

Helical Coordination Polymers and Cyclic Dimers Formed From Heteroleptic Thioether- Dipyrrinato Copper(II) Complexes

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Synthetic Procedures

General. Unless otherwise noted, starting materials were obtained from commercial suppliers and used without further purification. Elemental analysis was performed at NuMega Resonance Labs, San Diego, California. $^1\text{H}/^{13}\text{C}$ NMR spectra were recorded on a Varian FT-NMR spectrometer at the Department of Chemistry and Biochemistry, University of California, San Diego. Infrared spectra were collected on a Nicolet AVATAR 320 FT-IR instrument at the Department of Chemistry and Biochemistry, University of California, San Diego. UV-visible spectra were collected on a Perkin-Elmer Lambda 25 spectrophotometer.

3-Methylthiobenzaldehyde. 3-Methylthiobenzaldehyde was synthesized by a slightly modified literature procedure (M. Euerby and R. D. Waigh, *Synth. Commun.*, 1981, **11**, 849. N. Iqbal, C.-A. McEwen, and E. E. Knaus, *Drug Develop. Res.*, 2000, **51**, 177.). A Grignard reagent was prepared from 3-bromobenzaldehyde diethyl acetal (10 mL, 49 mmol) and crushed magnesium (~4 g) in dry THF (75 mL) under nitrogen. Once formation of the Grignard is complete (solution changes from a light yellow to a dark brown color), dimethyl disulfide (4.8 mL, 53 mmol) was added dropwise over ~30 min. The solution was refluxed for 3.5 h, cooled in an ice bath, and 20% NH_4Cl was added slowly. A trap was used to neutralize the evolution of methanethiol during this process. Extraction with ether gave the acetal as a light brown oil (11 g). The acetal was dissolved in THF (100 mL) and ~2M H_2SO_4 (150 mL), and the solution was stirred overnight. K_2CO_3 was added to neutralize the solution and the mixture was extracted with ether and dried over Mg_2SO_4 . Removal of Mg_2SO_4 by vacuum filtration and evaporation of the filtrate to dryness gave a brown oil. Yield 54% (4 g). ^1H NMR (CDCl_3 400 MHz, 25

°C): δ 2.50 (s, 1H), 7.40-7.68 (m, 4H), 9.93 (s, 1H). ^{13}C NMR (CDCl_3 100 MHz, 25 °C): δ 15.6, 125.9, 126.6, 129.1, 131.9, 136.7, 140.3, 191.6. GC-EIMS: m/z 152.3 $[\text{M}]^+$.

5-(3-Methylthiophenyl)dipyrromethane. 3-Methylthiobenzaldehyde (300 mg, 1.97 mmol) was dissolved in neat pyrrole (13.6 mL, 0.197 mol). The solution was degassed with nitrogen for 10 min. Trifluoroacetic acid (15.2 μL , 0.197 mmol) was added and the solution was stirred for 1 h under a nitrogen atmosphere. The reaction mixture was diluted with CH_2Cl_2 (50 mL), washed with 0.1 M NaOH (50 mL) and water (50 mL), followed by drying over Mg_2SO_4 . The Mg_2SO_4 was removed by vacuum filtration and the filtrate was evaporated to remove CH_2Cl_2 . The remaining pyrrole was removed by vacuum distillation with gentle heating. The product was purified by column chromatography (SiO_2 ; hexanes: CH_2Cl_2 , 1:4) to afford a yellow oil. Yield: 76% (403 mg). ^1H NMR (CDCl_3 300 MHz, 25 °C): δ 2.46 (s, 3H), 5.40 (s, 1H), 5.95 (bs, 2H), 6.20 (m, 2H), 6.67 (m, 2H), 7.00 (d, 1H, $J = 7.8$ Hz), 7.14-7.30 (m, 3H), 7.86 (bs, 2H, NH). ^{13}C NMR (CDCl_3 100 MHz, 25 °C): δ 15.5, 43.7, 107.1, 108.2, 117.2, 124.5, 124.9, 126.1, 128.8, 131.9, 138.4, 142.5. GC-EIMS: m/z 268.3 $[\text{M}]^+$. $\lambda_{\text{max}} = 228, 255$ nm.

[Cu(3-mtdpm)(hfacac)]. 5-(3-Methylthiophenyl)dipyrromethane (72 mg, 0.27 mmol) was dissolved in 60 mL of CHCl_3 and stirred in an ice bath. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (61 mg, 0.27 mmol) was dissolved in 60 mL benzene and added dropwise over ~30 min. Solid $[\text{Cu}(\text{hfacac})_2]\cdot\text{H}_2\text{O}$ (134 mg, 0.27 mmol) was added to the reaction mixture. The mixture was stirred for 10 min. to form the copper complex. The reaction mixture was evaporated to dryness, and the product was purified by column chromatography (SiO_2 ; CH_2Cl_2) to afford a red/green film. Yield: 86% (124 mg). APCI-MS: m/z 535.9 $[\text{M}+\text{H}]^+$. HR-EIMS Calcd for $\text{C}_{21}\text{H}_{14}\text{N}_2\text{O}_2\text{F}_6\text{SCu}$: 534.9971.

Found: 534.9976. λ_{\max} = 228, 260, 319, 490 nm. IR (film from CH₂Cl₂): ν 1001, 1033, 1145, 1154, 1207, 1251, 1549, 1646, 2854, 2925 cm⁻¹.

[Cu(4-mtdpm)(hfacac)]. The same procedure was used as in the synthesis of [Cu(3-mtdpm)(hfacac)] starting from 5-(4-methylthiophenyl)dipyrromethane (100 mg, 0.37 mmol). Yield: 54% (108 mg). APCI-MS: m/z 535.8 [M+H]⁺. HR-EIMS Calcd for C₂₁H₁₄N₂O₂F₆SCu: 534.9971. Found: 534.9973. λ_{\max} = 261, 377, 489 nm. IR (film from CH₂Cl₂): ν 1001, 1033, 1154, 1208, 1251, 1544, 1559, 1647, 2851, 2923 cm⁻¹.

[Cu(4-mtdpm)₂]. (*Note: This procedure is used to synthesize [Cu(4-mtdpm)(acac), but purification of the product afforded [Cu(4-mtdpm)₂].*) The same procedure was used in the synthesis of [Cu(3-mtdpm)(hfacac)], starting from 5-(4-methylthiophenyl)dipyrromethane (100 mg, 0.37 mmol) and [Cu(acac)₂] (97 mg, 0.37 mmol). Yield: 89% (98 mg). APCI-MS: m/z 593.92 [M+H]⁺. Anal Calcd for C₃₂H₂₆N₄S₂Cu: C, 64.68; H, 4.41; N, 9.43. Found: C, 64.79; H, 4.77; N, 9.56. λ_{\max} = 259, 374, 467, 499 nm. IR (film from CH₂Cl₂): ν 996, 1023, 1037, 1243, 1334, 1376, 1541, 1555, 2918, 3095 cm⁻¹.

X-Ray Crystallographic Data

Structure of [Cu(4-mtdpm)₂]. Green blocks were grown out of a solution of the complex in hexanes/CH₂Cl₂ by slow evaporation. CCDC deposition number 246586.

Structure of [Cu(4-mtdpm)(hfacac)]. Red/green blocks were grown out of a solution of the complex in CH₂Cl₂ by slow evaporation. CCDC deposition number 246587.

Structure of [Cu(3-mtdpm)(hfacac)]. Red/green rods were grown out of a solution of the complex in CH₂Cl₂/MeOH by slow evaporation. CCDC deposition number 246588.

Table S1. X-ray data for [Cu(4-mtdpm)₂], [Cu(4-mtdpm)(hfacac)], and [Cu(3-mtdpm)(hfacac)].

	[Cu(4-mtdpm) ₂]	[Cu(4-mtdpm)(hfacac)]	[Cu(3-mtdpm)(hfacac)]
Empirical Formula	C ₃₂ H ₂₆ N ₄ S ₂ Cu	C ₂₂ H ₁₆ Cl ₂ F ₆ N ₂ O ₂ SCu	C ₂₁ H ₁₄ F ₆ N ₂ O ₂ SCu
Formula Weight	594.23	620.87	535.94
Space Group	<i>Pbca</i>	<i>P2₁2₁2₁</i>	<i>P2₁/n</i>
Unit Cell dimensions	<i>a</i> = 18.082(2) Å <i>b</i> = 8.9956(11) Å <i>c</i> = 32.899(4) Å <i>α</i> = 90° <i>β</i> = 90° <i>γ</i> = 90°	<i>a</i> = 8.6561(8) Å <i>b</i> = 16.1930(15) Å <i>c</i> = 33.492(3) Å <i>α</i> = 90° <i>β</i> = 90° <i>γ</i> = 90°	<i>a</i> = 12.8881(11) Å <i>b</i> = 16.6327(14) Å <i>c</i> = 19.7978(17) Å <i>α</i> = 90° <i>β</i> = 96.5230(10)° <i>γ</i> = 90°
Volume, <i>Z</i>	5351.4(11) Å ³ , 8	4694.5(8) Å ³ , 8	4216.5(6) Å ³ , 8
Temperature (K)	100(2)	100(2)	100(2)
<i>λ</i>	0.71073 Å	0.71073 Å	0.71073 Å
<i>ρ</i> _{calcd}	1.475 g cm ⁻³	1.757 g cm ⁻³	1.689 g cm ⁻³
<i>μ</i>	1.003 mm ⁻¹	1.320 mm ⁻¹	1.210 mm ⁻¹
Final indices <i>I</i> > 2σ(<i>I</i>) ^a	<i>R</i> 1 = 0.0371 <i>wR</i> 2 = 0.0878	<i>R</i> 1 = 0.0476 <i>wR</i> 2 = 0.1150	<i>R</i> 1 = 0.0368 <i>wR</i> 2 = 0.0907
<i>R</i> indices (all data) ^a	<i>R</i> 1 = 0.0421 <i>wR</i> 2 = 0.0902	<i>R</i> 1 = 0.0518 <i>wR</i> 2 = 0.1178	<i>R</i> 1 = 0.0478 <i>wR</i> 2 = 0.0960

$$^a R_1 = \sum \|F_o\| - \|F_c\| / \sum \|F_o\|, R_2 = \left\{ \sum [w(F_o^2 - F_c^2)^2] / \sum [wF_o^4] \right\}^{1/2}$$

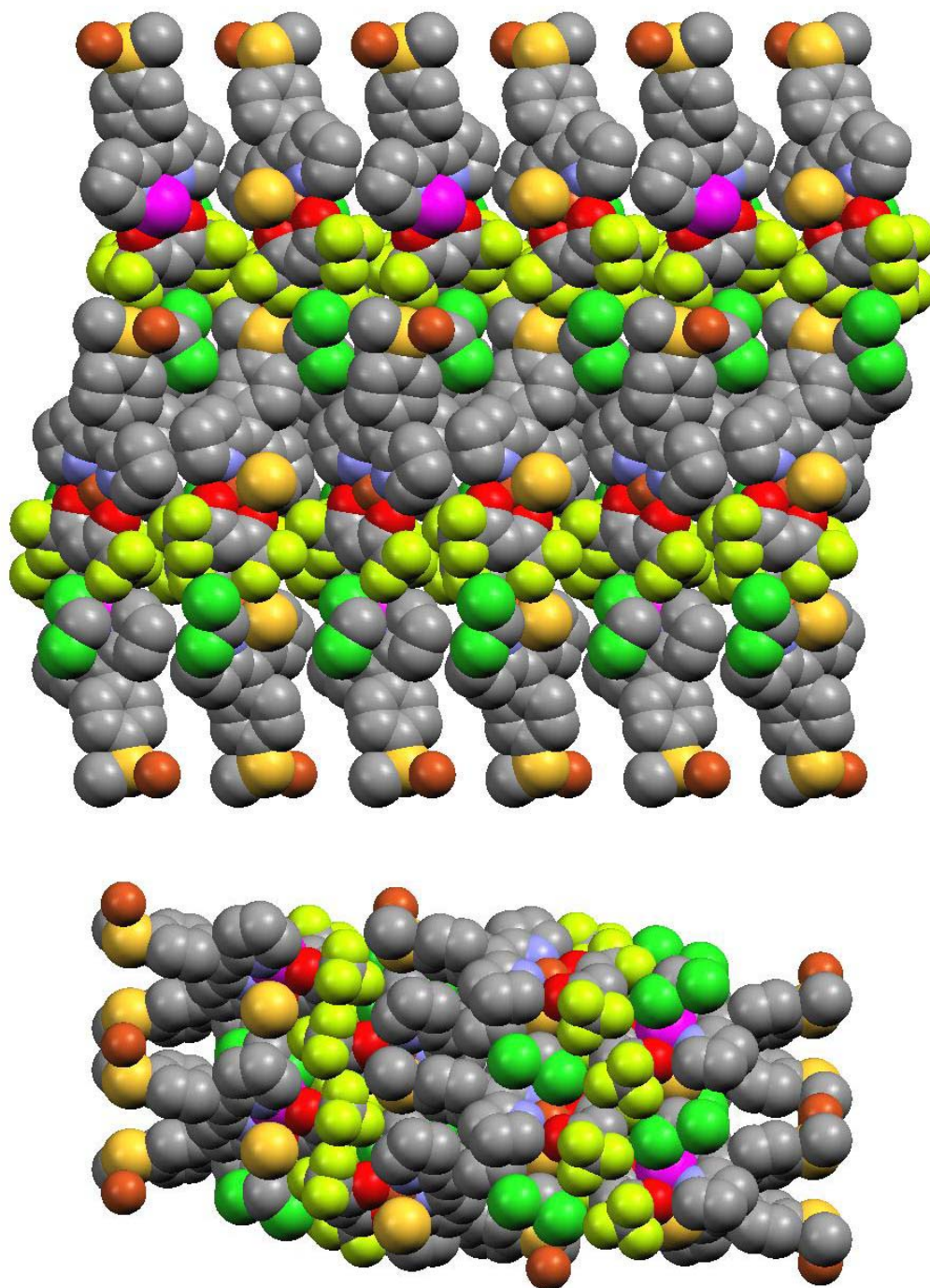


Fig. S1. Packing diagram (spacefill representation) of $[\text{Cu}(4\text{-mtdpm})(\text{hfacac})]$ viewed down the crystallographic a -axis (top) and b -axis (bottom). The spatial separation of the hfacac ligands (fluorine in yellow) can easily be seen in both perspectives. Hydrogen atoms have been removed for clarity.