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# Copper(II) complexes with neutral bis(pyrazolyl)methane ligands: The influence of steric hindrance on their structures and properties

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**Abstract**

By using the neutral bidentate nitrogen-containing ligands; bis(3,5-dimethyl-1-pyrazolyl)methane (L0″), bis(3,5-diisopropyl-1-pyrazolyl)methane (L1″), bis(3-tertiary-butyl-5-isopropyl-1-pyrazolyl)methane (L3″), and bis(3,5-ditertiary-butyl-1-pyrazolyl)methane (L4″), the copper(II) nitrato complexes $[Cu(L0'')_2(NO_3)]NO_3$ (**1NO$_3$**), $[Cu(L0'')(NO_3)_2]$ (**2**), $[Cu(L1'')(NO_3)_2]$ (**3**), $[Cu(L3'')(NO_3)_2]$ (**4**), and $[Cu(L4'')(NO_3)_2]$ (**5**), chloro complexes $[Cu(L0'')_2Cl]_2(CuCl_4)$ (**6CuCl$_4$**), $[Cu(L0'')_2Cl]_2(Cu_2Cl_6)$ (**6Cu$_2$Cl$_6$**), $[Cu(L1'')Cl_2]$ (**7**), and $[Cu(L3'')Cl_2]$ (**8**), nitrito complexes $[Cu(L0'')(ONO)_2]$ (**9**) and $[Cu(L1'')(ONO)_2]$ (**10**), and the complexes with perchlorate ions $[Cu(L0'')_2(CH_3OH)](ClO_4)_2$ (**11ClO$_4$**) and $[Cu(L1'')_2(H_2O)](ClO_4)_2$ (**12ClO$_4$**) were systematically synthesized and fully characterized by X-ray crystallography and by IR, far-IR, UV–Vis absorption, and ESR spectroscopy. In comparison with the obtained complexes with four bis(pyrazolyl)methanes having different bulkiness at pyrazolyl rings, the second coordination sphere effects on the ligands are discussed in detail. Moreover, the structures and physicochemical properties of these obtained complexes are compared with those of the related complexes with the neutral tridentate tris(pyrazolyl)methane ligand.


*Keywords:* Copper complex; Bis(pyrazolyl)methane; Coordination chemistry; Crystal structure; Nitrogen ligand

## 1. Introduction

Ligands containing N (nitrogen) donor atoms such as pyrazine and pyrimidine have been used for a long time in the field of coordination chemistry [1]. However, the study has been limited because of low solubility of these ligands in most organic solvents. On the other hand, many researchers have made use of organic ligands forming a chelate ring such as 2,2′-bipyridine (bipy) [2–4], ethylenediamine (en) [5], and 1,10-phenanthroline (phen) [4,6]. Therefore, the study of metal complexes with such N donor chelate ligands attracts much attention. In our laboratory, N3 tridentate ligands such as hydrotris(pyrazolyl)borate (tpzb) and tris(pyrazolyl)methane (tpzm) with various transition metal(II) ions have been reported [7–12]. The influences of the overall ligand charge, the overall ligand donor ability, and steric interactions at the pyrazolyl rings have been discussed in detail. In particular, the influences on structures and physicochemical properties of the complexes by changing the number of donor atoms from N3 tridentate to N2 bidentate of the coligands are of increasing interest. In our previous studies, we reported copper(I) and copper(II) complexes using bis(3,5-diisopropyl-1-pyrazolyl)methane (L1″) as an N2 bidentate ligand and compared the structures and characteristics of these complexes with those containing N3 tridentate ligands [13,14]. In this work, various bis(pyrazolyl)methane (bpzm) ligands with variable steric demands at the pyrazolyl rings are presented. The substituents introduced at both the 3rd and 5th positions of the pyrazolyl rings are: methyl (L0″), isopropyl (L1″), and tertiary-butyl (L4″), as shown in Fig. 1. L3″ has tertiary-butyl and isopropyl groups at the 3rd and 5th positions of pyrazolyl rings, respectively.

As described above, bipy, en, phen, and 1,8-naphthyridine (napy) [15] are well known as N2 bidentate ligands,

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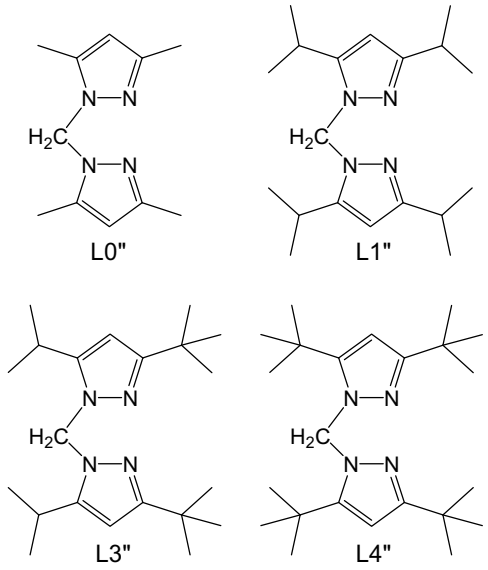


Fig. 1. Structures of N2 bidentate ligands discussed in this work: bis(3,5-dimethyl-1-pyrazolyl)methane (L0″), bis(3,5-diisopropyl-1-pyrazolyl)methane (L1″), bis(3-tertiary-butyl-5-isopropyl-1-pyrazolyl)methane (L3″), bis(3,5-ditertiary-butyl-1-pyrazolyl)methane (L4″).

and many copper(II) complexes with these ligands have been reported. For example, for $[Cu(bipy)X_2]$ ($X = NO_3$ [16], ONO [17], and Cl [18]), $[Cu(en)X'_2]$ ($X' = Cl$ [19] and $N(NO_2)CH_3$ [20]), and $[Cu(phen)(X'')_2]$ ($X'' = NO_3$ [21] and ONO [22]), and $[Cu(napy)(NO_3)_2]$ [23]. Some of the structures of these complexes were clarified by X-ray crystallography. In particular, nitrate and nitrite ions can coordinate to the central copper atom, in a unidentate or bidentate coordination mode. Differences in coordination modes of both nitrate and nitrite ions have been reported by Brill et al. for $[Cu(en)\{N(NO_2)CH_3\}_2]$ [20].

In this work, the copper(II) nitrato complexes $[Cu(L0'')_2(NO_3)]NO_3$ (**1NO$_3$**), $[Cu(L0'')(NO_3)_2]$ (**2**), $[Cu(L1'')(NO_3)_2]$ (**3**), $[Cu(L3'')(NO_3)_2]$ (**4**), and $[Cu(L4'')(NO_3)_2]$ (**5**), the chloro complexes $[Cu(L0'')_2Cl]_2(CuCl_4)$ (**6CuCl$_4$**), $[Cu(L0'')_2Cl]_2(Cu_2Cl_6)$ (**6Cu$_2$Cl$_6$**), $[Cu(L1'')Cl_2]$ (**7**), and $[Cu(L3'')Cl_2]$ (**8**), the nitrito complexes $[Cu(L0'')(ONO)_2]$ (**9**) and $[Cu(L1'')(ONO)_2]$ (**10**), and the complexes with perchlorate ions $[Cu(L0'')_2(CH_3OH)](ClO_4)_2$ (**11ClO$_4$**) and $[Cu(L1'')_2(H_2O)](ClO_4)_2$ (**12ClO$_4$**) were systematically synthesized using four different bpzm ligands that show a difference in bulkiness at the pyrazolyl rings. The complexes $[Cu(L1'')(NO_3)_2]$ (**3**), $[Cu(L1'')Cl_2]$ (**7**), and $[Cu(L1'')(ONO)_2]$ (**10**) with L1″ have been reported before [13,14]. All the complexes were characterized by X-ray crystallography and by IR, far-IR, UV–Vis absorption, and ESR spectroscopy. The influences of the second coordination sphere effects of the ligands on the complexes are examined. The structures and properties of the obtained complexes are also compared with those of the copper(II) complexes having tpzm as an N3 tridentate ligand.

## 2. Experimental

### 2.1. Materials

Preparation and handling of all of the complexes was performed under an argon atmosphere using standard Schlenk tube techniques. Dichloromethane were purified by refluxing and distilling under an argon atmosphere over phosphorous pentoxide. Diethyl ether, toluene, and heptane were purified by refluxing and distilling under an argon atmosphere over sodium benzophenone ketyl [24]. Chloroform, methanol, acetone, 2-propanol, and octane were spectroscopic grade and were used after bubbling with an argon gas. NMR solvents were obtained from Cambridge Isotope Laboratories, Inc. Silica gel for ligand purification was obtained from Merck KGaA. Other reagents are commercially available. The syntheses of ligands (L0″ [25], L1″ [13], and L4″ [26]) and complex $(Ph_4P)_2[Cu_2Cl_6]$ [27] and copper(II) complexes using L1″ ($[Cu(L1'')(NO_3)_2]$ (**3**), $[Cu(L1'')Cl_2]$ (**7**), and $[Cu(L1'')(ONO)_2]$ (**10**) [13,14]) were prepared by publish methods.

### 2.2. Measurements

IR and far-IR spectra were recorded on KBr pellets in the 4000–400 $cm^{-1}$ region and Nujol mull in the 650–150 $cm^{-1}$ region, respectively, using a JASCO FT/IR-550 spectrophotometer. $^1H$ NMR (600 MHz) and $^{13}C$ NMR (150 MHz) spectra were obtained on a Bruker AVANCE-600 NMR spectrometer in chloroform at room temperature. UV–Vis absorption spectra in dichloromethane at room temperature in the 240–1840 nm range were recorded with a JASCO V-570 spectrophotometer unless stated otherwise. ESR spectra as frozen solutions (dichloromethane/1,2-dichloroethane (1/1) or methanol/ethanol (9/1)) were recorded on a Bruker EMX-T ESR spectrometer at 140 K in quartz tubes (diameter 5 nm) with liquid nitrogen temperature controller BVT 3000. The elemental analyses (C, H, N) were performed by the Department of Chemistry at the University of Tsukuba.

### 2.3. Preparation of ligands

#### 2.3.1. $H_2C(3\text{-}tBu\text{-}5\text{-}iPrpz)_2$ L3″

Dichloromethane (130 $cm^3$) was added to a mixture of 3-tertiary-butyl-5-isopropylpyrazole [28] (6.16 g, 37.1 mmol), potassium carbonate (7.76 g, 56.2 mmol), and tetrabutylammonium hydrogensulfate (2.00 g, 5.89 mmol). This solution was bubbled with an argon gas for 15 min. This solution was then heated and gently refluxed for 2 weeks at ~110 °C (inner temperature of autoclave). During the reaction time, the color of the solution became dark brown. The mixture was allowed to cool to room temperature, and then the insoluble material was filtered off and washed with acetone. The filtrate was evaporated under reduced pressure. The remaining dark brown solid was dissolved in toluene (50 $cm^3$). The solution was