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Tetranuclear Copper(I)-Based Infinite One-Dimentional Chain Complex. Synthesis and X-Ray Crystal Structure of $\{[Cu_2(\mu\text{-3-methylpyridazine})_2(\mu\text{-pyrazine})_3](ClO_4)_2\}_\infty$

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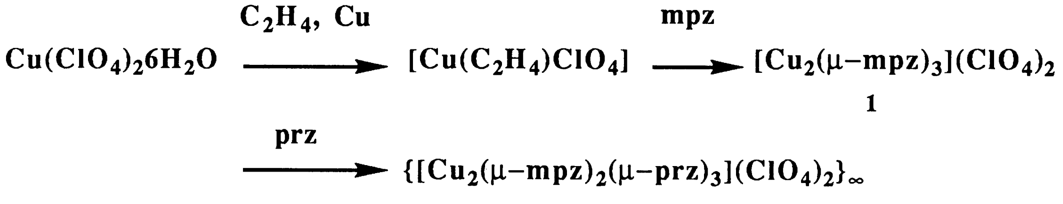
The title copper(I) compound has been isolated, whose X-ray crystallographic structure shows a rare polymerization mode in which the tetranuclear copper units, composed of three- and two-coordinate copper(I) atoms, are linked by pyrazines. This gives a cyclic voltammogram and a chrage transfer band characteristic of the polymeric structure in the solid state.

Coordination chemistry of copper(I) pyrazine has been relatively neglected although a large amount of information is available on their copper(II) complexes,[1)] where polynuclear structures including infinite chains have been well characterized. Copper(I) stereochemistry affords a wide variety of the coordination geometries,[2)] and therefore copper(I) could also provide polynuclear compounds of pyrazine as well as other metal compounds having bridging pyrazines.[3)] We have succeeded in synthesizing an novel infinite chain copper(I) polymer, which consists of tetranuclear copper(I) unit-based structure and has characteristic spectroscopic and electrochemical properties.

prz

mpz

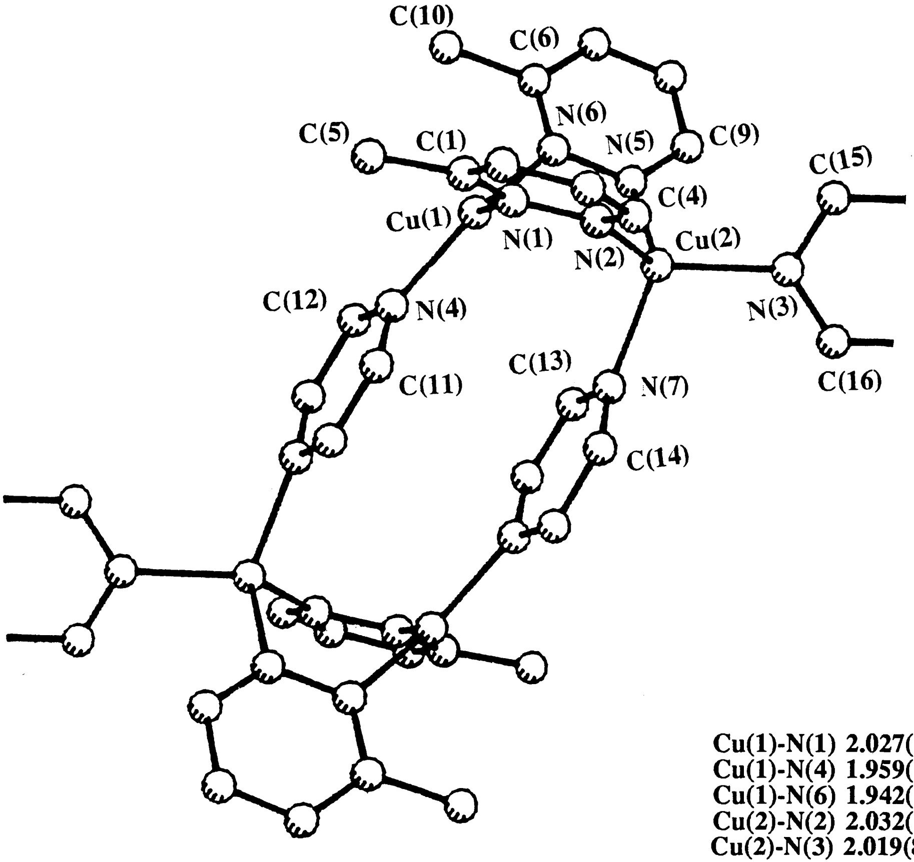
The stepwise reaction of copper(I) with prz and mpz gave orange crystal, **2**, as shown in the following scheme.[4)]



$$Cu(ClO_4)_2 6H_2O \xrightarrow{C_2H_4,\ Cu} [Cu(C_2H_4)ClO_4] \xrightarrow{mpz} \underset{\mathbf{1}}{[Cu_2(\mu\text{-}mpz)_3](ClO_4)_2}$$

$$\xrightarrow{prz} \underset{\mathbf{2}}{\{[Cu_2(\mu\text{-}mpz)_2(\mu\text{-}prz)_3](ClO_4)_2\}_\infty}$$

We have carried out an X-ray crystallographic study of **2**.5) The crystal data of **2** are as follows: $Cu_2N_7C_{16}H_{18}Cl_2O_8$, 634.36, monoclinic, $P2_1/c$, a=14.112(6) Å, b=12.395(4) Å, c=14.379(4) Å, β=107.46(3)°, V=2399(1) $Å^3$, Z=4, D_c=1.756 g/cm^3, $R(R_w)$ = 0.069 (0.080) for 2452 reflections. The crystal structure of **2** consists of infinite cation chains and perchlorate anions. The portion of the cation chain is shown in Figure 1. Three characteristic features are readily recognized. Firstly, there are two types of copper(I) geometry in this polymer; Cu(1) shows a three-coordinate Y-shape form while Cu(2) indicates a typical four-coordinate tetrahedral form. The Cu(1)-N(4) (1.959(9) Å) and Cu(1)-N(6) (1.942(9) Å) distances are shorter than Cu(1)-N(1) (2.027(9) Å) , while the N(4)-Cu(1)-N(6) angle (134.2(4)°) opens up more than 120°, coming close to a strained T-shape. The Cu(I) geometry follows the Y-T shape relationship in the bond distance and angle.6) Secondly, the unit in the polymer is quite a rare. The



Cu(1)-N(1)	2.027(9) Å
Cu(1)-N(4)	1.959(9) Å
Cu(1)-N(6)	1.942(9) Å
Cu(2)-N(2)	2.032(9) Å
Cu(2)-N(3)	2.019(8) Å
Cu(2)-N(5)	2.072(9) Å
Cu(2)-N(7)	2.042(9) Å

N(1)-Cu(1)-N(4)	113.5(4)°	N(1)-Cu(1)-N(6)	109.9(3)°
N(4)-Cu(1)-N(6)	134.2(4)°	N(2)-Cu(2)-N(3)	112.1(4)°
N(2)-Cu(2)-N(5)	109.4(3)°	N(2)-Cu(2)-N(7)	106.1(3)°
N(3)-Cu(2)-N(5)	107.4(3)°	N(3)-Cu(2)-N(7)	110.9(3)°
N(5)-Cu(2)-N(7)	111.1(4)°		

Fig.1. Structure of a portion of an infinite cation chain.
Selected bond distances(Å) and angles(deg) are shown.

mode of polymerization is best described by considering a fundamental tetracopper unit, in which the two mpz molecules bridge the two copper atoms and this dicopper unit is linked to another unit by two pyrazines (intraunit type), giving a tetranuclear copper unit. The closest Cu(1)...Cu(2) distance is 2.971(2) Å, indicating no direct metal-metal interaction. Finally, these units are furthermore linked to each other by a pyrazine (interunit type) to afford an infinite zig-zag cation chain(Fig. 2).

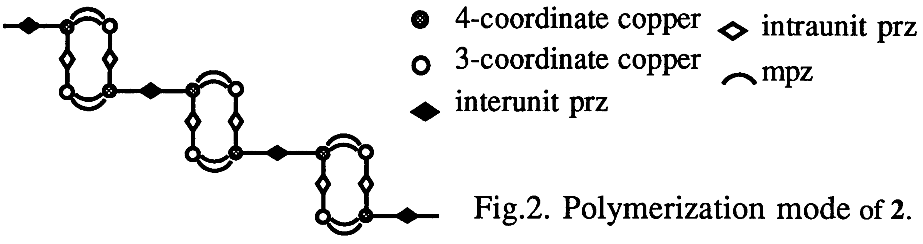


Fig.2. Polymerization mode of **2**.

Interestingly, the two methyl groups of the coordinated mpz are placed in the same direction so that they avoid the steric repulsion with the interunit prz and the Cu(1) results in a three-coordinate. The zig-zag mode is, thus, produced by controlling the direction of the methyl groups in mpz.

The reaction solution of this ternary system7) gives a band at 308 nm, which is attributed to the metal-to-ligand charge transfer band of Cu-mpz and/or Cu-prz moieties because both copper(I) complexes of mpz (**1**) and prz ($[Cu_2(mpz)_3(CH_3CN)_2](PF_6)_2$)8) show the band at *ca.*300 nm. This band encounters red shift (363 nm) in the case of crystals of **2**,9) which is associated with the polymeric structure. The cyclic voltammogram of the crystals **2** has two reversible redox couples with $E_{1/2}$= +0.22 and +0.53,10) which are ascribed to the $Cu^{I}Cu^{I} \leftrightarrow Cu^{I}Cu^{II}$ and $Cu^{I}Cu^{II} \leftrightarrow Cu^{II}Cu^{II}$ reactions of the closely contact dicopper moiety, respectively. Thermodynamic stability2)of copper(I) complexes lead to the conclusion that the copper with trigonal geometry has lower redox potential than that of tetrahedral one.

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4) 4.6 mg of $Cu(ClO_4)_2 6H_2O$ in 5 ml of methanol was reduced by copper wire under ethylene atmosphere. mpz (4.7 mg) was added to this solution and stirred for 5 min, followed by the addition of pyrazine (6.0 mg) in 5 ml of methanol. After ethylene was replaced with argon, the resultant deep yellow solution was kept at 5 °C for a week and orange crystals were obtained. This crystals are insoluble in usual organic solvents.

5) A brick-shaped crystal of the dimensions, 0.30x0.30x0.40 mm^3, was mounted on a glass fiber. All measurements were made on a Rigaku AFC-5R diffractometer with graphite monochromated MoKα radiation (λ = 0.71069 Å) and a 12 kW rotating anode generator. Intensities were gathered in an ω-2θ scan mode. Lorentz, polarization, and absorption corrections were applied. Of the 5757 unique reflections measured for $2\theta_{max}$ = 55°, 2452 reflections were considered observed($I>3\sigma(I)$). The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. The final cycle of full matrix least-squares refinement was converged with R, and R_w mentioned in the text.

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7)Possible species is not a polymer but a pyrazine adduct of dimeric **1** because of its good solubility. **1** is too unstable to isolate. ^1H NMR, 3.04(CH_3),8.20(4,5-H),9.45(6-H).

8) $[Cu_2(mpz)_3(CH_3CN)_2](PF_6)_2$, **3**, was obtained from $[Cu(CH_3CN)_4]PF_6$. Elemental analysis. Found: C,28.94; H, 3.02; N, 14.24%. Calcd for $C_{19}H_{24}N_8Cu_2P_2F_{12}$: C, 29.20; H, 3.10; N, 14.34%. ^1H NMR(ppm from TMS,-90 °C): **3**, 2.97(CH_3), 8.36(4.5-H), 9.56(6-H).

9)The absorption spectra of crystalline samples were measured by preparing KBr disc as well as IR spectra.

10)Cyclic voltammograms of the crystalline sample were recorded as follows. The pure crystals of **2** were added to carbon paste (graphite and mineral oil) and mixed well. By using this mixture working electrode was constructed; the mixture was set in a cavity of a teflon rod, which is connected with platinum wire. Another platinum wire was used as a counter electrode. The three-electrode systems and 0.1 M $NaClO_4$ aqueous solution were adopted. Ferrocene crystalline in the paste were used as a standard sample.

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