

Dinuclear copper(I) complexes of tris(3,5-dimethylpyrazol-1-yl)methane: Synthesis, structure, and reactivity

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Received 6 March 2007; received in revised form 18 April 2007; accepted 1 May 2007

Available online 8 May 2007

Abstract

The reaction of $[\text{Cu}(\text{NCMe})_4](\text{BF}_4)$ with equimolar amounts of the tris(substituted-pyrazolyl)methane ligand HCPz_3 or $\text{HC}(3,5\text{-Me}_2\text{Pz})_3$ yields the respective salts $[\text{Cu}(\text{HCPz}_3)(\text{NCMe})(\text{BF}_4)]$ (**1a**) or $[\text{Cu}(\text{HC}(3,5\text{-Me}_2\text{Pz})_3)(\text{NCMe})(\text{BF}_4)]$ (**1**). The acetonitrile ligand of **1** can be replaced by prazine, 4,4'-dipyridine or 1,4-diisocyanobenzene to yield related mononuclear complexes $[\text{Cu}(\text{HC}(3,5\text{-Me}_2\text{Pz})_3)(\text{pyrazine})(\text{BF}_4)]$ (**2**), $[\text{Cu}(\text{HC}(3,5\text{-Me}_2\text{Pz})_3)(4,4'\text{-bipyridine})(\text{BF}_4)]$ (**3**) or $[\text{Cu}(\text{HC}(3,5\text{-Me}_2\text{Pz})_3)(1,4\text{-CNC}_6\text{H}_4\text{NC})(\text{BF}_4)]$ (**7**), respectively. A series of binuclear copper(I) complexes $\{[\text{Cu}(\text{HC}(3,5\text{-Me}_2\text{Pz})_3)]_2(\mu\text{-BL})\}(\text{BF}_4)_2$ (**4**, BL = pyrazine; **5**, BL = 4,4'-dipyridine; **8**, BL = 1,4-diisocyanobenzene) were prepared by treating equal molar ratio of **1** with related mononuclear complexes **2**, **3** and **7**. In addition, binuclear copper(I) complexes were also prepared from treatment of 2 equiv of **1** with the related bridge ligand. Both of **4** and **5** reformed mononuclear starting complex **1** in acetonitrile solution. However, the more robust complex **8** was stable in acetonitrile solutions. The structure of complexes **1a**, **4**, **5**, and **7** were confirmed by X-ray crystallography. The redox properties of **4** and **8** were examined by cyclic voltammetry and exhibited two quasi-reversible waves suggesting that no significant structural reorganization occurs during the redox process on the electrochemical time scale.

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Keywords: Copper; Diisocyanobenzene; Tris(3,5-dimethylpyrazol-1-yl)methane

1. Introduction

During the past few decades, the structures and functions of some copper proteins have been elucidated, and the results of these studies have been recognized as among the most remarkable advances in biochemistry and bioinorganic chemistry [1,2]. Additionally, synthesis of low molecular weight models for copper containing proteins and their reactions with small molecule substrates are an important approach to understand catalytic mechanism of copper enzymes [3–5]. Model complexes not only provide a better understanding of the biological molecules but also assist in the development of new homogeneous catalysts for selective oxidations under mild conditions and also provide fundamental knowledge in copper(I) coordination chemistry which is necessary for a deeper understanding of copper enzymes. The model structures

of some copper(I)-containing proteins were obtained by X-ray crystallography or NMR spectroscopy [6–9]. In those structures, tris(pyrazolyl)methane, hydrotris(pyrazolyl)borate and other N3 ligand donor sets coordinate to the copper(I) centers are employed because of their facially coordinating ability [6,8–11]. Our interest is in developing copper(I) complexes containing nitrogen donor tripodal ligand sets [12], which are very important in bioinorganic chemistry area. Here, we report a series of novel mononuclear and binuclear copper(I) complexes containing tris(3,5-dimethylpyrazol-1-yl)methane ligand related to the fundamental copper coordination chemistry.

2. Experimental

2.1. Materials

All manipulations were carried out under an atmosphere of purified dinitrogen with standard Schlenk techniques.

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Chemical reagents were purchased from Aldrich Chemical Company Ltd., Lancaster Chemicals Ltd., or Fluka Ltd. All the reagents were used without further purification, apart from all solvents that were dried over Na (Et₂O, hexane, THF) or CaH₂ (CH₂Cl₂, CH₃CN) and then thoroughly degassed before use. [Cu(NCMe)₄](BF₄), HCPz₃, and HC(3,5-Me₂pz)₃ were prepared according to the literature procedures [13,14].

2.2. Measurements

IR spectra were recorded on a Perkin–Elmer System 2000 FT-IR spectrometer. UV–Visible spectra were recorded on a Jasco V-560 spectrophotometer using 1 cm path length quartz cell. ¹H NMR spectra were acquired on a Varian Gemini-200 proton/Carbon FT NMR or a Varian Gemini-500 proton/Carbon FT NMR spectrometer. ESI mass spectra were collected on a Bruker BioTOF Q Quadrupole-TOF mass spectrometer. Fast-atom bombardment (FAB) mass spectra were recorded by using a VG Blotch-5022 mass spectrometer. Elemental analyses were performed on a Heraeus CHN-OS Rapid Elemental Analyzer. Cyclic voltammetry were measured at a scan rate of 100 mV/s on 10⁻³ M MeCN solutions using 0.1 M (Bu₄N)(OTf) as supporting electrolyte and referenced to Fc⁺⁰. A platinum wire counter electrode, a glassy carbon working electrode, and an Ag/AgPF₆ (MeCN) reference electrode were used.

2.3. [Cu(HCPz₃)(NCMe)](BF₄) (1a)

A solid mixture of [Cu(NCMe)₄](BF₄) (0.31 g, 0.80 mmol) and HCPz₃ (0.17 g, 0.80 mmol) was charged in a 100 mL flask and suspended in CH₂Cl₂ (5 mL). After it was stirred for 1 h, the reaction mixture was treated with hexanes (20 mL). The mixture was filtered, and the remaining 0.24 g (81%) pale yellow solid and dried under vacuum. ¹H NMR (*d*₆-acetone): δ 2.45 (s, 3H, CH₃CN), 6.52 (dd, 3H, HCPz₃), 7.91 (dd, 3H, HCPz₃), 8.35 (dd, 3H, HCPz₃), 9.33 (s, 1H, HCPz₃); ESI-Mass: *m/z* = 318.1 [Cu(HCPz₃)(NCMe)]⁺, 277.2 [Cu(HCPz₃)]⁺. Anal. Calc. for C₁₂H₁₃BCuF₄N₇: C, 35.53; N, 24.17; H, 3.23. Found: C, 35.53; N, 23.77; H, 3.28%.

2.4. [Cu(HC(3,5-Me₂Pz)₃)(NCMe)](BF₄) (1)

A solution of HC(3,5-Me₂Pz)₃ (0.298 g, 1.0 mmol) in 10 mL acetone was added to a solution of [Cu(NCMe)₄](BF₄) (0.375 g, 1.0 mmol) in 20 mL acetone followed by stirring for 3 h at room temperature. The reaction mixture solution was reduced to <8 mL and 40 mL of ether was added followed by to yield white precipitates. The white precipitates were filtered and washed with ether to yield 0.376 g (78%) of product. ¹H NMR (*d*₆-acetone): δ 2.50 (s, 3H, CH₃CN), 2.30, 2.65 (s, s; 9H, 9H; 3,5Me-Pz), 6.15 (s, 3H, 4-*H* Pz), 7.91 (s, 1H, HC(3,5-Me₂Pz)₃); ESI-Mass: *m/z* = 402.5 [Cu(HC(3,5-Me₂Pz)₃)(NCMe)]⁺, 361.2

[Cu(HC(3,5-Me₂Pz)₃)]⁺. The spectroscopy data of this compound has been reported by Reger et al. [10].

2.5. [Cu(HC(3,5-Me₂Pz)₃)(pyrazine)](BF₄) (2)

A solution of **1** (0.505 g, 1.03 mmol) in 40 mL methanol and 10 mL acetone was added to a solution of pyrazine (0.482 g, 5.15 mmol) in 20 mL methanol followed by stirring for 3 h at room temperature. The reaction mixture solution was reduced to <8 mL and 20 mL of ether was added followed by to yield yellow precipitates. The yellow precipitates were filtered and washed with ether to yield 0.380 g (70%) of product. ¹H NMR (*d*₆-acetone): δ 8.991 (s, 4H, pyrazine), 8.051 (s, 1H, HC(3,5-Me₂Pz)₃), 6.147 (s, 3H, 4-*H* Pz), 2.699 (s, 9H, 3,5Me-Pz), 2.248 (s, 9H, 3,5Me-Pz). Positive FAB-Mass: *m/z* = 433 [Cu(HC(3,5-Me₂Pz)₃)(pyrazine)]⁺, 361 [Cu(HC(3,5-Me₂Pz)₃)]⁺. Anal. Calc. for C₂₀H₂₆BCuF₄N₈: C, 45.42; H, 4.96; N, 21.19. Found: C, 45.05; H, 5.08; N, 21.15%.

2.6. [Cu(HC(3,5-Me₂Pz)₃)(4,4'-dipyridine)](BF₄) (3)

A solution of **1** (0.503 g, 1.02 mmol) in 10 mL acetone was added to a solution of 4,4'-dipyridine (0.819 g, 5.11 mmol) in 20 mL methanol followed by stirring for 3 h at room temperature. The reaction mixture solution was reduced to <8 mL and 20 mL of ether was added followed by to yield yellow precipitates. The yellow precipitates were filtered and washed with ether to yield 0.463 g (75%) of product. ¹H NMR (*d*₆-acetone): δ 8.990 (s, 4H, 4,4'-dipyridine), 8.073 (s, 4H, 4,4'-dipyridine), 8.072 (s, 1H, HC(3,5-Me₂Pz)₃), 6.154 (s, 3H, 4-*H* Pz), 2.706 (s, 9H, 3,5Me-Pz), 2.244 (s, 9H, 3,5Me-Pz). Positive FAB-Mass: *m/z* = 517 [Cu(HC(3,5-Me₂Pz)₃)(4,4'-dipyridine)]⁺, 361 [Cu(HC(3,5-Me₂Pz)₃)]⁺. Anal. Calc. for C₂₆H₃₀BCuF₄N₈: C, 51.62; H, 5.00; N, 18.52. Found: C, 51.14; H, 5.05; N, 18.53%.

2.7. [Cu₂(HC(3,5-Me₂Pz)₃)₂(μ-pyrazine)](BF₄)₂ (4)

Method A. A solution of **1** (0.258 g, 0.553 mmol) in 30 mL acetone was added to a solution of **2** (0.278 g, 0.55 mmol) in 60 mL methanol and followed by stirring for 3 h at room temperature. The reaction mixture solution was reduced to 3 mL to yield yellow precipitates. The yellow precipitates were filtered and washed with ether to yield 0.386 g (71%) of product. Single crystals suitable for X-ray structure determination were grown from acetone/ether. ¹H NMR (*d*₆-acetone): δ 9.038 (s, 4H, pyrazine), 8.039 (s, 2H, HC(3,5-Me₂Pz)₃), 6.139 (s, 6H, 4-*H* Pz), 2.692 (s, 18H, 3,5Me-Pz), 2.24 (s, 18H, 3,5Me-Pz). Anal. Calc. for C₃₆H₄₈B₂Cu₂F₈N₁₄: C, 44.23; H, 4.95; N, 20.06. Found: C, 44.54; H, 4.85; N, 19.83%.

Method B. A solution of **1** (0.553 g, 1.0 mmol) in 30 mL acetone was added to a solution of pyrazine (0.04 g, 0.5 mmol) in 20 mL methanol and followed by stirring for 3 h at room temperature. The reaction mixture solution

was reduced to 5 mL to yield yellow precipitates. The yellow precipitates were filtered and washed with ether to yield 0.325 g (66%) of product.

2.8. $[\text{Cu}_2(\text{HC}(3,5\text{-Me}_2\text{Pz})_3)_2(\mu\text{-}4,4'\text{-dipyridine})](\text{BF}_4)_2$ (**5**)

Method A. A solution of **1** (0.134 g, 0.286 mmol) in 20 mL acetone was added to a solution of **3** (0.173 g, 0.286 mmol) in 60 mL methanol and followed by stirring for 3 h at room temperature. The reaction mixture solution was reduced to 5 mL to produce yellow precipitates. The yellow precipitates were collected and washed with ether to yield 0.201 g (67%) of product. Single crystals suitable for X-ray structure determination were grown from acetone/ether. ^1H NMR (d_6 -acetone): δ 9.180 (s, 4H, 4,4'-dipyridine), 8.258 (s, 4H, 4,4'-dipyridine), 8.073 (s, 2H, $\text{HC}(3,5\text{-Me}_2\text{Pz})_3$), 6.156 (s, 6H, 4-*H* Pz), 2.704 (s, 18H, 3,5-*Me*-Pz), 2.248 (s, 18H, 3,5-*Me*-Pz). Anal. Calc. for $\text{C}_{42}\text{H}_{52}\text{B}_2\text{Cu}_2\text{F}_8\text{N}_{14}$: C, 47.88; H, 4.97; N, 18.61. Found: C, 47.99; H, 5.06; N, 18.52%.

Method B. A solution of **1** (0.280 g, 0.573 mmol) in 30 mL acetone was added to a solution of 4,4'-dipyridine (0.045 g, 0.288 mmol) in 20 mL methanol and followed by stirring for 3 h at room temperature. The reaction mixture solution was reduced to 5 mL to yield yellow precipitates. The yellow precipitates were filtered and washed with ether to yield 0.191 g (63%) of product.

2.9. $[\text{Cu}(\text{HC}(3,5\text{-Me}_2\text{Pz})_3)(1,4\text{-CNC}_6\text{H}_4\text{NC})](\text{BF}_4)$ (**7**)

A solution of **1** (0.250 g, 0.51 mmol) in 20 mL acetone was added to a solution of 1,4-diisocyanobenzene (0.131 g, 1.02 mmol) in 20 mL acetone followed by stirring for 3 h at room temperature. The white precipitates formed were filtered and washed with ether to yield 0.179 g (17%) of product. Single crystals suitable for X-ray structure determination were grown from acetone/ether. ^1H NMR (d_6 -acetone): δ 8.035 (s, 1H, $\text{HC}(3,5\text{-Me}_2\text{Pz})_3$), 7.801 (dd, 2H, 1,4- $\text{CNC}_6\text{H}_4\text{NC}$), 7.717 (s, 2H, 1,4- $\text{CNC}_6\text{H}_4\text{NC}$), 6.117 (s, 3H, 4-*H* Pz), 2.699 (s, 9H, 3,5-*Me*-Pz), 2.289 (s, 9H, 3,5-*Me*-Pz). Positive FAB-Mass: $m/z = 488$ $[\text{Cu}(\text{HC}(3,5\text{-Me}_2\text{Pz})_3)(1,4\text{-CNC}_6\text{H}_4\text{NC})]^+$, 361 $[\text{Cu}(\text{HC}(3,5\text{-Me}_2\text{Pz})_3)]^+$. IR(nujol) $\nu(\text{CN}) = 2150\text{ cm}^{-1}$. Anal. Calc. for $\text{C}_{24}\text{H}_{27}\text{BCuF}_4\text{N}_8$: C, 49.88; H, 4.71; N, 19.39. Found: C, 49.65; H, 4.66; N, 19.28%.

2.10. $[\text{Cu}_2(\text{HC}(3,5\text{-Me}_2\text{Pz})_3)_2(\mu\text{-}1,4\text{-CNC}_6\text{H}_4\text{NC})](\text{BF}_4)_2$ (**8**)

Method A. A solution of **1** (0.140 g, 0.286 mmol) in 20 mL acetone was added to a solution of **7** (0.165 g, 0.286 mmol) in 60 mL methanol and followed by stirring for 2 h at room temperature. The reaction mixture solution was reduced to 1 mL to produce white precipitates. The white precipitates were collected and washed with ether to yield 0.202 g (69%) of product. ^1H NMR (d_3 -acetonitrile): δ 7.759 (s, 6H, 1,4- $\text{CNC}_6\text{H}_4\text{NC}$ and $\text{HC}(3,5\text{-Me}_2\text{Pz})_3$), 6.076 (s, 6H, 4-*H* Pz), 2.513 (s, 18H, 3,5-*Me*-Pz), 2.353 (s, 18H, 3,5-*Me*-Pz). ^{13}C NMR (d_3 -acetonitrile): δ 152.349 (s, C of 3,5-*Me*-Pz), δ 148.691 (s, br, 1,4- $\text{CNC}_6\text{H}_4\text{NC}$), δ 142.697 (s, C of 3,5-*Me*-Pz), δ 129.313 (s, 1,4- $\text{CNC}_6\text{H}_4\text{NC}$), δ 128.553 (s, 1,4- $\text{CNC}_6\text{H}_4\text{NC}$), δ 107.553 (s, C of 3,5-*Me*-Pz), δ 68.566 (s, $\text{HC}(3,5\text{-Me}_2\text{Pz})_3$), δ 13.924 (s, 3,5-*Me*-Pz), δ 11.216 (s, 3,5-*Me*-Pz). Positive FAB-Mass: $m/z = 937$ $[(\text{Cu}(\text{HC}(3,5\text{-Me}_2\text{Pz})_3))_2(1,4\text{-CNC}_6\text{H}_4\text{NC})]^{2+}$ (BF_4^-), 426 $[(\text{Cu}(\text{HC}(3,5\text{-Me}_2\text{Pz})_3))_2(1,4\text{-CNC}_6\text{H}_4\text{NC})]^{2+}$, 489 $[\text{Cu}(\text{HC}(3,5\text{-Me}_2\text{Pz})_3)(1,4\text{-CNC}_6\text{H}_4\text{NC})]^+$, 361 $[\text{Cu}(\text{HC}(3,5\text{-Me}_2\text{Pz})_3)]^+$. IR(nujol) $\nu(\text{CN}) = 2158\text{ cm}^{-1}$. Anal. Calc. for $\text{C}_{40}\text{H}_{48}\text{B}_2\text{Cu}_2\text{F}_8\text{N}_{14}$: C, 46.84; H, 4.72; N, 19.12. Found: C, 46.65; H, 4.70; N, 19.32%.

Method B. A solution of 1,4-diisocyanobenzene (0.012 g, 0.094 mmol) in 20 mL acetonitrile was added to a solution of **1** (0.109 g, 0.22 mmol) in 20 mL acetonitrile followed by stirring for 2 h at room temperature. The reaction mixture solution was reduced to <8 mL to yield white precipitates. The white precipitates were filtered and washed with ether to yield 0.042 g (40%) of product.

2.11. Crystallography

All crystals were mounted on a thin glass fiber by using oil (Paratone-N, Exxon) before being transferred to the diffractometer. Diffraction data for $[\text{Cu}(\text{HCPz}_3)(\text{NCMe})](\text{BF}_4)$ (**1a**), $[\text{Cu}_2(\text{HC}(3,5\text{-Me}_2\text{Pz})_3)_2(\mu\text{-pyrazine})](\text{BF}_4)_2$ (**4**), $[\text{Cu}_2(\text{HC}(3,5\text{-Me}_2\text{Pz})_3)_2(\mu\text{-}4,4'\text{-dipyridine})](\text{BF}_4)_2$ (**5**), and $[\text{Cu}(\text{HC}(3,5\text{-Me}_2\text{Pz})_3)(1,4\text{-CNC}_6\text{H}_4\text{NC})](\text{BF}_4)$ (**7**) were collected at 150(3) or 200(2) K on a Bruker Nonius Kappa CCD diffractometer (Mo $\text{K}\alpha$ radiation, $\lambda = 0.71073\text{ \AA}$). Data processing was performed with the integrated program package SHELXTL [15]. All structures were solved using direct methods and refined using full-matrix least squares on F^2 using the program SHELXL-97 [16]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using a riding model and included in the refinement at calculated positions. The data were corrected for absorption on the basis of Ψ scans. A summary of relevant crystallographic data for **1a**, **4**, **5**, and **7** is provided in Table 1.

3. Results and discussion

The copper(I) complex $[\text{Cu}(\text{HC}(3,5\text{-Me}_2\text{Pz})_3)(\text{NCMe})](\text{BF}_4)$ (**1**) and $[\text{Cu}(\text{HCPz}_3)(\text{NCMe})](\text{BF}_4)$ (**1a**) were generated in high yield by the reaction of $[\text{Cu}(\text{NCMe})_4](\text{BF}_4)$ with an equimolar amount of $\text{HC}(3,5\text{-Me}_2\text{Pz})_3$ and HCPz_3 at room temperature for ca. 60 min under N_2 . The molecular structure of the complex cation of $[\text{Cu}(\text{HCPz}_3)(\text{NCMe})](\text{BF}_4)$ (**1a**) is shown in Fig. 1. The coordination geometry around the copper atom is best described as a distorted tetrahedron with a facial tridentate ligand chelated. The intraligand N–Cu–N angles are restrained by the chelate rings to 87.83°, and the average angles from nitrogen atoms of acetonitrile donor to the

Table 1

Crystallographic data for [Cu(HCPz₃)(NCMe)](BF₄) (**1a**), [Cu₂(HC(3,5-Me₂Pz)₂(μ-pyrazine)](BF₄)₂ (**4**), [Cu₂(HC(3,5-Me₂Pz)₂(μ-4,4'-dipyridine)](BF₄)₂ (**5**), and [Cu(HC(3,5-Me₂Pz)₃](1,4-CNC₆H₄NC)](BF₄) (**7**)

	1a	4	5	7
Chemical formula	C ₂₄ H ₂₆ B ₂ Cu ₂ F ₈ N ₁₄	C ₄₂ H ₆₀ B ₂ Cu ₂ F ₈ N ₁₄ O ₂	C ₄₄ H ₅₆ B ₄ Cu ₂ F ₁₄ N ₁₄ O ₂	C ₂₇ H ₃₂ BCuF ₄ N ₈ O
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
Fw	811.29	1093.74	1249.35	634.96
<i>a</i> (Å)	21.1842(3)	10.7719(2)	27.2373(3)	13.8840(4)
<i>b</i> (Å)	10.8143(3)	11.55800(10)	7.69130(10)	15.1800(4)
<i>c</i> (Å)	15.4268(1)	11.7128(2)	31.4124(4)	15.0230(4)
α (°)	90	65.5150(10)	90	90
β (°)	109.8743(7)	80.5630(10)	109.1720(10)	99.9170(10)
γ (°)	90	72.3490(10)	90	90
<i>V</i> (Å ³)	3323.67(9)	1263.41(3)	1337.3(7)	3119.92(15)
<i>Z</i>	4	1	4	4
<i>D</i> _{calc} (g cm ⁻³)	1.621	1.438	1.335	1.352
<i>R</i> ^a	0.0387	0.0468	0.0712	0.0768
<i>R</i> _w ^a	0.0875	0.1310	0.2065	0.2036
GOF	1.004	1.046	1067	1.063

$$^a I > 2\sigma(I), R = \sum ||F_o| - |F_c|| / \sum |F_o|, R_w = [(\sum w(|F_o| - |F_c|)^2) / \sum wF_o^2]^{1/2}.$$

pyrazolyl nitrogen atoms is 126.61°. The Cu–N distances for the tridentate ligand vary from 2.053(2) to 2.1377(19) Å (average 2.087 Å). The fourth Cu–N distance to the nitrogen atom of acetonitrile is much shorter at 1.871(2) Å, which is similar to previously reported complex [Cu(HC(3-Bu¹Pz)₃)(NCMe)](PF₆) [10]. This may imply that the steric hindrance at the third position of the pyrazolyl rings does not significantly affect the bonding distance and strength of the acetonitrile complexes because this ligand is not very space demanding. The ESI-MS(+) spectrometry data of complexes **1** and **1a** show the molecular ion peaks and their corresponding fragment ion peaks, which lose one-coordinated MeCN. The ν_{CN} at 2273 and 2275 cm⁻¹ observed for **1** and **1a** also suggests the presence of a coordinated MeCN, consistent with the X-ray structure of **1a** Table 2.

The mononuclear complexes, [Cu(HC(3,5-Me₂Pz)₃](pyrazine)](BF₄) (**2**) and [Cu(HC(3,5-Me₂Pz)₃](4,4'-dipyridine)](BF₄) (**3**), were prepared by the reaction of excess

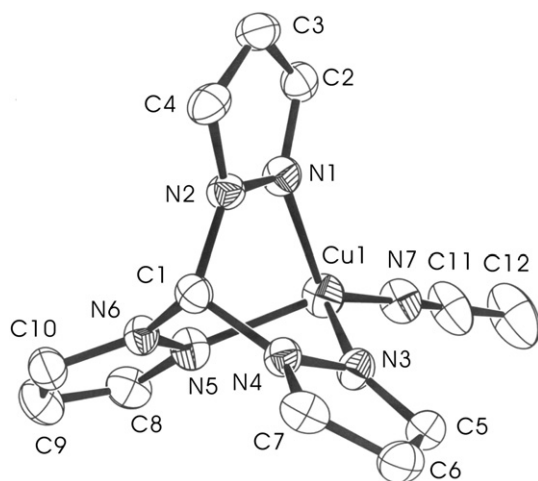


Fig. 1. Crystal structure of the cation of [Cu(HCPz₃)(NCMe)](BF₄) (**1a**).

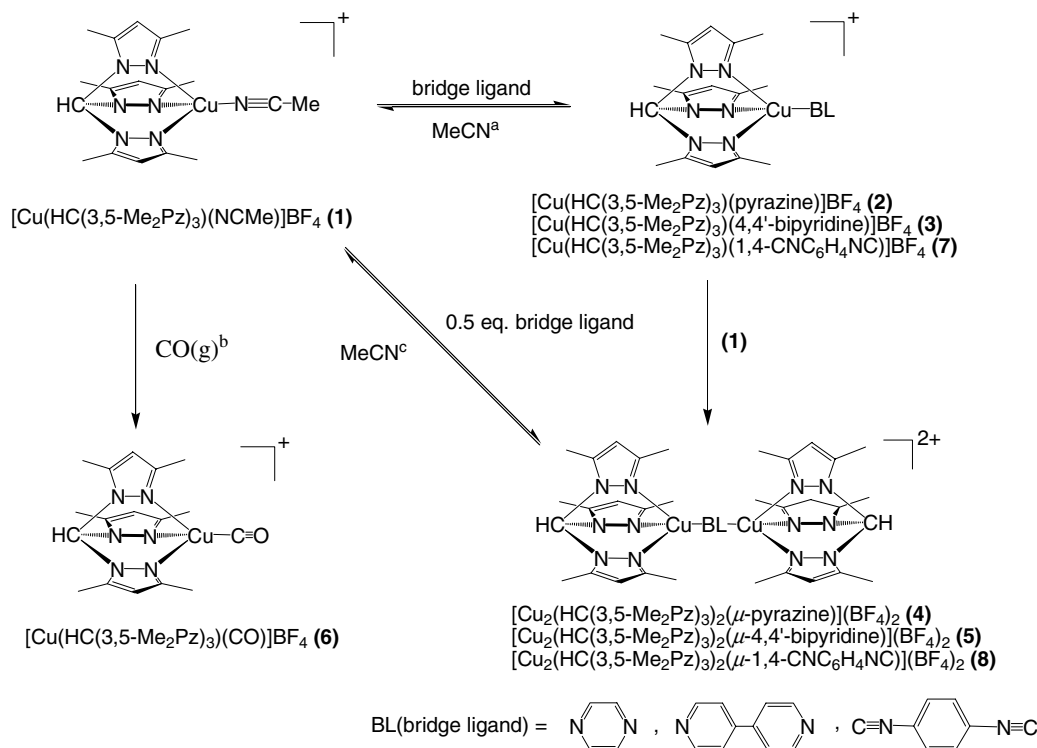
ligands (i.e. pyrazine and 4,4'-dipyridyl) with **1**. The reverse reactions took place by adding acetonitrile into an acetone solution of **2** and **3**, allowing the starting **1** to be recovered. The binuclear complexes, [Cu₂(HC(3,5-Me₂Pz)₂(μ-pyrazine)](BF₄)₂ (**4**) and [Cu₂(HC(3,5-Me₂Pz)₂(μ-4,4'-dipyridine)](BF₄)₂ (**5**), were also prepared by using equal molar ratio of **1** and mononuclear complexes **2** or **3**, respectively. In addition, **4** and **5** can also be prepared by the 2:1 molar ratio of **1** and its related ligand. In the present of acetonitrile donor, both of **4** and **5** reformed mononuclear starting complex **1**. The overall reactions are depicted in Scheme 1.

The X-ray structures of cations of [Cu₂(HC(3,5-Me₂Pz)₂(μ-pyrazine)](BF₄)₂ (**4**) and [Cu₂(HC(3,5-Me₂Pz)₂(μ-4,4'-dipyridine)](BF₄)₂ (**5**) are shown in Fig. 2. The complexes **4** and **5** consist of dinuclear cations and two BF₄⁻ anions. In the cations, the two Cu(I) centers are bridged by pyrazine or 4,4'-dipyridine, forming a

Table 2
Selected bond length (Å) and angles (°) of **1a**, **4**, **5**, and **7**

	1a	4	5	7
Cu(1)–N(1)	2.1377(19)	2.119(2)	2.077(2)	2.094(4)
Cu(1)–N(3)	2.053(2)	2.056(3)	2.133(3)	2.062(4)
Cu(1)–N(5)	2.0707(19)	2.141(2)	2.078(14)	2.056(4)
Cu(1)–N(7)	1.871(2)	1.941(3)	1.931(4)	
Cu(1)–C(17)				1.819(5)
C(17)–N(7)	1.163(7)			
C(24)–N(8)	1.189(8)			
N(1)–Cu(1)–N(7)	121.46(9)	117.09(10)	135.72(15)	
N(3)–Cu(1)–N(7)	130.27(8)	141.7(11)	121.17(5)	
N(5)–Cu(1)–N(7)	128.11(9)	119.57(10)	122.67(15)	
N(1)–Cu(1)–C(17)				122.3(2)
N(3)–Cu(1)–C(17)				130.26(19)
N(5)–Cu(1)–C(17)				129.0(2)
N(1)–Cu(1)–N(3)	85.59(8)	89.24(10)	87.79(13)	87.55(16)
N(1)–Cu(1)–N(5)	88.79(7)	88.50(9)	87.39(13)	87.22(16)
N(3)–Cu(1)–N(5)	89.14(8)	86.20(10)	88.62(13)	86.75(16)

Numbers in parentheses are estimated standard deviations of the last significant figure.



^a only **2** and **3**, detected by ¹H NMR monitoring. ^b detected by IR. ^c only **4** and **5**, detected by ¹H NMR monitoring.

Scheme 1. Reactions of copper(I) complexes.

centrosymmetrical homobinuclear complexes. Copper center of **4** and **5** is four-coordinate binding a tridentate HC(3,5-Me₂Pz)₃ ligand plus the nitrogen atom of pyrazine or 4,4'-dipyridine in a distorted tetrahedral geometry, respectively. The local geometry around the copper center of **4** and **5** is relatively similar to that of **1a**. The average Cu–N(Pz) distances for the tridentate ligand of **4** (2.105 Å) and **5** (2.096 Å) are slightly longer to **1a** (2.087 Å). The Cu–N(Pz) bond distances of **4** and **5** are also slightly longer, compared with the corresponding mean bond distances of Cu(HB(3,5-Me₂Pz)₃)(pyrazine) which bears a negative tridentate ligand bond to copper(I) atom [17]. The Cu–N(bridge) bond distances are slightly shorter by 0.1 Å, compared with that of Cu(HB(3,5-Me₂Pz)₃)(pyrazine) [17] and the literature values for Cu(I)–N(μ-pyrazine) (2.022–2.056 Å) [18,19]. This may be a consequence of the expected stronger σ-donation from the pyrazine or 4,4'-dipyridine ligand to copper atom between positive [Cu(HC(3,5-Me₂Pz)₃)] moiety than the neutral [Cu(HB(3,5-Me₂Pz)₃)] moiety.

The addition of CO to a solution of **1–5** in CH₂Cl₂ gave the mononuclear Cu^I-carbonyl [Cu(HC(3,5-Me₂Pz)₃](CO)](BF₄) (**6**), which was previously reported by Reger et al. as its PF₆[−] derivative [10]. The CO stretching frequency at 2112 cm^{−1} is in agreement with a terminal carbonyl in **6**. On the other hand, treatment of **1** with 1,4-diisocyanobenzene (isoelectron to CO) affords a mononuclear complex [Cu(HC(3,5-Me₂Pz)₃](1,4-CNC₆H₄NC)](BF₄) (**7**) as a colorless precipitate.

The molecular structure of the complex cation of [Cu(HC(3,5-Me₂Pz)₃](1,4-CNC₆H₄NC)](BF₄) (**7**) is shown in Fig. 3. The copper(I) ion has a distorted tetrahedral geometry with ligation to the tridentate HC(3,5-Me₂Pz)₃ ligand plus a carbon atom of 1,4-diisocyanobenzene. The Cu–N(Pz) bond distances of **7** are shorter than **1a**, **4** and **5** which may imply isocyanide having a strong σ-donor role toward copper(I) center to increase Cu–N(Pz) back bonding ability. The Cu–C bond of isocyanide is short (1.819 Å) and compares well with the shortest reported in the literature [20–24]. In addition, the C(17)–N(7) distance (1.163 Å) of copper bonded isocyanide is slightly shorter than the C(24)–N(8) distance (1.189 Å) of unbonded isocyanide indicating that the dominant mode of bonding of isocyanide is σ-donation with only minor contributions from π-acceptor interaction. The ¹H NMR spectrum of **7** exhibits well separated AA'BB' pattern for benzene ring protons, which is characteristic of two different coordinated environments on the *para*-diisocyanobenzene ring protons, one by copper coordinated and the other one free. The CNR stretching frequencies of **7** appear at 2150 and 2125(shoulder) cm^{−1}, also suggesting two different bonding mode, in agreement with the X-ray data.

The binuclear complex [Cu₂(HC(3,5-Me₂Pz)₃)₂](μ-1,4-CNC₆H₄NC)](BF₄)₂ (**8**) was prepared by using equal molar ratio of **1** and mononuclear complexes **7**. Treatment of **1** with 0.5 equiv. of 1,4-diisocyanobenzene also gives binuclear complex **8**. Complexes **7** and **8** do not take place reverse reactions by adding acetonitrile because the

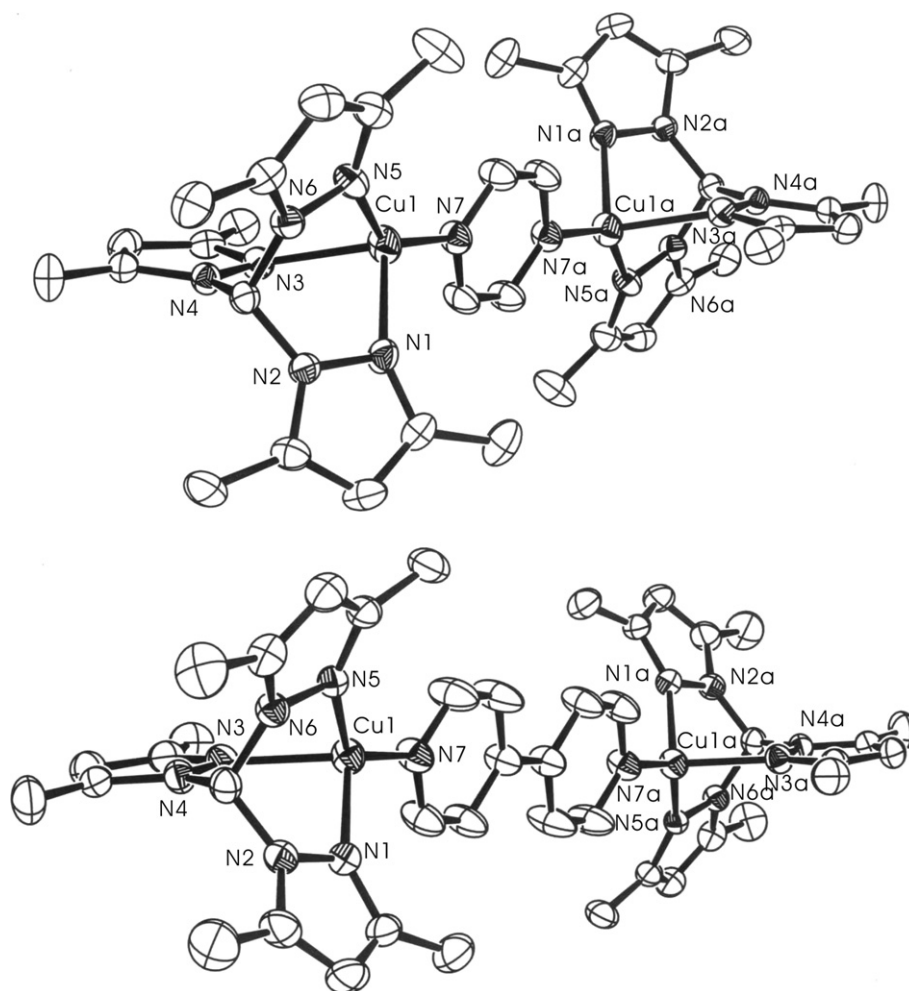


Fig. 2. ORTEP representation of the crystal structures of the cation of $[\text{Cu}_2(\text{HC}(3,5\text{-Me}_2\text{Pz})_3)(\mu\text{-pyrazine})](\text{BF}_4)_2$ (**4**) (up) and $[\text{Cu}_2(\text{HC}(3,5\text{-Me}_2\text{Pz})_3)_2](\mu\text{-4,4' -dipyridine})](\text{BF}_4)_2$ (**5**) (down).

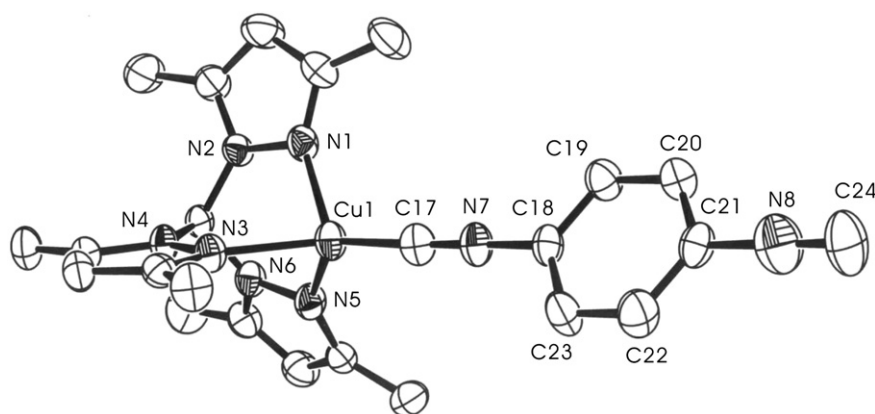


Fig. 3. ORTEP representation of the crystal structures of the cation of $[\text{Cu}(\text{HC}(3,5\text{-Me}_2\text{Pz})_3)(1,4\text{-CNC}_6\text{H}_4\text{NC})](\text{BF}_4)$ (**7**).

copper-isocyanide bond is stronger than copper–pyrazine (pyridine) bond. We are not able to grow single crystal for **8** to obtain its crystallographic data. However, the ^1H NMR spectrum of complex **8** shows a centrosymmetrical environment of 1,4-isocyanobenzene ring protons, which is

significant difference with **7**. The CNR stretching frequency only at 2158 cm^{-1} is also in agreement with a centrosymmetrical homobinuclear bridging isocyanide ligand in **8**.

Isocyanides are potential ligand-directed probes of metalloprotein coordination due to their strong IR absorption

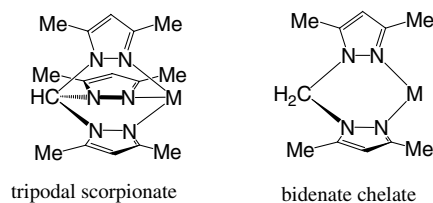
and preference for low-valence metal coordination chemistry [25,26]. Although the isocyanide ligand is isoelectronic with CO, its mode of bonding is rather different. Metal carbonyls exhibit strong π backbonding between the electron-rich low-valence metal and the empty antibonding orbitals of π symmetry on CO, which results in a weakening of the CO bond and a decrease in carbonyl stretching frequency, often well below the free-ligand value. In contrast, isocyanides are poorer π acceptors and stronger σ -donors. In Cu(I) isocyanide complexes, the frequency of the CNR stretch generally lies above the free-ligand value, implying that the dominant mode of bonding is σ -donation with only minor contributions from π -acceptor interactions. This is probably due to the inability of the closed d^{10} configuration to effectively engage in backbonding. Table 3 lists several copper(I) complexes containing N3 ligands and isocyanide donor. We observe the $\Delta\nu_{\text{CN}}$ of complexes **7** (32) and **8** (40) are higher than the value observed for similar complex [Cu(HB(Pz)₃)(CN^tBu)] (17), which is containing N3 anionic ligand [27]. This implies that N3 neutral ligand complexes **7** and **8** have more σ -donation character in the isocyanide bonding mode than N3 anionic ligand complex [Cu(HB(Pz)₃)(CN^tBu)]. On the other hand, the unusually high $\Delta\nu_{\text{CN}}$ value observed for [Cu(HB(3,5-(CF₃)₂Pz)₃)(CN^tBu)] (58) is a direct result of the fluorination of the tris(pyrazolyl)borate ligand [22].

Several related copper(I) complexes containing bis(pyrazolyl)methane (N2 ligand) and bridge by pyrazine ligand are reported very recently [19]. In complexes **1a**, **4**, **5**, and **7**, tris(pyrazolyl)methane coordinate by three nitrogen atoms with tripod scorpionate formation (N3 ligand) compare with N2 ligand as shown in Scheme 2. The coordinating ability of tris(pyrazolyl)methane and bis(pyrazolyl)methane are consequence of favorable electronic and geometric factors. For example, the bidentate chelating N2 ligand bis(pyrazolyl)methane react with [Cu(NCMe)₄]⁺ afforded the monomeric air stable bis chelates [Cu(H₂CPz₂)₂]⁺ and mono chelate air-sensitive Y-shaped [Cu(H₂CPz₂)(NCMe)]⁺ [19,28]. However, the N3 ligand tris(pyrazolyl)methane react with copper(I) source [Cu(NCMe)₄]⁺ only afford a stable monomeric complex **1a**. The raising of the ligand density from two to three will

Table 3
Cyanide stretching frequencies for copper(I) isocyanide complexes containing N3 ligands

	ν_{CN} (cm ⁻¹)	$\Delta\nu_{\text{CN}}$	Ref.
1,4-Diisocyanobenzene	2118		[25]
^t BuNC	2138		[22]
[Cu(HB(Pz) ₃)(CN ^t Bu)]	2155	17	[27]
[Cu(HB(3,5-(CF ₃) ₂ Pz) ₃)(CN ^t Bu)]	2196	58	[22]
[Cu(HC(3,5-Me ₂ Pz) ₃)]	2150, 2125(sh)	32	This
(1,4-CNC ₆ H ₄ NC)BF ₄ (7)			work
[Cu(HC(3,5-Me ₂ Pz) ₃) ₂]	2158	40	This
(μ -1,4-CNC ₆ H ₄ NC)(BF ₄) ₂ (8)			work

$\Delta\nu_{\text{CN}}$, difference of cyanide stretching frequencies between coordinating isocyanide and free ligand.



Scheme 2. Structure comparison for ligand tris(pyrazolyl)methane and bis(pyrazolyl)methane.

result in increase the stability if the copper(I) complexes with tripodal scorpionate ligand. Indeed, complexes **2–8** are air- and moisture-stable in solid state. In solution, complexes **2–5** will gradually react with dioxygen and turn to green in 5 h at room temperature. The isocyanide complexes **7** and **8** are air stable in both solid and solution state. These observations are similar related to complex **1**, which reacts with dioxygen to give a μ - η^2 : η^2 -peroxo complex, [Cu₂(HC(3,5-Me₂Pz)₃)₂ (μ -O₂)](PF₆)₂, at -80 °C to $+7$ °C and then gradually decomposes to a bis(μ -hydroxo) complex, [Cu₂(HC(3,5-Me₂Pz)₃)₂ (μ -OH)₂](PF₆)₂ [11]. On the other hand, the air-sensitive bis(pyrazolyl)methane copper(I) complex [Cu(H₂CPz₂)(NCCH₃)](ClO₄) react with dioxygen also gave the bis(μ -hydroxo) complex [28].

The redox properties of **4** and **8** were examined by cyclic voltammetry in methanol solution under N₂. Complexes **4** and **8** (Fig. 4) exhibited two quasi-reversible waves suggesting that no significant structural reorganization occurs during the redox process on the electrochemical time scale. These two quasi-reversible redox waves can be ascribed to electrode processes in the following equations:

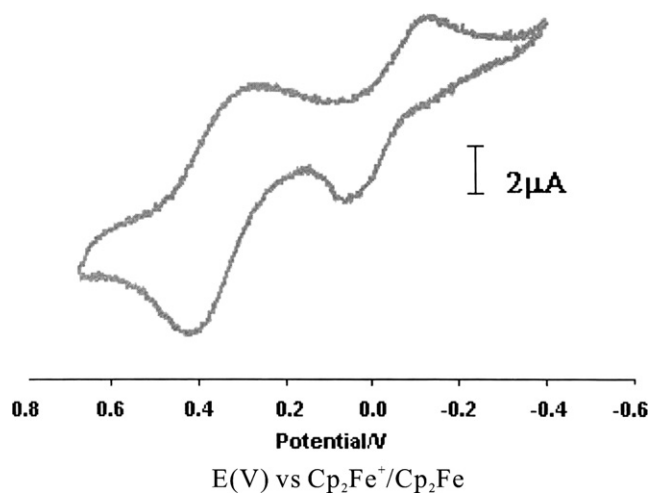
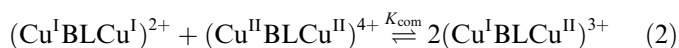
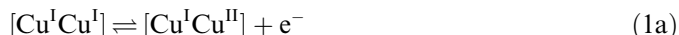


Fig. 4. CV of **8** in MeOH (1×10^{-3} M). Scan rate = 20 mV/s, electrolyte = (Bu₄N)(OTf) (0.1 M).

Table 4
CV data and comproportionation constant for dicopper complexes

Complex	$E_{1/2}^a$	ΔE	K_{com}	Ref.
$[\text{Cu}_2(\text{TDTO})(\text{MeCN})_2](\text{ClO}_4)_2^b$	+140 +568	124 122	2×10^7	[30]
$[\text{Cu}_2(\text{Ph}_4\text{bdptz})(\text{MeCN})_2](\text{OTf})_2^b$	+41 +516	122 124	1×10^8	[29]
$[\text{Cu}_2(\text{H}_2\text{C}(3,5\text{-Me}_2\text{Pz})_2)(\text{MeCN})_2(\mu\text{-pyrazine})](\text{ClO}_4)_2$	+164 +548	174 226	3×10^6	[19]
$[\text{Cu}(\text{HC}(3,5\text{-MePz})_3)]_2(\mu\text{-pyrazine})(\text{BF}_4)_2(\mathbf{4})$	-54 +354	146 186	8×10^6	This work
$[\text{Cu}(\text{HC}(3,5\text{-MePz})_3)]_2(\mu\text{-1,4-CNC}_6\text{H}_4\text{NC})(\text{BF}_4)_2(\mathbf{8})$	-32 +347	164 222	2.6×10^6	This work

^a mV (vs. $\text{Cp}_2\text{Fe}^+/\text{Cp}_2\text{Fe}$).

^b TDTO, 5,5,16,16-tetramethyl-23,24-dioxo-3,7,14,18-tetraazatricyclo[18.2.1.19,12]tetracosane-1(22), 2,7,9,11,13,18,20-octaene; Ph_4bdptz , 1,4-bis[bis(6-phenyl-2-pyridyl)methyl]phthalazine; OTf, triflate.

Electrochemical studies on a series of dicopper(I) complexes supported by nitrogen donor ligands (Table 4), including the complex $[\text{Cu}_2(\text{H}_2\text{C}(3,5\text{-Me}_2\text{Pz})_2)(\text{MeCN})_2(\mu\text{-pyrazine})](\text{ClO}_4)_2$, also showed well-resolved sequential one-electron redox waves at comparably high potentials than complexes **4** and **8** [19,29,30]. Redox potentials of copper complexes are influenced by many factors, including the type of donor atoms and the geometry of coordinated complexes. Here, complexes **4** and **8** have same type coordination geometry around copper center and donor atoms but different donor numbers to complex $[\text{Cu}_2(\text{H}_2\text{C}(3,5\text{-Me}_2\text{Pz})_2)(\text{MeCN})_2(\mu\text{-pyrazine})](\text{ClO}_4)_2$. The relatively low redox potentials of **4** and **8** are probably due to the facial tridentate N-donor vs. bidentate N-donor ligand, which making the oxidation to Cu(II) more easy. It also can be explained by the N3 ligand of tris(pyrazolyl)methane is more electron donating compared to the N2 ligand of bis(pyrazolyl)methane.

By using the $E_{1/2}$ values for the two redox couples, a comproportionation constant, K_{com} , for **4** and **8** were calculated according to the equilibrium in Eq. (2) [31,32]. The small value of K_{com} suggests that the mixed-valence species should have less thermodynamic stability. Therefore, attempts to generate the mixed-valence species from **4** and **8** have been unsuccessful. In contrast to the two redox waves seen with **4** and **8**, only one apparent wave, corresponding to the oxidation of both copper centers, is displayed by **5**. This result indicates that the two noninteracting copper ions in each of compound **5** are oxidized at approximately the same potential [33]. The bridging units in **4** and **8**, therefore, confer greater communication between the copper ions.

In summary, a family of dinuclear copper(I) complexes were prepared and characterized with tris(3,5-dimethylpyrazol-1-yl)methane containing pyrazine, 4,4'-bipyridine, and 1,4-diisocyanobenzene bridge ligand. Both of **4** and **5** lost bridge ligand (pyrazine and 4,4'-dipyridine) in acetonitrile solution to reform mononuclear starting com-

plex **1**. However, complex **8** does not take place ligand exchange reactions by adding acetonitrile. The synthesis and characterization of those compounds have provided fundamental knowledge about copper(I) complexes containing nitrogen donor ligand, necessary for a deeper understanding of the copper enzymes in particular as well as pyrazolyl complexes in general.

Acknowledgements

Financial support of the National Science Council of the Republic of China is highly appreciated. We thank Mr. T.-S. Kao for collecting X-ray data.

Appendix A. Supplementary material

CCDC 625281, CCDC 603434, CCDC 603436 and CCDC 603435 contain the supplementary crystallographic data for **1a**, **4**, **5** and **7**. These 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) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.05.006](https://doi.org/10.1016/j.jorganchem.2007.05.006).

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