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Metallic Complexation by Inner and Outer Nitrogens of Bis(diazine) Heterocycles: The Cases of 4,4′-Bipyrimidine and 2,2′-Bipyrazine

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The synthesis of [Cu(6,6′-dimethyl-2,2′-bipyrazine)$_2$][BF_4] (**4**), [Cu(2,2′-dimethyl-6,6′-diphenyl-4,4′-bipyrimidine)$_2$][PF_6] (**3**), and *catena*-poly-[(2,2′-dimethyl-4,4′-bipyrimidine-*N*,*N*′,*N*″)bis(acetonitrile)dicopper(I)] (**5**) was realized from the corresponding free heterocyclic ligands. X-ray structures of the two last products were determined, and their structural data are as follows. **3**: chemical formula ($CuN_8C_{44}H_{36}PF_6$; lattice constants with esd's ($a-c$, Å; $\alpha-\gamma$, deg) 12.089(1), 16.229(7), 21.196(3), 90, 98.46(1), 90; crystal system monoclinic; space group $P2_1/n$; $Z = 4$. **4**: chemical formula $CuN_8C_{20}H_{20}BF_4$. **5**: chemical formula $CuN_5C_{12}H_{13}PF_6$; lattice constants with esd's ($a-c$, Å; $\alpha-\gamma$, deg) 12.900(3), 8.773(3), 14.702(4); 90, 101.99(2), 90; crystal system monoclinic; space group $P2_1/n$; $Z = 4$. The proton NMR and crystallographic results of the unsubstituted 4,4′-bipyrimidine show that both inner and outer nitrogens are involved in the coordination metal center process, giving a structure of an infinite-chain copper(I) polymer.

Introduction

Recently, several papers have been devoted to the characterization of relevant heterocyclic complexes that merely involved copper(II) as the coordinated metal center[1,2] and bidentate or bis-bidentate phenanthroline,[3] 2,2′-bipyridine,[4] or 2,2′-bipyrimidine[1] heterocyclic ligands. The main interest of these complexes lies with their magnetic and electronic properties.[4] Other complexes with copper(I) developed by Lehn et al.[5] showed the same interesting properties. In one of our recent papers, based on the chemistry and electronic density determination of new bis-bidentate ligands, such as 2,2′-dimethyl-4,4′-bipyrimidine (Me_2bpm) and 6,6′-dimethyl-2,2′-bipyrazine (Me_2bpz), we reported the X-ray determination of their copper(I) complexes.[6]

This work reports here the synthesis and characterization of three original copper(I) complexes of Me_2bpm and Me_2bpz.

Experimental Section

Chemicals. The synthesis and handling of each complex were carried out under an argon atmosphere. Acetonitrile was freshly distilled under argon.

Preparation of [Cu(CH_3CN)$_4$][PF_6] (1). This complex was prepared by following the method initially described by Kubas.[7]

Preparation of [Cu(CH_3CN)$_4$][BF_4] (2). This complex was prepared by following the method described by Meerwein.[8]

Preparation of [Cu(Me_2bpm)$_2$][PF_6] (3). A 0.5 equiv amount of the complex [Cu(CH_3CN)$_4$][PF_6] (0.022 g, 0.06 mmol) was added at room temperature to a colorless acetonitrile solution (5.0 mL) of Me_2bpm (0.098 g, 0.11 mmol). A deep red solution immediately appeared, and the mixture was stirred 30 min more. The solvent was concentrated under *vacuum* to approximately 2 mL. Slow evaporation of the resultant solution yielded air-stable, deep red crystals.

Preparation of [Cu(Me_2bpz)$_2$][BF_4] (4). A 0.5 equiv amount of complex **2** was added at room temperature to a colorless acetonitrile solution (5.0 mL) of Me_2bpz (0.043 g, 0.23 mmol). The solution immediately turned deep red. The reaction medium was concentrated under *vacuum* until the first crystals appear in the liquid phase. Slow evaporation of the concentrate afforded air-stable, deep red crystals.

Preparation of *catena*-poly-[Cu_2(bis(acetonitrile))(2,2′-dimethyl-4,4′-bipyrimidine-*N*,*N*′,*N*″)][PF_6]$_2$ (5). To a colorless acetonitrile solution (5.0 mL) of 2,2′-dimethyl-4,4′-bipyrimidine (0.098 g, 0.53 mmol) was added at room temperature 0.5 equiv of the complex [Cu(CH_3CN)$_4$][PF_6] (0.098 g, 0.26 mmol). The solution turned rapidly to

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Table 1. Crystallographic data for compound (**3**) and (**4**)

Compound **3**	
$CuN_8C_{44}H_{36}PF_6$	fw 885.3
$a = 12.089(1)$ Å	space group $P2_1/n$
$b = 16.229(7)$ Å	$T = 25$ °C
$c = 21.196(3)$ Å	$\lambda = 1.540\,51$ Å
$\alpha = 90°$	$\varrho_{calcd} = 1.43$ g cm^{-3}
$\beta = 98.46(1)°$	$\mu = 15.3$ cm^{-1}
$\gamma = 90°$	$R(F) = 5.1\%$
$V = 4113(2)$ Å^3	$R_w(F) = 4.2\%$
$Z = 4$	
Compound **5**	
$CuN_5C_{12}H_{13}PF_6$	fw 435.5
$a = 12.900(3)$ Å	space group $P2_1/n$
$b = 8.773(3)$ Å	$T = 25$ °C
$c = 14.702(4)$ Å	$\lambda = 0.559\,36$ Å
$\alpha = 9°$	$\varrho_{calcd} = 1.78$ g cm^{-3}
$\beta = 101.99(2)°$	$\mu = 7.9$ cm^{-1}
$\gamma = 90°$	$R(F) = 6.2\%$
$V = 1627.7(8)$ Å^3	$R_w(F) = 5.8\%$
$Z = 4$	

[a] $R = \sum|F_o| - |F_c|/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(|F|_o)^2]^{1/2}$.

a deep red and was stirred 30 min more at room temperature. Workup procedure for crystallization was the same as above.

Instrumentation. ^1H NMR spectra were recorded at 200 and 400 MHz on Bruker DRX 400 and Bruker WP 200 spectrometers (Centre Nanceien de Résonance Magnétique Nucléaire), respectively. Spectra were measured for solutions of the complexes in deuterated solvents with tetramethylsilane as internal reference.

Crystal Data and X-ray Structures of [Cu(Me₂bpm)₂][PF₆] (3) and *catena*-poly-[Cu₂(bis acetonitrilo)-(2,2′-dimethyl-4,4′-Bipyrimidine-*N,N′,N″*)][PF₆]₂ (5). Suitable crystals of $[Cu\,(Me_2bpm)_2]$ $[PF_6]$ (**3**) and *catena*-poly-$[Cu_2$(bis(acetonitrile))(4,4′-bipyrimidine-*N,N′,N″*)$][PF_6]_2$ (**5**) were chosen for the X-ray diffraction experiment. These crystals were obtained by slow evaporation of acetonitrile solutions of **3** and **5**. The crystal of **3** used in experiment was a *b*-elongated red black platelet with a {101} prism of 0.02 × 0.9 × 0.07 mm dimensions. The sample of (**5**) was a red black parallelepiped of 0.1 × 0.3 × 0.2 mm dimensions. Data were collected at room temperature on an Enraf-Nonius CAD4F diffractometer using Cu Kα radiation ($\lambda = 1.540\,51$ Å) for **3** and Ag Kα radiation ($\lambda = 0.559\,36$ Å) for compound **5**. Unit cells parameters were determined by least squares fit to setting angles of 25 reflections with $16 \leq 2\theta \leq 40°$ for compound **3** and 25 reflections with $6 \leq 2\theta \leq 16°$ for compound **5**. Details of experimental conditions are given in Table 1. Both compounds crystallize in the $P2_1/n$ space group. A total of 3454 intensities were measured for complex **3** up to $((\sin\theta)/\lambda)_{max} = 0.53$ Å^{-1}, but only 1703 reflections with $I \geq 1.5\sigma(I)$ were used to refine the structure. For compound **5**, 3659 reflections were collected up to $((\sin\theta)/\lambda)_{max} = 0.61$ Å^{-1}, and 926 reflections with $I \geq 3\sigma(I)$ were used in the structure determination and refinements. Lorentz and polarization corrections, intensity scaling, and data reduction were carried out using the DREAR package[9,10] for the $[Cu(bpm)_2][PF_6]$ complex. The SDP package[11] was used for the *catena*-poly-$[Cu_2$(bis(acetonitrile))(4,4′-bipyrimidine-*N,N′,N″*)$][PF_6]_2$ compound. In both cases no absorption correction was applied.

The two structures were solved by Patterson function[12] and successive Fourier synthesis and refined by full-matrix least squares.[13] The scattering factors were taken from ref 14. Anisotropic thermal parameters were refined for all non-hydrogen atoms. Hydrogens were placed in calculated positions (C−H = 1.07 Å) and were assigned isotropic thermal parameters which were refined at the last cycles only for compound **5**. These parameters were not refined in the compound **3** structure according to the low number of reflections. Further details and final residual peak densities values are given in Table 1.

Table 2. Fractional Coordinates, Standard Deviations, and Equivalent Isotropic Temperature Factors (Å^2) of [Cu(2,2′-dimethyl-6,6′-diphenyl-4,4′-bipyrimidine)₂][PF₆]

atom	x	y	z	B_{eq}[a]
Cu	0.1582(1)	0.57706(9)	0.72086(6)	4.37(3)
C2	0.3107(6)	0.7195(5)	0.7671(4)	3.67(9)
C4	0.3272(6)	0.6673(5)	0.6692(3)	2.43(8)
C5	0.4202(7)	0.7163(5)	0.6687(4)	3.60(8)
C6	0.4600(6)	0.7640(5)	0.7202(4)	2.59(8)
C7	0.5629(6)	0.8118(5)	0.7257(4)	2.77(8)
C8	0.6313(7)	0.8112(5)	0.6778(4)	3.51(8)
C9	0.7318(7)	0.8530(5)	0.6869(4)	3.87(9)
C10	0.7674(7)	0.8943(6)	0.7414(4)	5.43(9)
C11	0.7006(8)	0.8952(6)	0.7901(4)	5.73(9)
C12	0.6014(7)	0.8538(6)	0.7805(4)	4.71(9)
C13	0.2563(7)	0.7275(6)	0.8267(4)	6.28(9)
N1	0.4020(5)	0.7685(4)	0.7696(3)	3.88(8)
N3	0.2721(5)	0.6693(4)	0.7209(3)	3.41(8)
C2′	0.1493(6)	0.5128(5)	0.5854(4)	3.96(9)
C4′	0.2813(6)	0.6096(5)	0.6196(4)	2.78(8)
C5′	0.3289(6)	0.5993(5)	0.5653(4)	3.25(8)
C6′	0.2818(6)	0.5409(5)	0.5226(4)	2.66(8)
C7′	0.3315(6)	0.5200(6)	0.4648(4)	3.19(8)
C8′	0.4127(7)	0.5669(6)	0.4423(4)	4.37(9)
C9′	0.4581(6)	0.5434(5)	0.3880(4)	3.78(9)
C10′	0.4227(7)	0.4720(6)	0.3574(4)	4.76(9)
C11′	0.3460(7)	0.4232(6)	0.3769(4)	5.23(9)
C12′	0.3002(6)	0.4472(6)	0.4322(4)	4.45(9)
C13′	0.0445(8)	0.4658(6)	0.5981(5)	6.49(9)
N1′	0.1923(5)	0.4974(4)	0.5318(3)	3.95(8)
N3′	0.1925(5)	0.5665(4)	0.6307(3)	3.28(8)
C2a	0.2960(6)	0.4351(6)	0.7931(4)	4.32(9)
C4a	0.1347(7)	0.4762(5)	0.8288(4)	3.33(8)
C5a	0.1611(6)	0.4251(6)	0.8806(4)	3.66(8)
C6a	0.2577(6)	0.3788(5)	0.8858(4)	2.80(8)
C7a	0.2998(7)	0.3224(5)	0.9394(4)	3.85(9)
C8a	0.4024(8)	0.2865(6)	0.9423(5)	6.56(9)
C9a	0.4396(8)	0.2334(7)	0.9947(5)	8.53(9)
C10a	0.3753(9)	0.2202(7)	1.0411(4)	7.76(9)
C11a	0.2743(8)	0.2554(6)	1.0384(4)	6.90(9)
C12a	0.2350(7)	0.3065(6)	0.9869(4)	6.07(9)
C13a	0.3729(8)	0.4396(7)	0.7429(5)	6.93(9)
N1a	0.3252(5)	0.3838(4)	0.8414(3)	4.17(8)
N3a	0.2033(5)	0.4836(4)	0.7847(3)	3.33(8)
C2a′	−0.0653(7)	0.6243(5)	0.7537(4)	3.77(9)
C4a′	0.0308(6)	0.5285(5)	0.8172(4)	2.63(8)
C5a′	−0.0545(7)	0.5211(5)	0.8520(4)	3.42(8)
C6a′	−0.1513(6)	0.5691(5)	0.8323(4)	3.28(8)
C7a′	−0.2518(6)	0.5602(5)	0.8637(4)	3.86(8)
C8a′	−0.2566(7)	0.5119(6)	0.9154(4)	5.05(9)
C9a′	−0.3557(8)	0.5026(7)	0.9424(5)	6.95(9)
C10a′	−0.4477(8)	0.5432(7)	0.9154(5)	7.76(9)
C11a′	−0.4451(7)	0.5911(7)	0.8654(5)	6.90(9)
C12a′	−0.3489(7)	0.6041(6)	0.8381(4)	6.07(9)
C13a′	−0.0673(7)	0.6825(6)	0.7004(5)	6.93(9)
N1a′	−0.1543(5)	0.6194(4)	0.7839(3)	4.33(8)
N3a′	0.0257(5)	0.5782(4)	0.7669(3)	3.53(8)
P	0.0987(3)	0.7014(2)	0.9826(1)	5.95(6)
F1	0.0351(4)	0.7635(3)	1.0235(2)	7.06(8)
F2	0.0488(5)	0.6281(4)	1.0187(3)	8.53(8)
F3	0.2035(4)	0.7030(4)	1.0361(3)	8.71(8)
F4	0.1590(5)	0.6390(4)	0.9427(3)	9.12(8)
F5	−0.0085(5)	0.7011(4)	0.9309(3)	9.87(8)
F6	0.1475(5)	0.7779(4)	0.9485(3)	9.16(8)

[a] $B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Tables 2 and 3 give final fractional coordinates and equivalent isotropic thermal parameters of non-hydrogen atoms for compounds **3** and **5**, respectively. Main bond distances and angles are listed in Table 4. Anisotropic thermal parameters for non-hydrogen atoms and fractional coordinates of hydrogens are reported as Supporting Information.

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Table 3. Fractional Coordinates, Standard Deviations, and Equivalent Isotropic Temperature Factors (Å^2) of *catena*-poly-[(2,2′-Dimethyl-4,4′-bipyrimidine-*N*,*N*′,*N*″)-bis(acetonitrile)dicopper(I)]

atom	*x*	*y*	*z*	B_{eq}[a]
Cu	0.0811(2)	0.2093(3)	0.2127(1)	2.95(4)
C2	0.251(1)	−0.046(2)	0.2325(9)	1.9(4)
C4	0.188(1)	0.050(2)	0.087(1)	2.3(4)
C5	0.270(1)	−0.027(2)	0.057(1)	3.2(4)
C6	0.337(1)	−0.113(2)	0.119(1)	3.2(4)
C7	0.236(1)	−0.056(2)	0.331(1)	3.3(4)
N1	0.324(1)	−0.132(1)	0.2069(9)	3.2(4)
N3	0.1814(9)	0.045(1)	0.1757(8)	2.1(3)
C2′	−0.041(1)	0.295(2)	0.019(1)	3.5(4)
C4′	0.103(1)	0.140(2)	0.027(1)	2.5(4)
C5′	0.085(1)	0.132(2)	−0.068(1)	2.3(4)
C6′	0.002(1)	0.215(2)	−0.117(1)	3.5(4)
C7′	−0.113(1)	0.379(2)	0.067(1)	4.7(5)
N1′	−0.0640(9)	0.292(2)	−0.0756(8)	3.1(3)
N3′	0.042(1)	0.225(2)	0.0712(8)	2.5(3)
N	−0.026(1)	0.166(2)	0.2832(9)	3.8(4)
C8	−0.083(1)	0.156(2)	0.330(1)	2.8(4)
C9	−0.157(1)	0.145(2)	0.393(1)	6.3(6)
P	0.0966(4)	0.3282(7)	−0.3486(4)	4.9(2)
F1	0.135(1)	0.187(2)	−0.2848(8)	8.9(4)
F2	0.108(1)	0.236(2)	−0.4365(7)	9.6(4)
F3	0.094(1)	0.418(2)	−0.2569(9)	10.8(5)
F4	0.2166(9)	0.381(2)	−0.3418(8)	9.5(4)
F5	0.064(1)	0.470(2)	−0.410(1)	11.6(5)
F6	−0.018(1)	0.281(2)	−0.3542(9)	12.7(6)

[a] See footnote *a* of Table 2.

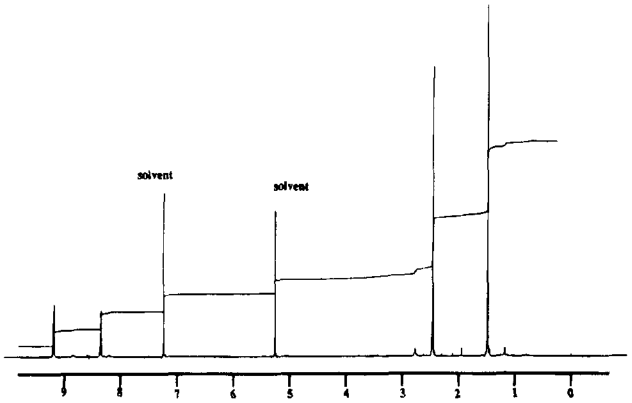

Figure 1. ^{1}H-NMR spectrum of *catena*-poly-[(2,2′-dimethyl-4,4′-bipyrimidine-*N*,*N*′,*N*″)bis(acetonitrile)dicopper(I)] (solvent $CDCl_3$).

Table 4. Selected Bond Distances (Å), Angles (deg) and Standard Deviations of [Cu(2,2′-dimethyl-6,6′-diphenyl-4,4′-bipyrimidine)$_2$][PF_6] (**3**) and *catena*-poly-[(2,2′-Dimethyl-4,4′-bipyrimidine-*N*,*N*′,*N*″)bis(acetonitrile)dicopper(I)] (**5**)

Distances for **3**

Cu−N3	2.034(6)	C2−N3	1.31(1)	C2′−N3′	1.34(1)
Cu−N3′	2.022(6)	C2−N1	1.36(1)	C2′−N1′	1.34(1)
Cu−N3a	2.053(6)	C6−N1	1.35(1)	C6′−N1′	1.33(1)
Cu−N3a′	1.994(6)	C4−N3	1.36(1)	C4′−N3′	1.33(1)
C4−C4′	1.46(1)	C4−C5	1.38(1)	C4′−C5′	1.37(1)
		C5−C6	1.37(1)	C5′−C6′	1.37(1)
		C2−C13	1.51(1)	C2′−C13′	1.54(1)
C2a−N3a	1.36(1)	C2a′−N3a′	1.33(1)		
C2a−N1a	1.33(1)	C2a′−N1a′	1.33(1)		
C6a−N1a	1.34(1)	C6a′−N1a′	1.31(1)		
C4a−N3a	1.34(1)	C4a′−N3a′	1.33(1)		
C4a−C5a	1.37(1)	C4a′−C5a′	1.36(1)		
C5a−C6a	1.38(1)	C5a′−C6a′	1.42(1)		
C2a−C13a	1.51(1)	C2a′−C13a′	1.47(1)		
C4a−C4a′	1.51(1)				

Angles for **3**

N3−Cu−N3′	80.2(3)	Cu−N3a−C4a	113.1(6)
N3−Cu−N3a′	125.8(3)	Cu−N3a′−C4a′	116.1(5)
N3′−Cu−N3a	119.3(3)	Cu−N3−C4	113.2(5)
N3a−Cu−N3a′	80.7(3)	Cu−N3′−C4′	113.8(5)
C2−N1−C6	116.9(7)	C2′-N1′−C6′	116.7(7)
N1−C2−N3	126.4(8)	N1′-C2′−N3′	124.7(7)
C2−N3−C4	117.0(7)	C2′-N3′-C4′	117.0(7)
N3−C4−C4′	114.6(6)	C4−C4′−N3′	116.3(7)
C4−C5−C6	120.8(8)	C4′-C5′-C6′	116.9(7)
C5−C6−N1	119.4(7)	C5′-C6′-N1′	122.6(7)
C7−C6−N1	116.4(7)	C7′-C6′-N1′	115.9(7)
C2a−N1a−C6a	117.4(7)	C2a′−N1a′-C6a′	118.9(7)
N1a-C2a-N3a	125.8(8)	N1a′−C2a′-N3a′	124.6(7)
C2a−N3a−C4a	116.1(7)	C2a′−N3a′-C4a′	116.8(7)
N3a−C4a−C4a′	115.0(7)	N3a′−C4a′-C4a′	115.0(7)
C4a−C5a−C6a	119.1(8)	C4a′−C5a′-C6a′	116.1(8)
C5a−C6a-N1a	120.5(7)	C5a′−C6a′-N1a′	120.1(7)
C7a−C6a-N1a	113.6(7)	C7a′−C6a′-N1a′	119.0(7)

Distances for **5**

Cu−N1″	2.06(1)	N3−C2	1.35(2)	N3′−C2′	1.33(2)
Cu−N	1.92(1)	N1−C2	1.32(2)	N1′−C2′	1.37(2)
Cu−N3	2.08(1)	N1−C6	1.34(2)	N1′−C6′	1.33(2)
Cu−N3′	2.04(1)	N3−C4	1.32(2)	N3′−C4′	1.35(2)
C4′-C4	1.48(2)	C4−C5	1.42(2)	C4′−C5′	1.37(2)
C8−C9	1.47(3)	C5−C6	1.35(2)	C5′−C6′	1.37(2)
N−C8	1.11(2)	C2−C7	1.50(2)	C2′−C7′	1.47(3)

Angles for **5**

N−Cu−N3	123.9(5)	Cu−N3−C4	113.8(9)
N−Cu−N1″	103.2(5)	Cu−N3′-C4′	113.9(9)
N3−Cu−N3′	79.4(5)	N−C8−C9	178.(1)
N3′-Cu−N1″	121.9(5)	Cu−N−C8	172.(1)
C2−N1−C6	116.(1)	C2′-N1′-C6′	117.(1)
N1−C2−N3	126.(1)	N1′-C2′-N3′	124.(2)
C2−N3−C4	117.(1)	C2′-N3′-C4′	118.(1)
N3−C4−C4′	115.(1)	N3′-C4′-C4	116.(1)
C4−C5−C6	118.(2)	C4′-C5′-C6′	118.(1)
N1−C6−C5	122.(2)	N1′-C6′-C5′	122.(1)

Table 5. ^{1}H-NMR Data for the Investigated Compounds **3**−**5**

			protons of R_1		protons of R_2		arom* protons		
compd	R_1	R_2	mult/ intens	δ	mult/ intens	δ	mult/ intens	δ	CH_3CN
3	CH_3	C_6H_5	s/6	2.75	m/3	8.15	s/1	8.35	
					m/2	8.77	s/1	9.11	
4	CH_3	H	s/6	2.60	s/1	8.55	s/1	9.30	
5	CH_3	H	s/6	2.46	d/1	8.30	d/1	9.15	s/3 1.49

Results and Discussion

Characterization of the Me_2bpm and Me_2bpz Complexes. All the complexes form deep red, air-stable crystals. In the literature, structural analyses of copper(II) complexes and polymer systems were recently reported with the diazine ligands[15,16] bpm and bpz (2,2′-isomers). These complexes present some interesting features, notably the presence of a distorted tetrahedral configuration around the copper atom. Proton NMR spectra of the Me_2bpm and Me_2bpz complexes are illustrated in Figures 1 and 2, and their spectral data are given in Table 5. The methyl protons (R_1) appear as a unique signal indicating they are isochronous. A comparison of the chemical shifts in the free ligands[17] and in the complexes revealed a general shielding effect on the R_1 protons (0.14−0.24 ppm) induced by the coordination with the metal and a deshielding effect on the phenyl and heterocyclic aromatic protons (R_2) (0.2−0.6 ppm); because of its unsolubility, complex **4** NMR data were obtained in CD_3CN instead of $CDCl_3$ as

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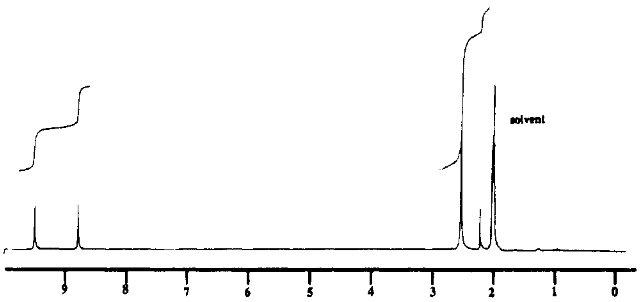

Figure 2. ^{1}H-NMR spectrum of [Cu(6,6′-dimethyl-2,2′-bipyrazine)$_2$]-[BF$_4$] (solvent CDCl$_3$).

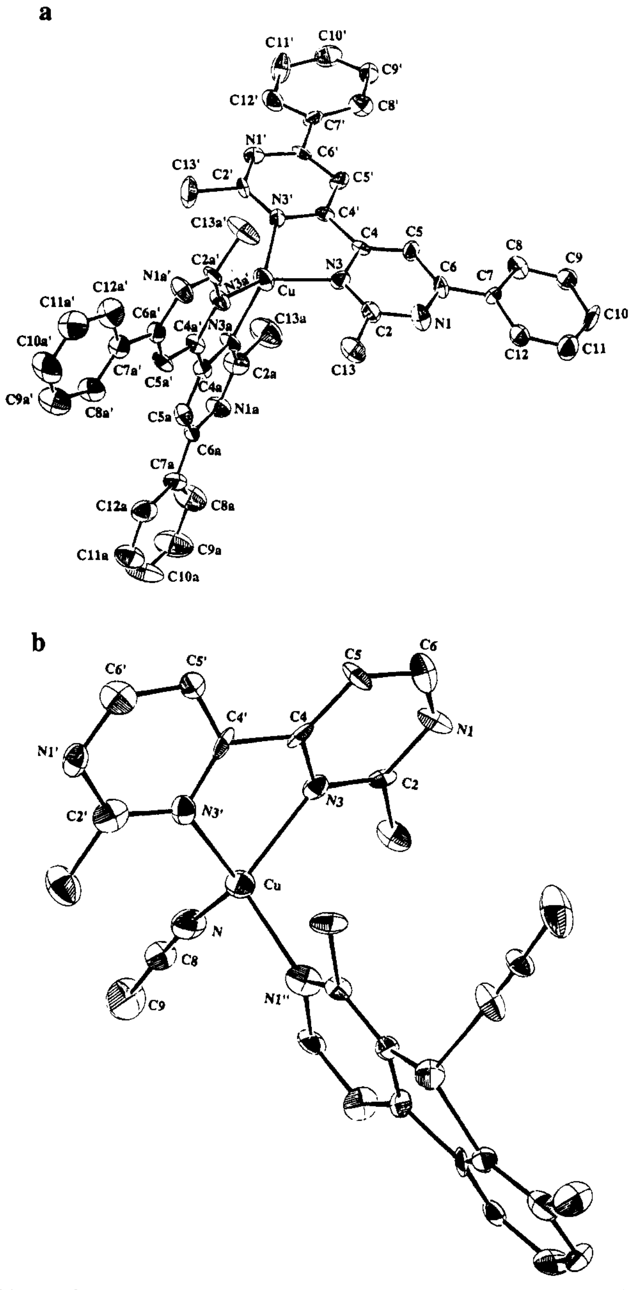

Figure 3. (a) ORTEP drawing and labeling scheme for [Cu(2,2′-dimethyl-6,6′-diphenyl-4,4′-bipyrimidine)$_2$][PF$_6$]. (b) ORTEP drawing and labeling scheme for *catena*-poly-[(2,2′-dimethyl-4,4′-bipyrimidine-*N,N′,N″*)bis(acetonitrilo)dicopper(I)].

solvent. Complex **5** showed a supplementary signal that corresponds to the CH$_3$CN−Cu coordinated molecule.

In the solid state, considering one isolated unit (one copper coordinated to two Me$_2$bpm) of the complex, the different methyl groups and the four aromatic protons in compound **5** are theoretically in a nonequivalent environment. Therefore, in solution, four different resonances for the methyl protons and for the aromatic protons are expected. Such a multiplicity is not observed. Concerning the polymeric nature of **5**, the observed methyl protons chemical shift value for CH$_3$CN clearly indicate that the latter is coordinated to the copper central atom (δ = 1.5 ppm instead of 2.0 ppm in a free molecule). This argument is in good agreement with the polymeric structure conservation of **5** in solution. Nevertheless, the magnetic unequivalency of the two aromatic protons in **3** may be attributed to a shielding and a deshielding effect induced by the proximity of the phenyl groups at the α position. Regarding compound **4**, one can see that the corresponding methyl cyanide

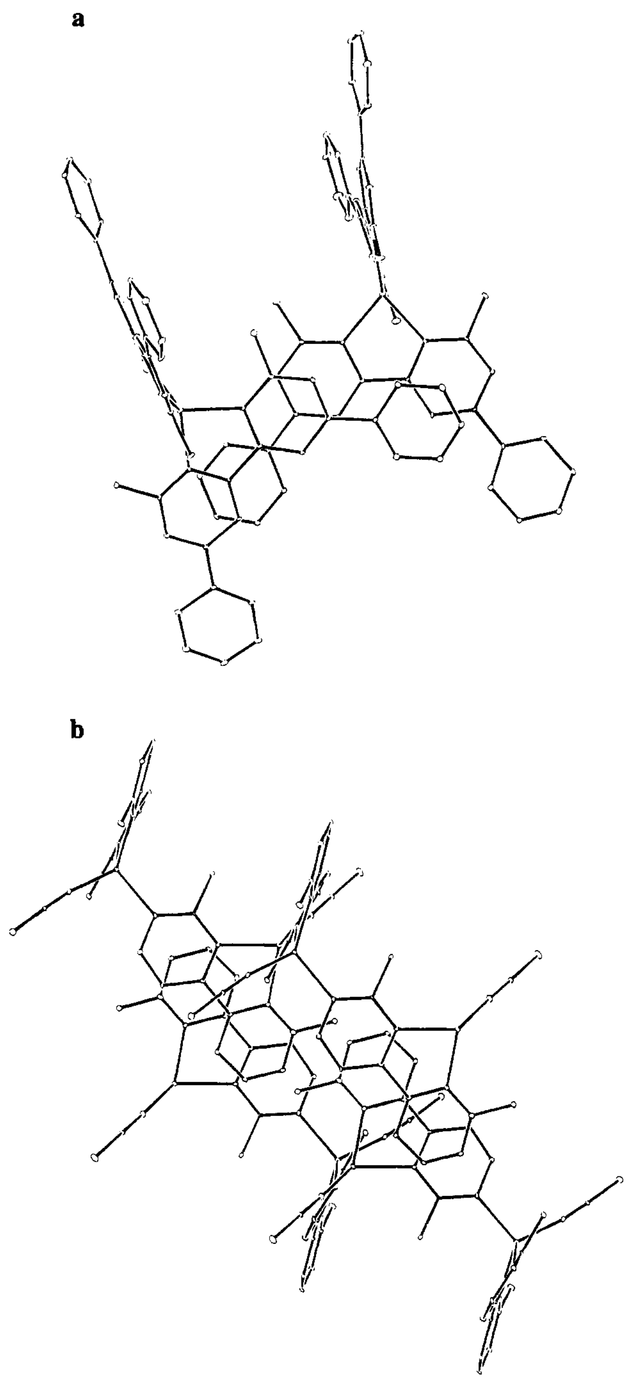

Figure 4. (a) Overlapping of two face to face molecules of [Cu(2,2′-dimethyl-6,6′-diphenyl-4,4′-bipyrimidine)$_2$][PF$_6$]. (b) Overlapping of two face to face molecules of *catena*-poly-[(2,2′-dimethyl-4,4′-bipyrimidine-*N,N′,N″*)bis(acetonitrilo)dicopper(I)].

signal is absent and therefore suggests a tetrahedral structure such as found in the complex **3**.

Molecular Configuration of [Cu(Me$_2$bpm)$_2$][PF$_6$] (3) and *catena*-poly-[Cu$_2$(bis(acetonitrile))(4,4′-bipyrimidine-*N*,*N*′,*N*″)]-[PF$_6$]$_2$ (5). ORTEP[18] views of the molecules are shown in Figures 3a,b with the atom-numbering schemes. A previous structure study of 2,2′-dimethyl-6,6′-diphenyl-4,4′-bipyrimidine[19] reveals an s-trans conformation and a low value of the rotational barrier energy along the C4−C4′ axis. No change in C4−C4′ distance was shown in the 2,2′-dimethyl-4,4′-bipyrimidine structure study so a low value of rotational barrier energy could also be assumed for this molecule.

As expected, the pyrimidine group rotates around this axis to present the two inner N3 nitrogen atoms toward the copper. The structure of compound **5** shows that inner nitrogens are not the only atoms involved in the complexation process but also outer nitrogens when the phenyl groups are removed. In comparison with previous structure determinations of bipyrimidine molecules[17,19] the distances C−C and C−N and angles N−C−N and C−N−C are not significantly modified by the metallic complexation. In these two compounds, the copper atom is in a distorted tetrahedral coordination. This distortion is mainly illustrated by different values of N−Cu−N angles varying from 79 to 123° for the two complexes. The smallest angles involve in the two cases the inner nitrogen belonging to the same bipyrimidine group (N3−Cu−N3′ = 79.4(5)° for compound **3** and 80.2(3)° for compound **5**. The average Cu−N distance is 2 Å when N belongs to pyrimidine ring, but this distance is a little shorter (Cu−N = 1.92 (1) Å) for the acetonitrile nitrogen as observed for the copper complex of phenanthroline.[3] The torsion angles between the two pyrimidine rings are respectively 3° for compound **3** and 9° for compound **5**. The phenyl groups are nearly in the same plane of pyrimidines. The greatest dihedral angle around the C6−C7 axis is 8° for complex **3**.

Molecular stacking of compound **3** exhibits a first planar pseudocompact hexagonal arrangement of the molecules at 0.5 fractionary coordinate along the *b* axis ($y = 0.43$ and 0.57 for the copper atoms) and a second planar one at 1.0 fractionary coordinate along the same axis ($y = 0.93$ and 1.07 for the copper atoms). The PF$_6^-$ anions are distributed by pairs in the *b*-axis elongated cavity surrounded by six 2,2′-dimethyl-6,6′-diphenyl-4,4′-bipyrimidine molecules. Two kinds of molecular interactions corresponding to the energy minimization occur in this compound; the first is between two parallel coplanar bipyrimidine−phenyl groups distanced by 3.5 Å (for example x, y, z and $^1/_2 - x$, $^1/_2 + y$, $^3/_2 - z$), as shown on Figure 4a, and the second corresponds to two perpendicular bipyrimidines (x, y, z and $1 + x$, y, z). These strong intermolecular interactions can explain the distortion of the copper tetrahedral coordination in which this atom plays the role of hinge.

The participation of outer, inner, and acetonitrile nitrogens bonding to copper in compound **5** yields a molecular arrangement as an infinite helicoidal polymeric chain around the 2_1 axis. The chains are interacting by two face-to-face bipyrimidines with overlapping distances of 3.6 Å (Figure 4b). As for compound **3**, this feature yields to two kinds of approximately perpendicular bipyrimidine planes in the crystal. PF$_6^-$ anions are located in the free spaces between two parallel chains; the shortest distances are N1′−F3 = 3.84(2) Å and N1−F3 = 3.44(2) Å.

Concluding Remarks. Previous electron density and electrostatic potential study of 2,2′-dimethyl-6,6′-diphenyl-4,4′-bipyrimidine[6] from low-temperature high-resolution X-ray diffraction have shown equivalent electronegative behavior of outer and inner nitrogens. This crystallographic study shows that both inner and outer nitrogens of bipyrimidine molecules may be potentially involved in the complexation process with transition metal atoms. In compound **3**, the phenyl rings prevent the complexation with outer nitrogens due to a steric effect. When these groups are removed, as in **5**, the two kinds of nitrogen are linked to the central copper atom. Concerning the apparent symmetry of **5** reflected in the NMR spectrum, this may be rationalized considering the tetrahedral geometry around the copper atom, the free rotation about the Cu−N1″ bond, and the coordination of both N1 nitrogens. Finally, the synthesis and structure of the copper(II) complexes are actually in progress.

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Supporting Information Available: Tables of anisotropic thermal parameters (U_{ij}'s) of non-hydrogen atoms and positional and isotropic thermal parameters and their estimated standard deviations of hydrogens (4 pages). Ordering information is given on any current masthead page.

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