Research Article

Syntheses and Crystal Structures of $[\text{Cu}_3\{\mu\text{-(NSPh}_2)_2\text{N}\}_2\text{Cl}_2]$ and $[\text{Cu}_3\{\mu\text{-(NSPh}_2)_2\text{N}\}_2\{(\text{NSPh}_2)_2\text{N}\}_2]\text{Cl}_2$

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We have prepared the trinuclear complexes $[\text{Cu}_3\{\mu\text{-(NSPh}_2)_2\text{N}\}_2\text{Cl}_2]$ (**3**) and $[\text{Cu}_3\{\mu\text{-(NSPh}_2)_2\text{N}\}_2\{(\text{NSPh}_2)_2\text{N}\}_2]\text{Cl}_2$ (**4**), from the reaction of CuCl_2 with $\{\text{N}(\text{Ph}_2\text{SN})(\text{Ph}_2\text{SNH})\}$ (**1**) and determined their structures by X-ray crystallographic analysis. In both complexes, two monoanions 1^- chelate the Cu(II) center in square-planar geometry, whereas the terminal Cu(II) center is four-coordinate and a distorted tetrahedron.

1. Introduction

The chemistry of λ^6 -sulfanenitrile, bearing an SN triple bond, shows some interesting and fascinating features. Mews et al. prepared trifluoro- λ^6 -sulfanenitrile ($\text{F}_3\text{S}\equiv\text{N}$) and its derivatives ($\text{F}_2\text{RS}\equiv\text{N}$, e.g., $\text{R} = \text{Me}_2\text{N}-$, $\text{F}_2(\text{O})\text{S}=\text{N}-$), and investigated their metal coordination chemistry [1–3]. Recently, we prepared fluoro(diphenyl)- λ^6 -sulfanenitrile ($\text{Ph}_2\text{FS}\equiv\text{N}$) and reported the formation of the various substituted λ^6 -sulfanenitriles [4–14]. Among them, new types of λ^6 -sulfanenitrile with nitrilo and imino groups (type **A**) or two nitrilo groups (ndsdsd, type **B**) at both ends have been shown to complexes as bidentate N, N' ligands. For example, the reaction of ndsdsd with MCl_2 ($\text{M} = \text{Co(II)}$, Ni(II) , and Cu(II)) gave the corresponding $[\text{MCl}_2(\text{ndsdsd})]$ and $[\text{M}(\text{ndsdsd})_2]\text{Cl}_2$, and their molecular structures were determined by X-ray crystallographic analysis [15]. The two terminal nitrogen atoms chelate to the metal center to form an eight-membered sulfur-nitrogen ring. We have also performed coordination studies of sulfanenitrile ligands of type **A** wherein the monoanions reacted with Ph_2SnCl_2 to give the corresponding tin-complexes $[\text{ClPh}_2\text{Sn}\{\text{E}(\text{Ph}_2\text{SN})_2\}]$ ($\text{E} = \text{CH}, \text{N}$) in good yields [16]. The crystal structures of both compounds were determined by X-ray crystallographic analysis and showed to consist with a monomeric chelate structure that contains a distorted trigonal bipyramidal tin

atom with a nitrogen and chlorine atom in the axial sites. In a further extension of these studies, we examined the reaction of **1** with CuCl_2 . Herein, we describe the preparation and crystal structure determination of $[\text{Cu}_3\{\mu\text{-(NSPh}_2)_2\text{N}\}_2\text{Cl}_2]$ (**3**) and $[\text{Cu}_3\{\mu\text{-(NSPh}_2)_2\text{N}\}_2\{(\text{NSPh}_2)_2\text{N}\}_2]\text{Cl}_2$ (**4**).

2. Experimental

2.1. Chemicals and General Methods. All reagents and solvents were obtained commercially and were further purified by general methods when necessary. The single crystal X-ray diffraction data were collected with a Rigaku RAXIS RAPID imaging plate using graphite monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71075 \text{ \AA}$). IR spectra were recorded on a Shimadzu FTIR-8400S spectrometer. Melting points were measured on a Yanaco Mp-J3 melting point apparatus. Elemental analyses were carried out at the Chemical Analysis

Center of the College of Science and Technology, Nihon University.

2.2. Syntheses. The free ligands $\{N(Ph_2SN)(Ph_2SNH)\}$ (**1**) was synthesized as described previously [7].

2.2.1. Preparation of $[Cu_3\{\mu-(NSPh_2)_2N\}_2Cl_4]$ (3**) and $[Cu_3\{\mu-(NSPh_2)_2N\}_2\{(NSPh_2)_2N\}_2]Cl_2$ (**4**).** A solution of **1** (166 mg, 0.4 mmol) and sodium methoxide (22 mg, 0.4 mmol) in methanol (1.0 mL) was slowly added to a solution of $CuCl_2$ (81 mg, 0.6 mmol or 41 mg, 0.4 mmol) in the same solvent (1.0 mL) at ambient temperature, which started to precipitate a solid within 1 minute. The precipitate was then filtered, washed with methanol, and dried under vacuum at 100°C for 24 hours. Crystals suitable for X-ray analysis were obtained from methanol-ether (**3**) and dichloromethane-ether (**4**).

Data for 3. Green-yellow; Yield 93%, relative to **1**; mp. 221–223°C (decomp.); IR (KBr) 3055, 1475, 1445, 1146, 1078, 1065, 1024, 1009, 984 cm^{-1} ; UV-vis (MeOH, λ_{max} , nm (ϵ , $M^{-1}cm^{-1}$)) 207 (9.3×10^4), 407 (sh, 3.5×10^3); Anal. Calcd for $C_{48}H_{40}Cl_4Cu_3N_6S_4$: C, 49.63; H, 3.47; N, 7.23; Found: C, 49.31; H, 3.38; N, 7.19.

Data for 4. Green; Yield 97%, relative to **1**; mp. 151–152°C (decomp.); IR (KBr) 3383, 3055, 1473, 1444, 1227, 1159, 1067, 1007, 972 cm^{-1} ; UV-vis (MeOH, λ_{max} , nm (ϵ , $M^{-1}cm^{-1}$)) 208 (1.4×10^5), 392 (sh, 9.9×10^3); Anal. Calcd for $C_{96}H_{88}Cl_2Cu_3N_{12}O_4S_8$: C, 57.89; H, 4.45; N, 8.44; Found: C, 57.82; H, 4.15; N, 8.42.

2.3. X-ray Crystallography. Diffraction data were collected with a Rigaku RAXIS RAPID imaging plate using graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71075 \text{ \AA}$). The data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied which resulted in transmission factors (see Table 1). The structures **2–4** were solved by the direct method using SHELXS-97 and were refined using SHELXL-97 [17]. Crystal data for $[Cu_3\{\mu-(NSPh_2)_2N\}_2Cl_4]$ (**3**) and $[Cu_3\{\mu-(NSPh_2)_2N\}_2\{(NSPh_2)_2N\}_2]Cl_2$ (**4**) are given in Table 1.

3. Results and Discussion

The addition of an equimolecular amount of **1** to $CuCl_2$ in methanol at ambient temperature immediately gave a green-yellow solution and green precipitates. After filtering the precipitates and removing the solvent, the recrystallization of the residue from methanol-ether gave yellow crystals **2**. On the other hand, the precipitates were recrystallized from methanol-ether to give green-yellow crystals **3**. The compositions of **2** and **3** were identified by elemental analysis and IR spectroscopy, and their structures were determined by X-ray crystallographic analysis (Figure 1 and Supplementary Figure S1, in Supplementary Material available online at doi:10.1155/2010/326568). Preliminary experiments indicated that **1** acts as the bridging ligands and base to form the

FIGURE 1: ORTEP drawing of **3** (50% probability thermal ellipsoids; H and C atoms (apart from the α atoms of the phenyl rings) have been omitted for clarity).

trinuclear complex, $[Cu_3\{\mu-(NSPh_2)_2N\}_2Cl_4]$ (**3**), and protonated compound, $\{N(Ph_2SNH)_2\}_2CuCl_4$ (**2**), respectively, (Scheme 1). Therefore, complex **3** was prepared effectively and almost quantitatively from the reaction of **1** and $CuCl_2$ (1.5 equivalents) in the presence of sodium methoxide as the base in methanol at ambient temperature (Scheme 1). Furthermore, the reaction of **1** and $CuCl_2$ in the ratio 4 : 3 under the above conditions gave the corresponding compound $[Cu_3\{\mu-(NSPh_2)_2N\}_2\{(NSPh_2)_2N\}_2]Cl_2$ (**4**) almost quantitatively (Scheme 1). Green crystals of **4** suitable for X-ray analysis were obtained by crystallization from dichloromethane-ether at ambient temperature.

In order to confirm the identity of $[Cu_3\{\mu-(NSPh_2)_2N\}_2Cl_4]$ (**3**) and $[Cu_3\{\mu-(NSPh_2)_2N\}_2\{(NSPh_2)_2N\}_2]Cl_2$ (**4**), single crystal X-ray structure determinations were carried out. ORTEP drawings of **3** and **4** are depicted in Figures 1 and 2. Selected bond lengths and angles for complexes **3** and **4** are collected in Table 2.

The X-ray structure of **3** shows two independent molecules with nearly identical bond lengths and angles (an ORTEP drawing of one of two independent molecules). The X-ray analysis clearly reveals that it is centrosymmetric trinuclear complex containing two six-membered CuN_3S_2 and two four-membered Cu_2N_2 rings (Figure 1). The two monoanions 1^- act as a bridging ligand to form the three linearly arranged copper(II) ions with a $Cu \cdots Cu$ separation of $3.0377(11) \text{ \AA}$. The ligand adopts a boat form conformation wherein the Cu(1) and the central nitrogen (N(2)) atoms lie 0.365 and $0.489 \text{ \AA}$, respectively, outside the quasi-plane formed by the S_2N_2 of the ring. The terminal nitrogen atoms of the ligand are fixed in a bridging position and the mean value of the terminal S–N bond lengths ($1.506 \text{ \AA}$) is considerably larger than that of the free ligand **1** (mean $1.486 \text{ \AA}$) [8] and is close to that of $[CuCl_2(\mu-NSPh_3)]_2$ ($1.505(4) \text{ \AA}$) [18]. The internal S–N bond lengths (mean $1.599 \text{ \AA}$) and S(1)–N(2)–S(2) angle ($118.1(3)^\circ$) are close to those of the free ligand **1** (S–N; mean $1.615 \text{ \AA}$, S–N–S; $117.5(1)^\circ$) [8]. The central Cu(II) atom adopts a square-planar geometry, being linked to four nitrogen atoms (N(1),

SCHEME 1: (i) CuCl₂ (1.0 equiv.), MeOH, r.t.; (ii) CuCl₂ (1.5 equiv.), MeONa, MeOH, r.t.; (iii) CuCl₂ (0.75 equiv.), MeONa, MeOH, r.t..

TABLE 1: Crystallographic Data for Compounds 3 and 4.

	3	4·4H ₂ O
Formula	C ₉₆ H ₈₀ Cl ₈ Cu ₆ N ₁₂ S ₈	C ₉₆ H ₈₈ Cl ₂ Cu ₃ N ₁₂ O ₄ S ₈
Fw	2323.04	1991.87
Cryst size (mm)	0.23 × 0.22 × 0.06	0.66 × 0.29 × 0.28
Temp (K)	296(2)	296(2)
λ(Å)	0.71075	0.71075
Cryst syst	triclinic	triclinic
Space group	P-1	P-1
a (Å)	9.294(4)	13.527 (6)
b (Å)	14.015(5)	15.760(6)
c (Å)	18.792(6)	16.493(6)
α (deg)	93.941(12)	60.552(14)
β (deg)	93.138(13)	64.828(14)
γ (deg)	94.280(12)	88.128(15)
V (Å ³)	2430.7(14)	2700.9(17)
Z	1	1
ρ _c (Mg/m ³)	1.587	1.220
μ (mm ⁻¹)	1.734	0.839
F(000)	1178	1021
T _{min} /T _{max}	0.6912/0.9031	0.6073/0.7989
θ range/deg	3.00–27.48	3.01–27.48
Reflns collcd	23995	26115
Indp reflns	10973	12146
R _{int}	0.096	0.04
Data/restraints/params	10973/0/589	12146/0/565
R ₁ , wR ₂	0.0688, 0.1074	0.0683, 0.1961
(I > 2σ[I])		
R ₁ , wR ₂ (all data)	0.1542, 0.1337	0.1110, 0.2293
GOF/F ²	1.024	1.018

TABLE 2: Selected Bond Lengths (Å) and angles (deg) Compounds 3 and 4.

3			
Cu(1)–N(1)	1.962(4)	Cu(2)–N(3)*	2.079(5)
Cu(1)–N(3)	1.990(4)	S(1)–N(1)	1.508(4)
Cu(2)–Cl(1)	2.227(2)	S(1)–N(2)	1.601(5)
Cu(2)–Cl(2)	2.196(2)	S(2)–N(2)	1.597(5)
Cu(2)–N(1)	1.975(4)	S(2)–N(3)	1.503(4)
N(1)–Cu(1)–N(3)	97.50(18)	N(2)–S(2)–N(3)	119.0(2)
N(1)–Cu(1)–N(3)*	82.50(18)	Cu(1)–N(1)–Cu(2)	100.99(19)
Cl(1)–Cu(2)–Cl(2)	101.58(8)	Cu(1)–N(1)–S(1)	124.8(3)
Cl(1)–Cu(2)–N(1)	104.63(15)	Cu(2)–N(1)–S(1)	132.8(3)
Cl(1)–Cu(2)–N(3)*	132.08(15)	S(1)–N(2)–S(2)	118.1(3)
Cl(2)–Cu(2)–N(1)	138.61(17)	Cu(1)–N(3)–Cu(2)*	96.55(18)
Cl(2)–Cu(2)–N(3)*	105.00(15)	Cu(1)–N(3)–S(2)	123.8(3)
N(1)–Cu(2)–N(3)*	79.95(18)	Cu(2)*–N(3)–S(2)	131.9(3)
N(1)–S(1)–N(2)	116.5(3)		
4			
Cu(1)–N(1)	1.966(4)	S(1)–N(2)	1.590(3)
Cu(1)–N(3)	1.976(3)	S(2)–N(2)	1.597(3)
Cu(2)–N(1)*	2.014(3)	S(2)–N(3)	1.480(4)
Cu(2)–N(3)	2.012(3)	S(3)–N(4)	1.472(4)
Cu(2)–N(4)	1.915(4)	S(3)–N(5)	1.590(4)
Cu(2)–N(6)	1.913(4)	S(4)–N(5)	1.586(4)
S(1)–N(1)	1.489(3)	S(4)–N(6)	1.478(4)
N(1)–Cu(1)–N(3)	97.50(14)	N(5)–S(4)–N(6)	123.5(2)
N(1)–Cu(1)–N(3)*	82.50(14)	Cu(1)–N(1)–Cu(2)*	98.69(15)
N(1)*–Cu(2)–N(3)	80.42(14)	Cu(1)–N(1)–S(1)	126.42(19)
N(1)*–Cu(2)–N(4)	143.23(19)	Cu(2)*–N(1)–S(1)	133.5(2)
N(1)*–Cu(2)–N(6)	100.69(15)	S(1)–N(2)–S(2)	119.0(2)
N(3)–Cu(2)–N(4)	100.60(16)	Cu(1)–N(3)–Cu(2)	98.39(15)
N(3)–Cu(2)–N(6)	143.14(19)	Cu(1)–N(3)–S(2)	126.4(2)
N(4)–Cu(2)–N(6)	99.65(16)	Cu(2)–N(3)–S(2)	133.9(2)
N(1)–S(1)–N(2)	118.63(18)	Cu(2)–N(4)–S(3)	125.5(2)
N(2)–S(2)–N(3)	118.64(18)	S(3)–N(5)–S(4)	118.6(2)
N(4)–S(3)–N(5)	123.3(2)	Cu(2)–N(6)–S(4)	125.2(2)

The atom labeling scheme is shown in Figure 1 and 2.

N(3), N(1)*, and N(3)*) of ligand 1[−]. The bond angles around the terminal Cu(II) atom with two nitrogen and two chlorine atoms span the range of 79.95(18)–138.61(17)°, substantially deviating from the ideal tetrahedral angle. The dihedral angle of 63.06° between the N(1)–Cu(2)–N(3) and Cl(1)–Cu(2)–Cl(2) planes shows significant deviation from the ideal 90° for a tetrahedral arrangement. The bond lengths of Cu–N (1.962(5)–2.079(5) Å; mean 2.002 Å) and Cu(2)–Cl (2.196(2)–2.227(2) Å; mean 2.212 Å) in **3**

are similar to those of [CuCl₂(μ-NSPh₃)]₂ (Cu–N; mean 2.016 Å, Cu–Cl; mean 2.217 Å [18]).

The structure of **4** consists of a separated [Cu₃{μ-(NSPh₂)₂N}₂[(NSPh₂)₂N]₂]²⁺ cation, two Cl[−] anions, and four water molecules. The cation moiety contains a square-planar central Cu(II) and two distorted tetrahedral Cu(II) atoms (Figure 2). The Cu(1)⋯Cu(2) distance is 3.0194(13) Å. Although the conformation of the bridging ligand (the Cu–N bond lengths in the four-membered Cu₂N₂

FIGURE 2: ORTEP drawing of **4** (50% probability thermal ellipsoids; H, C atoms (apart from the α atoms of the phenyl rings), two chloride anions, and uncoordinated water molecules have been omitted for clarity).

ring are 1.966(4)–2.014(3) Å; mean 1.992 Å) is similar to that of **3**, the bidentate ligand adopts a twist boat conformation (the Cu(2)–N bond lengths in the six-membered Cu(2)N₃S₂ ring are 1.913(3) and 1.915(3) Å, respectively). The terminal and internal S–N bond lengths of the bidentate ligand are slightly shorter than those of the corresponding bridging ligand.

4. Conclusions

In summary, we have demonstrated the formation of new types of λ^6 -sulfanenitrile-copper(II) complexes, [Cu₃{ μ -(NSPh₂)₂N₂}₂Cl₂] (**3**) and [Cu₃{ μ -(NSPh₂)₂N₂}₂{(NSPh₂)₂N₂}₂]Cl₂ (**4**), and determined their molecular structures. As magnetic orbital interactions between the copper ions in many multinuclear systems result in ferromagnetic coupling, further investigation of the chemistry of our trinuclear system including the magnetic properties is now in progress.

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