NOVEL N-DONOR HETEROCYCLIC LIGANDS AND THEIR COORDINATION CHEMISTRY TOWARDS A CU(II) SALT

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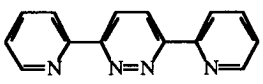
ABSTRACT

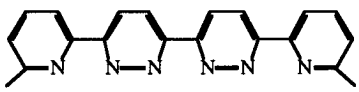
Two novel bridging-tridentate ligands, 4,6-di-(4,6-dimethyl-2-pyridylthio)-2-methyl pyrimidine, ***1****, and 4,6-di-(4,6-dimethyl-2-pyridylamino)-2-methylpyrimidine,* ***2****, have been synthesized and characterized. Both ligands* ***1*** *and* ***2*** *show an intriguing ability to reduce Cu(II) to Cu(I) ions. The ligand* ***1*** *reacts with* $Cu(O_3SCF_3)_2$ *to form the* ***Cu-1*** *complex which can be crystallized from the methanolic solution by adding diethylether: triclinic space group,* $\boldsymbol{P\bar{1}}$ *(No. 2) with a = 8.234 (6) Å, b = 11.224 (8) Å, c = 11.748 (6) Å, α = 96.40 (2)Å,, β = 100.43 (3)Å, γ = 102.70 (2)Å, Z =1, R = 0.0427, wR = 0.1155. The* ***Cu-1*** *complex contains two Cu(I) ions and two units of the ligand* ***1*** *in which each Cu(I) coordinates to 3 N donors oriented into a distorted trigonal planar geometry. Similarly, the ligand* ***2*** *reacts with* $Cu(O_3SCF_3)_2$ *to form the* ***Cu-2*** *complex. Spectroscopic and elemental analysis results reveal that* ***Cu-2*** *has a structure similar to* ***Cu-1****. The π-stacking interaction of the pyrimidine rings may be a significant factor to cause structural distortions in both* ***Cu-1*** *and* ***Cu-2*** *complexes.*

INTRODUCTION

Living organisms employ self-assembly processes, the spontaneous formation of higher-ordered structure, to construct components containing information and the functional units of their own assembly.[1] Chemists, on the other hand, have mimicked self-assembly process with metal ions and organic ligands which are allowed to arrange into specific arrays.[2] These fabricated substances can be used as molecular electronic devices such as molecular wires,[3] molecular sensors,[4] and others.[5] Compounds such as molecular-racks, -ladders and -grids[6] may potentially be developed into information storage devices.[7] Heterocyclic ligands containing nitrogen donor such as pyridine, pyrimidine and pyridazine derivatives have received much attention due to their ability to bind metal ions and to produce complexes in many forms and geometries.[8] The electronic communication between two or more metal centers can be accomplished by the π-conjugated system of the heterocyclic frameworks. Work done thus far employed quite rigid ligands such as 3,6-bis(2'-pyridyl)pyridazine, **a**,[9] and 6,6'-bis[2-(6-methylpyridyl)]-3,3'-bipyridazine, **b**,[10] which can chelate Cu(I) and Ag(I) ions in a bidentate fashion and form **Cu[2x2]** and **Ag[3x3]** molecular grids, respectively. The metal ions in both molecular grids are coordinating to 4 nitrogen donors oriented into a tetrahedral geometry.

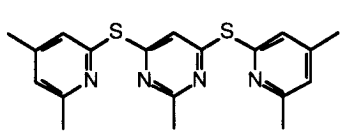


a

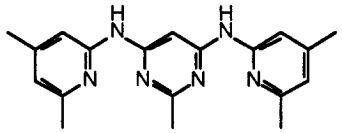


b

This article describes the preparation of two novel ligands, 4,6-di-(4,6-dimethyl-2-pyridylthio)-2-methylpyrimidine, **1**, and 4,6-di-(4,6-dimethyl-2-pyridylamino)-2-methyl pyrimidine, **2**, which are capable of fabricating molecular racks, ladders and grids. Both ligands **1** and **2** are composed of two pyridine units and one pyrimidine unit connecting by thioether sulfur and amine nitrogen atoms, respectively. These ligands are, therefore, more flexible than the ligands **a** and **b**. They are possibly able to bind metal ions in mono, di- or tridentate fashions; thus, they may accommodate metal ions that prefer 3, 4, 5 or 6 coordinates. We herein report the coordination chemistry of the ligands **1** and **2** with $Cu(O_3SCF_3)_2$.



1

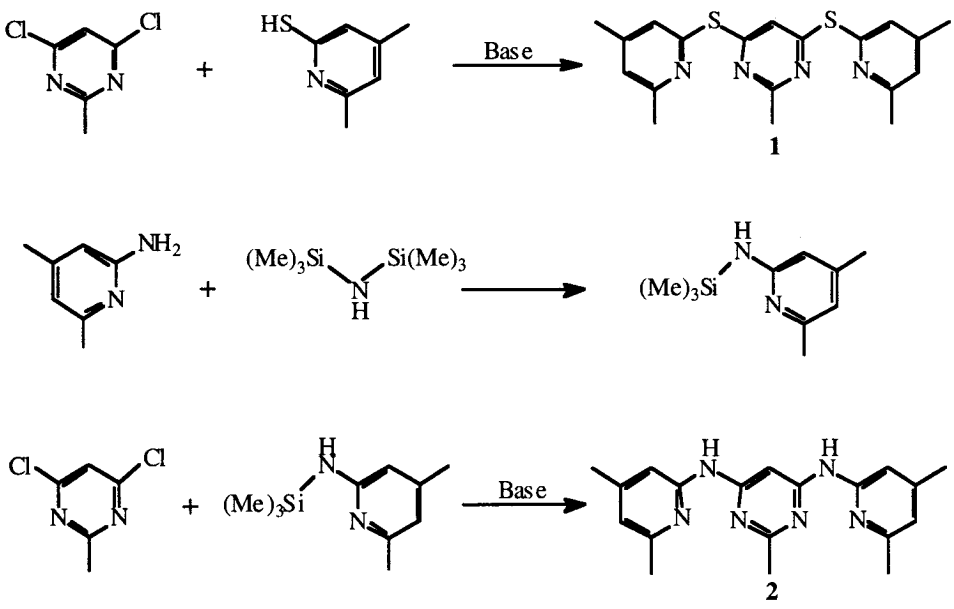


2

RESULT AND DISCUSSION

Preparation of the Ligands 1 and 2. The ligands **1** and **2** were basically prepared by nucleophilic aromatic substitution reactions as described in Scheme 1. The ligand 1, was synthesized in a similar fashion to the synthesis of 4,6-di-(2'-pyridylthio)pyrimidine reported by Thompson et al.[11] Nucleophilic substitution of chloride by 4,6-dimethyl-2-pyridinethiol in 4,6-dichloro-2-methylpyrimidine produced the sulfur bridging ligand **1** in 56% yield. The ^1H NMR spectrum of the ligand **1** is shown in Figure 1. The three signals at 2.28 (6H), 2.39 (6H) and 2.53 (3H) ppm are assigned to methyl protons 1, 2 and 3, respectively. Signals at 6.61 (1H), 6.90 (2H) and 7.20 (2H) ppm are assigned to the aromatic protons 4, 5, and 6, respectively. The FAB mass spectrum of the ligand **1** gives a very strong signal (100%) at 369 m/z consistent with the molecular weight of the ligand.

Scheme 1.

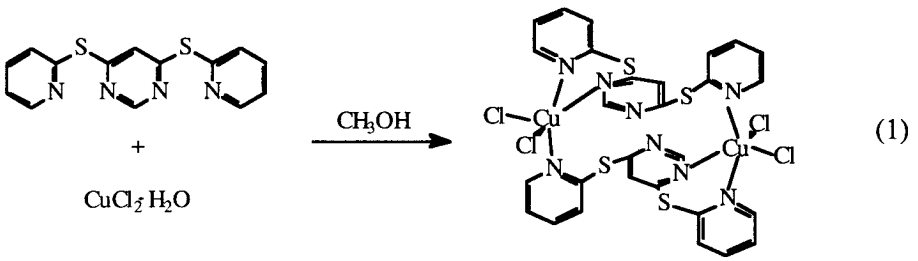


1

2

The amine bridging ligand, **2**, however, requires more steps for preparation than the analogue **1** does. The starting 2-amino-4,6-dimethylpyridine needed to be protected by a trimethylsilyl group before the substitution reaction took place. The reaction of the protected ligand with 4,6-dichloro-2-methylpyrimidine in the presence of n-butyllithium yielded the ligand **2**. The ^{1}H NMR spectrum of the ligand **2**, shown in Figure 2, is assigned in a similar manner to that of **1**. Three signals of methyl proton 1', 2' and 3' appear at 2.28 (6H), 2.39 (6H) and 2.53 (3H) ppm, respectively while the aromatic protons 4', 5', and 6', show signals at 6.60 (2H), 7.08 (2H) and 7.76 (1H) ppm, respectively. Signals from NH protons, however, cannot be observed in the spectrum probably due to the overlapping of signals with protons 1', 2' and 3'. The FAB mass spectrum of the ligand **2** gives a very strong signal (100%) at 335 m/z and thus comfirms the desired molecular structure. In addition, compared to **1**, the ligand **2** shows an intense blue fluoresence absorption at 254 nm. The complete spectral data of the ligands **1** and **2** are summarized in Table 1.

Coordination chemistry of 1 towards $Cu(O_3SCF_3)_2$. Thompson and coworkers reported the coordination chemistry of copper(II) with 4,6-di-(2'-pyridylthio)-pyrimidine, DPP. They found that the product of the reaction between DPP and $CuCl_2 \bullet H_2O$ gave a dimeric Cu(II) complex. Each Cu(II) ion was coordinated to 3 N donors and 2 Cl^- ions oriented into a distorted square pyramidal geometry, eq. 1. In the light of this result, we choose to use a metal salt that contains non-coordinating counter anions in order to avoid the coordination of anions to the metal centers. We, therefore, employed $Cu(O_3SCF_3)_2$ as the metal salt of choice to study coordination chemistry of the ligands **1** and **2**.



(1)

A reaction of the ligand **1** with $Cu(O_3SCF_3)_2$ in methanol resulted in a blue solution which turned yellowish green after stirring for 24 hours. The complex **Cu-1** could be crystallized by adding diethylether into the methanolic solution, yielding green crystals. The crystals were of good quality and suitable for single crystal X-ray analysis. The diffraction intensities of a green crystal of **Cu-1** complex were collected using a STOE IPDS diffractometer with Mo Ka radiation (0.71069 Å). Cell constants and the orientation matrix were obtained by least-squares refinements of the reflections in the range $2.38 < 2\theta < 25.96$. Based on a statistical analysis of the intensity distribution and the successful solution of the structure, the space group was determined to be $\boldsymbol{P\bar{1}}$ (No. 2). Machine and data collection parameters and crystal data are given in Table 2. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares requirement was based on 3739 observed reflections ($I > 2\sigma(I)$) and 392 variable parameters and converged with unweighted and weighted agreement factors of R = 0.0427 and wR = 0.1155. Atomic coordinates and equivalent isotropic displacement parameters for **Cu-1** are given in Table 3.

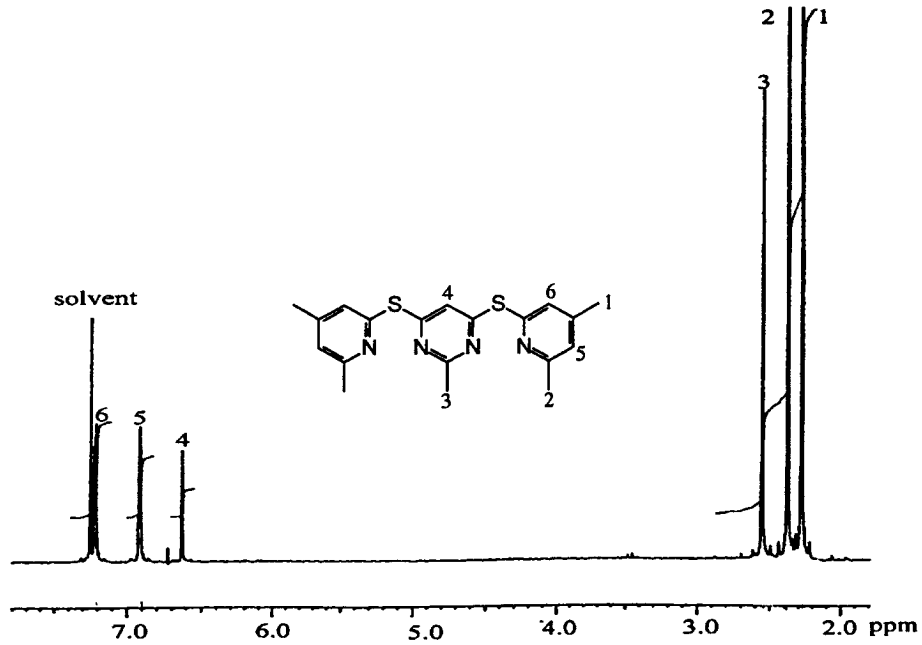


Fig.1 Proton NMR spectrum of the ligand **1**.

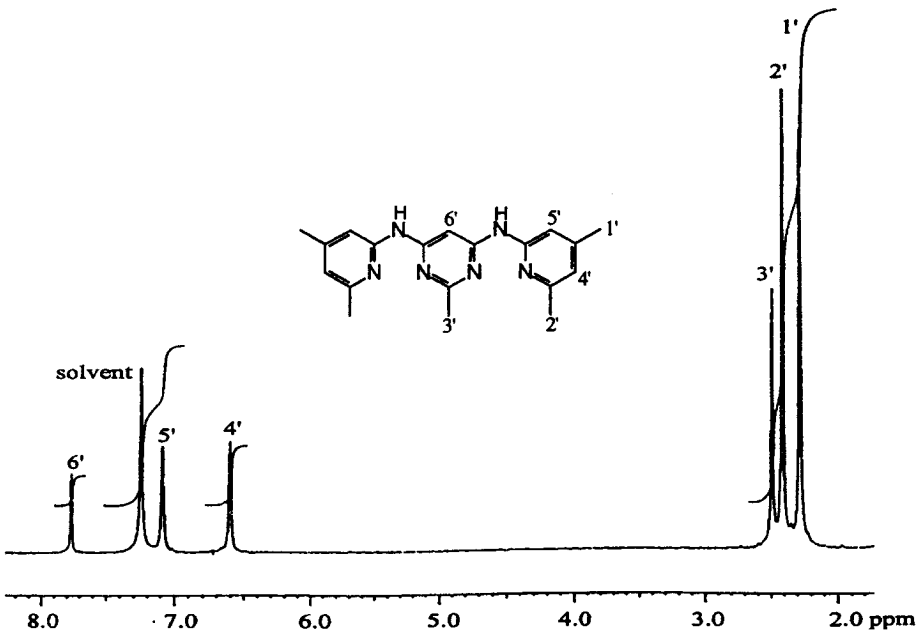


Fig.2 Proton NMR spectrum of the ligand **2**.

Table 1 Spectral data of ligands **1** and **2** and the complexes **Cu-1** and **Cu-2**.

Cmp.	IR (cm^{-1})	^1H NMR (ppm)	UV(nm)	FAB MS (m/z)
1	3142 (C-H, aromatic) 1598, 1523, 1443 (C=C, C=N)	2.28, 2.39, 2.53, 6.61, 6.90, 7.20	245, 292	369
2	3397, 3257 (N-H, aromatic) 3155, 3095, 3031 (C-H, aromatic) 1613, 1598, 1526, 1413 (C=C, C=N)	2.28, 2.41, 2.49, 6.60, 7.08, 7.76	260,292, 313	335
Cu-1	3098, 3057, 3004 (C-H, aromatic) 1608, 1526, 1511, 1444 (C=C, C=N)	2.36, 2.41, 7.46, 7.61	245, 292	1012[a]
Cu-2	3473, 3334, 3231 (N-H, aromatic) 3171, 3134, 3091, 3031 (C-H, aromatic) 1644, 1551, 1455 (C=C, C=N)	2.09, 2.24, 2.26, 6.51, 6.78, 6.81	255,277, 320	943[b]

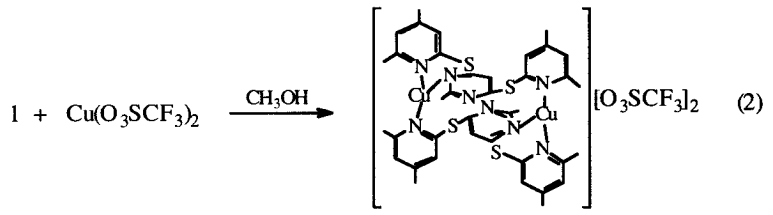
[a] signal due to $[Cu_2(N_4S_2C_{19}H_{20})_2(O_3SCF_3)]^+$

[b] signal due to $[Cu_2(N_6C_{19}H_{22})_2(O_3SCF_3)]^+$

Table 2 Crystal data and structure refinement for **Cu-1**.

Empirical formula	$[C_{19}H_{20}N_4S_2Cu]_2[0_3SCF_3]_2$
Formula weight	581.12
Temperature	200(1) K
Wavelength	.71069 Å
Crystal system	triclinic
Space group	$\boldsymbol{P}\bar{1}$ (No. 2)
Unit cell dimensions	a = 8.234(6) Å α = 96.40(2)° b = 11.224(8) Å β = 100.43(3)° c = 11.748(6) Å γ = 102.70(2)°
Volume	1028.6 (12) $Å^3$
Z	1
Density (calculated)	1.876 Mg/m^3
Absorption coefficient	1.429 mm^{-1}
F(000)	592
Theta range for data collection	2.38 to 25.96 deg.
Index ranges	$-9 \le h \le 9$, $-13 \le k \le 13$, $-14 \le l \le 14$
Reflections collected	11373
Independent reflections	3739 [R(int) = 0.0546]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3739 / 0 / 392
Goodness-of-fit on F^2	1.047
Final R indices [$I>2\sigma(I)$]	R1 = 0.0427, wR2 = 0.1155
R indices (all data)	R1 = 0.0521, wR2 = 0.1204
Largest diff. peak and hole	.401 and -.644 $eÅ^{-3}$

The stick and ball plot and the space filling diagram for **Cu-1** are presented in Fig. 3 and 4, respectively. The molecule crystallizes into a triclinic $P\bar{1}$ space group and, thus, possesses an inversion center. The structure consists of an unusual arrangement of two bridging-tridentate ligands which, however, are coordinated to two copper ions in monodentate and bidentate fashions. The complex is surrounded by only two triflate ions. This means that the copper ions in the complex possess +1 oxidation state. The ligand **1** is thus capable of reducing Cu(II) to Cu(I) as shown in eq. 2. This is quite intriguing compared to the analogous ligand DPP which does not show an ability to be oxidized. The low yield of the complex may be attributed to the transformation of the ligand after donating electrons to copper ions.[12]



(2)

The crystal structure shows that each Cu(I) centers coordinates to two pyridine and one pyrimidine nitrogen donors. The bond distances of Cu-N(1), Cu-N(4) and Cu-N(3) are 1.859(3), 1.853(3) and 2.146(3) Å, respectively. The first two distances are relatively short for this kind of ligand.[11] There may be weak interaction between copper ions and the sulfur donors as indicated by long distances of Cu-S of 2.925 and 2.966 Å. The crystal structure of a blue copper protein, plastocyanin, was found to have a Cu-$S_{methionine}$ bond distance of 2.90 Å similar to that of the complex **Cu-1**.[13] Schrauzer el al. found that the Zn(II), a d^{10} metal ion, in a zinc thioether complex also showed a weak interaction with a thioether-sulfur donor.[14] Normally, this type of bidentate heterocyclic ligand containing N donors forms complexes with Cu(I) ions in a tetrahedral geometry.[7] The failure of the ligand **1** to form a complex with Cu(I) in a bidentate fashion and give a tetrahedral geometry may stem from the preference of Cu(I), a soft acid, to interact with sulfur, a soft base. Fig. 3 and 4 reveal that the Cu(I) ions are surrounded by N(1), N(3), N(4), S(1) and S(2) donors while the N(2) donor is located outside the coordination sphere. This thus prohibits Cu(I) in **Cu-1** to interact with N(2) and renders a distorted trigonal planar geometry. Another cause of this distortion may stem from a π-stacking interactions-an important type of aromatic interactions that play a significant role in molecular recognition-which make the central pyrimidine rings of the two **1** units stacked onto each other via π-orbital interactions (Fig 4).[15] This behavior could lead to a severe twisting of the ligand and possibly caused N(2) to become inaccessible to the copper center. The angles of N(4)-Cu-N(1), N(1)-Cu-N(3) and N(4)-Cu-N(3) are 158.88(11)°, 96.34(10)° and 104.74(11)°, respectively indicating a severe distortion from a perfect trigonal planar geometry. The complete bond lengths and bond angles for **Cu-1** are compiled in Tables 4 and 5.

We also characterize **Cu-1** by spectroscopy. Complete spectral data for **Cu-1** is shown in Table 1. The Cu(I) ion possesses a filled d orbital and the complex is diamagnetic. The ^1H NMR spectrum of the complex **Cu-1** should be further evidence for the existence of Cu(I) ions. Unfortunately due to the low solubility of **Cu-1** in CD_3OD, only four signals at 2.36, 2.41, 7.46 and 7.61 ppm were observed, and their integral ratio could not be estimated. UV/vis spectrum shows only charge transfer bands at 245 and 292 nm similar to the ligand **1** where the S-Cu(II) charge transfer band of copper protein usually appears between 500-600 nm.[13] The FAB mass spectrum of **Cu-1** shows a signal at m/z 1012 due to $[Cu_2(N_4S_2C_{19}H_{20})_2(O_3SCF_3)]^+$. The elemental analysis results are also consistent with the determined structure.

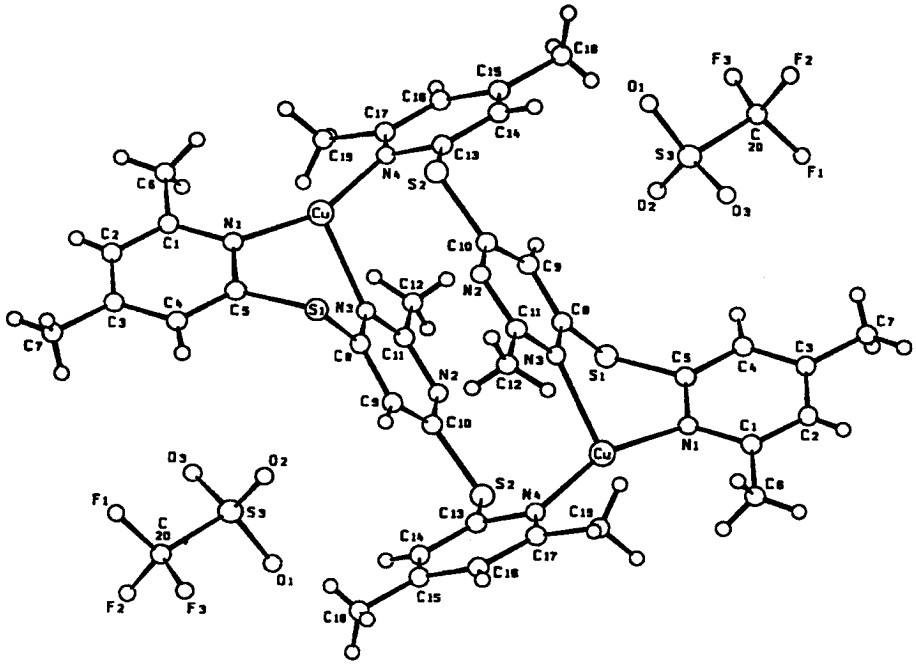


Fig.3 Stick and ball plot of **Cu-1**.

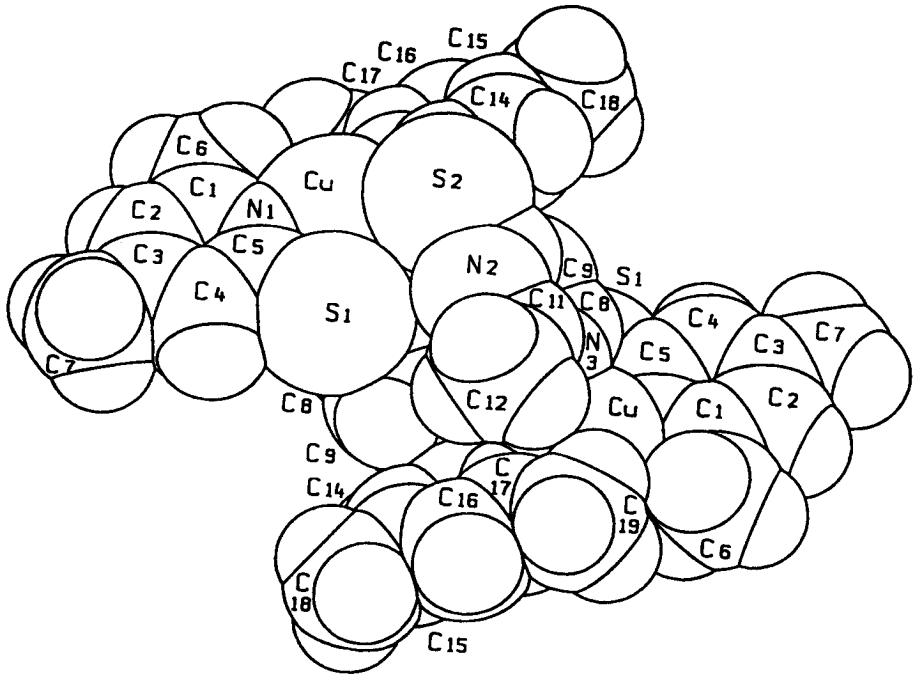


Fig.4 Space filling diagram of **Cu-1**.

Table 3 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **Cu-1**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tenser.

	x	y	z	U(eq)
Cu	1897(1)	2634(1)	8667(1)	34(1)
S(1)	-59(1)	4177(1)	7385(1)	33(1)
N(1)	2205(4)	2933(2)	7187(2)	29(1)
C(1)	3252(5)	2534(3)	6620(3)	32(1)
C(2)	3510(5)	2911(3)	5623(3)	36(1)
C(3)	2760(5)	3734(3)	5173(3)	35(1)
C(4)	1717(5)	4156(3)	5775(3)	33(1)
C(5)	1463(4)	3741(3)	6747(3)	30(1)
C(6)	4120(6)	1683(3)	7111(4)	40(1)
C(7)	3021(7)	4130(5)	4086(4)	48(1)
C(8)	1084(4)	5004(3)	8693(3)	28(1)
C(9)	821(4)	6105(3)	9024(3)	28(1)
C(10)	1600(4)	6671(3)	10086(3)	28(1)
N(2)	2613(3)	6212(2)	10772(2)	28(1)
C(11)	2815(4)	5154(3)	10382(3)	28(1)
C(12)	3923(5)	4641(4)	11171(3)	35(1)
N(3)	2073(3)	4516(2)	9373(2)	27(1)
S(2)	1443(1)	8054(1)	10727(1)	33(1)
C(13)	-156(4)	8385(3)	9763(3)	28(1)
C(14)	92(5)	8813(3)	8797(3)	32(1)
C(15)	-1199(5)	9093(3)	8097(3)	33(1)
C(16)	-2649(5)	8967(3)	8458(3)	31(1)
C(17)	-2828(4)	8553(3)	9458(3)	32(1)
C(18)	-976(8)	9540(5)	7021(4)	47(1)
C(19)	-4359(6)	8466(4)	9884(4)	43(1)
N(4)	-1596(3)	8238(2)	10106(2)	28(1)
S(3)	2713(1)	7742(1)	6742(1)	42(1)
O(1)	3161(4)	8806(2)	7567(2)	44(1)
O(2)	1061(4)	7074(3)	6596(3)	58(1)
O(3)	3917(5)	7067(3)	6780(3)	73(1)
C(20)	2728(6)	8317(4)	5433(4)	54(1)
F(1)	2453(4)	7448(3)	4566(3)	86(1)
F(2)	4180(4)	9024(3)	5445(3)	77(1)
F(3)	636(5)	8932(3)	5235(3)	90(1)

Table 4 Bond lengths [Å] for **Cu-1**.

Cu-N(4)#1	1.853(3)	C(11)-N(3)	1.283(4)
Cu-N(1)	1.859(3)	C(11)-C(12)	1.438(5)
Cu-N(3)	2.146(3)	S(2)-C(13)	1.710(3)
S(1)-C(8)	1.698(3)	C(13)-N(4)	1.303(4)
S(1)-C(5)	1.703(4)	C(13)-C(14)	1.312(5)
N(1)-C(1)	1.303(4)	C(14)-C(15)	1.340(5)
N(1)-C(5)	1.303(4)	C(15)-C(16)	1.322(5)
C(1)-C(2)	1.326(5)	C(15)-C(18)	1.438(5)
C(1)-C(6)	1.425(5)	C(16)-C(17)	1.331(5)
C(2)-C(3)	1.325(5)	C(17)-N(4)	1.293(4)
C(3)-C(4)	1.337(5)	C(17)-C(19)	1.427(6)
C(3)-C(7)	1.435(5)	N(4)-Cu#1	1.853(3)
C(4)-C(5)	1.314(5)	S(3)-O(2)	1.371(3)
C(8)-N(3)	1.287(4)	S(3)-O(3)	1.372(3)
C(8)-C(9)	1.330(4)	S(3)-O(1)	1.386(3)
C(9)-C(10)	1.314(5)	S(3)-C(20)	1.733(5)
C(10)-N(2)	1.284(4)	C(20)-F(3)	1.254(6)
C(10)-S(2)	1.690(3)	C(20)-F(2)	1.279(5)
N(2)-C(11)	1.281(4)	C(20)-F(1)	1.279(5)

Table 5 Bond angle (°) for **Cu-1**.

N(4)#1-Cu-N(1)	158.88(11)	C(11)-N(3)-Cu	131.0(2)
N(4)#1-Cu-N(3)	104.74(11)	C(8)-N(3)-Cu	111.6(2)
N(1)-Cu-N(3)	96.34(10)	C(10)-S(2)-C(13)	103.4(2)
C(8)-S(1)-C(5)	102.8(2)	N(4)-C(13)-C(14)	123.7(3)
C(1)-N(1)-C(5)	117.1(3)	N(4)-C(13)-S(2)	114.1(2)
C(1)-N(1)-Cu	126.1(2)	C(14)-C(13)-S(2)	122.2(3)
C(5)-N(1)-Cu	116.2(2)	C(13)-C(14)-C(15)	119,3(4)
N(1)-C(1)-C(2)	121.3(3)	C(16)-C(15)-C(14)	116.9(3)
N(1)-C(1)-C(6)	117.8(3)	C(16)-C(15)-C(18)	122.4(4)
C(2)-C(1)-C(6)	121.0(3)	C(14)-C(15)-C(18)	120.6(4)
C(3)-C(2)-C(1)	121.9(4)	C(15)-C(16)-C(17)	121.4(3)
C(2)-C(3)-C(4)	116.3(3)	N(4)-C(17)-C(16)	121.2(3)
C(2)-C(3)-C(7)	121.9(4)	N(4)-C(17)-C(19)	116.7(3)
C(4)-C(3)-C(7)	121.7(4)	C(16)-C(17)-C(19)	122.0(3)
C(5)-C(4)-C(3)	120.1(3)	C(17)-N(4)-C(13)	117.3(3)
N(1)-C(5)-C(4)	123.3(3)	C(17)-N(4)-Cu#1	122.9(2)
N(1)-C(5)-S(4)	118.5(3)	C(13)-N(4)-Cu#1	119.0(2)
C(4)-C(5)-S(1)	117.9(3)	O(2)-S(3)-O(3)	115.8(2)
N(3)-C(8)-C(9)	121.8(3)	O(2)-S(3)-O(1)	114.6(2)
N(3)-C(8)-S(1)	119.7(2)	O(3)-S(3)-O(1)	114 .8(2)
C(9)-C(8)-S(1)	118.3(3)	O(2)-S(3)-C(20)	103.0(2)
C(10)-C(9)-C(8)	116.9(3)	O(3)-S(3)-C(20)	103.2(2)
N(2)-C(10)-C(9)	122.4(3)	O(1)-S(3)-C(20)	102.9(2)
N(2)-C(10)-S(2)	111.4(2)	F(3)-C(20)-F(2)	107.5(4)
C(9)-C(10)-S(2)	126.3(3)	F(3)-C(20)-F(1)	108.6(4)
C(11)-N(2)-C(10)	116.8(3)	F(2)-C(20)-F(1)	106.0(4)
N(2)-C(11)-N(3)	125.3(3)	F(3)-C(20)-S(3)	111.7(3)
N(2)-C(11)-C(12)	116.1(3)	F(2)-C(20)-S(3)	111.2(4)
N(3)-C(11)-C(12)	118.6(3)	F(1)-C(20)-S(3)	111.6(3)
C(11)-N(3)-C(8)	116.8(3)		

Effects of the Bridging Amine on Coordination Chemistry of 2 towards $Cu(O_3SCF_3)_2$. The ligand **2** has almost the same structure as the ligand **1** but contains two amine bridging groups instead of thioether-sulfur donors. Reaction of the ligand **2** with $Cu(O_3SCF_3)_2$ salt in methanol gave a similar phenomenon observed in the **Cu-1** case. Addition of diethylether into the methanolic solution of **Cu-2** yielded green crystals. The ^1H NMR spectrum of the complex **Cu-2** in deuterated methanol shows signals similar to the starting ligand but displaced significantly upfield due to the influence of the charges of the copper ions. The result suggests that copper ions in this complex must have +1 oxidation state (diamagnetic) which means the ligand **2** can also act as a reductant and reduce Cu(II) ions to Cu(I) ions. As indicated in Table 1, **Cu-2** shows three absorptions due to charge transfer at 255, 277 and 320 nm. The FAB mass spectrum of the complex shows a strong signal at 943 m/z corresponding to $[Cu(C_{19}H_{22}N_6)]_2[O_3SCF_3]^+$. The elemental analysis results are consistent with the formula, $[Cu(C_{19}H_{22}N_6)]_2[O_3SCF_3]_2$. The structure of **Cu-2** can thus be deduced to be similar to the related **Cu-1** complex.

CONCLUDING REMARKS

The reactions of $Cu(O_3SCF_3)_2$ with the ligands **1** produce a dimetallic complex containing two Cu(I) centers in which each copper coordinates to 3 N donors oriented into a distorted trigonal planar geometry. The arrangement of the ligands and metals to provide these structures may be attributed to the electronic effects such as π-stacking interactions of two pyrimidine ligands and hard/soft acid/base behaviors of both metals and ligands. However, the ligand **2** containing two amine bridging groups can also react with $Cu(O_3SCF_3)_2$ to give **Cu-2** which has been shown to have a structure similar to **Cu-1**; the π-stacking interaction of the pyrimidine rings may thus be a greater contributor to the distortion of the ligands **1** and **2**. Other metal ions that can bind to both nitrogen and sulfur donors and provide tetrahedral (N_4) or octahedron (N_4S_2 or N_6) environments may be considered for the preparation of potentially useful architectures such as molecular grids. This subject will be further investigated in our laboratory.

EXPERIMENTAL SECTION

Materials. Dichloromethane was dried over phosphorus pentaoxide. Bis-trifuloro-sulfonate copper(II), 2-amino-4,6-dimethylpyridine and 1,1,1,3,3,3-hexamethyldisilazane were purchased form Aldrich Chemical Company. 4,6-dichloro-2-methylpyridine[16] and 4,6-dimethyl-2-pyridinethiol[17,18] were prepared by the published procedures. Unless otherwise noted, reactions were performed under argon or nitrogen atmosphere.

Physical Measurements. NMR spectra were recorded using a Bruker-200 FT NMR spectrometer. Mass spectra were determined at the mass spectrometry facility of the Chemistry Department, University Louis Pasteur, Strasbourg, France. IR spectra were recorded on a Nicolet Impact 410 FTIR spectrometer. Elemental analyses were carried out by the Scientific and Technological Research Equipment Center of Chulalongkorn University.

Preparation of 4,6-di-(4,6-dimethyl-2-pyridylthio)-2-methylpyrimidine, 1. Under argon atmosphere, 4,6-dimethyl-2-pyridinethiol (2.8 g, 20 mmol) was added to an ethanolic solution (30 mL) of Na (0.50 g, 22 mmol). The mixture was stirred until the sodium metal dissolved. Then, an ethanolic solution (30 mL) of 4,6-dichloro-2-methylpyrimidine (1.63 g, 10 mmol) was added, and the reaction mixture was heated at reflux for 4 h. The suspension was evaporated to dryness. The residue was subsequently redissolved in ether (100 mL) and heated at reflux for another 15 min. The suspension was filtered through a short alumina column (10

cm, 4 cm dia.) employing ether as an eluant. The solvent was removed by rotary evaporator, and an oily residue was obtained. The residue was redissolved in ether (10 mL) and n-hexane (30 mL) was then layered on. The mixture was left at -10°C overnight. The product **1** crystallized as colorless crystals which was subsequently washed with n-pentane (30 mL) and dried. (2.06 g, 56%)

^{1}H NMR (δ ppm, $CDCl_3$): 7.20 (d, 2H); 6.90 (d, 2H); 6.61 (s, 1H); 2.53 (s, 3H); 2.39 (s, 6H); 2.28 (s, 6H). IR (cm^{-1}, KBr pellet): 3142w, 2495w, 2911w, 1598vs, 1523vs, 1143vs, 1379s, 1338s, 1230s, 1180s, 1137s, 1034m, 913m, 901m, 861,s, 803s, 728m. UV/vis (nm): 245, 292. FAB MS (m/z): 369.

Preparation of 4,6-di-(4,6-dimethyl-2-pyridylamino)-2-methylpyrimidine, 2.

a. Preparation of N-trimethylsilyl-2-amino-4,6-dimethylpyridine. The following procedures were emulated with modification from a report by Smith *et al.*[19] Trimethylsilylchloride (0.6 g, 5.4 mmol) and LiI (0.24 g, 1.8 mmol) were added to a suspension of 2-amino-6-methylpyridine (9.0 g, 73.7 mmol) in 1,1,1,3,3,3-hexamethyldisilazane (32.28 g, 0.2 mol). The mixture was heated at reflux for 24 h. The clear solution was then distilled under reduced pressure (2 mm Hg). The product, N-trimethylsilyl-2-amino-6-methyl-pyridine was obtained at 62-64°C as a colorless oil (12.63 g, 88%) after a forerun of excess 1,1,1,3,3,3-hexamethyldisilazane (34°C).

b. Preparation of 2. A 1.6 M hexane solution (10 mL) of n-butyllithium was added slowly to a cool (-50°C) toluene solution (20 mL) of N-trimethylsilyl-2-amino-4,6-dimethylpyridine (3.11 g, 16 mmol). The solution was gradually warmed to room temperature, then heated to 50°C and was added dropwise a toluene solution (10 mL) of 4,6-dichloro-2-methylpyrimidine (1.30 g, 8.0 mmol). A deep red solution was formed and LiCl started to precipitate. The mixture was heated at reflux for 48 h and cooled to room temperature. A methanolic solution (20 mL) of KF (4.0 g, 68.8 mmol) was then added, and the mixture was held at 60°C for 30 min. The mixture was consequently evaporated to dryness. The products were eluted with acetone through a short silica column. The orange-brown solid obtained after evaporation contained the starting material, the monosubstituted pyrimidine and the desired **2**. Another chromatographic separation of the compounds (alumina, CH_2Cl_2/EtOAc 1:1) yielded a yellow solid which was recrystallized from ether/n-hexane (1:1) at -15°C. (0.83 g, 31%).

^{1}H NMR (δ ppm, $CDCl_3$): 7.76 (d, 2H); 7.08 (d, 2H); 6.60 (s, 1H); 2.49 (s, 3H); 2.41 (s, 6H); 2.28 (s, 6H). IR (cm^{-1}, KBr pellet): 3397w, 3257w, 3155w, 3095w, 2960w, 2904w, 1613s, 1598vs, 1526s, 1413s, 1337m, 1219s, 1199m, 1183m, 1035w, 983m, 830m. UV/vis (nm): 260, 292, 313. FAB MS (m/z): 335.

Preparation of Complex Cu-1 and Cu-2. $Cu(O_3SCF_3)_2$ (108.4 mg, 0.30 mmol) was added to a methanolic solution (5 ml) of the ligand **1** (110.5 mg, 0.30 mmol). The blue solution turned yellowish green after stirring for 24 hours. Then, 10 mL of dry diethylether was added. Green crystals of **Cu-1** were obtained after several hours. (54.3 mg, 31%)

Anal. Cald. For $[Cu_2(C_{19}H_{20}N_4S_2)_2][O_3SCF_3]_2$: C, 41.34; H, 3.47; N, 9.64 . Found: C, 41.45; H, 3.29; N, 9.68. ^{1}H NMR (δ ppm, CD_3OD): 7.61 (s, broad); 7.46 (s, broad); 2.41 (s); 2.36 (s). IR (cm^{-1}, KBr pellet): 3493b, 3098w, 3057w, 3004vw, 2945vw, 2914vw, 1608s, 1526s, 1444m, 1342m, 1275vs, 1219s, 1148s, 1030s, 856m, 635s. UV/vis (nm): 245, 292. FAB MS (m/z): 1012.

In a similar fashion to the synthesis of **Cu-1** complex, $Cu(O_3SCF_3)_2$ (36.2 mg, 0.10 mmol) was added to a methanolic solution (5 ml) of the ligand **2** (33.4 mg, 0.10 mmol). The solution became yellowish green after stirring for several hours and was allowed to stir for 24 hours. Then, 10 mL of dry diethylether was added. Green crystals of **Cu-2** were obtained in several days. (16.4 mg, 30%)

Anal. Cald. For $[Cu_2(C_{19}H_{22}N_6)_2][O_3SCF_3]_2$: C, 43.91; H, 4.05; N, 15.36 . Found: C, 43.85; H, 3.98; N, 15.40. ^1H NMR (d ppm, CD_3OD): 6.81 (δ, 4H); 6.78 (d, 4H); 6.51 (s, 2H); 2.26 (s, 6H); 2.24 (s, 12H); 2.09 (s, 12H). IR (cm^{-1}, KBr pellet): 3473b, 3334w, 3231w, 3171w, 3134vw, 3091vw, 3031vw, 2982vw, 2914vw, 1644s, 1614m, 1551s, 1455s, 1414s, 1352m, 1281s, 1250s, 1189s, 1168s, 1034s, 846m, 641m. UV/vis (nm): 255, 277, 320. FAB MS (m/z): 943.

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บทคัดย่อ

ได้ทำการสังเคราะห์ลิแกนด์ชนิดใหม่ประเภทสะพานเชื่อมไตรเดนเทตขึ้นคือ 4,6-di-(4,6-dimethyl-2-pyridylthio)-2-methylpyrimidine, **1**, และ 4,6-di-(4,6-dimethyl-2-pyridylamino)-2-methylpyrimidine, **2** ลิแกนด์ทั้งสองนี้สามารถรีดิวซ์ไอออนของโลหะทองแดงจาก +2 เป็น +1 ได้ ลิแกนด์ **1** ทำปฏิกิริยากับ $Cu(O_3SCF_3)_2$ เกิดเป็นสารประกอบเชิงซ้อน **Cu-1** ขึ้น และสามารถตกผลึก **Cu-1** ได้จากสารละลายเมธานอลโดยการเติมไดเอธิลอีเธอร์ ผลึกของ **Cu-1** นี้อยู่ในระบบผลึกแบบ ไตรคลินิก ซึ่งมี space group เป็น $P\bar{1}$ (No. 2) และมี a = 8.234 (6) Å , b = 11.224 (8) Å, c = 11.748 (6) Å, α = 96.40 (2)°, β = 100.43 (3)°, γ = 102.70 (2)°, Z = 1, R = 0.0427 และ wR = 0.1155 สารประกอบเชิงซ้อน **Cu-1** ประกอบด้วยไอออนของโลหะทองแดง 2 ไอออน และลิแกนด์ **1** 2 หน่วย ซึ่งโลหะไอออนแต่ละตัวจะจับกับ N-donor 3 อะตอมโดยจัดเรียงตัวอยู่ในรูป distorted trigonal planar ลิแกนด์ **2** ก็สามารถทำปฏิกิริยากับ $Cu(O_3SCF_3)_2$ แล้วเกิดสารประกอบเชิงซ้อน **Cu-2** ได้ ซึ่งจากการพิสูจน์ทราบโดยวิธีทางสเปกโตร-สโคปี และ การวิเคราะห์ธาตุองค์ประกอบ พบว่ามีโครงสร้างคล้ายกับสารประกอบเชิงซ้อน **Cu-1** จึงเชื่อว่าการบิดตัวของโครงสร้างของสารประกอบเชิงซ้อน **Cu-1** และ **Cu-2** เป็นผลส่วนใหญ่จาก π-stacking interaction ของวง pyrimidine