	Cu(1)–N(1)	2.006(3)	Cu(2)–N(4)	1.929(3)	Cu(1)–N(1)	1.862(8)
O(2)–N(3)	1.243(2)	N(1)–C(2)	1.353(4)	Cu(1)–N(2)	1.987(2)	Cu(1)–N(2)	2.023(3)	Cu(1)–N(2)	1.928(3)	Cu(2)–N(5)	2.017(3)	Cu(1)–N(2)*	1.877(8)
N(1)–C(2)	1.313(2)	N(2)–C(3)	1.295(4)	Cu(1)–N(4)	1.857(2)	Cu(1)–N(3)	1.854(3)	Cu(1)–N(6)	1.865(3)	Cu(2)–N(3)	1.850(2)	N(1)–C(2)	1.325(10)
N(1)–C(4)	1.434(2)	N(1)–C(5)	1.448(4)	N(1)–C(2)	1.301(3)	N(1)–C(2)	1.302(4)	N(1)–C(2)	1.278(4)	N(4)–C(30)	1.290(4)	N(1)–C(4)	1.462(13)
N(2)–C(3)	1.304(2)	N(2)–C(17)	1.457(5)	N(1)–C(4)	1.427(3)	N(1)–C(5)	1.450(4)	N(1)–C(5)	1.442(4)	N(4)–C(33)	1.423(4)	N(2)–C(3)	1.318(10)
N(2)–C(16)	1.428(2)	C(1)–C(2)	1.350(4)	N(2)–C(3)	1.306(2)	N(2)–C(3)	1.298(4)	N(2)–C(3)	1.293(4)	N(5)–C(31)	1.260(4)	N(2)–C(16)	1.451(11)
N(3)–C(1)	1.424(2)	C(1)–C(3)	1.425(5)	N(2)–C(16)	1.435(3)	N(2)–C(15)	1.431(4)	N(2)–C(17)	1.441(5)	N(5)–C(45)	1.448(5)	C(1)–C(2)	1.408(11)
C(1)–C(2)	1.407(2)	C(1)–C(4)	1.502(5)	N(3)–C(1)	1.419(3)	N(3)–C(4)	1.154(4)	N(3)–C(4)	1.149(5)	N(6)–C(32)	1.117(5)	C(1)–C(3)	1.402(10)
C(1)–C(3)	1.412(2)	N(2)–H(44)	1.646(4)	N(4)–C(28)	1.116(3)	C(1)–C(2)	1.416(4)	C(1)–C(2)	1.405(5)	C(29)–C(30)	1.423(5)	Cu(1)–Cu(1)*	4.9853(12)
		O(1)–H(40)*	1.864(4)	C(1)–C(2)	1.414(4)	C(1)–C(3)	1.412(4)	C(1)–C(3)	1.422(5)	C(29)–C(31)	1.458(5)		
				C(1)–C(3)	1.406(3)	C(1)–C(4)	1.419(4)	C(1)–C(4)*	1.418(5)	C(29)–C(32)	1.435(5)		
O(1)–N(3)–O(2)	122.1(1)	C(2)–N(1)–C(5)	120.4(3)	N(1)–Cu(1)–N(2)	96.94(7)	N(1)–Cu(1)–N(2)	99.0(1)	N(1)–Cu(1)–N(2)	96.6(1)	N(4)–Cu(2)–N(5)	97.0(1)	N(1)–Cu(1)–N(2)*	174.0(2)
C(2)–N(1)–C(4)	123.4(2)	C(3)–N(2)–C(17)	114.9(3)	N(1)–Cu(1)–N(4)	145.0(1)	N(1)–Cu(1)–N(3)	153.9(1)	N(1)–Cu(1)–N(6)	116.0(1)	N(4)–Cu(2)–N(3)	146.7(1)	Cu(1)–N(1)–C(2)	121.3(6)
C(3)–N(2)–C(16)	119.6(2)	C(2)–C(1)–C(4)	123.4(3)	N(2)–Cu(1)–N(4)	117.7(1)	N(2)–Cu(1)–N(3)	107.2(1)	N(2)–Cu(1)–N(6)	147.3(1)	N(5)–Cu(2)–N(3)	115.3(1)	Cu(1)–N(1)–C(4)	123.1(4)
N(3)–C(1)–C(2)	117.7(2)	C(3)–C(1)–C(4)	121.1(3)	Cu(1)–N(1)–C(2)	122.1(2)	Cu(1)–N(1)–C(2)	121.5(2)	Cu(1)–N(1)–C(2)	122.1(3)	Cu(2)–N(4)–C(30)	122.7(2)	Cu(1)–N(2)*–C(3)*	121.4(5)
N(3)–C(1)–C(3)	118.0(2)	C(2)–C(1)–C(3)	115.5(3)	Cu(1)–N(1)–C(4)	119.3(1)	Cu(1)–N(1)–C(5)	122.5(2)	Cu(1)–N(1)–C(5)	116.7(2)	Cu(2)–N(4)–C(33)	119.1(2)	Cu(1)–N(2)*–C(16)*	122.9(6)
C(2)–C(1)–C(3)	124.2(2)	N(1)–C(2)–C(1)	128.5(3)	Cu(1)–N(2)–C(3)	121.3(2)	Cu(1)–N(2)–C(3)	119.7(2)	Cu(1)–N(2)–C(3)	122.5(3)	Cu(2)–N(5)–C(31)	123.2(3)	C(2)–N(1)–C(4)	114.9(8)
N(1)–C(2)–C(1)	120.8(2)	N(2)–C(3)–C(1)	127.0(3)	Cu(1)–N(2)–C(16)	120.4(1)	Cu(1)–N(2)–C(15)	121.2(2)	Cu(1)–N(2)–C(15)	120.0(2)	Cu(2)–N(5)–C(45)	116.3(2)	N(2)–C(3)–C(1)	124.2(9)
N(2)–C(3)–C(1)	121.5(2)	C(29)–O(1)–H(44)	105.4	Cu(1)–N(4)–C(28)	169.2(3)	Cu(1)–N(3)–C(4)	163.7(3)	Cu(1)–N(6)–C(32)	170.6(4)	Cu(2)–N(3)–C(4)	170.0(4)	C(2)–C(1)–C(3)	123.1(9)

a) Estimated standard deviations are given in parentheses.

Table 3. Heat of Formation (ΔH_f, kcal mol^{-1}) of the Neutral Ligands Calculated by the PM3 Method

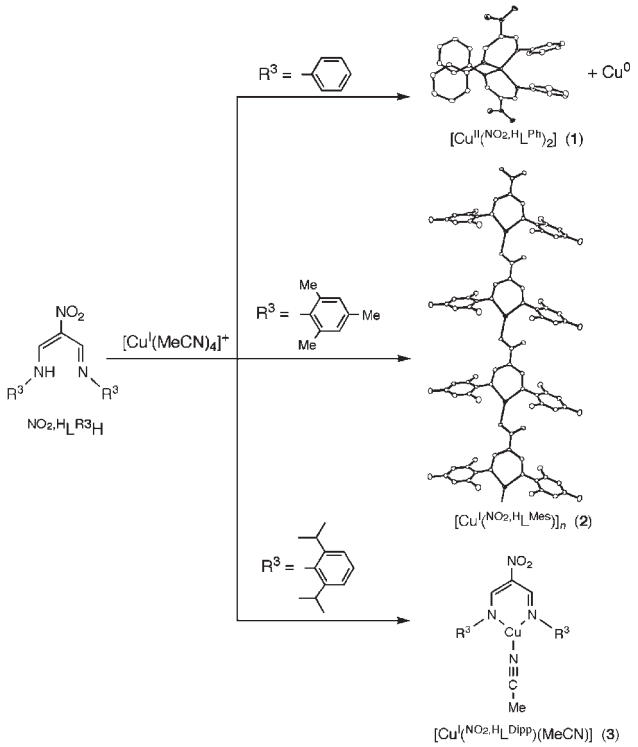
Ligand	Conformation **A**	Conformation **B**	$\Delta\Delta H_f$[a]
$^{H,H}L^{Dipp}H$	32.8	32.1	0.7
$^{Me,H}L^{Dipp}H$	24.0	25.4	−1.4
$^{CN,H}L^{Dipp}H$	65.1	68.1	−3.0
$^{NO_2,H}L^{Dipp}H$	17.6	25.9	−8.3
$^{H,Me}L^{Dipp}H$	10.9	21.8	−10.9

a) Difference of ΔH_f ($\Delta\Delta H_f = \Delta H_f^A - \Delta H_f^B$).

orbital calculations. In Table 3, the heats of formation ΔH_f calculated by the PM3 method are summarized. The calculated results clearly indicate that the closed conformation **A** is more stable than the open conformation **B**, except in the case of $^{H,H}L^{Dipp}H$, and that the stability of conformation **A** increases in the order of $^{Me,H}L^{Dipp}H < {}^{CN,H}L^{Dipp}H < {}^{NO_2,H}L^{Dipp}H < {}^{H,Me}L^{Dipp}H$. Thus, compounds $^{CN,H}L^{Dipp}H$, $^{NO_2,H}L^{Dipp}H$, and $^{H,Me}L^{Dipp}H$ mostly exhibit the closed conformation **A** as experimentally observed by the X-ray crystallographic analysis.[39] In this respect, compound $^{Me,H}L^{Dipp}H$ should also take the closed conformation **A**, since its closed conformation is more stable than its open conformation **B** by 1.4 kcal mol^{-1}. However, the crystal structure of $^{Me,H}L^{Dipp}H$ shown in Fig. 2 apparently exhibits conformation **B**. In this case, an intermolecular hydrogen-bonding network may stabilize the open conformation to give a linear molecular alignment. In this context, the nonsubstituted derivative $^{H,H}L^{Dipp}H$ may prefer the open conformation **B**. This is actually seen in the copper(I) complex discussed below. It should also be noted that the most popular ligand $^{H,Me}L^{Dipp}H$ highly prefers the closed conformation **A**. Thus, the ligand may stabilize the six-membered chelate ring seen in most of the β-diketiminato complexes of $^{H,Me}L^{Dipp}H$.[1]

Complex Formation of the Nitro-Ligands ($^{NO_2,H}L^{R3}H$) with $[Cu^I(MeCN)_4]PF_6$. In our previous communication,[29] we demonstrated that the treatment of $^{NO_2,H}L^{Mes}H$ and $[Cu^I(MeCN)_4]PF_6$ in methanol in the presence of triethylamine as a base gave a head-to-tail linear polymer complex $[\{Cu^I(^{NO_2,H}L^{Mes})\}_n]$ (**2**) with a dark purple color, where the copper(I) ion is adapted to a three-coordinate trigonal planar structure and the nitro group acts as a monodentate ligand to link the mononuclear copper(I) units (Scheme 2). When the mesityl group of $^{NO_2,H}L^{Mes}H$ was replaced by a simple phenyl group to give $^{NO_2,H}L^{Ph}H$, the same treatment caused a disproportionation reaction of Cu^I to give the corresponding bis(β-diketiminato)copper(II) complex, $[Cu^{II}(^{NO_2,H}L^{Ph})_2]$ (**1**)[40] and a black material of copper(0) (Scheme 2).

On the other hand, treatment of $[Cu^I(MeCN)_4]PF_6$ and $^{NO_2,H}L^{Dipp}H$ containing the bulkier 2,6-diisopropylphenyl group (Dipp) as the *N*-substituent under the same experimental conditions gave a mononuclear copper(I) complex, $[Cu^I(^{NO_2,H}L^{Dipp})(MeCN)]$ (**3**), the crystal structure of which is presented in Fig. 3 together with the crystallographic data and the selected bond lengths and angles summarized in Tables 1 and 2, respectively. Complex **3** exhibits a three-coordinate trigonal planar structure with an acetonitrile molecule as the external ligand, but its trigonal structure of copper center is significantly distorted [N(1)–Cu(1)–N(2): 96.94°, N(1)–Cu(1)–N(4): 145.0°, and N(2)–Cu(1)–N(4): 117.7°; deviation of Cu(I) from the least-squares plane defined by N(1), N(2), and N(4) is 0.063



Scheme 2.

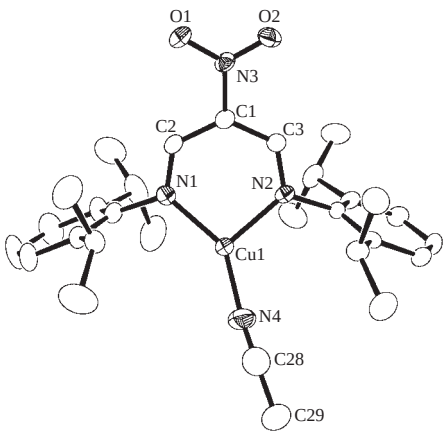


Fig. 3. ORTEP drawing of $[Cu^{I}(^{NO_2,H}L^{Dipp})(CH_3CN)]$ (**3**) with 50% probability thermal-ellipsoids. Hydrogen atoms are omitted for clarity.

Å] as compared to that of the polymer copper(I) complex **2** (the corresponding bond angles are 97.17, 125.86, and 136.96°; deviation of Cu(I) from the least-squares plane is 0.021 Å).[29]

These results clearly demonstrate that the complex formation of the nitro-ligands ($^{NO_2,H}L^{R3}H$) is largely affected by the *N*-aromatic substituents R^3 (Scheme 2). More specifically, the less bulky aromatic substituent (Ph) in $^{NO_2,H}L^{Ph}H$ may stabilize the bis(β-diketiminato)copper(II) complex $[Cu^{II}(^{NO_2,H}L^{Ph})_2]$ (**1**) causing the disproportionation reaction, whereas the larger aromatic substituent like 2,6-diisopropylphenyl (Dipp), prohibits the formation of not only the bis(β-diketiminato)copper(II) complex (**1**), but also of the linear polymer complex (**2**). Thus, the mononuclear copper(I) complex (**3**) was eventually formed.

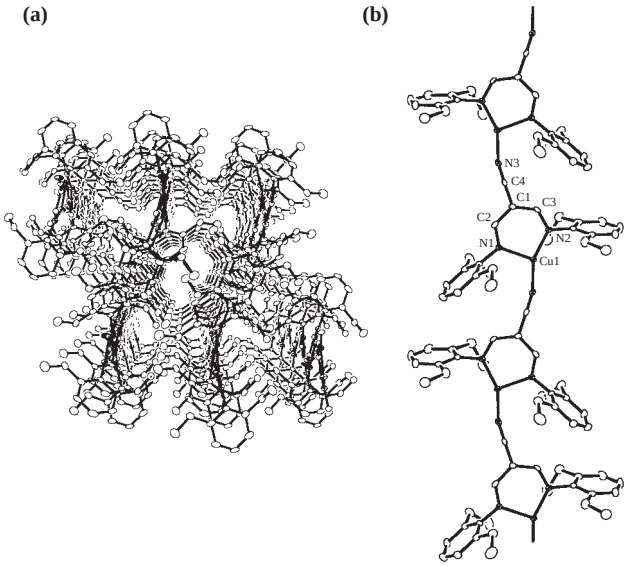


Fig. 4. ORTEP drawings of (a) a top view of the crystal packing of $[\{Cu^{I}(^{CN,H}L^{Dep})\}_n]$ (**6**) and (b) a side view of its linear chain structure with 50% probability thermal-ellipsoids. Hydrogen atoms are omitted for clarity.

Complex Formation of the Cyano-Ligands ($^{CN,R2}L^{R3}H$) with $[Cu^{I}(MeCN)_4]PF_6$. In contrast to the case of the nitro-ligand system, where the resulting copper complexes were largely different depending on the aromatic substituents R^3 (Scheme 2), reaction of cyano-ligands $^{CN,R2}L^{R3}H$ with $[Cu^{I}(MeCN)_4]PF_6$ always produced coordination polymer copper(I) complexes **4**–**8** regardless of the ligand substituents (R^2 and R^3). This can be attributed to the stronger binding of the cyano group to copper(I). All of the polymer complexes exhibit a yellow color and are hardly soluble to ordinary organic solvents except $[\{Cu^{I}(^{CN,H}L^{Dipp})\}_n]$ (**7**) which is soluble in nitrile solvents such as acetonitrile and propionitrile. Figures 4 and 5 show the X-ray structures of $[\{Cu^{I}(^{CN,H}L^{Dep})\}_n]$ (**6**) and $[\{Cu^{I}(^{CN,H}L^{Dipp})\}_n]$ (**7**), respectively. Their crystallographic data and the selected bond lengths and angles are also summarized in Tables 1 and 2, respectively. The similar polymeric structure of $[\{Cu^{I}(^{CN,H}L^{Mes})\}_n]$ (**5**) was also obtained in the X-ray crystallographic analysis, though the quality of the crystallographic data is not yet satisfactory.[41]

The copper(I) complexes of the cyano-ligands are head-to-tail coordination polymer complexes, where the cyano group on the ligand carbon framework acts as the bridging ligand connecting the (β-diketiminato)copper(I) monomer units. The copper(I) ion exhibits a three-coordinate trigonal planar structure with a N_3 donor set, in which the metal ion exists on the plane consisting of the three nitrogen atoms [deviations of the metal ion from the least-squares plane defined by the three nitrogen atoms are 0.001 Å and 0.0099 (molecule 1)–0.040 Å (molecule 2) for **6** and **7**, respectively]. However, the bond angles around the metal ion N–Cu–N are largely different between the two complexes. The N–Cu–N angles in $[\{Cu^{I}(^{CN,H}L^{Dep})\}_n]$ (**6**) are 99.0, 107.2, and 153.9° and those in $[\{Cu^{I}(^{CN,H}L^{Dipp})\}_n]$ (**7**) are 96.6, 116.0, and 147.3° (for molecule 1) and 97.0, 115.3, and 146.7° (for molecule 2), respectively (Table 2). Thus, the distortion from the trigonal

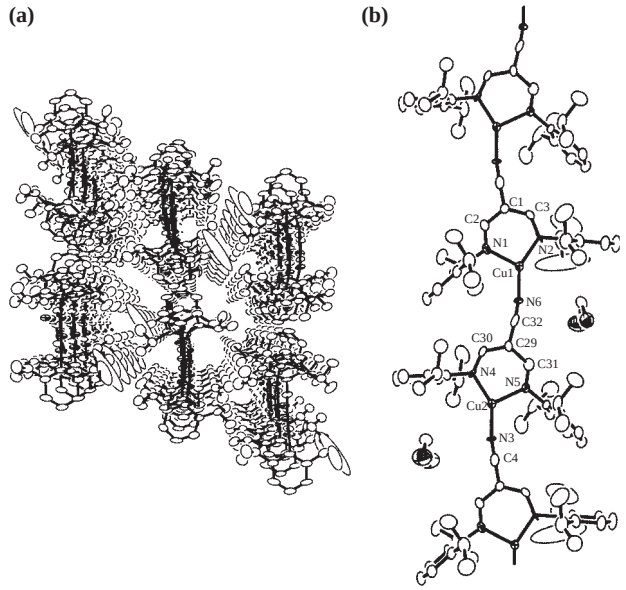


Fig. 5. ORTEP drawings of (a) a top view of the crystal packing of $[\{Cu^{I}(^{CN,H}L^{Dipp})\}_n]\cdot CH_2Cl_2$ (**7**) and (b) a side view of its linear chain structure with 50% probability thermal-ellipsoids. Hydrogen atoms are omitted for clarity.

structure becomes significantly larger in these cases as compared to that of the coordination polymer complex **2** of the nitro-ligand $^{NO_2,H}L^{Mes}H$. As a result, the linearity of the polymer chain in complexes **6** and **7** becomes zigzag shaped as indicated in Figs. 4b and 5b, respectively.

As seen in the top view of the crystal packing, relatively wide and long columns are constructed in each crystal [Cu–Cu distances in each complex are: 7.8 and 12.4 Å in **6**; 8.3 and 12.4 Å in **7**, see Figs. 4a and 5a], which could be applied as a gas adsorption material.

Copper(I) Complexes of $^{H,H}L^{Dipp}H$ and $^{Me,H}L^{Dipp}H$. So far, (β-diketiminato)copper(I) complexes supported by ligands with $-NO_2$ or –CN group at the α-position of the carbon framework have been described. In all of the cases, the ligands are adapted to the closed conformation **A** shown in Scheme 1. In this study, we have found that $^{H,H}L^{Dipp}H$ and $^{Me,H}L^{Dipp}H$ provide copper(I) complexes with the open conformation **B** as demonstrated below.

Reaction of $[Cu^{I}(MeCN)_4]PF_6$ and the lithium salt of $^{H,H}L^{Dipp-}$ (deprotonated form of $^{H,H}L^{Dipp}H$) gave the 12-membered macrocyclic dinuclear copper(I) complex **9** with the ligand exhibiting the open conformation **B** as shown in Fig. 6. The copper(I) ion exhibits a two-coordinate nearly linear coordination geometry (bond angle of N–Cu–N is 174.0°), and the distance between the two Cu(I) ions in the complex is about 4.99 Å. The macrocyclic ring is almost flat and the aromatic ring of the 2,6-diisopropylphenyl substituent is nearly perpendicular to the macrocyclic plane. The overall structure of this complex is very close to that of the similar macrocyclic dinuclear silver(I) complex of the same ligand recently reported by us.[42]

Another interesting copper(I) complex (**10**) was obtained in the reaction of $^{Me,H}L^{Dipp-}$ (lithium salt) and $[Cu^{I}(MeCN)_4]PF_6$ in THF. In this case, the product was a 24-membered macrocyclic tetranuclear copper(I) complex as illustrated in Fig. 7,

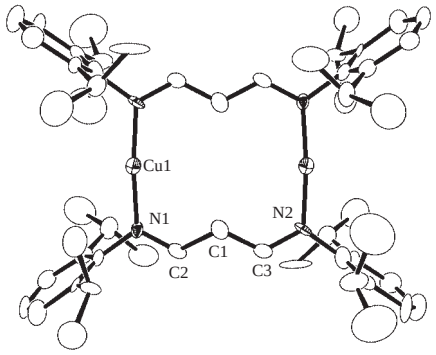


Fig. 6. ORTEP drawing of $[\{Cu^{I}(^{H,H}L^{Dipp})\}_2]\cdot CH_2Cl_2$ (**9**) with 50% probability thermal-ellipsoids. Hydrogen atoms are omitted for clarity.

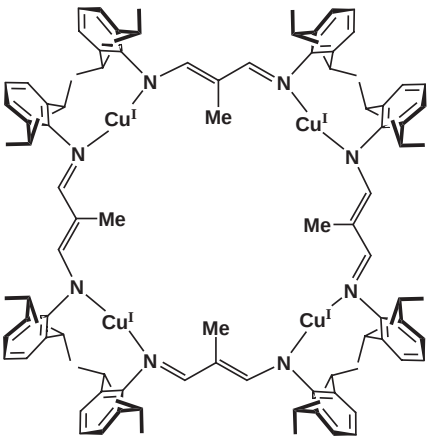


Fig. 7. Schematic drawing of the structure of tetranuclear copper(I) complex $[\{Cu^{I}(^{Me,H}L^{Dipp})\}_4]$ (**10**).

the structure of which has been confirmed by high-resolution FAB-MS, elemental analysis, and ^1H NMR data as presented in the Experimental section. Although the quality of the crystallographic data are not satisfactory due to the disorder problem of the solvent molecules, the tetranuclear copper(I) structure was seen in its preliminary X-ray study,[41] which was nearly the same as the structure of the macrocyclic tetranuclear silver(I) complex recently reported.[42] In this case as well, the ligand is adapted to the open conformation **B**, but the α-methyl substituent (R^1 = Me) may prevent the smaller macrocyclic structure shown in Fig. 6 from being taken due to the steric repulsion between the ligand substituents, thus providing the large 24-membered macrocyclic tetranuclear copper(I) complex **10**.

In summary, we have demonstrated that β-diketiminate ligands can be adopted for the synthesis of a variety of copper(I) complexes including mononuclear copper(I) complex **3**, one-dimensional coordination polymer complexes with different coordination geometry (**2** and **4**–**8**), and macrocyclic dinuclear and tetranuclear copper(I) complexes **9** and **10** supported by the ligand with the open conformation. The structures of copper(I) complexes are largely controlled by the steric and/or electronic effects of the substituents R^1 and R^3. We are currently studying the reactivity of the copper(I) complexes as well as applications of the polymer and macrocyclic copper(I) complexes to supramolecular chemistry.

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Supporting Information

Summary of X-ray crystallographic data of $[\{Cu^{I}(^{CN,H}L^{Mes})\}_n]$ (**5**) and $[\{Cu^{I}(^{Me,H}L^{Dipp})\}_4]$ (**10**) (Table S1) and preliminary X-ray structures of $[\{Cu^{I}(^{CN,H}L^{Mes})\}_n]$ (**5**) and $[\{Cu^{I}(^{Me,H}L^{Dipp})\}_4]$ (**10**) (Figs. S1 and S2). This material is available free of charge on the web at: http://www.csj.jp/journals/bcsj/.

References

1 L. Bourget-Merle, M. F. Lappert, J. R. Severn, *Chem. Rev.* **2002**, *102*, 3031.

2 N. M. Tsybina, V. G. Vinokurov, T. V. Protopopova, A. P. Skoldinov, *J. Gen. Chem. USSR* **1966**, *36*, 1383.

3 C. L. Honeybourne, G. A. Webb, *J. Chem. Soc., Chem. Commun.* **1968**, 739.

4 S. G. McGeachin, *Can. J. Chem.* **1968**, *46*, 1903.

5 M. Elder, B. R. Penfold, *J. Chem. Soc. A* **1969**, 2556.

6 Y. Murakami, K. Sakata, *Inorg. Chim. Acta* **1969**, *2*, 273.

7 D. Attanasio, A. A. G. Tomlinson, L. Alagna, *J. Chem. Soc., Chem. Commun.* **1977**, 618.

8 Y. Nishida, N. Oishi, S. Kida, *Inorg. Chim. Acta* **1979**, *32*, 7.

9 A. V. Kulichenko, V. P. Kurbatov, S. S. Kukharicheva, O. A. Osipov, *J. Gen. Chem. USSR* **1987**, *55*, 612.

10 R. Knorr, R. Zolch, K. Polborn, *Heterocycles* **1995**, *40*, 559.

11 P. L. Holland, W. B. Tolman, *J. Am. Chem. Soc.* **1999**, *121*, 7270.

12 P. L. Holland, W. B. Tolman, *J. Am. Chem. Soc.* **2000**, *122*, 6331.

13 D. W. Randall, S. D. George, P. L. Holland, B. Hedman, K. O. Hodgson, W. B. Tolman, E. I. Solomon, *J. Am. Chem. Soc.* **2000**, *122*, 11632.

14 B. A. Jazdzewski, P. L. Holland, M. Pink, V. G. Young, Jr., D. J. E. Spencer, W. B. Tolman, *Inorg. Chem.* **2001**, *40*, 6097.

15 N. W. Aboelella, E. A. Lewis, A. M. Reynolds, W. W. Brennessel, C. J. Cramer, W. B. Tolman, *J. Am. Chem. Soc.* **2002**, *124*, 10660.

16 S. Yokota, Y. Tachi, S. Itoh, *Inorg. Chem.* **2002**, *41*, 1342.

17 W. Z. Lee, W. B. Tolman, *Inorg. Chem.* **2004**, *41*, 5656.

18 D. J. E. Spencer, A. M. Reynolds, P. L. Holland, B. A. Jazdzewski, C. Duboc-Toia, L. Le Pape, S. Yokota, Y. Tachi, S. Itoh, W. B. Tolman, *Inorg. Chem.* **2002**, *41*, 6307.

19 C. Shimokawa, S. Yokota, Y. Tachi, N. Nishiwaki, M. Ariga, S. Itoh, *Inorg. Chem.* **2003**, *42*, 8395.

20 a) E. C. Brown, N. W. Aboelella, A. M. Reynolds, G. Aullón, S. Alvarez, W. B. Tolman, *Inorg. Chem.* **2004**, *43*, 3335. b) G. Aullón, S. Alvarez, *Eur. J. Inorg. Chem.* **2004**, 4430.

21 K.-H. Park, W. J. Marshall, *J. Am. Chem. Soc.* **2005**, *127*, 9330.

22 X. L. Dai, T. H. Warren, *Chem. Commun.* **2001**, 1998.

23 a) D. J. E. Spencer, N. W. Aboelella, A. M. Reynolds, P. L. Holland, W. B. Tolman, *J. Am. Chem. Soc.* **2002**, *124*, 2108. b) N. W. Aboelella, S. V. Kryatov, B. F. Gherman, W. W. Brennessel, V. G. Young, Jr., R. Sarangi, E. Rybak-Akimova, K. O. Hodgson, B. Hedman, E. I. Solomon, C. J. Cramer, W. B. Tolman, *J. Am. Chem. Soc.* **2004**, *126*, 16896.

24 D. A. Pantazis, J. E. McGrady, *Inorg. Chem.* **2003**, *42*, 7734.

25 D. S. Laitar, C. J. N. Mathison, W. M. Davis, J. P. Sadighi, *Inorg. Chem.* **2003**, *42*, 7354.

26 X. Dai, T. H. Warren, *J. Am. Chem. Soc.* **2004**, *126*, 10085.

27 L. D. Amisial, X. Dai, R. A. Kinney, A. Krishnaswamy, T. H. Warren, *Inorg. Chem.* **2004**, *43*, 6537.

28 A few examples of β-diketiminate copper complexes with functional group(s) (other than simple alkyl groups) on the ligand carbon framework have been reported in the literatures.[9,10,14,18,23,25]

29 S. Yokota, Y. Tachi, N. Nishiwaki, M. Ariga, S. Itoh, *Inorg. Chem.* **2001**, *40*, 5316.

30 D. D. Perrin, W. L. F. Armarego, D. R. Perrin, *Purification of Laboratory Chemicals*, 4th ed., Pergamon Press, Elmsford, NY, **1996**.

31 M. Cheng, D. R. Moore, J. J. Reczek, B. M. Chamberlain, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2001**, *123*, 8738.

32 J. Feldman, S. J. McLain, A. Parthasarathy, W. J. Marshall, J. C. Calabrese, S. D. Arthur, *Organometallics* **1997**, *16*, 1514.

33 S. D. Allen, D. R. Moore, E. B. Lobkovsky, G. W. Coates, *J. Organomet. Chem.* **2003**, *683*, 137.

34 J. J. P. Stewart, *J. Comput. Chem.* **1989**, *10*, 209; **1989**, *10*, 221.

35 V. T. Klimko, A. P. Skoldinov, *Zh. Obshch. Khim.* **1959**, *29*, 4027.

36 N. Nishiwaki, Y. Tohda, M. Ariga, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1997.

37 M. Stender, R. J. Wright, B. E. Eichler, J. Prust, M. M. Olmstead, H. W. Roesky, P. P. Power, *J. Chem. Soc., Dalton Trans.* **2001**, 3465.

38 S. Brownstein, E. J. Gabe, L. Prasad, *Can. J. Chem.* **1983**, *61*, 1410.

39 An energy difference ($\Delta\Delta H_f$) of 3.0 kcal mol^{-1} means that about 99.5% of the compound has the closed conformation **A** at 298 K.

40 X-ray structure of the authentic sample of complex **1** prepared by the reaction of $^{NO_2,H}L^{Ph}H$ and $Cu^{II}(OAc)_2$ has been reported in our previous paper.[19]

41 Preliminary results of the X-ray structural analyses for **5** and **10** are presented in Supporting Information. In the case of complex **5**, the size of single crystal was not sufficient to get enough diffraction spots. For complex **10**, on the other hand, there is a solvent molecule in the macrocyclic cavity, which is highly disordered preventing us to obtain high quality data.

42 C. Shimokawa, S. Itoh, *Inorg. Chem.* **2005**, *44*, 3010.