Synthesis and Crystal Structures of $[CuCl_2(\mu\text{-}NSPh_3)]_2$ and $[CuCl_2(Ph_3SN)_2]$: Novel Copper Complexes Bearing Organic λ^6-Sulfanenitrile as Ligand

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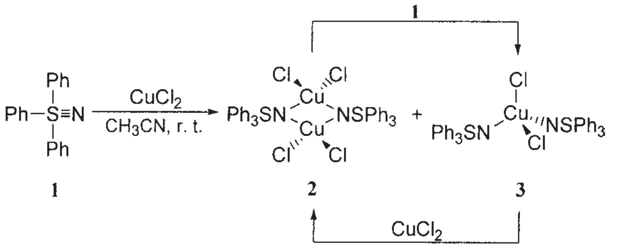
Dinuclear complex $[CuCl_2(\mu\text{-}NSPh_3)]_2$ (**2**) and mononuclear complex $[CuCl_2(Ph_3SN)_2]$ (**3**) were obtained concurrently by a reaction of $CuCl_2$ with triphenyl-λ^6-sulfanenitrile (**1**) in acetonitrile. They were characterized by elemental analysis, IR and NMR spectroscopy, and their molecular structures were determined by X-ray crystallographic analysis.



Scheme 1.

Thiazyl fluoride (FS≡N) and thiazyl trifluoride ($F_3S{\equiv}N$) were first prepared in inorganic field by Glemser and Mews et al., and their metal coordination chemistry has been investigated in recent years.[1,2] In 1992, we reported the synthesis of organic λ^6-sulfanenitrile, fluorodiphenyl-λ^6-sulfanenitrile ($FPh_2S{\equiv}N$).[3] We have subsequently succeeded in transforming fluoro-λ^6-sulfanenitrile to the various substituted λ^6-sulfanenitriles.[4] Their structures have been elucidated by X-ray crystallographic analysis and the reactivities have been clarified.[4–6] Sulfanenitriles have a nitrile-like nitrogen atom which is expected to coordinate toward metals. However there has been no report on the coordination chemistry of organic sulfanenitriles. As a part of continuing research on λ^6-sulfanenitrile, we have recently begun to study the coordination chemistry for sulfanenitrile as ligand toward transition metal center.

Triphenyl-λ^6-sulfanenitrile ($Ph_3S{\equiv}N$) (**1**) was prepared by the reaction of fluorodiphenyl-λ^6-sulfanenitrile with phenyllithium, and its molecular structure was revealed by X-ray crystallographic analysis.[4c] Compound **1** is thermally much more stable than other sulfanenitriles, and S≡N group has a stronger electron-donating nature,[4c,7] which is easier to incorporate into transition metal compounds as ligand. Therefore in the research project, reactions of **1** with transition metal salts were tried to prepare its metal complexes. We are stimulated to investigate the coordination chemistry of **1** as ligand toward copper center in the first place.

Addition of 1.2 equimolar amount of **1** to $CuCl_2$ in anhydrous acetonitrile at ambient temperature gave dark brown precipitates of **2** in 79% yield which was redissolve upon further treatment of another molar amount of **1** in acetonitrile. After removal of the precipitates and the solvent, recrystallization of the residue from acetonitrile–diethyl ether gave brown crystals **3** in 44% yield. Addition of $CuCl_2$ to the solution of **3** in acetonitrile afforded again **2**, and therefore the compounds **2** and **3** can be interconverted to one anther (Scheme 1).

The data from elemental analysis shows that the obtained complex **2** is a 1 : 1 complex of $CuCl_2$ and **1**.[8] The IR spectral data for **2** is also associated with its molecular structure.[8] As the SN stretching band is present at 1118 cm^{-1}, which is lower than that of **1** in the free ligand ($\nu_{SN} = 1267\ cm^{-1}$),[4c] it is suggested that there is a longer SN bond in **2**. The other signals are slightly shifted with respect to those shown in the free ligand. ^1H NMR spectroscopy of **2** exhibits reasonably sharp, isotropically shifted signals.[8,9] This is an evidence of the presence of two paramagnetic copper centers in **2**, and this is also associated with the speculation from the results of elemental analysis. All speculations about **2** were confirmed by X-ray crystallographic analysis.

The single crystals of **2** suitable for X-ray analysis were obtained finally by diffusing diethyl ether to DMF solution of **2**. The X-ray analysis clearly reveals that it is centrosymmetric dinuclear complex containing two bridging sulfanenitrile groups (Figure 1).[10] Each terminal copper atom of the cyclic Cu_2N_2 square exhibits a tetrahedral coordination with two chlorine atoms and two sulfanenitrile ligands bound by their nitrogen donors with Cu–N bonds of 2.016 Å in length. The nitrogen atom of sulfanenitrile is fixed in a bridging position, and the S–N bond (1.505 Å) of **2** is considerably longer than in the free ligand (1.462 Å),[4c] other bond lengths and angles of sulfanenitrile as

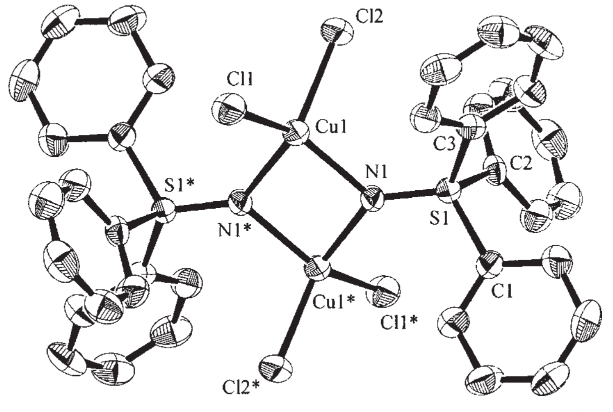


Figure 1. ORTEP drawings of **2**. Selected bond lengths (Å) and angles (°): S1–N1 1.505(4), S1–C1 1.790(4), S1–C2 1.802(5), S1–C3 1.795(4), Cl1–Cu1 2.205(1), Cl2–Cu1 2.229(1), N1–Cu1 2.016(3), N1–S1–C1 116.9(2), N1–S1–C2 113.2(2), N1–S1–C3 111.8(2), C1–S1–C2 104.5(2), C2–S1–C3 103.5(2), C3–S1–C1 105.6(2), Cu1–N1–S1 131.2(2), Cl1–Cu1–Cl2 102.6(5), N1–Cu1–N1* 83.3(1), Cu1–N1–Cu1* 96.7(1).

ligand correspond closely to those of the free state. As far as we are aware, this is the first instance of organic λ^6-sulfanenitrile as ligand in coordination chemistry.

Complex **3** obtained as minor product in the reaction of **1** and $CuCl_2$ was also investigated. The data from elemental analysis shows that **3** is a product with a $CuCl_2$: **1** molar ratio of 1 : 2.[8] Complex **3** exhibits a strong IR absorption at $1225\,cm^{-1}$ attributable to the SN stretching band.[8] The ^1H NMR spectroscopy of **3** does not show any signals for paramagnetic reason.

The structure of **3** was determined by X-ray crystallographic analysis, which revealed a pseudo-tetrahedral coordination geometry of the copper atom (Figure 2).[10] The copper atom which lies on symmetry center is coordinated by two chlorine atoms and two sulfanenitriles via their nitrogen donors with shorter Cu–N bonds (1.969 Å) than in **2**. The S–N bond (1.464 Å) of **3** is approximately considered not to be changed contrast to in the free ligand (1.462 Å),[4c] and is considerably shorter than in **2** (1.505 Å).

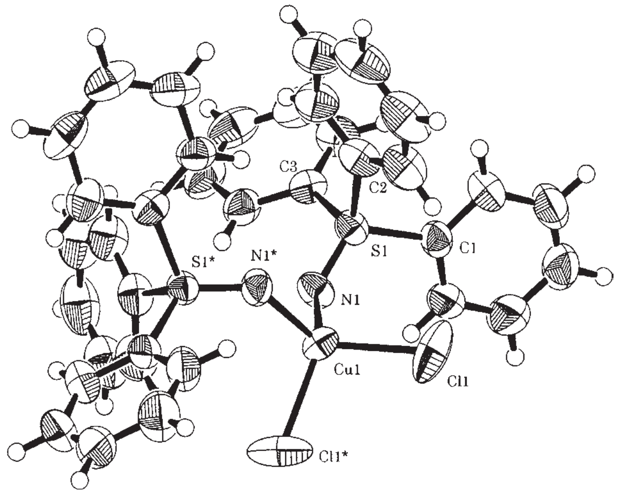


Figure 2. ORTEP drawings of **3**. Selected bond lengths (Å) and angles (°): S1–N1 1.464(4), S1–C1 1.811(5), S1–C2 1.805(5), S1–C3 1.802(5), Cl1–Cu1 2.249(2), N1–Cu1 1.969(4), N1–S1–C1 117.0(2), N1–S1–C2 111.1(2), N1–S1–C3 117.4(2), C1–S1–C2 102.5(2), C2–S1–C3 102.3(2), C3–S1–C1 104.7(2), Cu1–N1–S1 131.9(2), N1–Cu1–Cl1 102.7(1), N1–Cu1–N1* 96.9(3), Cl1–Cu1–Cl1* 105.2(1).

Further investigations on the coordination chemistry of **1** and $CuCl_2$ are in progress in our laboratory.

References and Notes

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8 For **2**: dark brown crystals, mp 228–230 °C, ^1H NMR (400 MHz, DMF-d_7): δ 7.65 (bs, 12H), 9.83 (bs, 18H); IR (KBr): $\nu_{SN} = 1118\,cm^{-1}$; Anal. Calcd for $C_{36}H_{30}Cl_4Cu_2N_2S_2$: C, 52.50; H, 3.67; N, 3.40%. Found: C, 52.66; H, 3.78; N, 3.54%. For **3**: brown crystals, mp 214–216 °C, IR (KBr): $\nu_{SN} = 1225\,cm^{-1}$; Anal. Calcd for $C_{36}H_{30}Cl_2Cu_1N_2S_2$: C, 62.74; H, 4.39; N, 4.06%. Found: C, 62.99; H, 4.46; N, 4.16%.

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10 Crystallographic data for **2**: $C_{36}H_{30}Cl_4Cu_2N_2S_2$, $M_r = 823.67$, orthorhombic, $a = 19.347(3)$, $b = 16.712(3)$, $c = 10.740(2)$ Å, $V = 3472(1)$ Å^3, $T = 296$ K, space group *Pbca* (No. 61), $Z = 4$, μ(Mo Kα) $= 16.82\,cm^{-1}$, 5597 reflections were collected, 5036 were unique; $R(I > 3\sigma(I)) = 0.043$, $R_w = 0.054$ for 2524 reflections and 208 parameters. Crystallographic data for **3**: $C_{36}H_{30}Cl_2Cu_1N_2S_2$, $M_r = 689.22$, orthorhombic, $a = 15.679(2)$, $b = 12.210(2)$, $c = 17.155(2)$ Å, $V = 3284(1)$ Å^3, $T = 296$ K, space group *Aba2* (No. 41), $Z = 4$, μ(Mo Kα) $= 9.83\,cm^{-1}$, 2655 reflections were collected, 2465 were unique; $R(I > 3\sigma(I)) = 0.034$, $R_w = 0.048$ for 1727 reflections and 194 parameters. Crystallographic data reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-191400 (**2**) and 191401 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk). Instruction for depositing the crystallographic data is available on the Web at http://www.ccdc.cam.ac.uk/conts/depositing.html.