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Coordination Chemistry of Sulfonyl Amides. 2 The Crystal Structure of Copper(II) and Silver(I) Complexes of *N,N*-4-toluenesulfonyl-2-pyridylaminato Ligand

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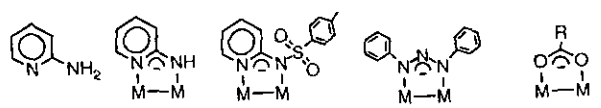
Three structures containing the *N,N*-4-toluenesulfonyl-2-pyridylaminato ligand are presented. The brown crystal of Cu_2L_4 (L = *N,N*-4-toluenesulfonyl-2-pyridylaminato) was found to crystallize in the monoclinic space group $P2_1/c$ with a = 15.762(12), b = 15.552(5), c = 20.505(11) Å, β = 104.14(7)°; V = 4874(5) Å^3; Z = 4; the final R_F = 0.050, R_{WF} = 0.049 for 5142 observed reflections and 612 variables. The Cu-Cu distance is small, 2.516(2) Å, and the complex is diamagnetic at room temperature. The colorless crystal of Ag_2L_2 was found to crystallize in the monoclinic space group $P2_1/n$ with a = 9.620(2), b = 5.625(2), c = 23.250(3) Å, β = 94.72(1)°; V = 1254.0(5) Å^3; Z = 2; the final R_F = 0.027; R_{WF} = 0.028 for 1929 observed reflections and 164 variables. The Ag-Ag distance is 2.739(1) Å. The green crystal of $CuL_2(py)_2$ was found to crystallize in the monoclinic space group $P2_1$ with a = 9.366(2), b = 20.615(7), c = 9.862(2) Å, β = 116.73(2)°; V = 1700.5(8) Å^3; Z = 2; the final R_F = 0.037; R_{WF} = 0.038 for 1636 observed reflections and 423 variables. A reversible transformation between Cu_2L_4 and $CuL_2(py)_2$ is reported.

INTRODUCTION

Amide groups are poorly coordinating systems, whereas amido anions are good σ donors. We have reported the synthesis and structure of various arene- and alkanesulfonylamido metal complexes.[1] The amino group of 2-aminopyridine (**1**) is a poor coordination site due to the delocalization of the lone pair electrons of the nitrogen atom to the pyridine ring. No metal complex of type (**2**) has been reported. After sulfonylation and deprotonation, aminopyridine becomes a good anionic ligand, *N*-aryl- or *N*-alkylsulfonyl-2-pyridylaminato (**3**) which resembles the 1,3-diphenyltriazenato[2] (**4**) and carboxylato ions[3] (**5**). They are all capable of forming bridged dinuclear complexes.



1 **2** **3** **4** **5**

We here describe the synthesis and structure of the Cu(II) dimer, Cu_2L_4 (L = *N,N*-4-toluenesulfonyl-2-pyridylaminato), the Ag(I) dimer complex, Ag_2L_2, and a Cu(II) monomer complex, $CuL_2(py)_2$. We report also the equilibrium between the Cu(II) dimer complex and the Cu(II) monomer complex in the presence of pyridine.

EXPERIMENTAL SECTION

Preparation of PtsampyH (LH)

The free ligand was prepared from the reaction of 2-aminopyridine and 4-toluenesulfonyl chloride in a 1:1 ratio in pyridine and subsequently quenched in HCl (15%, aq.). The product (80 % yield) was recrystallized from ethanol. IR (KBr) ν (N-H) 3220, ν (S=O) 1140 cm^{-1}; Anal. Calcd for $C_{12}H_{12}N_2SO_2$: C, 58.05; H, 4.87; N, 11.28, Found: C, 57.87; H, 4.50; N, 11.12.

Preparation of $[Cu_2(ptsampy)_4]$ (Cu_2L_4)

A solution of ptsampyH (1 mmol) in methanol (60 mL) was heated to boiling, mixed with a solution of copper acetate monohydrate (0.5 mmol in 15 mL methanol) and stirred for 30 min. The brown complex $[Cu_2(ptsampy)_4]$ (85 % yield) was obtained after filtration. Suitable crystals of $[Cu_2(ptsampy)_4]$ were grown by vapor diffusion of methanol into DMF solution of metal complex, UV-VIS (DMF solution) 438 nm (ε = 636.5 M^{-1}cm^{-1}); IR (KBr) ν (N-H) none, ν (S=O) 1130 cm^{-1}. Anal. Calcd for $Cu_2C_{48}H_{44}N_8S_4O_8$: C, 51.65; H, 3.97; N, 10.04, Found: C, 51.38; H, 3.43; N, 9.79.

Preparation of $[Cu(ptsampy)_2(py)_2]$ ($CuL_2(py)_2$)

Treatment of $[Cu_2(ptsampy)_4]$ microcrystal (0.01 g)

Dedicated to Professor Sheng-Lieh Liu (劉盛烈) on the occasion of his eightieth birthday.

with pyridine (ca. 10 mL) yielded a green solution. A single crystal of $[Cu(ptsampy)_2(py)_2]$ (50 % yield) was grown by the slow diffusion of diethyl ether vapor into the green solution. UV-VIS (pyridine solution) 424 nm (ε = 92 $M^{-1}cm^{-1}$), 605 nm (ε = 88 $M^{-1}cm^{-1}$); IR(KBr) ν (N-H) none, ν (S=O) 1136cm^{-1}; Anal. Calcd for $CuC_{34}H_{32}N_6S_2O_4$: C, 56.98; H, 4.47; N, 11.73, Found: C, 56.85; H, 4.06; N, 11.38.

Preparation of $[Ag_2(ptsampy)_2]$ (Ag_2L_2)

Addition of triethylamine (0.5 ml) to a mixture of $AgBF_4$ (1 mmol) and ptsampyH (1 mmol) in DMF 20 mL led to the formation of a white precipitate which was filtered off. The colorless needle crystals of $[Ag_2(ptsampy)_2]$ (70 % yield) were obtained by vapor diffusion of MeOH to the above solution. IR(KBr) ν (N-H) none, ν (S=O) 1129 cm^{-1}; Anal. Calcd for $Ag_2C_{24}H_{22}N_4S_2O_4$: C, 40.58; H, 3.12; N, 7.89, Found: C, 40.61; H, 2.60; N, 7.60.

X-ray Analysis

X-ray diffraction data were collected on a CAD-4 diffractometer. The structures were solved by Patterson maps and the heavy-atom method, and refined by a least-squares procedure. Atomic scattering factors were taken from International Tables for X-ray Crystallography. The computing programs were the NRCC VAX package.[4] The crystal data are summarized in Table 1, and the non-hydrogenic atomic coordinates are given in Tables 2-4. The bond parameters of the coordination sphere are summarized in Table 5 and of the ligand moiety are given in Table 6.

RESULT AND DISCUSSION

The ligand was prepared by mixing in stoichiometric proportions 2-aminopyridine and 4-toluenesulfonyl chloride; it was characterized by spectral means. The dinuclear metal complexes $Cu(II)_2L_4$, $Ag(I)_2L_2$ were prepared by the reaction of metal ions with the ligand LH in slightly basic condition and were characterized by IR, UV-VIS, and X-ray diffraction. The attempt to add the axial ligand, e.g. pyridine, to the Cu_2L_4 unit failed; instead, the monomeric $CuL_2(py)_2$ formed quantitatively.

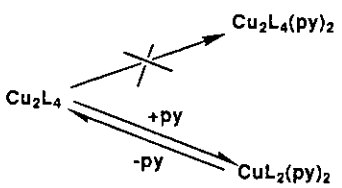


Table 1. Crystal Data

	Cu_2L_4	Ag_2L_2	CuL_2py_2
Formula	$Cu_2S_4O_8C_{48}N_8H_{44}$	$Ag_2S_2O_4C_{24}N_4H_{22}$	$CuS_2O_4C_{34}N_6H_{32}$
Fw	1116.33	710.31	716.34
Color	brown	colorless	green
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1$
a/Å	15.762(12)	9.620(2)	9.366(2)
b/Å	15.552(5)	5.625(2)	20.615(7)
c/Å	20.505(11)	23.250(3)	9.862(2)
β/deg	104.14(7)	94.72(1)	116.73(2)
V/$Å^3$	4874(5)	1254.0(5)	1700.5(8)
Z	4	2	2
Crystal dimensions/mm^3	0.30x0.30x0.50	0.20x0.20x0.40	0.20x0.20x0.40
F(000)	2296	704	742
d_{calcd}/g cm^{-3}	1.473	1.881	1.399
Radiation/Å	Mo Kα, 0.7093	Mo Kα, 0.7093	Mo Kα, 0.7093
Scan parameter	0.60+0.35tan(theta)	0.70+0.35tan(theta)	0.80+0.35tan(theta)
Scan speed/deg min^{-1}	16.48/10 to 16.48/2	16.48/10 to 16.48/2	16.48/8 to 16.48/2
hkl range h:	-18 18	-11 11	-10 8
k:	0 18	0 6	0 22
l:	0 24	0 27	0 10
Reflections collected (unique)	8571	2212	2284
Obs. reflections ($I>2\sigma(I)$)	5142	1929	1636
No. of variables	612	164	423
2θ limit/deg	49.8	49.8	44.9
Max. of c/s	0.102	0.027	0.055
Max. peak of DF-MAP/$e^-Å^{-3}$	1.170	0.610	0.700
R	0.050	0.027	0.037
R_w	0.049	0.028	0.038

Table 2. Atomic Parameters X,Y,Z and Biso of Cu_2L_4 Estimated Standard Errors Inparentheses Refer to the Last Digit Printed

	X	Y	Z	Biso
Cu1	0.70071(5)	0.42129(5)	0.21694(4)	2.32(4)
Cu2	0.80512(5)	0.54152(5)	0.26274(4)	2.44(4)
S1A	0.51349(12)	0.46889(13)	0.20189(9)	3.26(9)
N1A	0.7077(4)	0.6248(3)	0.2384(3)	3.1(3)
N2A	0.6091(3)	0.5113(3)	0.2245(3)	2.9(3)
C1A	0.7277(5)	0.7086(5)	0.2394(4)	4.1(4)
C2A	0.6633(6)	0.7715(5)	0.2286(5)	5.8(5)
C3A	0.5780(6)	0.7466(5)	0.2168(5)	5.5(5)
C4A	0.5558(5)	0.6610(5)	0.2137(4)	4.3(4)
C5A	0.6216(5)	0.5996(4)	0.2245(3)	3.0(3)
C6A	0.4589(5)	0.4863(4)	0.2666(4)	3.2(4)
C7A	0.4985(5)	0.4603(5)	0.3315(4)	3.6(4)
C8A	0.4554(5)	0.4741(5)	0.3822(4)	4.8(5)
C9A	0.3744(6)	0.5125(5)	0.3692(4)	5.1(5)
C10A	0.3291(7)	0.5289(7)	0.4238(5)	8.4(7)
C11A	0.3359(5)	0.5364(6)	0.3042(4)	5.4(5)
C12A	0.3782(5)	0.5253(5)	0.2521(4)	4.6(4)
O1A	0.5315(3)	0.3777(3)	0.19972(24)	3.8(3)
O2A	0.4598(3)	0.5078(4)	0.14215(24)	4.8(3)
S1B	0.78674(13)	0.26272(11)	0.18548(9)	3.10(9)
N1B	0.8998(4)	0.4545(3)	0.2854(3)	2.6(3)
N2B	0.8117(3)	0.3563(3)	0.2164(3)	2.5(3)
C1B	0.9763(5)	0.4796(4)	0.3278(4)	3.4(4)
C2B	1.0472(5)	0.4285(5)	0.3422(4)	4.6(4)
C3B	1.0433(5)	0.3476(5)	0.3118(4)	4.1(4)
C4B	0.9674(5)	0.3206(4)	0.2702(4)	3.5(4)
C5B	0.8930(4)	0.3752(4)	0.2574(3)	2.5(3)
C6B	0.8377(5)	0.2489(4)	0.1178(3)	3.1(3)
C7B	0.8222(6)	0.3088(5)	0.0672(4)	5.4(5)
C8B	0.8602(7)	0.2970(5)	0.0135(4)	5.9(6)
C9B	0.9107(5)	0.2252(5)	0.0098(4)	4.2(4)
C10B	0.9463(6)	0.2101(7)	-0.0511(5)	7.2(6)
C11B	0.9228(5)	0.1659(5)	0.0600(4)	4.9(5)
C12B	0.8867(5)	0.1779(5)	0.1141(4)	4.3(4)
O1B	0.6929(3)	0.2700(3)	0.15750(24)	3.8(3)
O2B	0.8169(3)	0.1940(3)	0.23180(24)	3.7(3)
S1C	0.81894(13)	0.57928(13)	0.40677(10)	3.59(9)
N1C	0.7083(3)	0.3815(3)	0.3111(3)	2.6(3)
N2C	0.7708(3)	0.5113(3)	0.3499(3)	2.6(3)
C1C	0.6766(5)	0.3045(4)	0.3194(3)	3.4(3)
C2C	0.6687(5)	0.2751(5)	0.3813(4)	4.3(4)
C3C	0.6977(5)	0.3301(5)	0.4361(4)	4.4(4)
C4C	0.7314(5)	0.4076(5)	0.4287(3)	3.5(4)
C5C	0.7390(4)	0.4346(4)	0.3642(3)	2.8(3)
C6C	0.7382(5)	0.6314(5)	0.4381(3)	3.4(4)
C7C	0.7611(5)	0.6699(5)	0.4991(4)	4.7(5)
C8C	0.6991(6)	0.7151(6)	0.5225(4)	6.0(5)
C9C	0.6141(6)	0.7211(6)	0.4873(4)	5.7(5)
C10C	0.5466(7)	0.7688(7)	0.5148(5)	8.6(7)
C11C	0.5920(6)	0.6808(7)	0.4260(5)	6.6(6)
C12C	0.6535(6)	0.6390(6)	0.4016(4)	5.9(5)
O1C	0.8558(3)	0.6411(3)	0.36899(24)	4.3(3)
O2C	0.8773(3)	0.5391(4)	0.46400(25)	4.8(3)
S1D	0.89920(13)	0.60787(12)	0.16257(10)	3.22(9)
N1D	0.6947(3)	0.4660(4)	0.1253(3)	2.6(3)
N2D	0.8180(3)	0.5481(3)	0.1669(3)	2.8(3)
C1D	0.6280(5)	0.4365(5)	0.0752(3)	3.4(4)
C2D	0.6195(5)	0.4599(5)	0.0091(3)	4.5(4)
C3D	0.6796(6)	0.5147(6)	-0.0062(4)	5.4(5)
C4D	0.7468(5)	0.5460(5)	0.0439(4)	4.4(4)
C5D	0.7532(5)	0.5204(4)	0.1110(3)	3.0(4)
C6D	0.9789(5)	0.5400(5)	0.1423(4)	3.94(17)
C7D	1.0370(13)	0.5033(12)	0.1822(10)	6.8(5)
C7D'	1.0656(11)	0.5761(10)	0.1568(8)	4.4(4)
C8D	1.0983(14)	0.4411(13)	0.1647(10)	7.8(6)
C8D'	1.1343(11)	0.5239(10)	0.1458(8)	4.6(4)
C9D	1.1004(7)	0.4305(7)	0.1148(5)	8.3(3)
C10D	1.1684(10)	0.3674(9)	0.1023(7)	13.8(5)
C11D	1.0279(13)	0.4633(12)	0.0490(9)	6.3(5)
C11D'	1.0340(11)	0.4005(10)	0.1230(8)	4.4(4)
C12D	0.9716(12)	0.5296(11)	0.0659(8)	5.4(4)
C12D'	0.9661(10)	0.4541(10)	0.1327(7)	4.0(3)
O1D	0.8779(3)	0.6727(3)	0.11108(25)	4.1(3)
O2D	0.9312(3)	0.6380(3)	0.23057(23)	4.0(3)

Table 3. Atomic Parameters X,Y,Z and Biso of Ag_2L_2 Estimated Standard Errors Inparentheses Refer to the Last Digit Printed

	X	Y	Z	Biso
Ag	0.02869(3)	0.04384(6)	0.057698(12)	4.032(15)
S	-0.08562(10)	-0.36170(17)	0.12864(4)	2.87(4)
O1	0.0202(3)	-0.2122(5)	0.15744(10)	3.50(11)
O2	-0.0657(3)	-0.6153(4)	0.13379(11)	3.57(12)
N1	0.1700(3)	0.3149(5)	0.03331(12)	3.23(13)
N2	-0.0995(3)	-0.2702(5)	0.06300(11)	2.82(13)
C1	0.2479(5)	0.4219(9)	0.07718(16)	4.72(21)
C2	0.3383(5)	0.6024(10)	0.06918(20)	5.9(3)
C3	0.3533(5)	0.6742(8)	0.01417(21)	5.40(24)
C4	0.2761(5)	0.5721(7)	-0.03110(17)	4.02(19)
C5	0.1828(4)	0.3880(6)	-0.02064(15)	2.78(15)
C6	-0.2460(4)	-0.2948(6)	0.15793(14)	2.74(15)
C7	-0.3015(4)	-0.4496(7)	0.19594(15)	3.26(16)
C8	-0.4249(4)	-0.3903(8)	0.21940(16)	3.90(19)
C9	-0.4929(4)	-0.1799(8)	0.20520(17)	3.84(19)
C10	-0.6280(5)	-0.1193(10)	0.23050(21)	5.8(3)
C11	-0.4348(4)	-0.0273(7)	0.16754(19)	4.15(20)
C12	-0.3116(4)	-0.0811(7)	0.14420(18)	3.85(19)

It was also found that the monomeric $CuL_2(py)_2$ was converted to dimeric Cu_2L_4 by dissolution of $CuL_2(py)_2$ in DMF or by heating the solid directly.

The crystal consists of discrete binuclear units of Cu_2L_4, the structure of which is shown in Fig. 1, with the bond parameters in Tables 5 and 6.

The binuclear Cu_2L_4 molecules have been shown to have the expected copper(II) acetate type structure without axial ligands in which pairs of closely separated metal atoms are bridged by the nitrogen atoms of the four ptsampy groups, such that the environment of each metal atom is almost square-planar with respect to its bonded nitrogen atoms. The array of nitrogen atoms about each metal atom is almost planar but the metal atom lies outside this plane by ca. 0.2 Å. The two N_4-planes of each complex are almost parallel, but when the structure is viewed down

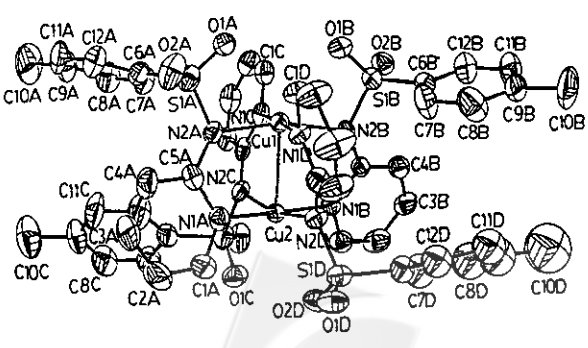


Fig. 1. ORTEP drawing of Cu_2L_4.

Table 4. Atomic Parameters X,Y,Z and Biso of CuL_2py_2 Estimated Standard Errors Inparentheses Refer to the Last Digit Printed

	X	Y	Z	Biso
Cu	0.99291(12)	0.25031	0.24620(12)	4.22(5)
S1A	1.1614(3)	0.41295(13)	0.4414(4)	7.10(18)
N1A	1.0133(8)	0.3088(3)	0.0987(7)	4.8(4)
N2A	1.1119(8)	0.3544(3)	0.3293(8)	5.3(4)
O1A	1.0631(8)	0.4695(3)	0.3766(10)	9.5(6)
O2A	1.1693(8)	0.3877(3)	0.5762(8)	7.6(5)
C1A	0.9786(10)	0.3047(5)	-0.0517(10)	5.8(5)
C2A	1.0167(11)	0.3523(5)	-0.1240(11)	7.7(7)
C3A	1.0874(12)	0.4069(5)	-0.0440(13)	8.5(7)
C4A	1.1206(12)	0.4143(5)	0.1037(12)	7.5(7)
C5A	1.0818(9)	0.3614(4)	0.1777(10)	5.2(5)
C6A	1.3577(10)	0.4348(4)	0.4775(11)	5.4(6)
C7A	1.4802(11)	0.3915(5)	0.5401(12)	7.5(7)
C8A	1.6330(12)	0.4100(6)	0.5628(13)	8.8(7)
C9A	1.6651(11)	0.4718(5)	0.5377(11)	6.9(6)
C10A	1.8340(13)	0.4919(7)	0.5745(14)	10.6(9)
C11A	1.5476(11)	0.5144(5)	0.4772(12)	6.8(7)
C12A	1.3888(12)	0.4966(5)	0.4469(13)	8.1(8)
S1B	0.6907(3)	0.14446(14)	-0.1073(3)	6.87(17)
O1B	0.8202(9)	0.1115(4)	-0.1133(9)	9.9(6)
O2B	0.5801(9)	0.1748(4)	-0.2443(7)	10.2(5)
N1B	0.7657(7)	0.2743(3)	0.1810(7)	4.7(4)
N2B	0.7647(8)	0.1913(3)	0.0302(8)	5.1(4)
C1B	0.7022(11)	0.3197(4)	0.2352(11)	6.3(7)
C2B	0.5394(13)	0.3312(6)	0.1700(15)	9.1(8)
C3B	0.4447(12)	0.2961(6)	0.0468(15)	9.8(9)
C4B	0.5054(11)	0.2493(6)	-0.0107(11)	7.8(6)
C5B	0.6774(9)	0.2351(4)	0.0608(9)	5.3(5)
C6B	0.5838(9)	0.0834(4)	-0.0659(8)	4.2(4)
C7B	0.6611(9)	0.0459(4)	0.0594(9)	4.9(5)
C8B	0.5771(12)	-0.0019(4)	0.0903(10)	6.1(6)
C9B	0.4151(11)	-0.0123(5)	0.0015(10)	6.1(6)
C10B	0.3240(13)	-0.0629(6)	0.0445(14)	8.9(8)
C11B	0.3409(11)	0.0262(5)	-0.1218(10)	6.3(6)
C12B	0.4250(11)	0.0736(5)	-0.1561(9)	5.8(5)
N1C	1.1896(8)	0.2007(3)	0.2687(7)	4.6(4)
C1C	1.1749(11)	0.1585(5)	0.1606(10)	6.4(6)
C2C	1.3132(14)	0.1297(6)	0.1618(11)	9.6(9)
C3C	1.4607(14)	0.1438(6)	0.2802(12)	9.4(9)
C4C	1.4718(11)	0.1839(6)	0.3872(12)	8.1(7)
C5C	1.3320(11)	0.2115(5)	0.3794(10)	6.1(6)
N1D	1.0010(7)	0.2055(3)	0.4295(7)	4.1(4)
C1D	1.0668(11)	0.2313(4)	0.5663(9)	6.2(6)
C2D	1.0603(14)	0.1998(6)	0.6902(10)	8.7(8)
C3D	0.9931(12)	0.1408(5)	0.6719(11)	7.3(7)
C4D	0.9308(12)	0.1145(5)	0.5356(11)	6.9(7)
C5D	0.9370(12)	0.1487(4)	0.4177(10)	5.8(6)

Table 5. Bond Parameters of Coordination Sphere

	Distances/Å		Angles/deg	
Cu_2L_4	Cu(1)-Cu(2)	2.516(2)	Cu(2)-Cu(1)-N(2A)	82.7(2)
	Cu(1)-N(2A)	2.044(5)	Cu(2)-Cu(1)-N(2B)	83.4(2)
	Cu(1)-N(2B)	2.022(5)	Cu(2)-Cu(1)-N(1C)	89.4(2)
	Cu(1)-N(1C)	2.003(5)	N(2A)-Cu(1)-N(2B)	166.0(2)
	Cu(1)-N(1D)	1.984(5)	N(2A)-Cu(1)-N(1C)	90.8(2)
	Cu(2)-N(1A)	1.978(6)	N(2A)-Cu(1)-N(1D)	87.8(2)
	Cu(2)-N(1B)	1.983(5)	N(2B)-Cu(1)-N(1C)	90.1(2)
	Cu(2)-N(2C)	2.044(5)	N(2B)-Cu(1)-N(1D)	90.7(2)
	Cu(2)-N(2D)	2.027(5)	N(1C)-Cu(1)-N(1D)	177.4(2)
			Cu(1)-Cu(2)-N(1A)	89.7(2)
			Cu(1)-Cu(2)-N(1B)	88.1(2)
			Cu(1)-Cu(2)-N(2C)	82.3(2)
			Cu(1)-Cu(2)-N(2D)	83.5(2)
			N(1A)-Cu(2)-N(1B)	177.8(2)
			N(1A)-Cu(2)-N(2C)	90.9(2)
			N(1A)-Cu(2)-N(2D)	88.7(2)
			N(1B)-Cu(2)-N(2C)	89.0(2)
			N(1B)-Cu(2)-N(2D)	90.8(2)
			N(2C)-Cu(2)-N(2D)	165.9(2)
Ag_2L_2	Ag-Ag	2.739(1)	Ag-Ag-N(1)	87.1(1)
	Ag-N(1)	2.149(3)	Ag-Ag-N(2)	80.7(1)
	Ag-N(2)	2.163(3)	N(1)-Ag-N(2)	165.9(1)
CuL_2Py_2	Cu-N(1A)	1.964(6)	N(1A)-Cu-N(2A)	61.1(3)
	Cu-N(2A)	2.386(6)	N(1A)-Cu-N(1B)	93.1(3)
	Cu-N(1B)	1.989(6)	N(1A)-Cu-N(2B)	89.9(3)
	Cu-N(2B)	2.547(7)	N(1A)-Cu-N(1C)	90.3(3)
	Cu-N(1C)	2.030(6)	N(1A)-Cu-N(1D)	167.4(3)
	Cu-N(1D)	2.001(6)	N(2A)-Cu-N(1B)	98.9(2)
			N(2A)-Cu-N(2B)	143.4(2)
			N(2A)-Cu-N(1C)	98.9(3)
			N(2A)-Cu-N(1D)	106.4(3)
			N(1B)-Cu-N(2B)	58.4(2)
			N(1B)-Cu-N(1C)	161.3(3)
			N(1B)-Cu-N(1D)	90.4(3)
			N(2B)-Cu-N(1C)	103.3(2)
			N(2B)-Cu-N(1D)	102.2(2)
			N(1C)-Cu-N(1D)	90.3(2)

the metal-metal line the two sets of coordinating nitrogen atoms are seen to be twisted markedly from the eclipsed position by about 17°. The only closely related structure is $[Cu_2(dpt)_4]$ (dpt = 1,3-diphenyltriazenato).[2] Both structure have small Cu-Cu dlstances, 2.441(2) Å for $[Cu_2(dpt)_4]$ and 2.516(2) Å for $[Cu_2L_4]$ and both are diamagnetic at room temperature.

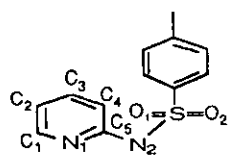
Fig. 2 shows a perspective view of Ag_2L_2. The dimer has a crystallographic inversion center. The entire central group, $Ag_2(NCN)_2$, is essentially planar. The silver ions are linearly coordinated by two nitrogen atoms. A closely related structure is $[Ag_2(form)_2]$ (form = *N,N'*-di-*p*-tolylformamidinato).[5] Both structures have small Ag-Ag distances, 2.705(1) Å for $[Ag_2(form)_2]$ and 2.739(1) Å for Ag_2L_2.

Because of these small metal-metal distances in Cu_2L_4 and Ag_2L_2, the question naturally arises whether there is metal-metal bonding. It is still controversial for the d^9-d^9 and d^{10}-d^{10} metal-metal bonds.[6] In all cases, there are

Table 6. Bond Parameters of Ligand

	Cu_2L_4	Ag_2L_2	$CuL_2(py)_2$
Distances/Å			
S-O(1)	1.449(5)	1.442(3)	1.430(8)
S-O(2)	1.439(5)	1.443(3)	1.413(8)
S-N(2)	1.607(6)	1.606(3)	1.556(7)
N(1)-C(1)	1.342(9)	1.356(5)	1.357(11)
N(1)-C(5)	1.361(9)	1.335(5)	1.368(11)
N(2)-C(5)	1.374(9)	1.386(5)	1.370(11)
C(1)-C(2)	1.372(11)	1.359(7)	1.368(14)
C(2)-C(3)	1.386(11)	1.360(7)	1.356(17)
C(3)-C(4)	1.356(11)	1.364(6)	1.361(17)
C(4)-C(5)	1.409(10)	1.405(5)	1.458(12)
N(1)···N(2)	2.308(8)	2.299(4)	2.253(10)
Angles/deg.			
O(1)-S-O(2)	117.6(3)	117.0(2)	117.2(4)
O(1)-S-N(2)	103.0(3)	104.8(2)	105.6(4)
O(2)-S-N(2)	113.4(3)	113.3(2)	109.4(4)
S-N(2)-C(5)	122.6(5)	121.3(2)	122.3(6)
C(1)-N(1)-C(5)	120.3(6)	118.8(3)	122.1(7)
N(1)-C(1)-C(2)	122.0(6)	123.3(4)	122.1(9)
C(1)-C(2)-C(3)	118.2(7)	118.0(4)	117.9(9)
C(2)-C(3)-C(4)	120.7(7)	120.5(4)	122.0(9)
C(3)-C(4)-C(5)	119.5(6)	119.5(4)	119.5(9)
N(1)-C(5)-N(2)	115.1(6)	115.3(3)	112.3(7)
N(1)-C(5)-C(4)	119.2(6)	120.0(3)	116.5(8)
N(2)-C(5)-C(4)	125.7(6)	124.7(3)	131.2(8)

L =



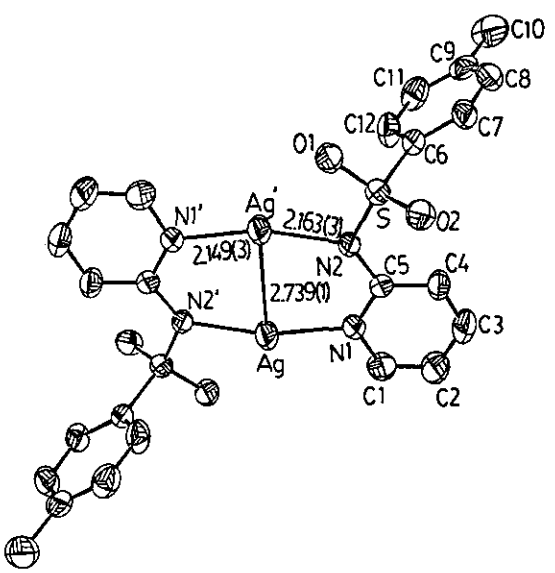


Fig. 2. ORTEP drawing of Ag_2L_2.

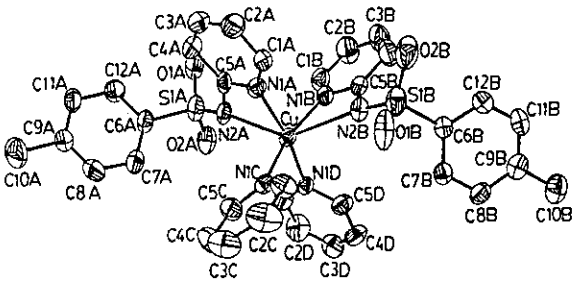


Fig. 3. ORTEP drawing of $CuL_2(py)_2$.

bridging ligands which hold together the cluster. Even the results of molecular orbital calculations do not agree with each other.[5,7]

The molecular structure of the monomeric copper complex is depicted in Fig. 3. The copper atom has a distorted octahedral geometry in which four nitrogen atoms of pyridine form a square base and two nitrogen atoms of amido groups occupy the axial positions. The Cu-N (basal) distances, ranging from 1.964(6) to 2.030(6) Å, are normal whereas the Cu-N (axial) distances are large, 2.386(6) and 2.547(7) Å, resulting from a Jahn-Teller distortion. The nonbridge bidentate mode of the *N,N* -4-toluenesulfonyl-2-pyridylaminato ligand is uncommon. Because of the rigidity of the ligand, the ligand dimensions (Table 6) are remarkably consistent in all three structures.

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Key Words

Crystal structure; Metal complexes of sulfonyl amides; Metal-metal bond.

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