# Crystal Structure of Pyrazolato-bridged Copper(I) Polynuclear Complexes

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We prepared a series of copper(I) polynuclear complexes bridged by three different alkyl substituted pyrazolate anions. From X-ray analysis, these differences reflected their molecular structures. These structural changes also reflected some properties in their IR, far-IR, UV–vis, and NMR spectra.
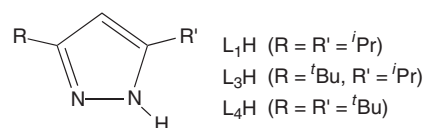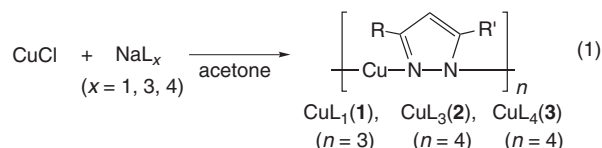
Designs and researches of d^{10} metal complexes with polynuclear structures are a subject of current interest because of their potential abilities for selective transport of metal ions in biological systems, catalyses for efficient chemical transformations, and other physicochemical properties such as luminescence for useful inorganic materials.[1] Pyrazole is one of bidentate ligands, which are easily obtained from β-diketones and hydrazine. Fackler and co-workers have reported the syntheses and crystal structures of $[M(\mu\text{-}3,5\text{-}Ph_2pz)]_3$ (M = Cu(I), Ag(I), and Au(I)) (pz = pyrazolate anion).[2] These complexes formed trimeric metallocycle. However, the relationships between coordinated metal ions and substituent groups of pyrazole rings are unclear. Moreover, the syntheses and crystal structures of $[Cu(\mu\text{-}3,5\text{-}Me_2pz)]_3$, $[Au(\mu\text{-}3,5\text{-}(CF_3)_2pz)]_3$, and $[Au(\mu\text{-}4\text{-}Mepz)]_3$ have been reported by Thompson,[3] Banditelli[4] and Omary,[5] and Raptis,[6] respectively. We are concerted with the relationship between coordination mode and bulkiness of ligand.[7] In this research, we used three different alkyl substituted pyrazoles such as 3,5-diisopropyl-1-pyrazole (3,5-$^{i}Pr_2pzH = L_1H$), 3-*tert*-butyl-5-isopropyl-1-pyrazole (3-^{t}Bu-5-$^{i}PrpzH = L_3H$) and 3,5-di-*tert*-butyl-1-pyrazole (3,5-$^{t}Bu_2pzH = L_4H$) (Scheme 1) for syntheses of polynuclear copper(I) complexes. By use of these ligands, we can obtain the first examples of tetranuclear copper(I) complexes with square and diamond geometry, depending on the hindrance of pyrazole rings. These obtained complexes were

Scheme 1.

characterized by X-ray diffraction, IR, far-IR, UV–vis, and NMR spectroscopies.

In an analogous manner applied to the preparation of silver(I) compound $[Ag(\mu\text{-}3,5\text{-}Ph_2pz)]_3$,[2] copper(I) polynuclear complexes, $[Cu(\mu\text{-}3,5\text{-}^{i}Pr_2pz)]_3$ (**1**), $[Cu(\mu\text{-}3\text{-}^{t}Bu\text{-}5\text{-}^{i}Prpz)]_4$ (**2**), and $[Cu(\mu\text{-}3,5\text{-}^{t}Bu_2pz)]_4$ (**3**), were prepared by the reaction of a sodium salt of appropriate pyrazoles with CuCl in acetone.[8]

The structures of all the complexes (**1–3**) with their atomic numbering schemes are shown in Figure 1 (Side views of complexes **2** and **3** are also shown in Graphical Abstract).[9] The complex **1** is formed trimeric metallocycle, in which the nitrogen atoms of the pyrazole rings bridge metal ions. This structure resembles the complexes described in introduction. Its central nine-membered ring, Cu_3N_6 is a qualitatively planar with almost linear coordination mode (av N–Cu–N angle; 172.5°). On the other hand, by use of larger substituents of pyrazoles (L_3H and L_4H), the obtained complexes are not trimeric metallocycle but tetrameric one. To our knowledge, these are the first examples of tetranuclear copper(I) complexes bridged by alkyl substi-
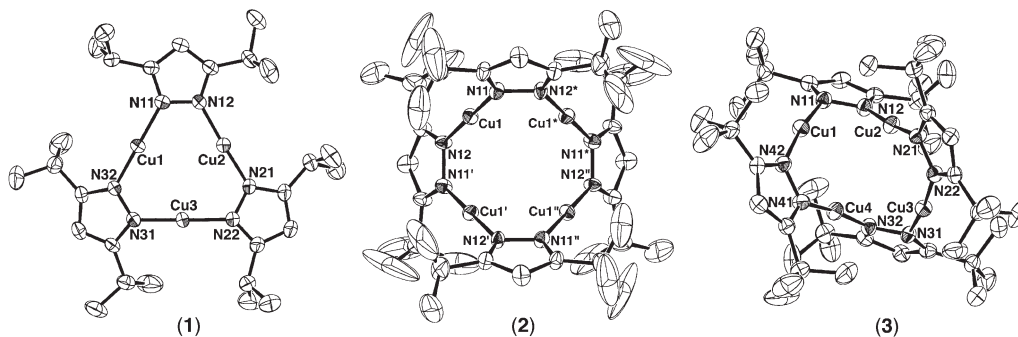
Figure 1. Molecular structures of **1–3** (ORTEP, 50% (**1** and **3**) 30% (**2**) probability ellipsoids) with atomic numbering. Selected bond distances (Å) and angles (deg) are as follows. **1**: Cu1–N11, 1.861(3); Cu1–N32, 1.863(3); Cu2–N12, 1.843(3); Cu2–N21, 1.843(3); Cu3–N22, 1.863(3); Cu3–N31, 1.859(3); Cu1···Cu2, 3.1907(6); Cu2···Cu3, 3.1997(7); Cu3···Cu1, 3.2370(6); N11–Cu1–N32, 171.4(1); N12–Cu2–N21, 176.9(1), N22–Cu3–N31, 169.1(1). **2**: Cu1–N11, 1.833(8); Cu1–N12, 1.851(8); N11–Cu1–N12, 179.6(4), Cu1···Cu1′, 3.071(2); Cu1···Cu1″, 4.343(2). **3**: Cu1–N11, 1.851(3); Cu1–N42, 1.849(3); Cu2–N12, 1.862(3); Cu2–N21, 1.858(3); Cu3–N22, 1.854(3); Cu3–N31, 1.855(3); Cu4–N32, 1.857(3); Cu4–N41, 1.865(3); Cu1···Cu2, 2.9877(7); Cu2···Cu3, 2.9708(7); Cu3···Cu4, 2.9783(7); Cu4···Cu1, 2.9718(7); Cu1···Cu3, 4.8488(7); Cu4···Cu2, 3.3999(7); N11–Cu1–N42, 169.3(1); N12–Cu2–N21, 173.5(1); N22–Cu3–N31, 169.9(1); N32–Cu4–N41, 172.7(1).

tuted pyrazoles.[5,10,11] Each of their bonds distances (av Cu–N; **2**: 1.84 Å, **3**: 1.86 Å) shows almost the same value with **1** (av Cu–N; 1.86 Å). The bond angles of **2** and **3** (av N–Cu–N; **2**: 179.6°, **3**: 171.4°) reveal central copper atoms are two-coordinate in a nearly linear arrangement as the same case as **1**. The central four copper atoms of **2** and **3** are on the same plane but four pyrazole rings are not. The intramolecular Cu···Cu distances (neighboring Cu···Cu) of **2** and **3** are av 3.07 Å and av 2.98 Å, respectively. In **2**, the two intramolecular Cu···Cu distances (diagonal Cu···Cu) is the same (4.34 Å), so it is clear that the central four Cu atoms form a square geometry. On the other hand, in **3**, the two intramolecular Cu···Cu distances (diagonal Cu···Cu) is different (4.85 Å and 3.40 Å). It shows that the central four copper atoms form a diamond geometry.[10] In the case of copper(I) ion in central metal ion, when the substituent groups in their 3- and/or 5-position of the pyrazole rings are bulkier than isopropyl group, the complexes cannot have trimeric structure any more. Because these larger substituent groups are the sterically hindered by some repulsive interaction. For this reason, **2** and **3** are tetranuclear geometry, although they have the same linear coordination as **1**. In addition, only **1** has intermolecular Cu···Cu interactions (≈3.03 Å) on the basis of the X-ray structure.

The IR spectra of **1**–**3** provided additional evidence in that the band attributed primarily to a C=N stretching is shifted to ≈1520 cm^{-1} in the copper(I) complexes from ≈1570 cm^{-1} in pyrazolate anion, which are consistent with a weakening of the bonds in the pyrazole rings of the copper(I) complexes.

The solution and solid electronic absorption spectra of three complexes were measured as compared with those of ligands and sodium salts of ligands. From the same spectroscopic behavior in solid and solution states, each of complexes in solid state keeps their conformation in solution state. It was observed that the substituent groups in their 3- and/or 5-position of the pyrazole rings are so bulky that their Cu–N charge-transfer bands shifted to higher energy (**1**; 238 nm, **2**; 236 nm, **3**; 227 nm). These differences were also reflected in their Cu–N stretching vibrations in far-IR regions.

The ^{1}H NMR and ^{13}C NMR spectra of the trimeric structure **1** and the tetrameric complex **3** give quite simple peaks. It seems that this result occurs because of the symmetrical substituent groups on their 3- and 5-position of the pyrazole rings. On the other hand, the ^{1}H NMR and ^{13}C NMR spectra of **2** are complicated. This result shows that **2** has the asymmetrical substituent (^{t}Bu and ^{i}Pr) groups on their 3- and 5-position of the pyrazole. We are now underway to elucidate the steric hindrances and electronic effects of pyrazole rings with group 11 metal ions.

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8　**1**: (Yield 37%) Anal. Calcd for C$_{27}$H$_{45}$N$_6$Cu$_3$: C, 50.33; H, 7.04; N, 13.04. Found: C, 50.54; H, 7.21; N, 13.00. IR (KBr, cm^{-1}): 2956(C–H), 1523(C=N). Far-IR (CsI, cm^{-1}): 501 (Cu–N). UV–vis (MeCN, rt, nm (cm^{-1} mol^{-1} dm^3)): 238 (21700), 274 (sh, 2200). UV–vis (nujor mull, rt, nm): 238, 274. ^{1}H NMR (CDCl$_3$, 600 MHz): δ 1.35 (d, J = 7 Hz, 36H, CH*Me*$_2$), 3.08 (sept, J = 7 Hz, 6H, C*H*Me$_2$), 5.92 (s, 3H, Pz). ^{13}C NMR (CDCl$_3$, 150 MHz): δ 24.05 (CH*Me*$_2$), 29.07 (*C*HMe$_2$), 96.71 (4-Pz), 161.09 (3,5-Pz). **2**: (Yield 39%) Anal. Calcd for C$_{40}$H$_{68}$N$_8$Cu$_4$: C, 52.50; H, 7.49; N, 12.24. Found: C, 52.38; H, 7.55; N, 12.33. IR (KBr, cm^{-1}): 2958(C–H), 1521(C=N). Far-IR (CsI, cm^{-1}): 519(Cu–N). UV–vis (MeCN, rt, nm (cm^{-1} mol^{-1} dm^3)): 236 (16600), 264 (sh, 3000). UV–vis (nujor mull, rt, nm): 236, 265. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 1.07–1.39 (24H, CH*Me*$_2$), 1.50–1.55 (36H, C*Me*$_3$), 2.83–3.08 and 3.10–3.49 (4H, C*H*Me$_2$), 5.83–5.96 (4H, Pz). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 23.12–23.93 (CH*Me*$_2$), 28.10–28.48 (CHMe$_2$), 31.39–31.67 (*C*Me$_3$), 95.77–96.87 (4-Pz), 159.32–163.10 (3,5-Pz). **3**: (Yield 42%) Anal. Calcd for C$_{44}$H$_{76}$N$_8$Cu$_4$·CH$_2$Cl$_2$: C, 51.17; H, 7.44; N, 10.61. Found: C, 51.28; H, 7.38; N, 10.63. IR (KBr, cm^{-1}): 2958(C–H), 1520(C=N). Far-IR (CsI, cm^{-1}): 516(Cu–N), 493(Cu–N). UV–vis (MeCN, rt, nm (cm^{-1} mol^{-1} dm^3)): 227(15200), 240(sh, 11000), 265(sh, 3000). UV–vis (nujor mull, rt, nm): 227, 242. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 1.34 (s, 72H, C*Me*$_3$), 5.83 (s, 4H, Pz). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 31.46 (C*Me*$_3$) 31.54 (*C*Me$_3$), 97.08 (4-Pz), 161.42 (3,5-Pz).
9　**1** (fw 644.33, at 208 K) crystallized in the monoclinic space group $P2_1/a$ with a = 17.407(3) Å, b = 13.585(4) Å, c = 14.493(3) Å, β = 112.94(1)°, V = 3156(1) Å^3, Z = 4, D_{calcd} = 1.34 g cm^{-3}. Of 7257 unique reflections measured, 5771 [$I > 2\sigma(I)$] were used in refinement (R = 0.046, R_w = 0.055). **2** (fw 933.23, at 212 K) crystallized in the tetragonal space group $I4_1/a$ with a = 19.033(3) Å, b = 19.033(3) Å, c = 14.277(2) Å, V = 5172(2) Å^3, Z = 4, D_{calcd} = 1.20 g cm^{-3}. Of 2963 unique reflections measured, 1377 [$I > 2\sigma(I)$] were used in refinement (R = 0.074, R_w = 0.098). **3** (fw 1056.25, at 211 K) crystallized in the monoclinic space group $P2_1/n$ with a = 25.760(5) Å, b = 18.971(8) Å, c = 10.813(2) Å, β = 93.37(2)°, V = 3156(3) Å^3, Z = 4, D_{calcd} = 1.33 g cm^{-3}. Of 12113 unique reflections measured, 7471 [$I > 2\sigma(I)$] were used in refinement (R = 0.043, R_w = 0.050). Crystallographic data reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-222966 to 222968. Copies of the data can be obtained free of charge via 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; or deposit@ccdc.cam.ac.uk).
10　Very recently, the structure of [Au(3,5-^{t}Bu$_2$pz)]$_4$ has been published in ref. 5 (only brief comments in the text).
11　We also determined the crystal structure of [Au(3,5-^{t}Bu$_2$pz)]$_4$. From our data, the complex has a square geometry as the same as **2**. This difference comes from ionic radii of Au(I) ion.