Structural Diversity of Copper Complexes with 2,2'-Dipyridyldisulfide. From Dimer to Infinite Sheet Structure Both in Solid State and in Solution

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Reaction of 2,2'-dipyridyldisulfide (dpds) with $CuBr_2$ in methanol provide a extended sheet or a discrete dimer structrue. The discrete dimer $[CuBr(dpds)]_2$ change to the sheet structure of $[CuBr(dpds)]_n$ by heat in the solid state or prolonged standing in reaction system.

Copper complexes have a variety of one to three dimensional infinite structures[1] and show the prominent functionality like superconductivity.[2] Recently, rational synthesis of the coordination polymer has been performed using the rigid coordination sphere as a back born for the supramolecular unit.[3] Another method to produce variety of polymer structure is use of more flexible ligating system.[4] We have used 2,2'-dipyridyldisulfide (dpds) for for preparation of a extended structure containing S-S bond. There have been prepared several dpds coordinated complexes[5] and diselenide analog,[6] even though, there are still a lot of possibility of coordination pattern due to the flexibility of dpds ligand. Using this ligand we have produced a variety of coordination compound of Cu(I)/(II) and found interesting polymerization reaction in solid state.

Because of the polymorphism of Cu-dpds complexes, careful treatment is required to reproduce specific structure. To two legs of an H–shaped cell for reaction and crystallization, (ϕ 2 cm, l 7.5 cm for leg part, and ϕ 2 cm, l 10 cm for bridging part), methanol solutions of $CuBr_2$ (0.30 g 1.3 mmol) and dpds (0.32 g, 1.5 mmol) were settled separately. After addition of methanol to immerse the bridging part, this solution was stand for 1 week. From the bridging part of H-tube, red crystals **1** of a dimer-structure complex $[CuBr(dpds)]_2$ were appeared with small amount of yellow crystals **3** as sheet-structure compound $[CuBr(dpds)]_n$. Deeply colored red crystals **2** of $[CuBr_2(dpds)]$ formed from the bottom where initially $CuBr_2$ solution was settled. Yield of pure red crystal **1** was ca. 50 mg, and total yields including **1**, **2**, and **3** ($[CuBr(dpds)]_n$) was ca. 300 mg. Unfortunately, prolonged standing of this solution causes the conversion of **1** to **3** with a significant decrease of the yield for **1**. Crystal **3** can prepare easily from CuBr (0.05 g, 0.35 mmol) with dpds (0.52 g, 2.4 mmol) in CH_3CN(35ml). Initially, the mixture made red turbidity, then became light yellow clear solution and produce yellow crystals of **3**.

The infinite sheet network for **3** is consisted with 6 Cu ions just like the Cu in the network found for $[Cu(pz)_{1.5}(CH_3CN)]PF_6$ crystal.[7] Every Cu atom in **3** is surrounded by two bromides and two dpds ligands tetrahedrally that works as bridge to neiboring Cu atoms. As a result, two $CuBr_2Cu$ units are linked by two dpds–Cu–dpds– units. The net work makes infinite sheet structure spread out toward *ab* plane and stacked along crystallographic *c* axis. Cu–L bond distances are 2.4961(9) Å} and 2.070(4) Å} for Cu–Br and Cu–N respectively. Br–Cu–Br and N–Cu–N planes orthogonarized to each other. The red crystal **1** consists of the discrete dimer molecule, $[(dpds)Cu(\mu\text{-}Br)_2Cu(dpds)]$. Dpds works as a bidentate ligand through pyridyl N atoms to Cu(I) two Br^- ions bridge Cu(I) ions.

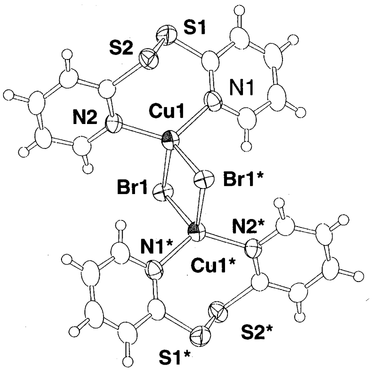

Figure 1. Ortep drawing of **1**.

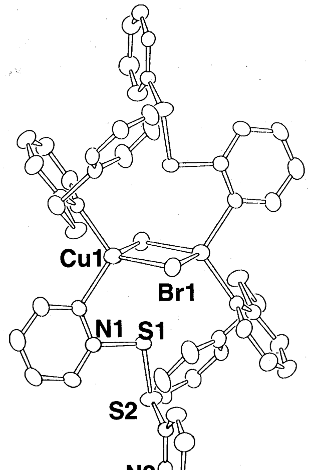

Figure 2. Ortep drawing of a circumstance in **3**.

Divalent copper salt, $CuBr_2$ was used as starting materials for complex **1** and **2** in protic solvent. The improvement of the yields for **1** is difficult under any condition due to the conversion toward sheet structure. This phenomenon was observed even at the solid states. The conversion from **1** to **3** is achieved by heated to 104-105℃. Resulting yellow solid shows only powder pattern by X-ray analysis, even though, the IR spectrum exactly match to that of infinite sheet dimer.[8] Without light, the crystal **1** gradually changed to yellow during several month at room temperature.

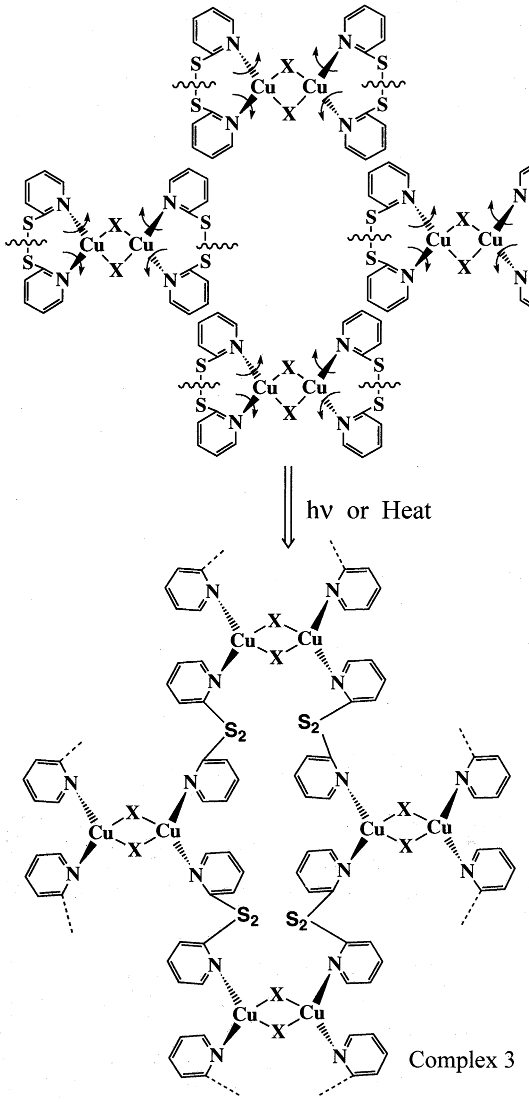

Figure 3. Schematic presentation of interconversion of dimer (**1**) to sheet (**3**).

Within the structure **1**, Cu–Br_2–Cu units lie in the same plane and neighbour S–S units has significant short contact to each other. The array of Cu unit in crystal **3** make following expectation possible. The presence of adjacent S–S expect the structural change from **1** to **3** concerted with S–S bond creavage reforming rearrangement. If the part of the crystalof **1** changed, rest of the crystal will change within a day to crystal **3**. This observation suggests the kind of chain reaction through either heterolytic or homolytic creavage of S-S bond acceptable above rearrangement mechanism.

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8 Crystal data for **1**: $CuBrC_{10}H_8N_2S_2$, M_w = 363.76, triclinic, space group $P1$ a = 9.454(1), b = 9.641(1), c = 7.6181(9) Å}, α = 106.573(9), β = 111.787(9)°, γ= 86.81(1), V = 617.0(1) Å}^{3}, Z =2, D_x = 1.96 g/cm^3, $\mu(MoK\alpha)$ = 53.27 cm^{-1}, Intensity data were measured on a Rigaku AFC7S diffractometer using ω-2θ scan technique with graphite monochromated Mo$K\alpha$ radiation (λ = 0.71069 Å}). 3608 unique refractions within 4≤ 2θ ≤60° were collected. The data were corrected for Lorentz and polarization effects. Decay correction was increase 0.31 %. The structure was solved and refined by using the teXsan programs. The current R value is 0.032 (R_w = 0.035) for 2536 independent absorption-corrected reflections (I ≥ 3σ(I)) by empirical Ψ scan method.

9 Crystal data for **2**: CuBrC10H8N2S2, M_w = 363.76, monoclinic, space group $P21/n$ a = 7.987(2), b = 15.218(3), c = 10.378(3) Å}, β = 112.03(2)°, V = 1169.3(4) Å}^{3}, Z = 4, D_x = 2.066 g/cm^3, $\mu(MoK\alpha)$ = 56.22 cm^{-1}, Intensity data were measured on a Rigaku AFC7S diffractometer using ω-2θ scan technique with graphite monochromated Mo$K\alpha$ radiation (λ = 0.71069 Å}). 3544 unique refractions within 4≤ 2θ ≤60° were collected. The data were corrected for Lorentz and polarization effects. No decay correction was applied. The structure was solved and refined by using the teXsan programs. The current R value is 0.047 (R_w = 0.049) for 2577 independent absorption-corrected reflections (I ≥ 3σ(I)) by empirical Ψ scan method.