Inorg. Chem. **2004**, *43*, 1242–1249

Inorganic Chemistry
Article

Heteroleptic Copper Dipyrromethene Complexes: Synthesis, Structure, and Coordination Polymers

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Received October 24, 2003

The synthesis of neutral [Cu(dpm)$_2$] and [Cu(dpm)(acac)] (dpm = dipyrromethene, acac = acetylacetonato) complexes is presented. The formation of the asymmetric metal complexes was monitored by electronic absorption and infrared spectroscopy. Two of the complexes investigated, containing pyrdpm ligands (pyrdpm = pyridyldipyrromethene), form 1-dimensional coordination polymers. The coordination polymers formed by these complexes have been characterized by single-crystal X-ray diffraction, differential scanning calorimetry, and thermogravimetric analysis. The complexes possess square pyramidal coordination geometries with the apical position occupied by the *meso*-pyridyl donor of a neighboring complex in the crystal lattice. The features of these coordination complexes that facilitate formation of extended solids have been probed. Symmetric [Cu(pyrdpm)$_2$] complexes are unable to form coordination solids due to steric hindrance at the metal center. Use of cyano donors in complexes such as [Cu(cydpm)(acac)] (cydpm = cyanodipyrromethene) in lieu of pyridyl donors also fail to form network solids. Through these systematic studies, both the basic coordination chemistry of these complexes and the fundamental design requirements for synthesizing this novel class of coordination polymers have been defined.

Introduction

Coordination polymers have rapidly developed into an active area of chemical research as a route to materials with useful electronic, magnetic, and zeolitic properties. To this end, a wide variety of coordination solids that form 1-, 2-, and 3-dimensional networks have been prepared and studied.[1-5] Attempts to control the dimensionality and topology of these materials have focused on judicious selection of multidentate ligands with metal ions of the appropriate coordination geometry. Typically these structures consist of rigid, symmetric ligands complexed to isolated metal centers or metal clusters.[6-10] Significantly fewer examples exist that use multidentate, asymmetric ligand systems.[11-14] Among the many systems studied, a number of coordination solids containing copper ions have been prepared, frequently with the use of rigid, multidentate poly(pyridyl) ligands as the organic spacer group. Among these copper-containing compounds, several utilize [Cu(hfacac)$_2$] or [Cu(tfacac)$_2$] (hfacac = hexafluoroacetylacetonato, tfacac = trifluoroacetylacetonato) as a building block.[15-18] In these

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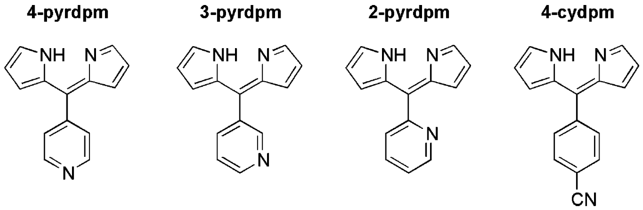
(1) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319–330.
(2) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629–1658.
(3) Yaghi, O. M.; Li, H.; Davis, C.; Richardson, D.; Groy, T. L. *Acc. Chem. Res.* **1998**, *31*, 474–484.
(4) Tulsky, E. G.; Long, J. R. *Chem. Mater.* **2001**, *13*, 1149–1166.
(5) Evans, O. R.; Lin, W. *Acc. Chem. Res.* **2002**, *35*, 511–522.
(6) Hamilton, B. H.; Kelly, K. A.; Malasi, W.; Ziegler, C. J. *Inorg. Chem.* **2003**, *42*, 3067–3073.
(7) Hamilton, B. H.; Kelly, K. A.; Wagler, T. A.; Espe, M. P.; Ziegler, C. J. *Inorg. Chem.* **2002**, *41*, 4984–4986.
(8) Näther, C.; Greve, J.; Je*β*, I. *Chem. Mater.* **2002**, *14*, 4536–4542.
(9) Bernhard, S.; Goldsmith, J. I.; Takada, K.; Abruña, H. D. *Inorg. Chem.* **2003**, *42*, 4389–4393.
(10) Shin, D. M.; Lee, I. S.; Chung, Y. K.; Lah, M. S. *Inorg. Chem.* **2003**, *42*, 5459–5461.
(11) Saalfrank, R. W.; Maid, H.; Hampel, F.; Peters, K. *Eur. J. Inorg. Chem.* **1999**, 1859–1867.
(12) Turner, S. S.; Collison, D.; Mabbs, F. E.; Halliwell, M. *J. Chem. Soc., Dalton Trans.* **1997**, 1117–1118.
(13) Chen, B.; Fronczek, F. R.; Maverick, A. W. *Chem. Commun.* **2003**, 2166–2167.
(14) Lin, W.; Wang, Z.; Ma, L. *J. Am. Chem. Soc.* **1999**, *121*, 11249–11250.
(15) Dong, Y.-B.; Smith, M. D.; Layland, R. C.; zur Loye, H.-C. *Inorg. Chem.* **1999**, *38*, 5027–5033.
(16) Lee, B.-W.; Twamley, B.; Shreeve, J. M. *J. Fluorine Chem.* **2001**, *108*, 111–116.

10.1021/ic0352295 CCC: $27.50

Chart 1. Multidentate *meso*-Substituted Dipyrromethene Ligands Used in This Study



extended solids, the acac-derived ligand makes up the square plane of the copper(II) coordination environment and multidentate nitrogen-based donor ligands link the complexes by binding to the open axial sites on the copper center. An unusual example of an asymmetric ligand system in these types of structures is the use of combined acetylacetonate−pyridine ligands that result in self-complementary complexes that form square-grid and 3-dimensional interpenetrated topologies.[12,13]

In the devising of building blocks for coordination polymers that utilize copper or other transition metal ions, *meso*-substituted dipyrromethene ligands have a rigid, easily derivatized structure that make them attractive targets for use in the synthesis of extended solids (Chart 1). Dipyrromethenes (dipyrrins) are monoanionic ligands that form stable complexes with a variety of transition metal ions.[19−21] Several discrete, neutral supramolecular structures with α- or β-linked dipyrrins have been described, which were found to be easily purified by conventional flash chromatography.[22,23] Synthetically, a wide range of functionalized arylaldehydes can be used to prepare *meso*-substituted dipyrrin ligands with two distinct binding sites and a strictly defined binding geometry.[19,20] The spacing of these functional groups can be systemically varied by using rigid aromatic or phenylalkyl extensions, as has been previously described.[24] Such compounds should allow for the synthesis of metal-containing building blocks with 2-fold or 3-fold symmetry[25,26] for further elaboration as homo- or heterometallic coordination solids.[2,27−29] Furthermore, asymmetrically substituted complexes can also potentially form coordination solids of lower dimensionality (Figure 1).

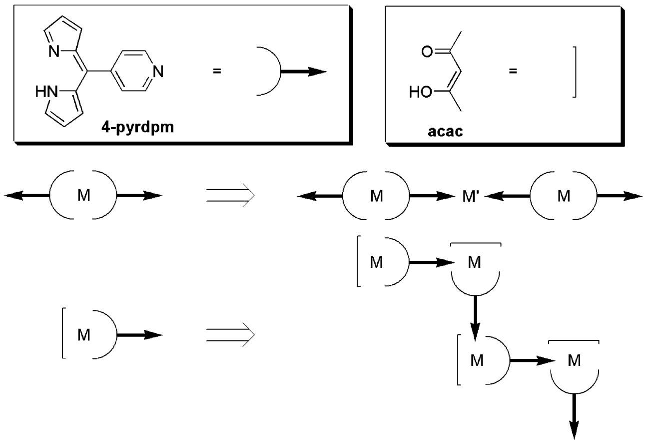


Figure 1. Structure of a dipyrrin ligand (pyrdpm = pyridyldipyrromethene) and some plausible schemes for the formation of homo- and heterometallic coordination solids. Heterometallic (top) and homometallic 1-dimensional (bottom) coordination polymers may both be accessible.

As part of an effort to prepare heterometallic coordination polymers based on multidentate dipyrrin ligands, several *meso*-pyridyldipyrromethene (pyrdpm) ligands have been synthesized and characterized. In the process of using [Cu(acac)$_2$] (acac = acetylacetonato) as the metal source to make copper(II) complexes of these ligands, it was found that both the [Cu(pyrdpm)$_2$] and asymmetric [Cu(pyrdpm)(acac)] complexes were stable compounds. In addition, two of the [Cu(pyrdpm)(acac)] complexes were found to form 1-dimensional coordination polymers with the metal centers connected by distal *meso*-pyridyl nitrogen atom ligation. Several other dipyrrin compounds were synthesized to explore the coordination chemistry of these ligands and to determine what features of the dipyrromethene ligand promote the formation of extended solids. All of the complexes have been examined by electronic absorption and infrared spectroscopy, and the solid-state structures of each compound have been determined. Two novel coordination polymers have been synthesized, and a number of other complexes reveal the properties of the ligand and metal geometry that facilitate formation of these unusual polymeric structures.

Experimental Section

General Methods. Unless otherwise noted, starting materials were obtained from commercial suppliers and used without further purification. The dipyrromethane precursors for the ligands 4-pyrdpm, 3-pyrdpm, 2-pyrdpm, and 4-cydpm were synthesized according to literature procedures.[30,31] Elemental analysis data were obtained through NuMega Resonance Labs, Inc. (San Diego, CA). Infrared spectra were collected on a Nicolet AVATAR 320 FT-IR instrument at the Department of Chemistry and Biochemistry, University of California at San Diego. UV−visible spectra were recorded in CH$_2$Cl$_2$ using a Hewlett-Packard 4582A spectrophotometer under PC control using the ChemStation software suite.

[Cu(4-pyrdpm)$_2$]. 5-(4-Pyridyl)dipyrromethane[31] (0.30 g, 1.34 mmol) was dissolved in 150 mL of CHCl$_3$, and the solution was

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(17) Bunn, A. G.; Carroll, P. J.; Wayland, B. B. *Inorg. Chem.* **1992**, *31*, 1297−1299.

(18) Sano, Y.; Tanaka, M.; Koga, N.; Matsuda, K.; Iwamura, H.; Rabu, P.; Drillon, M. *J. Am. Chem. Soc.* **1997**, *119*, 8246−8252.

(19) Brückner, C.; Zhang, Y.; Rettig, S. J.; Dolphin, D. *Inorg. Chim. Acta* **1997**, *263*, 279−286.

(20) Brückner, C.; Karunaratne, V.; Rettig, S. J.; Dolphin, D. *Can. J. Chem.* **1996**, *74*, 2182−2193.

(21) Cohen, S. M.; Halper, S. R. *Inorg. Chim. Acta* **2002**, *341*, 12−16.

(22) Zhang, Y.; Thompson, A.; Rettig, S. J.; Dolphin, D. *J. Am. Chem. Soc.* **1998**, *120*, 13537−13538.

(23) Thompson, A.; Rettig, S. J.; Dolphin, D. *Chem. Commun.* **1999**, 631−632.

(24) Halper, S. R.; Cohen, S. M. *Chem.*−*Eur. J.* **2003**, *9*, 4661−4669.

(25) Choe, W.; Kiang, Y.-H.; Xu, Z.; Lee, S. *Chem. Mater.* **1999**, *11*, 1776−1783.

(26) Kiang, Y.-H.; Gardner, G. B.; Lee, S.; Xu, Z.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **1999**, *121*, 8204−8215.

(27) Dong, Y.-B.; Smith, M. D.; zur Loye, H.-C. *Inorg. Chem.* **2000**, *39*, 1943−1949.

(28) Shorrock, C. J.; Jong, H.; Batchelor, R. J.; Leznoff, D. B. *Inorg. Chem.* **2003**, *42*, 3917−3924.

(29) Leznoff, D. B.; Xu, B.-Y.; Batchelor, R. J.; Einstein, F. W. B.; Patrick, B. O. *Inorg. Chem.* **2001**, *40*, 6026−6034.

(30) Rao, P. D.; Dhanalekshmi, S.; Littler, B. J.; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 7323−7344.

(31) Gryko, D.; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 2249−2252.

stirred in an ice bath. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (0.31 g, 1.34 mmol) was dissolved in 100 mL of benzene, and the solution was added slowly dropwise. After addition, the solvent was evaporated to half the volume and [$CuCl_2 \cdot 2H_2O$] (0.092 g, 0.54 mmol) dissolved in 50 mL of MeOH was added. The mixture was stirred for 10 min to form the copper complex. The solution was evaporated to dryness, and the product was purified by column chromatography (SiO_2; $CHCl_3$ with 1.0% MeOH) to afford a dichroic red/green film. Yield: 25%. FAB-MS: *m/z* 504.5, $[M + H]^+$. Anal. Calcd for $C_{28}H_{20}N_6Cu$: C, 66.72; H, 4.00; N, 16.67. Found: C, 66.35; H, 3.70; N, 16.45. $\lambda_{max} = 230, 302, 378, 470, 502$ nm. IR (film from CH_2Cl_2): ν 995, 1022, 1037, 1244, 1335, 1376, 1404, 1536, 2924, 3094 cm^{-1}.

[Cu(3-pyrdpm)$_2$]. The same procedure was used as in the synthesis of [Cu(4-pyrdpm)$_2$] starting from 5-(3-pyridyl)dipyrromethane.[31] Yield: 16%. FAB-MS: *m/z* 504.5, $[M + H]^+$. Anal. Calcd for $C_{28}H_{20}N_6Cu$ $0.5H_2O$: C, 64.42; H, 4.25; N, 16.10. Found: C, 64.50; H, 4.11; N, 15.90. $\lambda_{max} = 232, 318, 372, 468, 502$ nm. IR (film from CH_2Cl_2): ν 995, 1023, 1037, 1244, 1335, 1376, 1405, 1547, 2925, 3094 cm^{-1}.

[Cu(4-cydpm)$_2$]. The same procedure was used as in the synthesis of [Cu(4-pyrdpm)$_2$] starting from 5-(4-cyanophenyl)-dipyrromethane.[30] Yield: 51%. MALDI-TOF-MS: *m/z* 551.2, $[M]^+$. Anal. Calcd for $C_{32}H_{20}N_6Cu \cdot 1.5H_2O$: C, 66.37; H, 4.00; N, 14.51. Found: C, 66.66; H, 4.01; N, 14.69. $\lambda_{max} = 236, 306, 472, 498$ nm. IR (film from CH_2Cl_2): ν 994, 1028, 1247, 1337, 1383, 1406, 1561, 1592, 2225, 2916 cm^{-1}.

[Cu(4-pyrdpm)(acac)]. 5-(4-Pyridyl)dipyrromethane[31] (0.50 g, 2.24 mmol) was dissolved in 150 mL of $CHCl_3$ and the solution was stirred in an ice bath. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (0.51 g, 2.24 mmol) was dissolved in 100 mL of benzene, and the solution was added slowly dropwise. [Cu(acac)$_2$] (0.59 g, 2.24 mmol) was dissolved in 20 mL of $CHCl_3$ and the solution was added to the reaction mixture, which was stirred for 10 min to form the copper complex. The solution was evaporated to dryness, and the product was purified by column chromatography (SiO_2; $CHCl_3$ with 0.5% MeOH) to afford brown/red crystals. Yield: 40%. FAB-MS: *m/z* 383.4, $[M + H]^+$, 283.2, $[M - acac]^+$. Anal. Calcd for $C_{19}H_{17}N_3O_2Cu$: C, 59.60; H, 4.48; N, 10.97. Found: C, 59.68; H, 4.68; N, 11.04. $\lambda_{max} = 230, 300, 364, 496$ nm. IR (film from CH_2Cl_2): ν 993, 1025, 1245, 1338, 1387, 1520, 1557, 1592, 2920, 3045, 3093 cm^{-1}.

[Cu(3-pyrdpm)(acac)]. The same procedure was used as in the synthesis of [Cu(4-pyrdpm)(acac)] starting from 5-(3-pyridyl)-dipyrromethane.[31] Yield: 58%. FAB-MS: *m/z* 383.4, $[M + H]^+$. Anal. Calcd for $C_{19}H_{17}N_3O_2Cu \cdot 0.5CH_2Cl_2$: C, 55.06; H, 4.27; N, 9.88. Found: C, 55.01; H, 4.67; N, 9.94. $\lambda_{max} = 232, 302, 362, 496$ nm. IR (film from CH_2Cl_2): ν 993, 1026, 1244, 1337, 1378, 1520, 1549, 1591, 2919, 3094 cm^{-1}.

[Cu(2-pyrdpm)(acac)]. The same procedure was used as in the synthesis of [Cu(4-pyrdpm)(acac)] starting from 5-(2-pyridyl)-dipyrromethane.[31] Yield: 17%. ESI-MS: *m/z* 383.1, $[M + H]^+$. Anal. Calcd for $C_{19}H_{17}N_3O_2Cu \cdot 0.5CH_2Cl_2$: C, 55.06; H, 4.27; N, 9.88. Found: C, 55.32; H, 4.34; N, 9.95. $\lambda_{max} = 230, 300, 366, 498$ nm. IR (film from CH_2Cl_2): ν 996, 1028, 1246, 1337, 1384, 1520, 1555, 1586, 2854 cm^{-1}.

[Cu(4-cydpm)(acac)]. The same procedure was used as in the synthesis of [Cu(4-pyrdpm)(acac)] starting from 5-(4-cyanophenyl)-dipyrromethane.[30] Yield: 41%. FAB-MS: *m/z* 406.3, $[M + H]^+$. Anal. Calcd for $C_{21}H_{17}N_3O_2Cu$: C, 61.98; H, 4.21; N, 10.33. Found: C, 62.34; H, 4.51; N, 10.73. $\lambda_{max} = 236, 306, 496, 506$ nm. IR (film from CH_2Cl_2): ν 996, 1028, 1245, 1336, 1403, 1555, 1588, 2229, 2340, 2360.

X-ray Crystallographic Analysis. Single crystals of each compound suitable for X-ray diffraction structural determination were mounted on quartz capillaries with Paratone oil and were cooled in a nitrogen stream on the diffractometer. Data were collected on either a Bruker AXS or a Bruker P4 diffractometer each equipped with area detectors. Peak integrations were performed with the Siemens SAINT software package. Absorption corrections were applied using the program SADABS. Space group determinations were performed by the program XPREP. The structures were solved by either Patterson or direct methods and refined with the SHELXTL software package.[32] All hydrogen atoms were fixed at calculated positions with isotropic thermal parameters, and all non-hydrogen atoms were refined anisotropically unless otherwise noted.

Differential Scanning Calorimetry and Thermogravimetric Analysis. Differential scanning calorimetry (DSC) experiments were performed on a Shimadzu DSC-50 instrument in a helium atmosphere with a flow rate of 30 cm^3/min. Crystalline samples were heated from ~25 to 500 °C at a rate of 10 °C/min. Thermogravimetric analysis (TGA) experiments were performed on a Shimadzu TGA-50 with a flow rate of 40 cm^3/min of nitrogen. Crystalline samples were heated from ~25 to 800 °C at a rate of 4 °C/min.

Results

The syntheses of the dipyrromethane precursors (**1** and **2**; Scheme 1) were performed according to literature procedures.[30,31] The dipyrromethanes were oxidized to the corresponding dipyrrins by reaction with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in a chloroform/benzene solution. The dipyrrin ligands were not isolated but were used in situ to generate the desired metal complexes.[19−21,24] To form heteroleptic [Cu(dpm)(acac)] complexes, the oxidation reaction mixtures containing the dipyrrin ligand were combined with ~1 molar equiv (based on the quantity of dipyrromethane precursor) of [Cu(acac)$_2$]. The desired complexes were formed at room temperature within 30 min, after which the products were purified by silica column chromatography as bright orange-red compounds that generally appeared lustrous green upon removal of solvent. The solids were readily dissolved in a variety of organic solvents such as benzene, chloroform, methylene chloride, and acetone. The heteroleptic [Cu(dpm)(acac)] complexes were found to be stable in solution and in the presence of silica gel. However, when exposed to basic alumina, the complexes were found to rapidly decompose to the homoleptic [Cu(dpm)$_2$] complexes. To prepare the homoleptic [Cu(dpm)$_2$] complexes, the same general procedure was used, but only ~0.4 equiv (based on dipyrromethane precursor) of [Cu(acac)$_2$] or [$CuCl_2 \cdot 2H_2O$] was combined with the oxidized dipyrrin mixture. Again, column chromatography was used to isolate the complexes in modest yields. All of the metal complexes were characterized by mass spectrometry, elemental analysis, infrared spectroscopy, and absorption spectroscopy.

Formation of the desired hetero- or homoleptic complex was confirmed by examination of the absorption and infrared spectra of the compounds. Indeed, the UV−visible spectra of the crude oxidation/complexation mixtures could be used to follow the progress of the reaction. Figure 2 shows the

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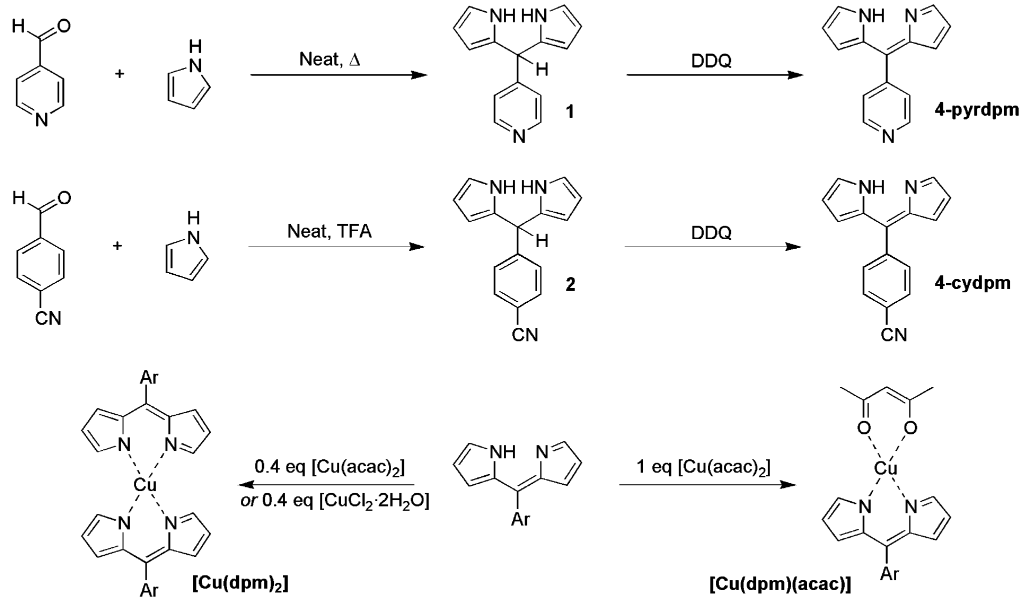
[32] Sheldrick, G. M. In *SHELXTL vers. 5.1 Software Reference Manual*; Brucker AXS: Madison, WI, 1997.

Scheme 1. General Approach for Preparing dpm Ligands, [Cu(dpm)(acac)] Complexes, and [Cu(dpm)$_2$] Complexes



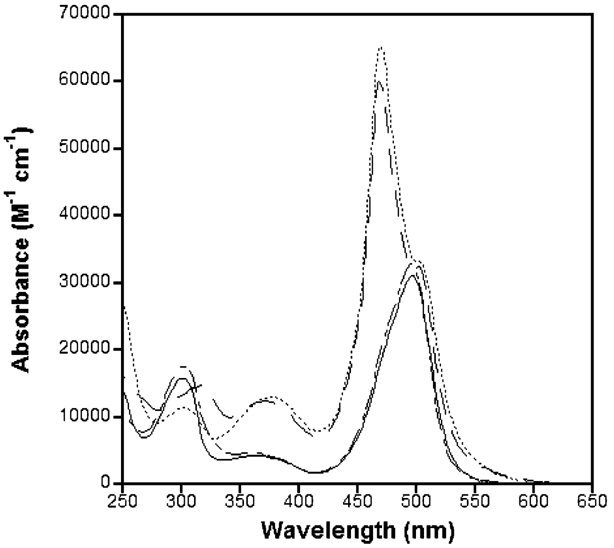


Figure 2. Electronic absorption spectra for [Cu(4-pyrdpm)(acac)] (solid, —), [Cu(4-pyrdpm)$_2$] (dotted, ···), [Cu(3-pyrdpm)(acac)] (dashed dotted, —·—), and [Cu(3-pyrdpm)$_2$] (dashed, – –).

absorption spectra for [Cu(4-pyrdpm)(acac)], [Cu(3-pyrdpm)(acac)], [Cu(4-pyrdpm)$_2$], and [Cu(3-pyrdpm)$_2$]. The heteroleptic complexes [Cu(4-pyrdpm)(acac)] and [Cu(3-pyrdpm)(acac)] show characteristic absorption maxima around 301 and 495 nm, while the homoleptic complexes show major transitions at 302/318 (4-pyrdpm/3-pyrdpm), 378/372, and 469 nm with a shoulder feature around 503 nm.[24] The intense low-energy bands (495/469 nm) have been previously assigned to charge-transfer processes associated with the dipyrrin ligand.[19,20,24] In the infrared spectra (Figure S1), characteristic features between 800 and 1800 cm^{-1} could be used to distinguish the two complexes. The bis(dipyrrin) complexes have several features at approximately 995, 1022, 1244, 1335, 1375, and 1545 cm^{-1} characteristic of the dipyrrin ligand. The [Cu(dpm)(acac)] complexes retain these features but also display two additional bands at ~1520 and ~1590 cm^{-1} that are found in [Cu(acac)$_2$] (1517 and 1580 cm^{-1}). The distinct spectroscopic features of the symmetric and asymmetric complexes allow for facile evaluation of the reaction products.

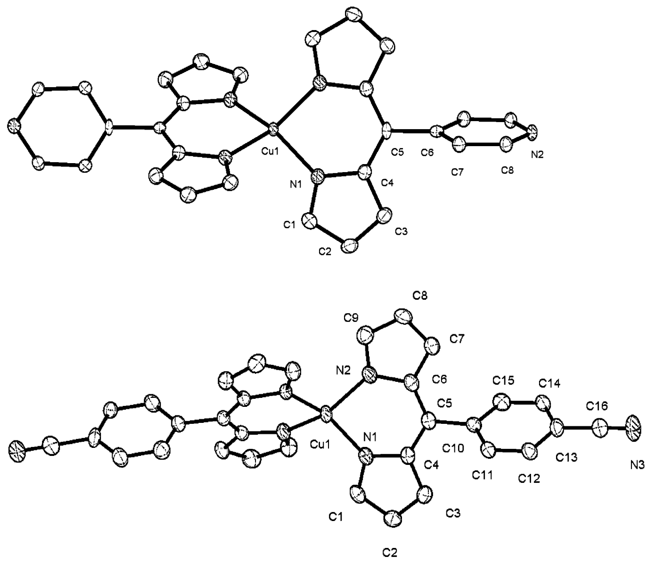


Figure 3. Structural diagram of [Cu(4-pyrdpm)$_2$] (top) and [Cu(4-cydpm)$_2$] (bottom) with partial atom numbering schemes (ORTEP, 50% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

The structures of [Cu(4-pyrdpm)$_2$], [Cu(4-cydpm)$_2$], [Cu(4-pyrdpm)(acac)], [Cu(3-pyrdpm)(acac)], [Cu(2-pyrdpm)(acac)], and [Cu(4-cydpm)(acac)] were determined by single-crystal X-ray diffraction studies. The complexes [Cu(4-pyrdpm)$_2$] and [Cu(4-cydpm)$_2$] show 4-coordinate, distorted square planar metal environments with average Cu−N bond distances of ~1.95 Å (Figure 3). The twist angle between the two chelators in each structure is ~44°. As expected, the *meso*-pyridyl/phenyl substituents are twisted out of plane with the dipyrrin π-system by ~65°. No significant intermolecular interactions, particularly those associated with the pyridine or cyano nitrogen atoms, are found in the structures. The [Cu(4-pyrdpm)$_2$] and [Cu(4-cydpm)$_2$] structures are quite

Table 1. X-ray Data for [Cu(4-pyrdpm)$_2$] and [Cu(4-cydpm)$_2$]

	[Cu(4-pyrdpm)$_2$]	[Cu(4-cydpm)$_2$]
empirical formula	$C_{28}H_{20}N_6Cu$	$C_{32}H_{20}N_6Cu$
fw	504.04	552.09
space group	*Aba*2 (No. 41)	$P2_1/n$ (No. 14)
unit cell dimens (Å, deg)	$a = 8.9282(7)$ $\alpha = 90$ $b = 8.9150(7)$ $\beta = 90$ $c = 28.113(2)$ $\gamma = 90$	$a = 11.9165(12)$ $\alpha = 90$ $b = 16.0218(17)$ $\beta = 91.223(2)$ $c = 12.9956(14)$ $\gamma = 90$
V (Å^3), Z	2237.7(3), 4	2480.6(5), 4
temp (K)	100(2)	100(2)
λ (Å)	0.710 73	0.710 73
D_{calcd} (Mg m^{-3})	1.496	1.478
μ (mm^{-1})	1.007	0.916
final R indices ($I > 2\sigma(I)$)[a]	R1 = 0.0266 wR2 = 0.0728	R1 = 0.0565 wR2 = 0.1111
R indices (all data)[a]	R1 = 0.0268 wR2 = 0.0730	R1 = 0.0798 wR2 = 0.1181

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

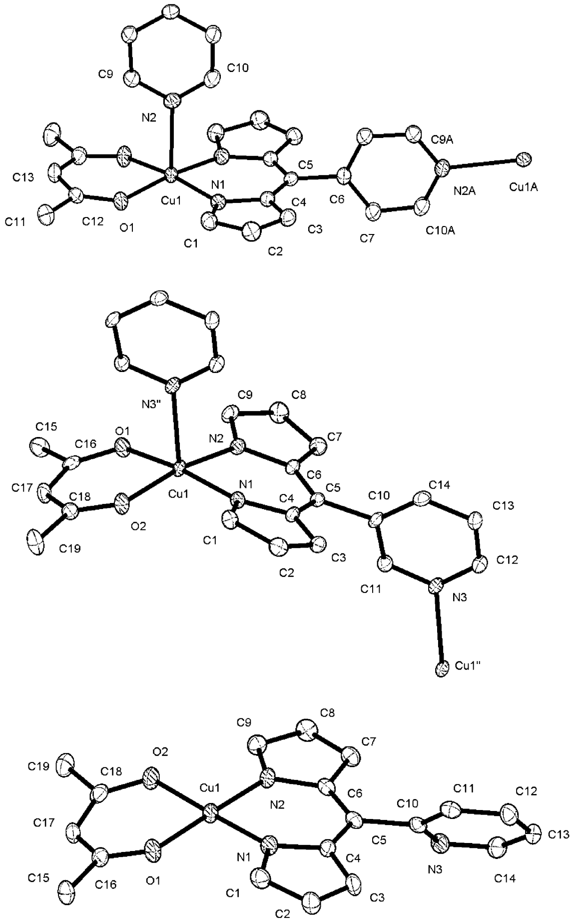


Figure 4. Structural diagrams of [Cu(4-pyrdpm)(acac)] (top), [Cu(3-pyrdpm)(acac)] (middle), and [Cu(2-pyrdpm)(acac)] (bottom) with partial atom numbering schemes (ORTEP, 50% probability ellipsoids). Hydrogen atoms and solvent molecules have been omitted for clarity. Coordination from the adjacent *meso*-pyridyl donor and to the neighboring copper(II) center are shown for [Cu(4-pyrdpm)(acac)] and [Cu(3-pyrdpm)(acac)] to illustrate the polymeric nature of these structures.

typical of other 4-coordinate α-unsubstituted dipyrrin complexes (Table 1) of copper(II) and nickel(II).[20,24]

The structure of [Cu(4-pyrdpm)(acac)] is quite distinct from the homoleptic complex [Cu(4-pyrdpm)$_2$] (Table 2). [Cu(4-pyrdpm)(acac)] displays a square pyramidal coordination geometry (Figure 4). The base of the square pyramid geometry is provided by the acac and dipyrrin ligands with Cu−O and Cu−N bond lengths of 1.96 and 1.98 Å, respectively. Unlike the symmetric complex [Cu(4-pyrdpm)$_2$], the square plane in [Cu(4-pyrdpm)(acac)] is not distorted and is essentially an idealized geometry. The copper atom is only slightly displaced ~0.05 Å out of the square plane toward the apical ligand. The apical position of the square pyramid is occupied by a pyridine nitrogen donor atom from an adjacent molecule of [Cu(4-pyrdpm)(acac)] with a substantially longer Cu−N bond distance of 2.32 Å. The pyridyl ring of the 4-pyrdpm ligand is nearly orthogonal to the plane of the dipyrrin chelator with a dihedral angle of ~88°. Binding of the pyridyl nitrogen atom results in the formation of an infinite 1-dimensional zigzag coordination polymer.

The structure of [Cu(3-pyrdpm)(acac)] also forms a 1-dimensional coordination polymer like [Cu(4-pyrdpm)(acac)] (Table 2), but the structure of the complex and the resulting polymer is noticeably different (Figure 4). The [Cu(3-pyrdpm)(acac)] complex has a square pyramidal coordination sphere about the copper(II) ion. The bond lengths at the base of the square pyramid are 1.96 Å for the Cu−O bonds (acac) and 1.98 Å for the Cu−N bonds (dipyrrin), nearly identical with those found in [Cu(4-pyrdpm)(acac)]. Again, the copper(II) ion resides slightly above the square plane (~0.06 Å) toward the apical site, which is occupied by the pyridyl nitrogen atom from an adjacent molecule in the polymeric chain (Cu−N bond length 2.29 Å, Table 3). The pyridyl ring is twisted perpendicular relative to the dipyrrin plane with a dihedral angle of ~73°. A notable feature of [Cu(3-pyrdpm)(acac)] is the apparent curvature in the overall profile of the complex, which appears to have a concave shape away from the face of the molecule where the pyridyl nitrogen is bound.

Unlike [Cu(4-pyrdpm)(acac)] and [Cu(3-pyrdpm)(acac)], the structure of [Cu(2-pyrdpm)(acac)] shows that this complex is a simple, discrete mononuclear metal complex (Table 2). The copper(II) ion possesses a square planar coordination geometry as observed in the other heteroleptic complexes, but there is no apparent axial coordination by an additional ligand (Figure 4). The Cu−O and Cu−N bond lengths are slightly shorter than the other complexes described above (Table 3). The pyridyl ring is less twisted relative to the dipyrrin group with a dihedral angle of ~52°. The shortest distance between the 2-pyridyl nitrogen of one complex and its nearest neighbor is >6.0 Å, which is too long for a Cu−N bond. In addition, the molecules are not positioned in any particular orientation in the solid state that would suggest ordering in a coordinate-covalent, polymeric fashion.

The structure of [Cu(4-cydpm)(acac)] shows that this compound is a square planar copper(II) complex (Figure 5). The bond lengths are comparable to those found in the other asymmetric complexes described (Table 3). Unlike the [Cu(4-pyrdpm)(acac)] complex, [Cu(4-cydpm)(acac)] does not form a coordination polymer but is rather a simple, discrete complex similar to [Cu(2-pyrdpm)(acac)] (Figure 5). The

Table 2. X-ray Data for [Cu(4-pyrdpm)(acac)], [Cu(3-pyrdpm)(acac)], [Cu(2-pyrdpm)(acac)], and [Cu(4-cydpm)(acac)]

	[Cu(4-pyrdpm)(acac)]	[Cu(3-pyrdpm)(acac)]	[Cu(2-pyrdpm)(acac)]	[Cu(4-cydpm)(acac)]
empirical formula	$C_{25.33}H_{22.67}N_4O_{2.67}Cu_{1.33}$	$C_{19.5}H_{18}N_3O_2ClCu$	$C_{19}H_{17}N_3O_2Cu$	$C_{21}H_{17}N_3O_2Cu$
fw	510.35	425.36	382.90	406.92
space group	*Pnma* (No. 62)	$P\bar{1}$ (No. 2)	$P2_12_12_1$ (No. 19)	*C*2/*c* (No. 15)
unit cell dimens (Å, deg)	$a = 14.0337(10)$	$a = 8.3811(5)$	$a = 9.4788(6)$	$a = 11.9543(10)$
	$\alpha = 90$	$\alpha = 117.520(1)$	$\alpha = 90$	$\alpha = 90$
	$b = 11.9862(9)$	$b = 15.5837(10)$	$b = 9.9354(6)$	$b = 20.6386(18)$
	$\beta = 90$	$\beta = 91.737(1)$	$\beta = 90$	$\beta = 103.165(2)$
	$c = 10.4162(7)$	$c = 16.5921(11)$	$c = 35.677(2)$	$c = 7.6606(7)$
	$\gamma = 90$	$\gamma = 98.950(1)$	$\gamma = 90$	$\gamma = 90$
V (Å^3), Z	1752.1(2), 3	1714.7(2), 4	3359.9(4), 8	1840.3(3), 4
temp (K)	100(2)	100(2)	100(2)	218(2)
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73
D_{calcd} (Mg m^{-3})	1.452	1.498	1.514	1.469
μ (mm^{-1})	1.263	1.319	1.317	1.208
Final R indices ($I > 2\sigma(I)$)[a]	R1 = 0.0268	R1 = 0.0545	R1 = 0.0330	R1 = 0.0372
	wR2 = 0.0778	wR2 = 0.1473	wR2 = 0.0726	wR2 = 0.0995
R indices (all data)[a]	R1 = 0.0293	R1 = 0.0647	R1 = 0.0359	R1 = 0.0392
	wR2 = 0.0787	wR2 = 0.1544	wR2 = 0.0738	wR2 = 0.1010

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

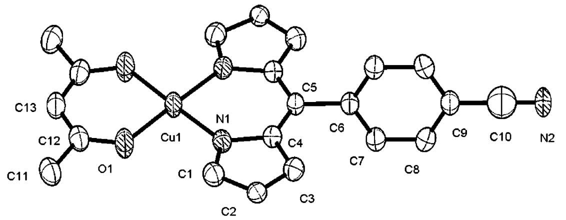


Figure 5. Structural diagram of [Cu(4-cydpm)(acac)] with partial atom numbering schemes (ORTEP, 50% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

Table 3. Selected Bond Lengths for Each Copper(II) Complex

compd	Cu−$N_{dipyrrin}$ (Å)	Cu−O_{acac} (Å)	Cu−$N_{pyridyl}$ (Å)
[Cu(4-pyrdpm)$_2$]	1.95	n/a	n/a
[Cu(4-cydpm)$_2$]	1.96	n/a	n/a
[Cu(4-pyrdpm)(acac)]	1.98	1.96	2.32
[Cu(3-pyrdpm)(acac)]	1.98	1.96	2.29
[Cu(2-pyrdpm)(acac)]	1.96	1.94	n/a
[Cu(4-cydpm)(acac)]	1.95	1.92	n/a

closest distance between a copper(II) ion and a cyano nitrogen atom from a neighboring molecule is ~6.0 Å clearly indicating that no intermolecular bonding interactions are present.

The polymeric materials, [Cu(4-pyrdpm)(acac)] and [Cu(3-pyrdpm)(acac)], were further examined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). DSC experiments on dried samples [Cu(4-pyrdpm)(acac)] and [Cu(3-pyrdpm)(acac)] gave similar results with sharp, endothermic thermal decompositions at around 225 °C. The DSC profile for [Cu(3-pyrdpm)(acac)] shows an additional broader, endothermic feature centered at ~94 °C (Figure 6). On the basis of the crystallographic and elemental analysis data (vide supra), this observation was tentatively assigned to the loss of CH_2Cl_2 from the coordination polymer. TGA analysis showed that this DSC event corresponded to an 8.3% weight loss from the material. The stoichiometry of CH_2Cl_2 was 1 molecule/2 [Cu(3-pyrdpm)(acac)] complexes (on the basis of both the X-ray structure and elemental analysis), which would give a predicted weight loss of 9.98%, in satisfactory agreement with the experimental data. Even after drying at ~50 °C under vacuum, the [Cu(3-pyrdpm)(acac)] polymer does not readily release the cocrystallized solvent and can effectively trap this volatile compound. Furthermore, TGA experiments revealed that the endotherm observed at ~225 °C was associated with a sharp weight loss of 18.1%, followed by another gradual weight loss of 4.8% up to 470 °C (data not shown). The exact nature of this weight loss is unclear, but it may be associated with liberation of the acac ligand (predicted weight loss 23.3%). A similar weight loss (20.2%) was also found for the [Cu(4-pyrdpm)(acac)] polymer (Figure 6). Above 470 °C an additional break point was observed in both compounds followed by a gradual weight loss with increasing temperature consistent with decomposition of the samples. In contrast, DSC measurements on [Cu(2-pyrdpm)(acac)], which does not form an extended solid, showed a single endothermic event at substantially lower temperature (~120 °C) than found for the polymeric compounds (data not shown).

Discussion

The initial goal of this study was to design multidentate dipyrromethene ligands for preparing extended solids[25,26,33] via the formation of bis(dipyrrin)copper complexes.[20,24] During the course of these investigations, it became apparent that heteroleptic [Cu(dpm)(acac)] complexes were stable, isolatable species. These complexes could be readily distinguished from the [Cu(dpm)$_2$] complexes by examination of their electronic absorption and infrared spectroscopy. Furthermore, solid-state structural characterization revealed that some of these asymmetric complexes, namely [Cu(4-pyrdpm)(acac)] and [Cu(3-pyrdpm)(acac)], were "self-complementary" and spontaneously formed 1-dimensional coordination polymers (Figure 4). The ability of these complexes to form polymers in the solid state and the nature of the resulting polymers was found to be strongly influenced by the position of the nitrogen atom in the pyridine heterocycle. Placement of the coordinating nitrogen atom in the 4- or

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(33) Kiang, Y.-H.; Lee, S.; Xu, Z.; Choe, W.; Gardner, G. B. *Adv. Mater.* **2000**, *12*, 767−770.

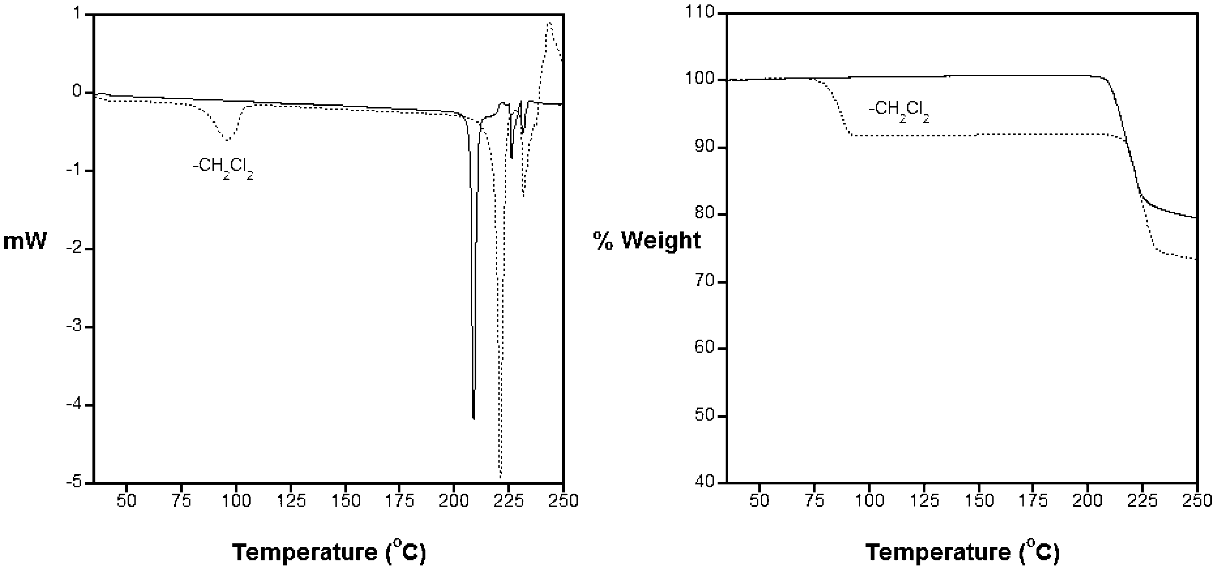

Figure 6. DSC (left) and TGA (right) analysis of the coordination polymers [Cu(4-pyrdpm)(acac)] (solid, —) and [Cu(3-pyrdpm)(acac)] (dotted, ···). The experiments show the generally similar behavior of the two compounds, except for the loss of trapped CH_2Cl_2 from [Cu(3-pyrdpm)(acac)].

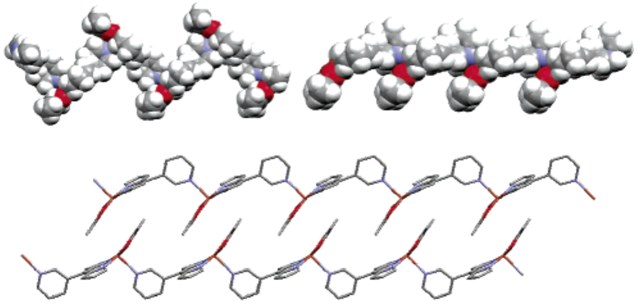

Figure 7. Space-filling representation of the coordination polymers formed by [Cu(4-pyrdpm)(acac)] (top left) and [Cu(3-pyrdpm)(acac)] (top right). A stick representation of [Cu(3-pyrdpm)(acac)] (bottom) is viewed down the crystallographic *c*-axis, which shows the interdigitation of the acac ligands between paired polymer chains. Solvent molecules (top right, bottom) and hydrogen atoms (bottom only) have been omitted for clarity.

3-position allowed for the formation of two related, but topologically distinct, coordination polymers (Figure 7). The typical motifs for 1-dimensional coordination polymers are zigzag chains and helicies,[2] the latter being a rather rare morphology. Both [Cu(4-pyrdpm)(acac)] and [Cu(3-pyrdpm)(acac)] form structures quite typical of zigzag chains.[27,34,35] [Cu(3-pyrdpm)(acac)] shows a particularly intriguing arrangement in the solid state: the packing diagram of [Cu(3-pyrdpm)(acac)] (Figure 7, bottom) shows that two coordination chains assemble in an antiparallel fashion with interdigitation of the acac ligands in an alternating manner. This results in a tight packing of the bulk structure into paired polymeric chains.

Formation of these extended polymers has little effect on the metal and ligand geometry. The Cu−O and Cu−N bond distances for the acac and dipyrrin chelators are essentially the same as the mononuclear, square planar complexes that do not form polymeric structures (Table 3). The copper(II) ion is somewhat puckered out of the square plane geometry toward the axial pyridine donor, and the pyridine ring system is directed nearly perpendicular to the dipyrrin π-system in both polymeric complexes. In contrast to [Cu(4-pyrdpm)(acac)] and [Cu(3-pyrdpm)(acac)], the 2-pyridyl derivative, [Cu(2-pyrdpm)(acac)], did not form a coordination polymer although the complex maintains a similar square planar coordination geometry with respect to the dipyrrin and acac ligands. The lack of intermolecular interactions is supported by the long Cu−N distances between neighboring molecules and the "relaxed" conformation of the pyridine heterocycle relative to the plane of the dipyrrin moiety. Inspection of space-filling models of the [Cu(2-pyrdpm)(acac)] complex suggests that the 2-pyridyl ligand is situated such that the nitrogen donor is sterically prevented from establishing a proximate relationship with a neighboring copper(II) center.

In an attempt to extend the general motif of these complexes toward coordination polymers with different donor ligands, the [Cu(4-cydpm)(acac)] complex, which possesses a cyano functionality extending from the *meso*-phenyl group of the dipyrrin ligand, was synthesized. The cyano group was chosen on the basis of a select number of earlier examples of copper-containing coordination polymers linked by this functional group.[11,17] Structural characterization of [Cu(4-cydpm)(acac)] showed that a 4-coordinate square planar metal complex rather than a coordination polymer was isolated. Apparently the cyano group is not a sufficiently strong donor to drive polymer formation. This finding is not completely surprising because although copper-containing coordination polymers based on cyano bridges are known, the failure of this moiety to generate such interactions has been documented in several attempts to synthesize related structures.[15,16,36]

Structural characterization of [Cu(4-pyrdpm)$_2$] and [Cu(3-pyrdpm)$_2$] reveals that these compounds are mononuclear

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(34) Mimura, M.; Matsuo, T.; Nakashima, T.; Matsumoto, N. *Inorg. Chem.* **1998**, *37*, 3553−3560.

(35) Stocker, F. B.; Troester, M. A.; Britton, D. *Inorg. Chem.* **1996**, *35*, 3145−3153.

(36) Zhang, W.; Jeitler, J. R.; Turnbull, M. M.; Landee, C. P.; Wei, M.; Willett, R. D. *Inorg. Chim. Acta* **1997**, *256*, 183−198.

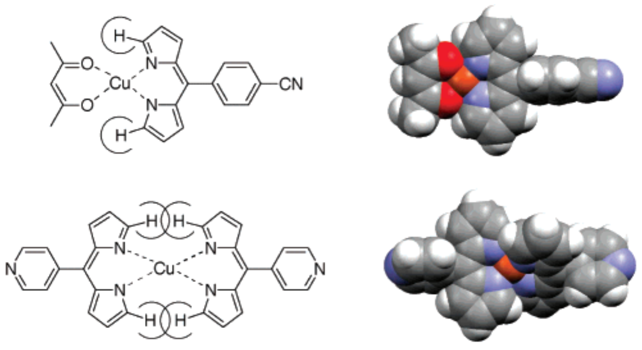

Figure 8. Chemical (left) and space-filling (right, from X-ray coordinates) representations of [Cu(4-cydpm)(acac)] (top) and [Cu(4-pyrdpm)$_2$] (bottom). The structures clearly show that the steric interactions between the α-pyrrolic protons play a major role in controlling the coordination geometry of these complexes. Note that the axial positions in [Cu(4-pyrdpm)$_2$] are largely blocked by the twisting of the dipyrrin ligands relative to one another.

metal complexes. The solid-state structure of these complexes show the metal centers possess a highly distorted square planar geometry that is more typical of bis(dipyrrin)metal complexes.[20,24] The inability of these compounds to form more idealized square planar geometries is attributed to a steric clash between the α-pyrrole protons on opposing ligands (Figure 8).[20] The severely distorted square planar geometry in these complexes obstructs coordination of a fifth ligand such as a pyridyl nitrogen atom, although on the basis of spectroscopic studies it has been suggested that such coordination is possible.[20] Although these compounds do not form self-complementary coordination polymers, they hold promise as building blocks for heterometallic coordination polymers by subsequent reaction with salts of silver(I), cadmium(II), or other metal ions that can form coordinate bonds with nitrogenous ligands.[2,13,25,26,33,37,38]

In summary, a series of homo- and heteroleptic copper(II) dipyrromethene complexes were synthesized and characterized. Certain heteroleptic complexes containing *meso*-pyridyl substituents were found to form 1-dimensional coordination polymers of varying topologies while similar complexes containing *meso*-4-cyanophenyl or geometrically inaccessible *meso*-pyridyl substituents formed discrete compounds. In addition, homoleptic compounds were found to be unable to form coordination polymers with either cyano or pyridyl donors due to steric constraints. Ongoing studies are focused on varying both the dipyrrin and acac ligands to better understand the formation of these compounds and to discover new polymer structures. In addition, studies focused on using homoleptic complexes as monomers for heterometallic coordination polymers are underway and will be reported in due course.

Acknowledgment. We thank Prof. Arnold L. Rheingold, Dr. Lev N. Zakharov, and David T. Puerta (U.C. San Diego) for help with the X-ray structure determinations, Prof. Emmanuel A. Theodorakis (U.C. San Diego) for use of his FT-IR, and Melissa A. Grunlan and Prof. William P. Weber (U.S.C.) for instruction and use of their TGA and DSC instruments. This work was supported by the University of California, San Diego, a Chris and Warren Hellman Faculty Scholar award, and a Hellman Fellows award. Acknowledgment is made to the donors of the American Chemical Society Petroleum Research Fund for support of this research. H.M.D. was supported by the NSF-MASEM program through the U.C. San Diego Summer Training Academy for Research in the Sciences (STARS), and S.R.H. was supported in part by GAANN Fellowship No. GM-602020-03. This material is based upon work supported under a National Science Foundation Graduate Research Fellowship (S.R.H.).

Supporting Information Available: An additional figure, experimental details, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. X-ray crystallographic files in CIF format are available free of charge via the Internet at http://www.ccdc.cam.ac.uk. Refer to CCDC reference numbers 222290, 222291, 222292, 222293, 222294, and 222295.

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(37) Fujita, M.; Umemoto, K.; Yoshizawa, M.; Fujita, N.; Kusukawa, T.; Biradha, K. *Chem. Commun.* **2001**, 509−518.

(38) Hirsch, K. A.; Wilson, S. R.; Moore, J. S. *Chem. Commun.* **1998**, 13−14.