Acta Chemica Scandinavica, 1997: 51: 462–469
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ACTA
CHEMICA SCANDINAVICA
ISSN 0904–213X

Synthesis and Characterization of Some New Bipyridyl-Based Multidentate Ligands and Their Cu^{I} Complexes

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Laitinen, R. H., Csoban, K., Pursiainen, J., Huuskonen, J. and Rissanen, K., 1997. Synthesis and Characterization of Some New Bipyridyl-Based Multidentate Ligands and Their Cu^{I} Complexes. – Acta Chem. Scand. 51: 462–469. © Acta Chemica Scandinavica 1997.

Four new 2,2′-bipyridyl-based ligands: 6,6′-bis(methylthiomorpholine)-2,2′-bipyridine ($\mathbf{L}^1$), 4,4′-dimethyl-6,6′-bis(methylthiomorpholine)-2,2′-bipyridine ($\mathbf{L}^2$), 6,6′-bis(methylpiperidine) −2,2′-bipyridine ($\mathbf{L}^3$) and 4,4′-dimethyl-6,6′-bis(methylpiperidine)-2,2′-bipyridine ($\mathbf{L}^4$), and dimeric Cu^{I} complexes of the ligands $\mathbf{L}^1$ and $\mathbf{L}^2$ have been synthetized. The X-ray crystal structures of the ligands $\mathbf{L}^1$ and $\mathbf{L}^2$ and the $\mathbf{L}^1$–Cu^{I} complex have been determined. Complexation of these ligands with other metals produced mainly compounds having very low solubilities.

2,2′-Bipyridine and its derivatives are well known for their ability to form stable coordination compounds with a large number of metal ions. Therefore 2,2′-bipyridine has become a widely used building block for metal-binding large ligands.[1] For example, macrocyclic polypyridine ligands allow the control of metal-ion binding as well as of photophysical and photochemical behaviour via ligand design, while at the same time they increase the thermal and photostability of the complexes.[2] 2,2′-Bipyridines and their metal complexes have strongly influenced both biological and non-biological coordination chemistry, especially in catalytic processes.[1] For example ruthenium–bipyridine compounds are widely studied because they are highly luminescent species and powerful reactants for light-induced and light-generating electron transfer processes.[3,4]

In this work we have prepared bipyridyl based multidentate ligands containing thiomorpholine and piperidine as side chains in 6,6′-positions. Being structural analogues of piperazine, which is widely used in macrocyclic chemistry, they also could allow comparison of the complexes of structurally related cyclic and open-chain structures. Corresponding ligands with methyl groups in 4,4′-positions were also studied. These ligands form easily complexes with Cu^{I}, Cu^{II}, Ag^{I}, Ru^{II} and Rh^{I} metal centres. However, owing to low solubilities of these complexes, full structural characterization was possible only for the copper(I) compounds.

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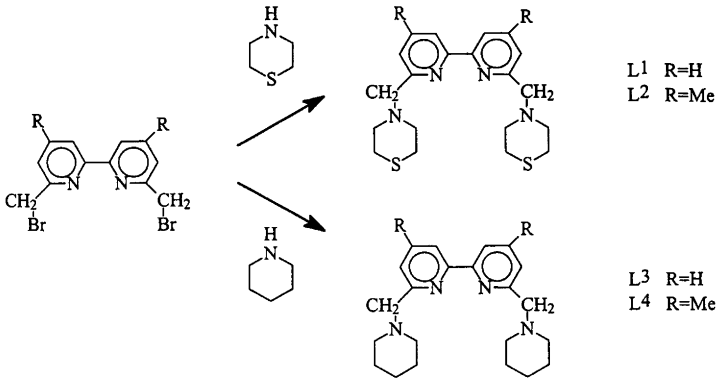
Results and discussion

Synthesis of the ligands. Treatment of thiomorpholine or piperidine with bipyridine building block afforded a series of bipyridyl based multidentate ligands which all have closely related basic structure (Scheme 1). The ligands offer S-donors and two different types of N-donors for the coordination of metals.

Suitable crystals of 6,6′-bis(methylthiomorpholine)-2,2′-bipyridine ($\mathbf{L}^1$) and 4,4′-dimethyl-6,6′-bis(methylthiomorpholine)-2,2′-bipyridine ($\mathbf{L}^2$) for X-ray diffraction analysis were obtained by slow evaporation of chloroform solution. The crystal structures of $\mathbf{L}^1$ and $\mathbf{L}^2$ are shown in Fig. 1. Both structures adopt a linear chain-type conformation where the nitrogen atoms of bipyridine are pointed to opposite directions.

Studies of the ligands $\mathbf{L}^1$ and $\mathbf{L}^2$ with copper. Copper was chosen as metal atom for the new bipyridyl-based ligands for two reasons. It has a biological importance in the reactions involving the catalytic synthesis, and it forms soluble complexes for further research. The treatment of the ligands with Cu^{I} afforded a dimeric structure where two ligand molecules bind to two copper(I) atoms (Fig. 2).

The crystals of complex $\mathbf{L}^1$–Cu^{I} for X-ray diffraction analysis were grown from acetone (contains small amount of water). Cu^{I} has a tetrahedral coordination chemistry which makes the coordination to all four nitrogens of the ligands $\mathbf{L}^1$ or $\mathbf{L}^2$ difficult. Therefore the



Scheme 1.

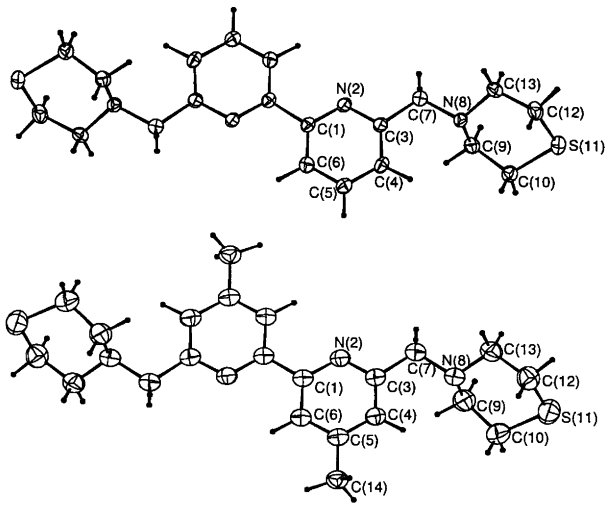


Fig. 1. The molecules of L^1 (above) and L^2 (below) showing the atom labeling. The thermal ellipsoids are shown at the 50% probability level, and H atoms are of arbitary size.

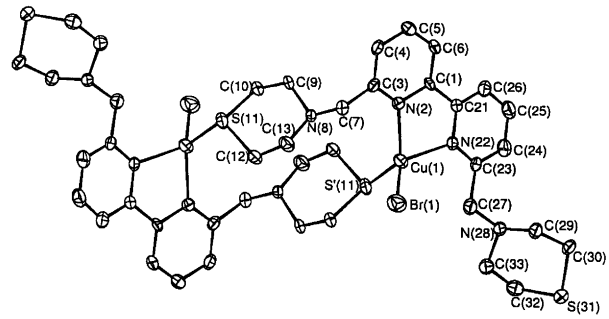


Fig. 2. The dimeric structure of L^1–Cu^I complex showing the atom labeling. The thermal ellipsoids are at the 50% probability level, and H atoms have been excluded for clarity.

characterized Cu^I complex shows a dimeric structure where the metal atom is bonded to the nitrogen atoms of a bipyridine and to the sulfur of a thiomorpholine. The coordination geometry of Cu^I in the complex L^1–Cu^I is twisted from optimal tetrahedral geometry (Fig. 3) owing to the sterical strain caused by bipyridine group.

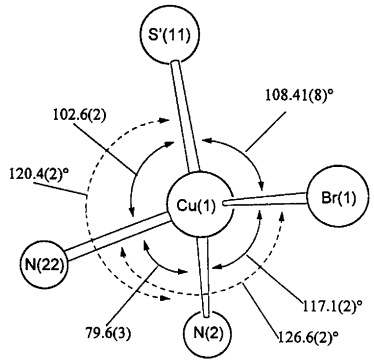


Fig. 3. The coordination geometry of Cu^I in the L^1–Cu^I complex. The H-atoms are excluded for clarity.

The distances between Cu(1)–N(2), Cu(1)–N(22), Cu(1)–Br(1) and Cu(1)–S(11) are 2.113(7), 2.113(6), 2.418(2) and 2.306(3) (in Å), respectively. These values are typical for Cu^I complexes.[5]

L^1–Cu^I complex forms endless pseudo-helical structure (Fig. 4a). The packing structure of the complex shows that the dimeric assemblies are bound together by intermolecular contacts between sulfur atom S(31) and hydrogen atom H(121) (Fig. 4b) The distances between S(31)–H(121) is 2.66 Å, which is less than van der Waals S···H distance of 3.05 Å.

The ^{1}H-NMR data of the L^2–Cu^I complex proved its basic structure similar to L^1–Cu^I complex. Crystallization for crystallographic determination was not successful.

Experimental

NMR spectra were recorded on a Bruker DPX400 spectrometer. Spectra were recorded in the solvent indicated, locked on solvent deuterium and referenced to residual solvent protons. Elemental analyses were recorded on a Perkin Elmer 2400 series II CHNS/O analyzer. Single-crystal X-ray determinations were recorded on a SYNTEX $P2_1$ and an Enraf-Nonius CAD4 diffractometer. Column chromatography was carried out on Aldrich silica gel (70–230 mesh). Commercially available

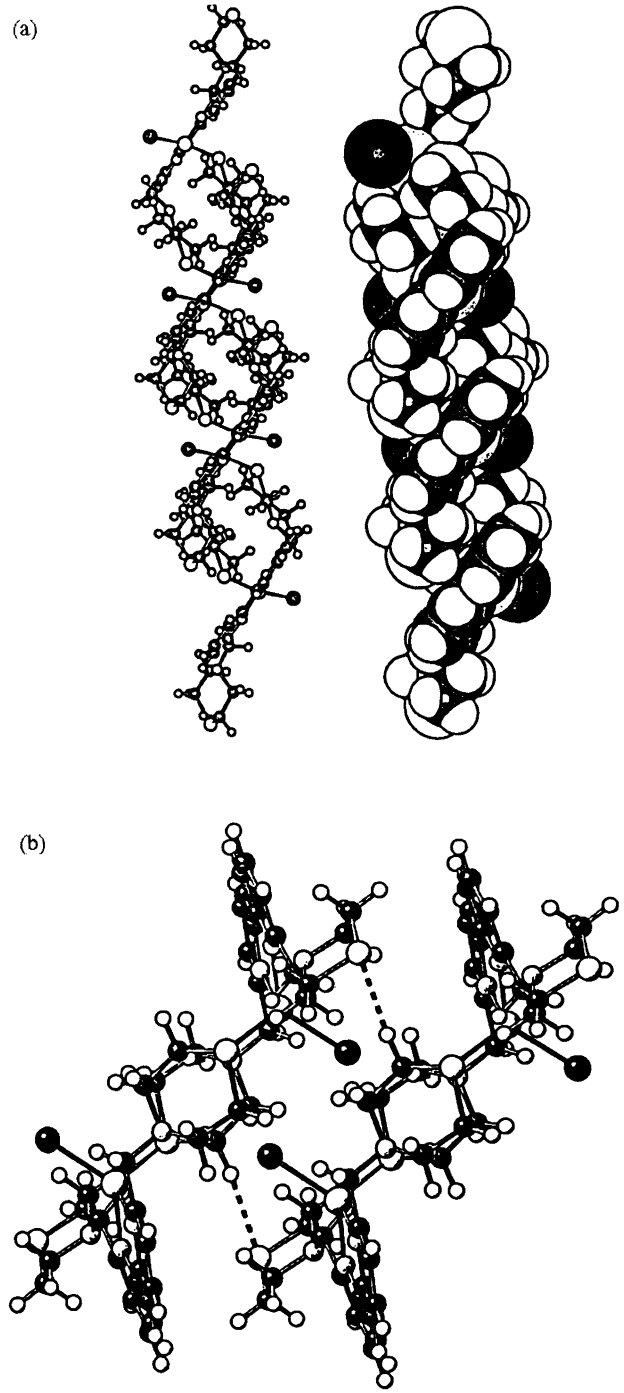


Fig. 4. (a) A side view of helical packing structure of the L^1–Cu^I complex. Space filling model on the right. (b) A view of L^1–Cu^I chains showing the S···H interaction between dimeric complexes.

reagents were used without further purification. All reactions were carried out in a nitrogen atmosphere using Schlenk techniques. The ligands are stable in air, but the Cu^I complexes seemed to oxidize with time.

Preparation of the starting materials. 6,6′-Dimethyl-2,2′-bipyridine and 4,4′,6,6′-tetramethyl-2,2′-bipyridine were prepared according to a procedure which was modified from the original published procedures for 6,6′-dimethyl-2,2′-bipyridine.[6,7]

2-Bromo-6-methylpyridine. 48% hydrobromic acid (95 ml) was cooled in an ethanol bath (−20 °C). Pulverized 2-amino-6-methylpyridine (27.0 g, 0.25 mol) was added carefully in small portions. After 2-amino-6-methylpyridine had been dissolved, 30 ml (0.6 mol) of bromine were added dropwise to the mixture. The mixture was stirred for 30 min and $NaNO_3$ (40.85 g, 0.775 mol) in water (63 ml) was then added. The temperature was not allowed to exceed −10 °C. The mixture was stirred for 30 min, after which the cooling bath was removed. Stirring was continued for 90 min. The reaction mixture was neutralised by adding NaOH (150 g, 3.75 mol) in water (375 ml). (The temperature was kept below 20 °C). The mixture was extracted four times with 75 ml portions of cloroform, and the organic phase was dried with Na_2SO_4. After filtration the solvent was evaporated and the 2-bromo-6-methylpyridine, a yellowish oil, (34.4 g, 80%) was distilled *in vacuo*.

6,6′-Dimethyl-2,2′-bipyridine-N,N′-*nickel dibromide.* Dry and activated Raney nickel catalyst (5.87 g, 0.1 mol), absolute toluene (130 ml) and 2-bromo-6-methylpyridine (34.4 g, 0.20 mol) were added to a dry 250 ml reaction flask (in nitrogen atmosphere). The mixture was refluxed for 20 h under nitrogen. In 1 h a violet product began to form. After 20 h of reaction time the mixture was cooled, and a violet solid product, 6,6′-dimethyl-2,2′-bipyridine-*N,N′*-nickel dibromide (30.0 g, 74.5%) was filtered and washed using a small amount of toluene, followed by drying *in vacuo*.

6,6′-Dimethyl-2,2′-bipyridine. 250 ml of water were warmed to about 40 °C, and 6,6′-dimethyl-2,2′-bipyridine-*N,N′*-nickel dibromide (15 g, 37.2 mmol) was added to water portion-wise. The mixture was warmed to 40 °C for 90 min. The green suspension formed was filtered, and the precipitate was washed with a small amount of cloroform. The crude product was extracted four times with 60 ml portions of cloroform, and the organic phase was dried with $MgSO_4$. After filtration the solvent was evaporated and 6,6′-dimethyl-2,2′-bipyridine (6.0 g, 87%) was recrystallised from petroleum ether.

6,6′-Bis(bromomethyl)-2,2′-bipyridine. A mixture of 6,6′-dimethyl-2,2′-bipyridine (3.8 g, 20.7 mmol), *N*-bromosuccinimide (7.4 g, 41.4 mmol), a small amount of α,α′-azoisobutyronitrile and carbontetrachloride (140 ml) was refluxed under a 1000 W lamp until succinimide flowed in the surface of the solution. The mixture was cooled to room temperature, succinimide was filtered off and the filtrate was evaporated. The precipitate was dissolved in a cloroform–methanol 1:1 volumetric mixture (25 ml), cooled in a refrigerator and filtered. The 6,6′-bis(bromomethyl)-2,2′-bipyridine (1.7 g, 24.1%) was

washed with methanol (20 ml), dried *in vacuo* and recrystallized from *N,N*-dimethylformamide.

Preparation of the ligands.

6,6'-Bis(methylthiomorpholine)-2,2'-bipyridine (L^1). A twofold excess of thiomorpholine was added dropwise to a solution of 6,6'-bisbromomethyl-2,2'-bipyridine (150.0 mg, 0.44 mmol) and potassium carbonate (303.0 mg, 2.19 mmol) in *N,N*-dimethylformamide (25 ml) at room temperature. The reaction mixture was stirred for 1 h and filtered using a double ended needle. The solution was evaporated and the precipitate subjected to chromatography on silica (CH_2Cl_2:EtOH:acetone, 2:2:1). The major yellow band was collected, the solvent was removed and the light yellow 6,6'-bis(methylthiomorpholine)-2,2'-bipyridine (126.8 mg, 74.8%) was crystallised from chloroform to give single crystals suitable for crystallographic analysis. M.p. 153 °C. Found: C 61.7; H 6.6; N 14.2%. Calc. for $C_{20}H_{26}N_4S_2$ C 62.1; H 6.8; N 14.5%. δ_H (400 MHz; solvent $CDCl_3$; standard TMS): 8.26 [1H, d, *J* 8 Hz, H(6)], 7.78 [1H, t, *J* 8 Hz, H(5)], 7.43 [1H, d, *J* 8 Hz, H(4)], 3.79 [2H, s, H(7)], 2.85 [4H, m, H(9, 13)], 2.73 [4H, m, H(10, 12)].

4,4'-Dimethyl-6,6'-bis(methylthiomorpholine)-2,2'-bipyridine. (L^2). A twofold excess of thiomorpholine was added dropwise to a solution of 4,4'-dimethyl-6,6'-bisbromomethyl-2,2'-bipyridine (135.4 mg, 0.37 mmol) and potassium carbonate (252.9 mg, 1.83 mmol) in *N,N*-dimethylformamide (30 ml) at room temperature. The reaction followed the same procedure as L^1. 4,4'-dimethyl-6,6'-bis-(methylthiomorpholine)-2,2'-bipyridine (102.9 mg, 67.1%) was crystallised from chloroform to give single crystals for crystallographic analysis. M.p. 168 °C. Found: C 61.7; H 7.3; N 11.0%. Calcd. for $C_{22}H_{30}N_4S_2$ C 63.7; H 7.3; N 13.5%. δ_H (400 MHz; solvent $CDCl_3$; standard TMS): 8.07 [1H, s, H(6)], 7.26 [1H, s, H(4)], 3.79 [2H, s, H(7)], 2.88 [4H, m, H(9, 13)], 2.76 [4H, m, H(10, 12)], 2.43 [3H, s, H(14)].

6,6'-Bis(methylpiperidine)-2,2'-bipyridine. (L^3). A twofold excess of piperidine was added dropwise to a solution of 6,6'-bisbromomethyl-2,2'-bipyridine (139.5 mg, 0.41 mmol) and potassium carbonate (281.8 mg, 2.04 mmol) in *N,N*-dimethylformamide (20 ml) at room temperature. Preparation of 6,6'-bis(methylpiperidine)-2,2'-bipyridine (92.9 mg, 65.0%) followed the same procedure as L^1. M.p. 94 °C. Found: C 68.6; H 8.5; N

Table 1. Crystallographic data.

	L^1	L^2	L^1–Cu^I
Chemical formula	$C_{20}H_{26}N_4S_2$	$C_{22}H_{30}N_4S_2$	$C_{20}H_{26}Cu_1Br_1N_4S_2 \cdot H_2O$
Molecular weight	386.580	414.626	548.037
Crystal size/mm	0.20 × 0.25 × 0.30	0.20 × 0.40 × 0.40	0.15 × 0.20 × 0.20
Color, habit	Pale yellow cube	Yellowish plate	Red rod
Crystal system	Orthorombic	Triclinic	Triclinic
Space group	Pbca (no. 61)	P-1 (no. 2)	P-1 (no. 2)
a/Å	8.459(1)	9.1239(8)	9.799(3)
b/Å	10.552(2)	9.518(2)	10.416(1)
c/Å	22.823(3)	7.3299(7)	12.947(1)
α/°	90	95.26(9)	66.186(9)
β/°	90	107.805(7)	73.45(2)
γ/°	90	112.17(1)	85.07(2)
V/Å^3	2037.2(6)	545.6(1)	1158.2(4)
Z	8	1	2
D_c/g cm^{-3}	1.185	1.293	1.567
F(000)	774	222	560
No. of measured reflections	2795	2050	3434
No. of centring reflections	25	25	25
2θ limits/°	4.0–113.0	2.0–50.0	2.0–50.0
No. of unique reflections	1329	1916	3212
Obs. data (>3σ)	858	1402	1541
μ/mm^{-1}	2.56	0.254	0.284
No. of parameters	118	127	271
F_o/parameter ratio	7.27	11.02	5.69
R^a	0.034	0.074	0.047
$R_w{}^b$	0.038	0.092	0.049
Weighting coefficients	(0.467, −0.106, 0.148, −0.146)	(10.7, 5.24, 6.59)	(6.83, −5.12, 5.44)
Conv. max shift error	<0.01	<0.01	<0.01
Res. electron density, Δρ/Å^3	0.19	0.31	0.84
T/K	296±1	296±1	296±1
λ/Å	Cu K_α 1.5418	Mo K_α 0.7107	Mo K_α 0.7107

$^a R = (\Sigma \| F_o| - |F_c\|)/\Sigma|F_o|$. $^b R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, $w = w'[1.0 - (\Delta F/6\sigma F)^2]^2$, where w' was a Chebychev polynomial for F_c.

Table 2. Fractional coordinates and equivalent isotropic factors for L^1.

Atom	*x/a*	*y/b*	*z/c*	*U*(iso)
S(11)	0.1877(1)	0.15191(9)	0.21957(4)	0.0515
N(2)	−0.3280(3)	0.4650(2)	0.0432(1)	0.0361
N(8)	−0.0585(3)	0.3230(2)	0.1517(1)	0.0353
C(1)	−0.4750(4)	0.4513(3)	0.0218(1)	0.0316
C(3)	−0.2783(4)	0.3834(3)	0.0840(1)	0.0365
C(4)	−0.3708(4)	0.2837(3)	0.1035(1)	0.0381
C(5)	−0.5199(4)	0.2680(3)	0.0801(1)	0.0452
C(6)	−0.5726(4)	0.3533(3)	0.0385(1)	0.0428
C(7)	−0.1162(4)	0.4134(3)	0.1078(2)	0.0486
C(9)	0.0024(4)	0.2086(3)	0.1236(1)	0.0398
C(10)	0.0347(4)	0.1066(3)	0.1682(1)	0.0454
C(12)	0.1044(4)	0.3026(3)	0.2403(1)	0.0475
C(13)	0.0622(4)	0.3831(3)	0.1882(1)	0.0430

Table 3. Selected bond distances (in Å) and angles (in °) for L^1.

Bond distances			
S(11)–C(10)	1.810(3)	C(1)–C(1)	1.492(5)
S(11)–C(12)	1.803(3)	C(1)–C(6)	1.377(4)
N(2)–C(1)	1.344(4)	C(3)–C(4)	1.385(4)
N(2)–C(3)	1.335(3)	C(3)–C(7)	1.508(4)
N(8)–C(7)	1.467(4)	C(4)–C(5)	1.380(4)
N(8)–C(9)	1.460(4)	C(5)–C(6)	1.382(4)
N(8)–C(13)	1.463(4)	C(9)–C(10)	1.506(4)
		C(12)–C(13)	1.505(4)
Angles			
C(10)–S(11)–C(12)	97.1(1)	C(4)–C(3)–C(7)	123.9(3)
C(1)–N(2)–C(3)	118.4(3)	C(3)–C(4)–C(5)	118.9(3)
C(7)–N(8)–C(9)	110.8(2)	C(4)–C(5)–C(6)	118.9(3)
C(7)–N(8)–C(13)	109.8(2)	C(1)–C(6)–C(5)	119.1(3)
C(9)–N(8)–C(13)	111.2(2)	N(8)–C(7)–C(3)	114.3(3)
N(2)–C(1)–C(1)	115.6(3)	N(8)–C(9)–C(10)	111.0(2)
N(2)–C(1)–C(6)	122.3(3)	S(11)–C(10)–C(9)	112.3(2)
C(1)–C(1)–C(6)	122.1(3)	S(11)–C(12)–C(13)	112.5(2)
N(2)–C(3)–C(4)	122.4(3)	N(8)–C(13)–C(12)	111.8(2)
N(2)–C(3)–C(7)	113.7(3)		

Table 4. Fractional coordinates and equivalent isotropic factors for L^2.

Atom	*x/a*	*y/b*	*z/c*	*U*(iso)
S(11)	0.7807(2)	0.4074(2)	0.6243(2)	0.0927
N(2)	0.2093(4)	0.1020(4)	−0.3089(4)	0.0608
N(8)	0.5471(4)	0.3187(4)	0.1753(5)	0.0651
C(1)	0.0387(4)	0.0471(4)	−0.3967(5)	0.0545
C(3)	0.2833(5)	0.1894(4)	−0.1229(5)	0.0616
C(4)	0.1894(5)	0.2212(4)	−0.0205(5)	0.0616
C(5)	0.0152(5)	0.1642(4)	−0.1102(5)	0.0575
C(6)	−0.0615(4)	0.0744(4)	−0.3017(5)	0.0574
C(7)	0.4747(5)	0.2555(6)	−0.0376(6)	0.0738
C(9)	0.5342(6)	0.1975(5)	0.2822(7)	0.0781
C(10)	0.5690(7)	0.2573(6)	0.4971(7)	0.0890
C(12)	0.7788(6)	0.5276(5)	0.4500(7)	0.0824
C(13)	0.7212(5)	0.4387(5)	0.2417(6)	0.0736
C(14)	−0.0882(5)	0.1984(5)	−0.0024(6)	0.0665

12.2%. Calcd. for $C_{22}H_{30}N_4$ C 75.4; H 8.6; N 16.0%. δ_H (400 MHz; solvent $CDCl_3$; standard TMS): 8.27 [1H, d, *J* 8 Hz, H(6)], 7.78 [1H, t, *J* 8 Hz, H(5)], 7.52 [1H, d, *J* 8 Hz, H(4)], 3.82 [2H, s, H(7)], 2.61 [4H, m, H(9, 13)], 1.68 [6H, m, H(10, 11, 12)].

4,4'-Dimethyl-6,6'-bis(methylpiperidine)-2,2'-bipyridine (L^4). A fourfold excess of piperidine was added dropwise to a solution of 4,4'-dimethyl-6,6'-bisbromomethyl-2,2'-bipyridine (40.5 mg, 0.11 mmol) and potassium carbonate (81.8 mg, 0.59 mmol) in *N,N*-dimethylformamide

Table 5. Selected bond distances (in Å) and angles (in °) for L^2.

Bond distances			
S(11)–C(10)	1.792(5)	C(1)–C(6)	1.387(5)
S(11)–C(12)	1.792(5)	C(3)–C(4)	1.391(5)
N(2)–C(1)	1.350(4)	C(3)–C(7)	1.506(5)
N(2)–C(3)	1.346(5)	C(4)–C(5)	1.378(5)
N(8)–C(7)	1.460(5)	C(5)–C(6)	1.385(5)
N(8)–C(9)	1.441(5)	C(5)–C(14)	1.504(5)
N(8)–C(13)	1.456(5)	C(9)–C(10)	1.516(6)
C(1)–C(1)	1.489(7)	C(12)–C(13)	1.504(6)
Angles			
C(10)–S(11)–C(12)	97.4(2)	C(3)–C(4)–C(5)	120.0(3)
C(1)–N(2)–C(3)	117.7(3)	C(4)–C(5)–C(6)	118.1(3)
C(7)–N(8)–C(9)	111.9(3)	C(4)–C(5)–C(14)	120.7(3)
C(7)–N(8)–C(13)	112.2(3)	C(6)–C(5)–C(14)	121.2(3)
C(9)–N(8)–C(13)	111.6(3)	C(1)–C(6)–C(5)	119.3(3)
N(2)–C(1)–C(1)	116.3(3)	N(8)–C(7)–C(3)	113.3(3)
N(2)–C(1)–C(6)	122.7(3)	N(8)–C(9)–C(10)	111.8(4)
C(1)–C(1)–C(6)	120.9(4)	S(11)–C(10)–C(9)	112.3(3)
N(2)–C(3)–C(4)	122.1(3)	S(11)–C(12)–C(13)	113.2(3)
N(2)–C(3)–C(7)	115.2(3)	N(8)–C(13)–C(12)	111.2(3)
C(4)–C(3)–C(7)	122.6(3)		

Table 6. Fractional coordinates and equivalent isotropic factors for the L^1–Cu^I complex.

Atom	*x/a*	*y/b*	*z/c*	*U*(iso)
Br(1)	0.3068(1)	0.3242(1)	0.7537(1)	0.0661
Cu(1)	0.1697(1)	0.5345(1)	0.7188(1)	0.0432
S(11)	0.2156(3)	0.6598(3)	0.5188(2)	0.0417
S(31)	0.8578(2)	0.9204(3)	0.6304(2)	0.0482
N(2)	−0.0397(7)	0.5154(7)	0.8293(6)	0.0341
N(8)	−0.1155(7)	0.3642(7)	0.6854(6)	0.0326
N(22)	0.1780(7)	0.6925(7)	0.7803(6)	0.0334
N(28)	0.5412(7)	0.8426(8)	0.6525(6)	0.0373
C(1)	−0.0653(9)	0.6080(9)	0.8839(7)	0.0306
C(3)	−0.1386(9)	0.4156(9)	0.8605(7)	0.0343
C(4)	−0.2678(9)	0.411(1)	0.9409(8)	0.0404
C(5)	−0.292(1)	0.504(1)	0.9950(8)	0.0430
C(6)	−0.191(1)	0.602(1)	0.9659(7)	0.0373
C(7)	−0.1027(9)	0.3117(9)	0.8050(8)	0.0381
C(9)	0.2636(9)	0.616(1)	0.3172(7)	0.0355
C(10)	0.281(1)	0.549(1)	0.4393(8)	0.0428
C(12)	0.043(1)	0.6873(9)	0.4918(8)	0.0416
C(13)	0.049(1)	0.738(1)	0.3645(9)	0.0494
C(21)	0.0496(9)	0.7126(9)	0.8475(8)	0.0365
C(23)	0.2845(9)	0.785(1)	0.7454(7)	0.0345
C(24)	0.267(1)	0.903(1)	0.7717(9)	0.0491
C(25)	0.138(1)	0.923(1)	0.840(1)	0.0523
C(26)	0.028(1)	0.826(1)	0.8780(8)	0.0441
C(27)	0.424(1)	0.753(1)	0.6733(8)	0.0442
C(29)	0.656(1)	0.847(1)	0.5512(8)	0.0445
C(30)	0.770(1)	0.954(1)	0.5179(8)	0.0494
C(32)	0.6966(9)	0.906(1)	0.7453(8)	0.0437
C(33)	0.594(1)	0.799(1)	0.7572(8)	0.0462
O(34)	0.460(3)	0.040(2)	0.974(1)	0.0581
O(35)	0.463(1)	0.182(1)	0.9643(8)	0.0442

(20 ml) at room temperature. The preparation of 4,4′-dimethyl-6,6′-bis(methylpiperidine)-2,2′-bipyridine (28.6 mg, 69.1%) followed the same procedure as L^1. M.p. 252 °C. Found: C 59.1; H 7.3; N 9.8%. Calcd. for $C_{24}H_{34}N_4$ C 76.2; H 9.1; N 18.8%. δ_H (400 MHz; solvent $CDCl_3$; standard TMS): 8.17 [1H, s, H(6)], 7.55 [1H, s, H(4)], 4.05 [2H, s, H(7)], 2.60 [4H, m, H(9, 13)], 2.47 [3H, s, H(14)], 1.88 [6H, m, H(10, 11, 12)].

Preparation of the copper(I) complexes.

L^1–Cu^I. 6,6′-Bis(methylthiomorpholine)-2,2′-bipyridine (193.3 mg, 0.5 mmol) was dissolved in an ethanol–water

Table 7. Selected bond distances (in Å) and angles (in °) for L^1–Cu^I complex.

Bond distances			
Br(1)–Cu(1)	2.418(2)	N(28)–C(33)	1.47(1)
Cu(1)–S(11)	2.306(3)	C(1)–C(6)	1.36(1)
Cu(1)–N(2)	2.113(7)	C(1)–C(21)	1.47(1)
Cu(1)–N(22)	2.113(6)	C(3)–C(4)	1.38(1)
S(11)–C(10)	1.804(9)	C(3)–C(7)	1.49(1)
S(11)–C(12)	1.796(9)	C(4)–C(5)	1.38(1)
S(31)–C(30)	1.80(1)	C(5)–C(6)	1.35(1)
S(31)–C(32)	1.802(9)	C(9)–C(10)	1.50(1)
N(2)–C(1)	1.38(1)	C(12)–C(13)	1.50(1)
N(2)–C(3)	1.34(1)	C(21)–C(26)	1.37(1)
N(8)–C(7)	1.46(1)	C(23)–C(24)	1.39(1)
N(8)–C(9)	1.46(1)	C(23)–C(27)	1.52(1)
N(8)–C(13)	1.48(1)	C(24)–C(25)	1.38(1)
N(22)–C(21)	1.36(1)	C(25)–C(26)	1.38(1)
N(22)–C(23)	1.33(1)	C(29)–C(30)	1.50(1)
N(28)–C(27)	1.44(1)	C(32)–C(33)	1.49(1)
N(28)–C(29)	1.45(1)		
Angles			
Br(1)–Cu(1)–S(11)	108.41(8)	N(2)–C(3)–C(4)	120.5(8)
Br(1)–Cu(1)–N(2)	117.1(2)	N(2)–C(3)–C(7)	117.3(8)
S(11)–Cu(1)–N(2)	120.4(2)	C(4)–C(3)–C(7)	122.3(8)
Br(1)–Cu(1)–N(22)	126.6(2)	C(3)–C(4)–C(5)	119.8(9)
S(11)–Cu(1)–N(22)	102.6(2)	C(4)–C(5)–C(6)	119.6(9)
N(2)–Cu(1)–N(22)	79.6(3)	C(1)–C(6)–C(5)	119.8(8)
Cu(1)–S(11)–C(10)	111.7(4)	N(8)–C(7)–C(3)	114.2(7)
Cu(1)–S(11)–C(12)	104.8(3)	N(8)–C(9)–C(10)	113.3(7)
C(10)–S(11)–C(12)	96.9(4)	S(11)–C(10)–C(9)	111.1(7)
C(30)–S(31)–C(32)	95.4(4)	S(11)–C(12)–C(13)	113.5(6)
Cu(1)–N(2)–C(1)	113.3(5)	N(8)–C(13)–C(12)	111.7(8)
Cu(1)–N(2)–C(3)	127.2(6)	N(22)–C(21)–C(1)	116.8(7)
C(1)–N(2)–C(3)	119.0(7)	N(22)–C(21)–C(26)	121.5(8)
C(7)–N(8)–C(9)	111.6(6)	C(1)–C(21)–C(26)	121.7(8)
C(7)–N(8)–C(13)	107.3(7)	N(22)–C(23)–C(24)	121.9(8)
C(9)–N(8)–C(13)	110.9(6)	N(22)–C(23)–C(27)	115.4(8)
Cu(1)–N(22)–C(21)	113.2(5)	C(24)–C(23)–C(27)	122.7(8)
Cu(1)–N(22)–C(23)	127.0(6)	C(23)–C(24)–C(25)	119.6(9)
C(21)–N(22)–C(23)	118.8(7)	C(24)–C(25)–C(26)	118.4(8)
C(27)–N(28)–C(29)	111.3(6)	C(21)–C(26)–C(25)	119.8(9)
C(27)–N(28)–C(33)	111.2(7)	N(28)–C(27)–C(23)	113.2(7)
C(29)–N(28)–C(33)	110.7(7)	N(28)–C(29)–C(30)	112.4(7)
N(2)–C(1)–C(6)	121.2(8)	S(31)–C(30)–C(29)	113.4(7)
N(2)–C(1)–C(21)	116.1(7)	S(31)–C(32)–C(33)	111.5(6)
C(6)–C(1)–C(21)	122.7(7)	N(28)–C(33)–C(32)	111.9(8)

4:1 mixture (50 ml). Solid CuCl (99.0 mg, 1.0 mmol) was added to that solution in one portion. The reaction mixture changed colour from green to orange under 1 h stirring. The exess of CuCl was filtered by a double-ended needle and the solvent was evaporated. The precipitate was subjected to chromatography on silica using acetone as an eluent. The dark orange band was collected, the solvent removed and the product (158.0 mg, 57.7%) crystallised from acetone–water mixture to give single crystals for crystallographic analysis. The crystallization proved difficult and the crystallographically satisfactory crystals (containing Br^-) were finally obtained from a reaction, where the starting material had not been properly purified. M.p. 102 °C. δ_H (400 MHz; solvent $CDCl_3$; standard TMS): 8.19 [2H, br, H(6, 26)], 7.82 [2H, br, H(5, 25)], 7.52 [2H, br, H(4, 24)], 3.80 [4H, br, H(7, 27)], 2.85 [8H, br, H(9, 13, 29, 33)], 2.72 [8H, br, H(10, 12, 30, 32)].

L^2–Cu^I. 4,4′-Dimethyl-6,6′-bis(methylthiomorpholine)-2,2′-bipyridine (35.2 mg, 0.1 mmol) was dissolved in an ethanol–water 4:1 mixture (20 ml). Solid CuCl (18.4 mg, 0.2 mmol) was added to that solution in one portion. Preparation of the copper complex of L^2 (26.6 mg, 46.1%) followed the same procedure as the complex of L^1. δ_H (400 MHz; solvent $CDCl_3$; standard TMS): 8.04 [2H, br, H(6, 26)], 7.51 [2H, br, H(4, 24)], 3.75 [4H, br, H(7, 27)], 2.84 [8H, br, H(9, 13, 29, 33)], 2.74 [8H, br, H(10, 12, 30, 32)], 2.18 [6H, s, H(14, 24)].

Crystal structure determinations and refinements. The crystals of $C_{20}H_{26}N_4S_2$ (L^1) and $C_{22}H_{30}N_4S_2$ (L^2) were obtained by recrystallisation from chloroform and the crystals of $C_{20}H_{26}Cu_1Br_1N_4S_2$ (L^1–Cu^I-complex) from an acetone–water mixture and mounted on a diffractometer. Diffraction data were collected at 296 ± 1 K with a Syntex $P2_1$ diffractometer using graphite-monochrom-

ated Cu K_α radiation for L^1 and a Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo K_α radiation for L^2 and the L^1–Cu^I complex. Crystal data and data collection parameters are compiled in Table 1. Two standard reflections showed no significant variation in intensity. The data of the ligands L^1 and L^2 were corrected with an empirical absorption correction (DIFABS)[8] with minimum and maximum correction coefficients of 0.877, 1.156 (L^1) and 0.645, 1.249 (L^2), respectively. The empirical absorption correction of the L^1–Cu^I complex was based on ψ-scans.

All structures were solved by direct methods[9] and subjected to full-matrix refinement.[10] Non-H atoms were refined anisotropically. The hydrogen atoms were calculated in their idealized positions (C–H distances 1.00 Å) and refined as riding atoms with fixed temperature factors ($U=0.08$ Å^2). Fractional coordinates and equivalent isotropic factors are listed in Tables 2, 4 and 6. Selected bond distances and angles are listed in Tables 3, 5 and 7.

Supplementary material contains coordinates of hydrogen atoms, anisotropic temperature factors and abstracts, and is available from the Cambridge Crystallographic Data Centre.

Acknowledgements. Financial support from Neste Foundation is gratefully acknowledged.

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Received June 20, 1996.