

Assembly of Heteroleptic Copper Complexes with Silver Salts: From Discrete Trinuclear Complexes to Infinite Networks

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Received October 16, 2009

The use of heteroleptic copper complexes functionalized with two differentiated coordinating groups for the elaboration of heterometallic extended networks is presented. Two novel 5-phenyl-dipyrin (dpm) ligands appended with an imidazole or a pyrazole function, dpm-imid and dpm-pz, have been prepared and used as ligands for the synthesis of a series of heteroleptic (acacR)Cu(dpm) complexes (acacH = acetylacetonate; acacCN = 3-cyanoacetylacetonate). The X-ray crystal structures of these complexes revealed that, albeit no particular association mode is observed for the acac capping ligand, one-dimensional networks are formed with the acacCN capping ligand. Whereas the imidazole peripheral ligand is coordinated to the copper center of a neighboring complex in the structure of (acacCN)Cu(dpm-imid), such an interaction is absent for the pyrazole appended derivative, (acacCN)Cu(dpm-pz), leading to an association mode involving the peripheral nitrile group of the acacCN ligand. Upon reaction of the imidazole functionalized complexes, (acac)Cu(dpm-imid) and (acacCN)Cu(dpm-imid), with silver salts, trinuclear species, $\{[(acacR)Cu(dpm-imid)]_2Ag\}^+$, are formed as a result of the coordination of the azole nitrogen atom of two copper complexes to the silver ion. As expected, in the case of (acac)Cu(dpm-imid), these species do not self-assemble into an extended network owing to the absence of a peripheral coordinating group. However, for the (acacCN)Cu(dpm-imid) complex, the trinuclear species are equipped with peripheral nitrile groups, thus allowing the binding of metal centers. Consequently, these species self-assemble into one-dimensional polymers with association modes varying with the nature of the anion present in the silver salt.

Introduction

Coordination polymers (CPs) have attracted considerable interest over the past decade, as they hold promise in the fields of gas storage and catalysis.¹ While the vast majority of these compounds are homometallic, the synthesis of their heterometallic counterpart remains challenging. Indeed, a one-pot synthetic approach can lead to a statistical mixture of

homo- and heterometallic architectures. To circumvent this synthetic issue, a sequential strategy can be envisioned.^{2–8}

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(1) (a) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460–1494. (b) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O'Keefe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319–330. (c) Kitagawa, S.; Kitaura, R.; Noro, S. I. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334–2375. (d) Férey, G.; Mellot-Drazniewski, C.; Serre, C.; Millange, F. *Acc. Chem. Res.* **2005**, *38*, 217–225. (e) MasPOCH, D.; Ruiz-Molina, D.; Veciana, J. *Chem. Soc. Rev.* **2007**, *36*, 770–818. (f) *Chem. Soc. Rev.* **2009**, *38* (5), themed issue on metal–organic frameworks.

(2) (a) Kahn, O. *Acc. Chem. Res.* **2000**, *33*, 647–657. (b) Andruh, M. *Chem. Commun.* **2007**, 2565–2577. (c) Pardo, E.; Ruiz-Garcia, R.; Cano, J.; Ottenwaelder, X.; Lescouëzec, R.; Jourmaux, Y.; Lloret, F.; Julve, M. *Dalton Trans.* **2008**, 2780–2805. (d) Constable, E. C. *Coord. Chem. Rev.* **2008**, *252*, 842–855. (e) Goldberg, I. *CrystEngComm.* **2008**, *10*, 637–645.

(3) (a) Baudron, S. A.; Hosseini, M. W. *Inorg. Chem.* **2006**, *45*, 5260–5262. (b) Baudron, S. A.; Hosseini, M. W.; Kyritsakas, N.; Kurmoo, M. *Dalton Trans.* **2007**, 1129–1139.

(4) (a) Dawe, L. N.; Miglioi, J.; Turnbow, L.; Taliaferro, M. L.; Shum, W. W.; Bagnato, J. D.; Zakharov, L. N.; Rheingold, A. L.; Arif, A. M.; Fourmigué, M.; Miller, J. S. *Inorg. Chem.* **2005**, *44*, 7530–7539. (b) Silva, R. M.; Gwengo, C.; Lindeman, S. V.; Smith, M. D.; Gardinier, J. R. *Inorg. Chem.* **2006**, *45*, 10998–11007. (c) Deiters, E.; Bulach, V.; Hosseini, M. W. *New. J. Chem.* **2006**, *30*, 1289–1294. (d) Deiters, E.; Bulach, V.; Hosseini, M. W. *Dalton Trans.* **2007**, 4126–4131. (e) Paw, W.; Eisenberg, R. *Inorg. Chem.* **1997**, *36*, 2287–2293. (f) Deiters, E.; Bulach, V.; Hosseini, M. W. *New. J. Chem.* **2008**, *32*, 99–104.

(5) (a) Chen, B.; Fronczek, F. R.; Maverick, A. W. *Inorg. Chem.* **2004**, *43*, 8209–8211. (b) Vreshch, V. D.; Lysenko, A. B.; Chernega, A. N.; Howard, J. A. K.; Krautscheid, H.; Sieler, J.; Domasevitch, K. V. *Dalton Trans.* **2004**, 2899–2903. (c) Zhang, Y.; Chen, B.; Fronczek, F. R.; Maverick, A. W. *Inorg. Chem.* **2008**, *47*, 4433–4435.

(6) (a) Burrows, A. D.; Cassar, K.; Mahon, M. F.; Warren, J. E. *Dalton Trans.* **2007**, 2499–2509. (b) Kondracka, M.; Englert, U. *Inorg. Chem.* **2008**, *47*, 10246–10257.

(7) (a) Halper, S. R.; Cohen, S. M. *Inorg. Chem.* **2005**, *44*, 486–488. (b) Murphy, D. L.; Malachowski, M. R.; Campana, C. F.; Cohen, S. M. *Chem. Commun.* **2005**, 5506–5508. (c) Halper, S. R.; Do, L.; Stork, J. R.; Cohen, S. M. *J. Am. Chem. Soc.* **2006**, *128*, 15255–15268. (d) Garibay, S.; Stork, J. R.; Wang, Z.; Cohen, S. M.; Telfer, S. G. *Chem. Commun.* **2007**, 4881–4883. (e) Stork, J. R.; Thoi, V. S.; Cohen, S. M. *Inorg. Chem.* **2007**, *46*, 11213–11223.

(8) (a) Salazar-Mendoza, D.; Baudron, S. A.; Hosseini, M. W. *Chem. Commun.* **2007**, 2252–2254. (b) Salazar-Mendoza, D.; Baudron, S. A.; Hosseini, M. W. *Inorg. Chem.* **2008**, *47*, 766–768.

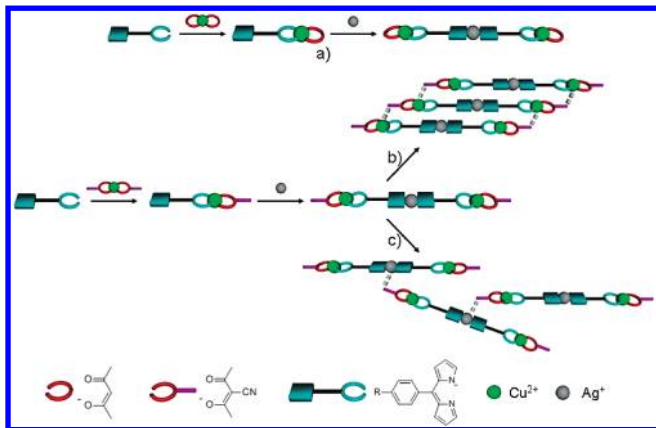


Figure 1. Coordination of an (acac)Cu(dpm) complex with silver ions, leading to a trinuclear complex (a). With the nitrile appended (acacCN)Cu(dpm) complexes, coordination polymers can be obtained (b and c).

The latter relies on the use of ligands bearing differentiated coordination sites, hence allowing the stepwise elaboration of heterometallic architectures. Reaction of such a ligand with a first metal center leads to the formation of a metal complex, or metallatecton,⁹ bearing peripheral coordinating sites available for ligation to another metal center. Among the many potential differentiated ligands, the dipyrriins, dpm,¹⁰ represent a particularly interesting class of compounds. Indeed, their rather easy synthesis and functionalization as well as the monoanionic and chelating nature of their conjugate base have made them appealing candidates. In particular, the 5-aryl-dipyrriin derivatives have been successfully used for the elaboration of extended heterometallic architectures based, for the major part, on the association of homoleptic metallatectons with silver salts.^{7,8} Only a few examples have reported the elaboration of extended heterometallic systems based on heteroleptic metallatectons incorporating a dpm.⁸ These examples involve a Ag- π interaction between the silver ion and the pyrrolic system of the dpm. In the absence of such interaction, heteroleptic metallatectons such as (acac)Cu(dpm)^{8,11} or (salen)Co(dpm)⁸ complexes (acac = acetylacetonate, salen = *N,N'*-bis(salicylidene)ethylenediamine) incorporating a dpm bearing a coordinating site in the para position should only lead to discrete heterometallic complexes upon reaction with a second metal center, as illustrated in Figure 1a. Two approaches can be considered to obtain extended systems with such species. The first one consists of using a dpm ligand bearing more than one peripheral coordinating site. An example of such a unit may be obtained by functionalizing both meta positions on the aryl moiety. The second strategy relies on the use of the capping ligand itself for further coordination. For example, when considering the association of a (acac)Cu(dpm) heteroleptic complex with silver salts (Figure 1b and c), introduction of a coordinating group on the

capping ligand should allow the self-assembly by coordination processes of the heterometallic discrete complexes. It is worth noting that at least two modes of self-assembly can be foreseen for these species. The silver ion can feature coordination numbers higher than 2 and is therefore capable of interaction with the additional peripheral coordinating group (Figure 1c). It has also been demonstrated that (acac)Cu(dpm) complexes self-assemble upon coordination of the peripheral group on the dpm to a metal center of another complex leading to a penta-coordinated Cu ion.¹¹ In the case of discrete heterometallic complexes bearing peripheral coordinating sites, such a self-assembly mode should also lead to extended architectures (Figure 1b). Recently, several homoleptic complexes with the acacPy or acacCN ligands (acacPy = 3-(4-pyridyl)acetylacetonate; acacCN = 3-cyanoacetylacetonate) have been prepared and used for the elaboration of heterometallic CPs.^{5,6} Interestingly, no (acacCN)-Cu(dpm) or (acacPy)Cu(dpm) complexes have, to our knowledge, been reported. Such species would be suitable candidates for the application of the sequential construction strategy illustrated in Figure 1b and c. To illustrate this approach, we report herein on the synthesis of (acacCN)Cu(dpm), with the novel dipyrriins **5** and **6** (Scheme 1) bearing peripheral imidazole and pyrazole groups, respectively, and the study of their self-assembly as well as their reaction with silver salts to afford heterometallic CPs. The imidazole and pyrazole groups have been chosen for their known ability to form complexes with silver salts.^{12,13}

Experimental Section

Synthesis. The starting Cu(acacCN)₂ complex was prepared as described.¹⁴ Aldehydes **1** and **2** were synthesized following a modified version of the reported procedure.¹⁵ Pyrrole was purified over an alumina column before use. All other reagents were obtained commercially and used without further purification. ¹H and ¹³C NMR spectra were recorded at 25 °C on a Bruker AV 300 (300 MHz) with the deuterated solvent as

(9) (a) Hosseini, M. W. *Acc. Chem. Res.* **2005**, *38*, 313–323. (b) Hosseini, M. W. *Chem. Commun.* **2005**, 582–589.

(10) (a) Wagner, R. W.; Lindsey, J. S. *Pure Appl. Chem.* **1996**, *68*, 1373–1380. (b) Brückner, C.; Karunaratne, V.; Rettig, S. J.; Dolphin, D. *Can. J. Chem.* **1996**, *74*, 2182–2193. (c) Wood, T. E.; Thompson, A. *Chem. Rev.* **2007**, *107*, 1831–1861. (d) Maeda, H. *Eur. J. Org. Chem.* **2007**, 5313–5325.

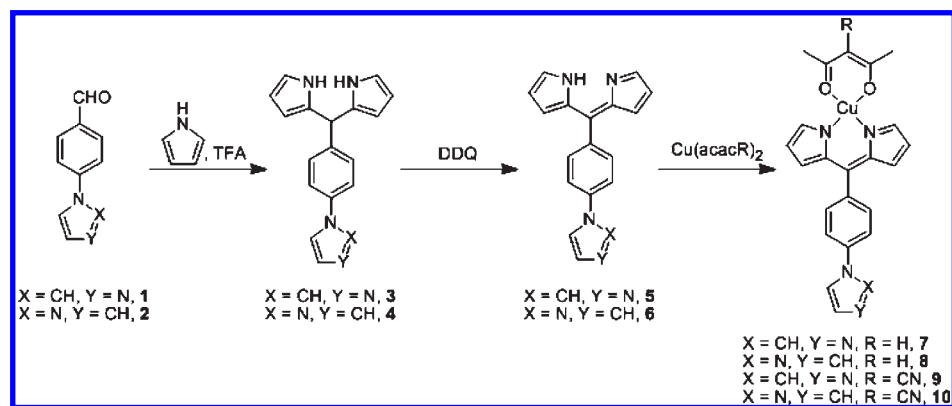
(11) (a) Halper, S. R.; Malachowski, M. R.; Delaney, H. M.; Cohen, S. M. *Inorg. Chem.* **2004**, *43*, 1242–1249. (b) Halper, S. R.; Cohen, S. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 2385–2388. (c) Do, L.; Halper, S. R.; Cohen, S. M. *Chem. Commun.* **2004**, 2662–2663. (d) Halper, S. R.; Cohen, S. M. *Inorg. Chem.* **2005**, *44*, 4139–4141. (e) Heinze, K.; Reinhart, A. *Inorg. Chem.* **2006**, *45*, 2695–2703.

(12) See, for example: (a) Hoskins, B. F.; Robson, R.; Slizys, D. A. *J. Am. Chem. Soc.* **1997**, *119*, 2952–2953. (b) Fan, J.; Sun, W.-Y.; Okamura, T.; Tang, W.-X.; Ueyama, N. *Inorg. Chem.* **2003**, *42*, 3168–3175. (c) Fan, J.; Zhu, H.-F.; Okamura, T.; Sun, W.-Y.; Tang, W. X.; Ueyama, N. *Chem.—Eur. J.* **2003**, *9*, 4724–4731. (d) Dobrzańska, L.; Llyod, G. O.; Raubenheimer, H. G.; Barbour, L. J. *J. Am. Chem. Soc.* **2005**, *127*, 13134–13135. (d) Zhu, H.-F.; Fan, J.; Okamura, T.; Sun, W.-Y.; Ueyama, N. *Cryst. Growth Des.* **2005**, *5*, 289–294. (e) Liu, C.-S.; Chen, P.-Q.; Yang, E.-C.; Tian, J.-L.; Bu, X.-H.; Li, Z.-M.; Sun, H.-W.; Lin, Z. *Inorg. Chem.* **2006**, *45*, 5812–5821. (f) Jin, C.-M.; Lu, H.; Wu, L.-Y.; Huang, J. *Chem. Commun.* **2006**, 5039–5041.

(13) (a) Francisco, R. H. P.; Mascarhenas, Y. P.; Lechat, J. R. *Acta Crystallogr., Sect. B* **1979**, *35*, 177–178. (b) Loi, M.; Hosseini, M. W.; Jouaiti, A.; De Cian, A.; Fischer, J. *Eur. J. Inorg. Chem.* **1999**, 1981–1985. (c) Jouaiti, A.; Hosseini, M. W.; Kyritsakas, N. *Eur. J. Inorg. Chem.* **2003**, 57–61. (d) Shu, M.; Tu, C.; Xu, W.; Jin, H.; Sun, J. *Cryst. Growth Des.* **2006**, *6*, 1890–1896. (e) Liddle, B. J.; Hall, D.; Lindeman, S. V.; Smith, M. D.; Gardinier, J. R. *Inorg. Chem.* **2009**, *48*, 8404–8414. (f) Ehrhart, J.; Planeix, J.-M.; Kyritsakas-Gruber, N.; Hosseini, M. W. *Dalton Trans.* **2009**, 2552–2257. (g) Ehrhart, J.; Planeix, J.-M.; Kyritsakas-Gruber, N.; Hosseini, M. W. *Dalton Trans.* **2009**, 6309–6314.

(14) (a) Angelova, O.; Petrov, G.; Macicek, J. *Acta Crystallogr., Sect. C* **1989**, *45*, 710–713. (b) Angelova, O.; Macicek, J.; Atanasov, M.; Petrov, G. *Inorg. Chem.* **1991**, *30*, 1943–1949. (c) Tsiamis, C.; Tzavellas, L. C.; Stergiou, A.; Anesti, V. *Inorg. Chem.* **1996**, *35*, 4984–4988. (d) Tsiamis, C.; Hatzidimitriou, A. G.; Tzavellas, L. C. *Inorg. Chem.* **1998**, *37*, 2903–2909. (e) Silvernail, C. M.; Yap, G.; Sommer, R. D.; Rheingold, A. L.; Day, V. W.; Belot, J. A. *Polyhedron* **2001**, *20*, 3113–3117. (f) Burdukov, A. B.; Roschuplina, G. I.; Gatilov, Y. V.; Gromilov, S. A.; Reznikov, V. A. *J. Supramol. Chem.* **2002**, *2*, 359–363. (g) Yoshida, J.; Nishikiori, S.; Kuroda, R. *Chem.—Eur. J.* **2008**, *14*, 10570–10578.

(15) Sreedhar, B.; Shiva Kumar, K. B.; Srinivas, P.; Balasubrahmanyam, V.; Venkanna, G. T. *J. Mol. Catal. A: Chem.* **2007**, *265*, 183–185.

Scheme 1. Synthesis of the Dipyrins **5** and **6** and the Heteroleptic Copper Complexes **7–10**

the lock and residual solvent as the internal reference. NMR chemical shifts and J values are given in parts per million and in hertz, respectively.

Aldehyde 1. A DMSO solution (60 mL) of CuI (0.21 g, 1.1 mmol) and L-histidine (0.34 g, 2.2 mmol) was stirred in a preheated oil bath (100 °C) under nitrogen for 30 min. Then, 4-bromobenzaldehyde (2 g, 1.11 mmol), imidazole (0.9 g, 1.32 mmol), and potassium carbonate (3.06 g, 2.22 mmol) were added. After 36 h, the reaction mixture was washed with aqueous NaHCO₃ (750 mL), and the product was extracted in chloroform (3 × 500 mL). Organic extracts were dried over MgSO₄ and concentrated. The crude product was purified by chromatography (SiO₂, EtOAc Rf = 0.37) to afford compound **1** as a white solid (0.76 g, 40%). ¹H NMR (300 MHz, CDCl₃): δ 10.04 (s, 1H), 8.01 (d, J = 8.7 Hz, 2H), 7.96 (s, 1H), 7.57 (d, J = 8.7 Hz, 2H), 7.37 (t, J = 1.4 Hz, 1H), 7.24 (t, J = 1.1 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 190.6, 141.7, 135.4, 135.0, 131.6, 131.4, 121.1, 117.7. Anal. Calcd for C₁₀H₈N₂O: C, 69.76; N, 16.27; H, 4.68. Found: C, 69.72; N, 16.55; H, 4.87.

Aldehyde 2. A DMSO solution (60 mL) of CuI (0.5 g, 2.6 mmol) and L-histidine (0.34 g, 2.2 mmol) was stirred in a preheated oil bath (100 °C) under nitrogen for 30 min. Then, 4-bromobenzaldehyde (5 g, 27.70 mmol), pyrazole (2.26 g, 33.2 mmol), and K₂CO₃ (7.65 g, 55.43 mmol) were added. After 36 h, the reaction mixture was washed with aqueous K₂CO₃ (1.5 L), and the product was extracted in chloroform (4 × 500 mL). Organic extracts were dried over dry MgSO₄ and concentrated. The crude product was purified by flash chromatography (SiO₂, CHCl₃, Rf = 0.34) in CHCl₃/pentane (1/1) and then in CHCl₃ to afford product **2** as a white solid (1.25 g, 26.4%). ¹H NMR (300 MHz, CDCl₃): δ 10.01 (s, 1H), 8.03 (d, J = 2.6 Hz, 1H), 8.00–7.96 (m, 2H), 7.91–7.87 (m, 2H), 7.78 (d, J = 1.8 Hz, 1H), 6.53 (dd, J^1 = 2.6, J^2 = 1.8 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 191.0, 144.3, 142.3, 134.1, 131.3, 127.0, 118.8, 108.9. Anal. Calcd for C₁₀H₈N₂O: C, 69.76; N, 16.27; H, 4.68. Found: C, 68.95; N, 16.07; H, 4.41.

Dipyrromethane 3. Several drops of trifluoroacetic acid (TFA) were added to a solution of **1** (2.5 g, 15.52 mmol) in an excess of degassed pyrrole (40 mL). The mixture was heated at 75 °C for 24 h under nitrogen and protected from light. Pyrrole was then removed under vacuum, and the resulting residue was dissolved in CHCl₃ (300 mL) and washed with a 0.1 M NaOH (3 × 150 mL) solution. The organic extracts were dried over MgSO₄ and concentrated. The crude product was purified by flash chromatography (SiO₂, CHCl₃, Rf(EtOAc) = 0.53). The resulting solid was washed with EtOAc to afford **3** as a beige solid (2.63 g, 69.1%). ¹H NMR (300 MHz, acetone-d₆): δ 9.81 (s, 1H), 7.97 (s, 1H), 7.53 (dt, J^1 = 2.3 Hz, J^2 = 8.7 Hz, 2H), 7.34 (dt, J^1 = 2.3 Hz, J^2 = 8.7 Hz, 2H), 7.08 (t, J = 1.1 Hz, 1H), 6.70 (m, 2H), 6.00 (dd, J^1 = 2.8 Hz, J^2 = 5.8 Hz, 2H), 5.76 (m, 2H), 5.52 (s, 1H). ¹³C NMR (75 MHz, DMSO-d₆): δ 143.1, 135.9, 135.5, 133.2, 130.2, 129.8, 120.3, 118.5, 106.6, 43.3. Anal. Calcd

for C₁₈H₁₆N₄: C, 74.98; N, 19.43; H, 5.59. Found: C, 74.32; N, 19.46; H, 5.56.

Dipyrromethane 4. Several drops of TFA were added to a solution of **2** (1.25 g, 6.98 mmol) in an excess of degassed pyrrole (40 mL). The mixture was heated at 75 °C for 24 h under nitrogen and protected from light. A few drops of Et₃N were added to the mixture, and pyrrole was removed under vacuum. The resulting residue was dissolved in CHCl₃ (300 mL) and washed with 0.1 M NaOH (3 × 150 mL). The organic extracts were dried over MgSO₄ and concentrated. The crude product was purified by flash chromatography on SiO₂ (CHCl₃) and then on Al₂O₃ (CHCl₃/pentane: 1/1, Rf(CHCl₃) = 0.17) to afford **4** as a yellow solid (1.61 g, 76.9%). ¹H NMR (300 MHz, CDCl₃): δ 8.00 (s, 2H), 7.89 (d, J = 2.4 Hz, 1H), 7.71 (d, J = 1.6 Hz, 1H), 7.65–7.60 (m, 2H), 7.31–7.27 (m, 2H), 6.72 (dd, J^1 = 4.2, J^2 = 2.8 Hz, 2H), 6.46 (t, J = 2.1 Hz, 1H), 6.17 (dd, J^1 = 6.0 Hz, J^2 = 2.6 Hz, 2H), 5.93 (m, 2H), 5.51 (s, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 141.1, 140.5, 139.1, 132.2, 129.4, 126.8, 119.5, 117.4, 108.6, 107.6, 107.4, 43.5. Anal. Calcd for C₁₈H₁₆N₄: C, 74.98; N, 19.43; H, 5.59. Found: C, 74.64; N, 19.59; H 5.45.

Dipyrin 5. A benzene solution (100 mL) of DDQ (2.75 g, 12.09 mmol) was added dropwise over a period of 30 min to a THF solution (300 mL) of **3** (2.63 g, 11.52 mmol). Thin-layer chromatography (TLC) analysis indicated complete consumption of the starting material after stirring for 1 h. The solvent was removed under vacuum, and the resulting residue was dissolved in CHCl₃ (300 mL) and purified by mixing with activated carbon. The CHCl₃ solution was separated by filtration, and the crude product was purified by flash chromatography (SiO₂, EtOAc with addition of Et₃N, Rf = 0.45) to afford **5** as a yellow solid (1.6 g, 61.4%). ¹H NMR (300 MHz, acetone-d₆): δ 8.21 (s, 1H), 7.78 (dt, J^1 = 8.52 Hz, J^2 = 2.1 Hz, 2H), 7.76 (t, J = 1.4, 2H), 7.71 (t, J = 1.4, 1H), 7.65 (dt, J^1 = 8.5 Hz, J^2 = 2.1 Hz, 2H), 7.17 (t, J = 1.1 Hz, 1H), 6.60 (dd, J^1 = 4.2, J^2 = 1.3 Hz, 2H), 6.44 (dd, J^1 = 4.2, J^2 = 1.3 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 0.144.1, 140.8, 140.1, 137.7, 136.5, 135.5, 132.3, 130.8, 128.5, 121.5, 120.4, 118.1, 118.0, 117.6, 108.5, 107.4. UV–vis (CH₂Cl₂), λ_{max} (nm)/ε (mol⁻¹ L cm⁻¹): 228 (30 000), 323 (11 000), 434 (26 000). Anal. Calcd for C₁₈H₁₄N₄: C, 75.51; N, 19.57; H, 4.93. Found: C, 75.52; N, 19.86; H, 5.21.

Dipyrin 6. A benzene solution (100 mL) of DDQ (1.3 g, 5.73 mmol) was added dropwise over a period of 30 min to a THF solution (200 mL) of **4** (1.5 g, 6.57 mmol). TLC analysis indicated complete consumption of the starting material after stirring for 12 h. Then, the solvent was removed under vacuum, and the resulting residue was dissolved in CHCl₃ (300 mL) and purified by mixing with activated carbon. The organic solution was separated by filtration, and the crude product was purified by flash chromatography (SiO₂, CHCl₃/pentane: 1:1 with addition of Et₃N, Rf(CHCl₃) = 0.66) to afford **6** as a yellow solid (1.2 g, 80.1%). ¹H NMR (300 MHz, CDCl₃): δ 8.01 (d, J = 2.5 Hz, 2H), 7.82–7.77 (m, 3H), 7.66 (t, J = 1.2 Hz, 2H), 7.62–7.57 (m, 2H),

Table 1. Crystallographic Data for Compounds 3, 4, and 7–10·(C₄H₈O₂)

	3	4	7	8	9	10·(C ₄ H ₈ O ₂)
formula	C ₁₈ H ₁₆ N ₄	C ₁₈ H ₁₆ N ₄	C ₂₃ H ₂₀ CuN ₄ O ₂	C ₂₃ H ₂₀ CuN ₄ O ₂	C ₂₄ H ₁₉ CuN ₅ O ₂	C ₂₈ H ₂₇ CuN ₅ O ₄
fw	288.35	288.35	447.99	447.97	472.98	561.10
cryst syst	triclinic	monoclinic	triclinic	monoclinic	monoclinic	triclinic
space group	P $\bar{1}$	P2 ₁ /n	P $\bar{1}$	P2 ₁ /c	P2 ₁ /c	P $\bar{1}$
a, Å	8.5724(10)	9.2680(3)	8.6097(2)	14.0618(6)	9.0755(3)	7.7529(2)
b, Å	9.7289(10)	17.7535(5)	10.6165(3)	17.0890(8)	21.5983(6)	11.9322(2)
c, Å	10.4170(11)	9.3468(3)	11.0140(3)	8.8153(4)	21.3201(6)	14.8002(4)
α, deg	62.616(4)		82.1660(10)			84.4710(10)
β, deg	80.140(4)	109.2900(10)	87.9790(10)	107.739(2)	94.0810(10)	74.8250(10)
γ, deg	83.840(4)		88.6640(10)			72.3840(10)
V, Å ³	759.63(14)	1451.58(8)	996.54(5)	2017.62(16)	4168.5(2)	1259.23(5)
Z	2	4	2	4	8	2
T, K	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)
μ, mm ⁻¹	0.078	0.081	1.124	1.110	1.081	0.913
reflns collected	6871	15557	12188	13780	39063	26130
ind. reflns (R _{int})	3260 (0.0395)	3298 (0.0255)	4525 (0.0249)	4593 (0.0309)	9592 (0.0398)	7313 (0.0261)
R ₁ (I > 2σ(I)) ^a	0.0758	0.0415	0.0339	0.0403	0.0385	0.0353
wR ₂ (I > 2σ(I)) ^a	0.1639	0.0947	0.0914	0.0975	0.0998	0.0857
R ₁ (all data) ^a	0.1038	0.0508	0.0392	0.0528	0.0623	0.0409
wR ₂ (all data) ^a	0.1774	0.1016	0.0970	0.1163	0.1161	0.0897
GOF	1.146	1.067	1.072	1.100	1.082	1.085

$$^a R_1 = \sum |F_o| - |F_c| / \sum |F_o|; wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}.$$

6.64 (dd, $J^1 = 4.2$ Hz, $J^2 = 1.0$ Hz, 2H), 6.52 (t, $J = 2.2$ Hz, 1H), 6.42 (dd, $J^1 = 4.2$ Hz, $J^2 = 1.5$ Hz, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 143.8, 141.5, 140.8, 140.8, 140.6, 135.4, 132.0, 128.6, 126.8, 118.2, 117.8, 108.1. UV-vis (CH₂Cl₂) λ_{max}(nm)/ε (mol⁻¹ L cm⁻¹): 227 (18 000), 258 (22 000), 338 (12 000), 437 (22 000), 461 (18 000). HRMS (ESI), m/z : [M + H]⁺ calcd for C₁₈H₁₅N₄, 287.129; found, 287.126.

[(acac)Cu(5)], 7. A solution of 5 (25 mg, 0.087 mmol) in THF (8 mL) was mixed with a THF (8 mL) solution of Cu(acac)₂ (22.9 mg, 0.087 mmol). The reaction mixture was stirred for 20 min. The solvent was then removed under vacuum. The crude product was purified by flash chromatography (SiO₂, EtOAc, Rf = 0.47). The resulting solid was washed with *n*-pentane (50 mL) to afford 7 as a red solid (25.5 mg, 65%). Dichroic red-green crystals were grown by slow diffusion of ether into a CHCl₃ solution of the complex. UV-vis, (CH₂Cl₂) λ_{max}(nm)/ε (mol⁻¹ L cm⁻¹): 229 (34 000), 297 (15 000), 329 (11 000), 479 (25 000), 493 (32 000). Anal. Calcd for C₂₃H₂₀N₄O₂Cu: C, 61.67; N, 12.51; H, 4.50. Found: C, 61.19; N, 12.16; H, 4.51.

[(acac)Cu(6)], 8. A THF (8 mL) solution of 6 (25 mg, 0.087 mmol) was mixed with a THF (8 mL) solution of Cu(acac)₂ (22.8 mg, 0.087 mmol). The reaction mixture was stirred for 20 min and then was evaporated to dryness under vacuum. The crude product was purified by chromatography (SiO₂, CHCl₃, Rf = 0.44). The resulting solid was washed with *n*-pentane (50 mL) to afford 8 as a red solid (27.3 mg, 69.5%). Dichroic red-green crystals were grown by slow evaporation of a CHCl₃ solution of the complex. UV-vis, (CH₂Cl₂) λ_{max}(nm)/ε (mol⁻¹ L cm⁻¹): 227 (33 000), 294 (24 000), 342 (15 000), 482 (32 000), 493 (39 000). Anal. Calcd for C₂₃H₂₀N₄O₂Cu: C, 61.67; N, 12.51; H, 4.50. Found: C, 61.62; N, 12.67; H, 4.82.

[(acacCN)Cu(5)], 9. A THF (30 mL) solution of Cu(acacCN)₂ (109 mg, 0.349 mmol) was added to a THF (20 mL) solution of 5 (100 mg, 0.349 mmol). After stirring for 20 min, the resulting precipitate was filtered off and washed with ether (3 × 75 mL) to afford 9 as a green-red solid (136 mg, 82.4%). Dichroic red-green crystals were grown by slow evaporation of a CHCl₃ solution. UV-vis (CH₂Cl₂) λ_{max}(nm)/ε (mol⁻¹ L cm⁻¹): 227 (28 000), 288 (12 000), 333 (9 000), 479 (21 000), 491 (27 000). IR (ATR, cm⁻¹): ν_{CN} 2206. HRMS (ESI), m/z : [M + H]⁺ calcd for C₂₄H₂₀N₅O₂Cu, 473.091; found, 473.091.

[(acacCN)Cu(6)], 10. A THF solution (20 mL) of 6 (55 mg, 0.19 mmol) was mixed with a THF solution (30 mL) of Cu(acacCN)₂ (60 mg, 0.19 mmol). The reaction mixture was stirred

for 20 min, before removal of the solvent under a vacuum. The crude product was purified by flash chromatography (SiO₂, CHCl₃, Rf = 0.42). The resulting solid was washed with *n*-pentane (150 mL) to afford 10 as dichroic red-green crystals (53 mg, 58.1%). Green-red single crystals were grown either by slow diffusion of *n*-pentane into a dioxane solution of the complex or by slow diffusion of *n*-pentane into a CHCl₃ solution of the complex. UV-vis (CH₂Cl₂) λ_{max}(nm)/ε (mol⁻¹ L cm⁻¹): 229 (69 000), 263 (30 000), 349 (12 000), 478 (23 000), 489 (27 000). IR (ATR, cm⁻¹): ν_{CN} 2197. Anal. Calcd for C₂₈H₂₇N₅CuO₄: C, 59.94; N, 12.48; H, 4.85. Found: C, 60.12; N, 12.73; H, 5.01.

Heterometallic Complex 11. A solution of 7 (34.5 mg, 0.076 mmol) in THF (20 mL) was slowly diffused into a benzene solution (15 mL) of AgSbF₆ (13.3 mg, 0.038 mmol) in a tube (16 × 1 cm) protected from light. After two weeks, dichroic green-orange crystals were grown (39 mg, 73.0%). UV-vis, (THF) λ_{max}(nm)/ε (mol⁻¹ L cm⁻¹): 237 (65 000), 301 (40 000), 475 (57 000), 494 (98 000). Anal. Calcd for C₃₈H₅₂AgCu₂F₆N₈O₄Sb: C, 49.91; N, 8.03; H, 3.75. Found: C, 48.94; N, 7.70; H, 3.78.

Coordination Polymer 12. In a vial (Ø22.00 × 65 × 1 mm) protected from light, a solution of 9 (10 mg, 0.021 mmol) in THF (10 mL) was slowly diffused into an EtOH solution (5 mL) of AgPF₆ (2.67 mg, 0.0106 mmol). After two weeks, dichroic green-orange crystals were obtained (7.7 mg, 51.2%) and analyzed by X-ray diffraction on a single crystal. IR (ATR, cm⁻¹): ν_{CN} 2196. Anal. Calcd for C₅₂H₄₆AgCu₂F₆N₁₀O₅P: C, 49.14; N, 11.02; H, 3.65. Found: C, 48.87; N, 11.35; H, 3.91.

Coordination Polymer 13. In a crystallization tube (Ø22.00 × 65 × 1 mm) protected from light, a solution of 9 (10 mg, 0.021 mmol) in CHCl₃ (7 mL) was slowly diffused into a benzene solution (7 mL) of AgBF₄ (2.10 mg, 0.0106 mmol). After two weeks, dichroic green-orange crystals were obtained (7.2 mg, 55.9%) and analyzed by X-ray diffraction on a single crystal. IR (ATR, cm⁻¹): ν_{CN} 2194. Anal. Calcd for C₅₄H₄₄AgBCu₂F₄N₁₀O₄: C, 53.22; N, 11.49; H, 3.64. Found: C, 52.28; N, 11.62; H, 3.88.

Coordination Polymer 14. A solution of 9 (9 mg, 0.019 mmol) in *o*-xylene (4 mL) was mixed with an *o*-xylene (2 mL) solution of AgOTf (4.8 mg, 0.0095 mmol) and stirred for 1 min. A red precipitate appeared, which was dissolved upon the addition of CH₃CN (2.5 mL). Slow evaporation of CH₃CN in the absence of light afforded the product as dark-green crystals (7.8 mg, 62.7%). IR (ATR, cm⁻¹): ν_{CN} 2251.

X-Ray Crystallography. Data (Tables 1 and 2) were collected on a Bruker SMART CCD diffractometer with Mo Kα

Table 2. Crystallographic Data for Compounds 10–14

	10	11	12	13	14
formula	C ₂₄ H ₁₉ CuN ₅ O ₂	C ₅₈ H ₅₂ AgCu ₂ F ₆ N ₈ O ₄ Sb	C ₅₂ H ₄₆ AgCu ₂ F ₆ N ₁₀ O ₅ P	C ₅₄ H ₄₄ AgBCu ₂ F ₄ N ₁₀ O ₄	C ₅₇ H ₄₈ AgCu ₂ F ₃ N ₁₀ O ₇ S
fw	472.98	1395.78	1270.91	1218.78	1309.09
cryst syst	monoclinic	triclinic	triclinic	triclinic	triclinic
space group	<i>P</i> 2 ₁	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> , Å	7.0712(3)	10.2596(2)	6.8023(7)	6.8931(3)	11.9313(2)
<i>b</i> , Å	15.8916(7)	15.4490(3)	8.5991(10)	8.5345(4)	12.1710(3)
<i>c</i> , Å	9.4970(4)	19.2748(4)	22.727(3)	22.8014(10)	21.7466(5)
α , deg		110.1590(10)	82.210(4)	79.907(2)	74.9010(10)
β , deg	105.4930(10)	97.3400(10)	81.502(4)	83.993(2)	82.2040(10)
γ , deg		95.1390(10)	79.614(4)	78.969(2)	64.6080(10)
<i>V</i> , Å ³	1028.42(8)	2814.97(10)	1285.1(2)	1292.71(10)	2753.35(10)
<i>Z</i>	2	2	1	1	2
<i>T</i> , K	173(2)	173(2)	173(2)	173(2)	173(2)
μ , mm ⁻¹	1.095	1.637	1.642	1.261	1.229
reflns collected	11992	33360	12020	23641	31895
ind. reflns (<i>R</i> _{int})	4294 (0.0280)	12742 (0.0342)	5716 (0.0318)	5824 (0.0267)	12394 (0.0280)
<i>R</i> ₁ (<i>I</i> > 2 σ (<i>I</i>)) ^a	0.0272	0.0452	0.0456	0.0302	0.0464
<i>wR</i> ₂ (<i>I</i> > 2 σ (<i>I</i>)) ^a	0.0661	0.1070	0.0991	0.0723	0.1131
<i>R</i> ₁ (all data) ^a	0.0290	0.0649	0.0772	0.0384	0.0552
<i>wR</i> ₂ (all data) ^a	0.0678	0.1332	0.1099	0.0755	0.1191
GOF	1.096	1.129	1.016	1.033	1.172

$$^a R_1 = \sum |F_o| - |F_c| / \sum |F_o|; wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}.$$

radiation. The structures were solved using SHELXS-97 and refined by full matrix least-squares on F^2 using SHELXL-97 with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were introduced at calculated positions and not refined (riding model).

CCDC 751566–751576 contain the supplementary crystallographic data for compounds 3, 4, 7–10 (C₄H₈O₂), and 10–14. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Synthesis. The aldehyde precursors 1 and 2 were prepared by a Cu(I)-catalyzed reaction of *p*-bromobenzaldehyde with imidazole and pyrazole, respectively.¹⁵ Their subsequent reaction in neat pyrrole in the presence of a catalytic amount of TFA, as developed by Lindsey and co-workers,¹⁶ leads to the formation of dipyrromethanes 3 and 4 in 69 and 77% yields, respectively. The latter are readily oxidized with DDQ to afford dipyrrens 5 and 6 in 61 and 80% yields, respectively, after purification by column chromatography (SiO₂). Reaction of either dipyrren 5 or 6 with 1 equiv of Cu(acacR)₂ (R = H, CN) affords the corresponding heteroleptic Cu(acacR)(dpm) complexes 7–10, in 58–82% yield. All four complexes feature two absorption bands between 470 and 495 nm in CH₂Cl₂ solutions, which are in agreement with reported data in the literature¹¹ for (acac)Cu(dpm) complexes. The CN vibration stretch is observed in the IR spectra of complexes 9 and 10 at 2206 and 2197 cm⁻¹, respectively, again in agreement with values reported for other Cu(acacCN)₂ derivatives.^{14,17}

Crystal Structure of the Ligands and the Mononuclear Complexes. Both dipyrromethane derivatives 3 and 4 were crystallized by the slow diffusion of *n*-pentane in a THF solution. The former crystallizes in the triclinic space group *P* $\bar{1}$, while the latter crystallizes in the monoclinic space group *P*2₁/*n* with one molecule in a general position.

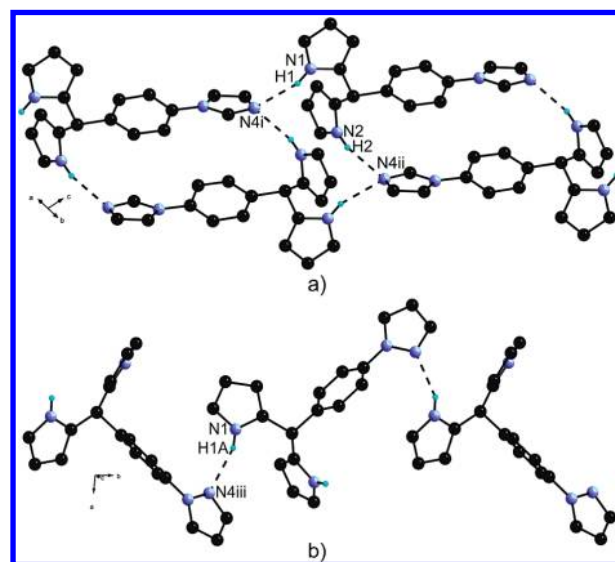


Figure 2. Hydrogen-bonded networks in 3 (a) and 4 (b). Only N–H hydrogen atoms are shown for clarity. Selected bond distances (Å) and angles (deg), for 3: N1⋯N4i, 3.051(6); N2⋯N4ii, 3.031(7); N1–H1⋯N4i, 160.3; N2–H2⋯N4ii, 164.1. For 4: N1⋯N4iii, 3.036(2); N1–H1A⋯N4iii, 153.4. *i* = 1 + *x*, *y*, –1 + *z*; *ii* = 1 – *x*, 1 – *y*, 2 – *z*; *iii* = 1/2 – *x*, –1/2 + *y*, 3/2 – *z*.

In 3, one imidazole nitrogen atom forms hydrogen bonds with the pyrrolic N–H of two neighboring molecules, leading thus to the formation of one-dimensional chains along *c* (Figure 2a). This type of arrangement is reminiscent of the recently reported crystal structures of other α,β -unsubstituted dipyrromethanes.^{7e,18} In 4, a single hydrogen bond is identified between a pyrrolic N–H and a pyrazole N atom leading again to a 1D chain (Figure 2b) analogous to the organization of dpm-py.^{7c}

Crystals of 7 were obtained by slow diffusion of Et₂O vapors into a CHCl₃ solution. Complex 7 crystallizes in

(16) Littler, B. J.; Miller, M. A.; Hung, C.-H.; Wagner, R. W.; O'Shea, D. F.; Boyle, P. D.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 1391–1396.

(17) Fackler, J. P. *J. Chem. Soc.* **1962**, 1957–1960.

(18) (a) Heinze, K.; Reinhart, A. *Z. Naturforsch.* **2005**, *60b*, 758–762. (b) Baudron, S. A.; Salazar-Mendoza, D.; Hosseini, M. W. *CrystEngComm.* **2009**, *11*, 1245–1254.

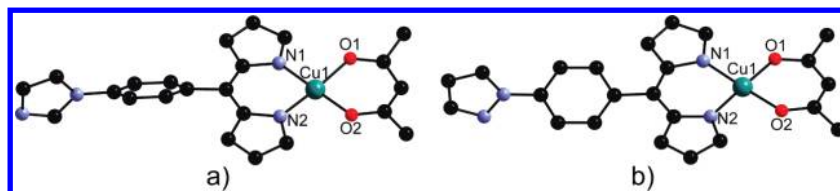


Figure 3. Crystal structure of complexes **7** (a) and **8** (b). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å), for **7**: Cu1–O1, 1.9554(17); Cu1–O2, 1.9478(16); Cu1–N1, 1.9286(15); Cu1–N2, 1.9391(14). For **8**: Cu1–O1, 1.9411(19); Cu1–O2, 1.9225(19); Cu1–N1, 1.942(2); Cu1–N2, 1.961(2).

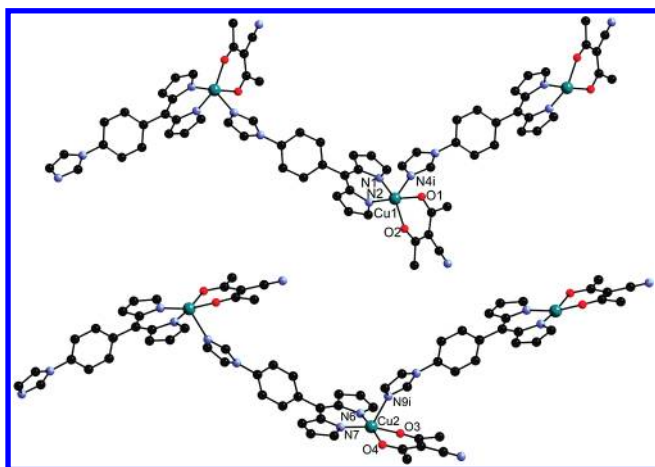


Figure 4. Two independent 1D polymers in the crystal structure of complex **9**; Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Cu1–O1, 1.9732(18); Cu1–O2, 1.9931(19); Cu1–N1, 1.966(2); Cu1–N2, 1.948(2); Cu1–N4i, 2.245(2); Cu2–O3, 1.9694(19); Cu2–O4, 1.9930(19); Cu2–N6, 1.968(2); Cu2–N7, 1.957(2); Cu2–N9, 2.302(2). $i = 1 - x, 1/2 + y, 3/2 - z$; $ii = -x, 1/2 + y, 1/2 - z$.

the triclinic space group $P\bar{1}$ with one molecule in a general position. Complex **8**, obtained upon slow evaporation of CHCl_3 , crystallizes in the monoclinic space group $P2_1/c$ with one molecule in a general position. In both compounds, the copper atom is in a square planar environment with Cu–N and Cu–O distances close to those reported for other analogous complexes (Figure 3).^{8,11} Interestingly, unlike other reported (acac)Cu(dpm) or (hfac)Cu(dpm) species,¹¹ the peripheral coordinating group, the diazole here, does not coordinate the Cu(II) center. A difference between the two complexes lies in the angle between the diazole and the phenyl ring, 30.9° for **7** and 13.9° for **8**. The angle for the latter might explain the absence of coordination to a neighboring complex, as reported for the analog incorporating the 5-(2-pyridyl)dipyrrin.^{11a}

Crystals of **9** were obtained by slow evaporation of a CHCl_3 solution. Complex **9** crystallizes in the monoclinic space group $P2_1/c$ with two molecules in general positions. In both molecules, the Cu ion is coordinated to both chelates, the dpm and the acacCN, and to the imidazole group of a neighboring complex with Cu–N_{imid} distances of 2.245(2) and 2.302(2) Å, leading to the formation of 1D coordination polymers (Figure 4). This parallels the crystal structure of other heteroleptic (acac)Cu(dpm)'s where the dpm bears a coordinating peripheral nitrogen atom, such as pyridine or quinoline.¹¹ The main difference between the two independent complexes lies in the coordination geometry around the copper atoms. While one complex deviates from planarity with an angle of

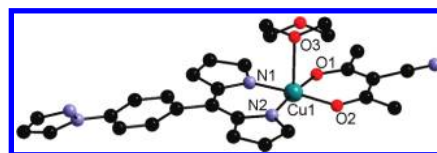


Figure 5. Crystal structure of the **10**· $\text{C}_4\text{H}_8\text{O}_2$ solvate showing the axially coordinated dioxane molecule. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å), for **7**: Cu1–O1, 1.9573(11); Cu1–O2, 1.9470(12); Cu1–N1, 1.9534(12); Cu1–N2, 1.9628(13); Cu1–O3, 2.443(2).

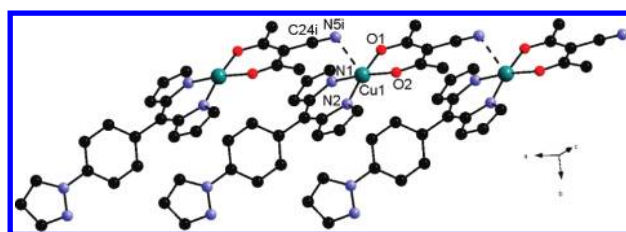


Figure 6. One-dimensional polymer in the crystal structure of complex **10**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angle (deg): Cu1–O1, 1.9706(16); Cu1–O2, 1.9465(16); Cu1–N1, 1.9586(18); Cu1–N2, 1.9648(19); Cu1–N5i, 2.489(2); C24i–N5i–Cu1, 114.4° . $i = 1 + x, y, z$.

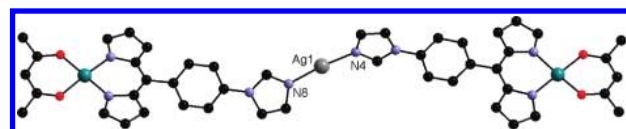


Figure 7. Complex $[\text{Ag}(\mathbf{7})_2]^+$ in **11**. Hydrogen atoms, solvent molecules, as well as the SbF_6^- anion have been omitted for clarity. Selected bond lengths (Å) and angle (deg): Ag1–N4, 2.079(3); Ag1–N8, 2.074(3); N4–Ag1–N8, $171.89(14)$.

42.9° between the acacCN and the dpm chelates (Figure 4a), the other is less distorted with an angle of 8.8° between the two groups. Such a concave arrangement away from the additional coordinating atom has been observed for other (acac)Cu(dpm) species.¹¹ The difference in the organizations of **7** and **9** is surprising but might be due to packing effects preventing the formation of a polymer with the earlier complex.

For compound **10**, depending on the solvent of crystallization used, two different crystal structures were obtained. In both cases, the arrangement of the copper complexes is quite different from the one observed for **9**. Upon slow diffusion of *n*-pentane vapors into a dioxane solution of **10**, dioxane solvate crystals **10**· $\text{C}_4\text{H}_8\text{O}_2$ were obtained (see Figure 5). The latter crystallizes in the triclinic space group $P\bar{1}$ with one copper complex and one solvent molecule in a general position. The copper center features a square pyramidal coordination

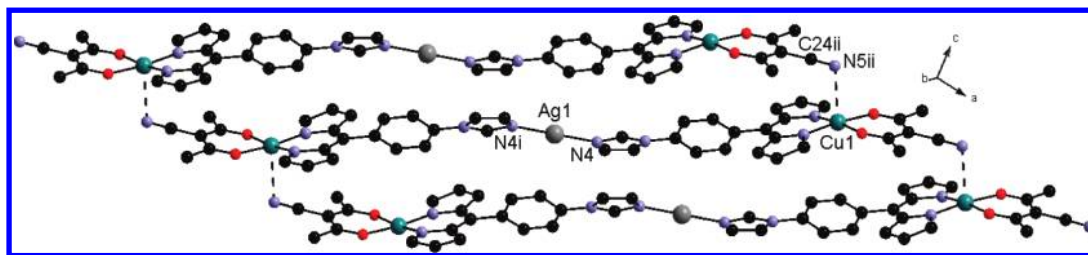


Figure 8. Coordination ribbon $[\text{Ag}(\mathbf{9})_2]^+_{\infty}$ observed for **12** and **13**. Hydrogen atoms, solvent molecules, as well as the anions have been omitted for clarity. Selected bond lengths (Å) and angles (deg), for **12**: Ag1–N4, 2.090(3); Cu1–N5ii, 2.631(4); N4–Ag1–N4i, 180.0(3); C24ii–N5ii–Cu1, 103.6. For **13**: Ag1–N4, 2.084(3); Cu1–N5ii, 2.620(4); N4–Ag1–N4i, 180.0(3); C24ii–N5ii–Cu1, 105.4. $i = -2 - x, 2 - y, -z$, $ii = 1 + x, y, z$.

geometry, being coordinated to the acacCN and the dpm chelates, as well as to an oxygen atom of the dioxane molecule. Unlike in the case of **9**, the azole nitrogen atom is not coordinated to the copper center.

Upon slow vapor diffusion of *n*-pentane in a CHCl_3 solution of the complex, crystals of **10** (nonsolvated) were obtained. Complex **10** crystallizes in the monoclinic space group $P2_1$ with one molecule in a general position. The copper ion is coordinated to the acacCN and dpm chelates with bond distances as expected for such complexes. Here again, the azole nitrogen atom is not coordinated to the copper center, but a one-dimensional chain is nonetheless formed owing to a weak interaction of the metal center with the nitrogen atom of the CN group of a neighboring complex (Figure 6). The Cu–N_{acacCN} distance of 2.489(2) Å is rather long, and the CNCu angle of 114.4° deviates largely from linearity. These geometrical parameters are however similar to the ones observed in the crystal structure of other reported $\text{Cu}(\text{acacCN})_2$ complexes.^{14,19} This structure illustrates the coordination, although weak, of the peripheral nitrile group to the copper center, as depicted in Figure 1b.

Heterometallic Architectures. With these four complexes in hand, the preparation of heteronuclear species was attempted by their reaction with silver salts. Unfortunately, the two pyrazole functionalized complexes **8** and **10** did not form crystalline heterometallic systems upon reaction with silver salts either by slow evaporation of benzene/MeCN mixtures or by slow liquid/liquid diffusion in a tube. This is rather surprising given that some phenyl–pyrazole derivatives have been reported to coordinate silver ions.¹³ This might be related to the position of the azole donor atom. We will illustrate hereafter the strategy presented in Figure 1 using complexes **7** and **9**.

To prepare a discrete heteronuclear complex such as the one presented schematically in Figure 1a, complex **7** was reacted with silver salts. Upon slow diffusion of a benzene solution of AgSbF_6 into a THF solution of **7**, crystals of the heterometallic complex $[\text{Ag}(\mathbf{7})_2](\text{SbF}_6)_2$ (C_6H_6)₂, **11**, were obtained. This compound crystallizes in the triclinic space group $P\bar{1}$ with two complexes **7**, one silver ion, a SbF_6^- anion, and two benzene molecules in general positions. The coordination geometry around the

copper atoms is similar to the one observed in the structure of **7**. The Ag^+ cation is coordinated in a linear fashion to two imidazole groups belonging to two copper complexes (Figure 7) with a Ag–N_{imid} distance close to the one previously observed for similar compounds.¹² As expected (Figure 1a), the absence of a further coordinating group in **7** prevents the self-assembly process through coordination bonds to take place, and thus a discrete species is formed. To investigate the role played by a peripheral nitrile group on the copper complexes, **9** was reacted with silver salts in a 2:1 stoichiometry.

Interestingly, upon reacting complex **9** with either AgPF_6 or AgBF_4 salts, isomorphous heterometallic systems were obtained. Orange crystals of $[\text{Ag}(\mathbf{9})_2]_{\infty}(\text{PF}_6)$ (THF), **12**, were obtained upon slow diffusion of an EtOH solution of AgPF_6 into a THF solution of **9**, while crystals of $[\text{Ag}(\mathbf{9})_2]_{\infty}(\text{BF}_4)$ (C_6H_6), **13**, were obtained from a CHCl_3 /benzene mixture (see Figure 8). Only the structure of **12** will be discussed hereafter. This compound crystallizes in the triclinic space group $P\bar{1}$ with a silver ion on an inversion center, one copper complex **9** and one PF_6^- anion, both in general positions, and one THF molecule on an inversion center. The silver ion is coordinated linearly to the imidazole group of two molecules of **9**, as in **11**, hence forming a trinuclear species. Owing to the interaction of the peripheral nitrile groups with copper atoms of neighboring complexes, the trinuclear complexes are interconnected ($d_{\text{Cu}-\text{NacacCN}} = 2.631(4)$ Å), affording 1D polymers along the *c* axis. Consequently, the copper centers are in a square pyramidal environment. As stated above, this type of coordination mode has been also observed for complex **10**. Although the Cu–N_{acacCN} distance observed for **12** is longer than the one observed for **10**, it is nevertheless in the same range as those observed for other self-assembled heteroleptic complexes incorporating the $[(\text{acacCN})\text{Cu}]^+$ fragment.^{14,19}

Slow evaporation of a MeCN/*o*-xylene solution of **9** and AgOTf afforded orange crystals of $[\text{Ag}(\mathbf{9})_2(\text{OTf})]_{\infty}$ (C_8H_{10}), **14**. It crystallizes in the triclinic space group $P\bar{1}$ with two complexes **9**, one Ag^+ cation, one triflate anion, and an *o*-xylene molecule in a general position. The two complexes **9** differ in the geometry around the copper centers. While one shows a square planar arrangement, the other is in a square pyramidal coordination environment owing to an interaction with an oxygen atom of the triflate anion ($d_{\text{Cu}-\text{O}} = 2.405(3)$ Å). As in the case of **11**, the Ag^+ center is coordinated to the two copper complexes via the imidazole groups (Figure 9). The coordination geometry around the silver ion however deviates

(19) (a) Soldatov, D. V.; Ripmeester, J. A.; Shergina, S. I.; Sokolov, I. E.; Zanina, A. S.; Gromilov, S. A.; Dyadin, Y. A. *J. Am. Chem. Soc.* **1999**, *121*, 4179–4188. (b) Ma, B.-Q.; Gao, S.; Yi, T.; Xu, G.-X. *Polyhedron* **2001**, *20*, 1255–1261. (c) Soldatov, D. V.; Tinnemans, P.; Enright, G. D.; Ratcliffe, C. I.; Diamante, P. R.; Ripmeester, J. A. *Chem. Mater.* **2003**, *15*, 3826–3840. (d) Yoshida, J.; Nishikiori, S.; Kuroda, R. *Chem. Lett.* **2007**, *36*, 678–679.

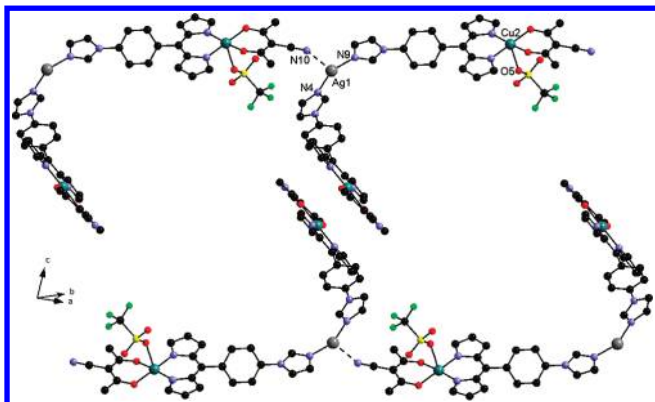


Figure 9. Portions of 1-D polymers $[\text{Ag}(\mathbf{9})_2(\text{OTf})]_\infty$ in **14** showing the interdigitation of consecutive polymers. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ag1–N4, 2.135(3); Ag1–N9, 2.141(3); Ag1–N10, 2.627(3); Cu2–O5, 2.405(3); N4–Ag1–N9, 154.93(10); N4–Ag1–N10, 109.79(10); N9–Ag1–N10, 93.94(10).

from linearity with a $\text{N}_{\text{imid}}\text{–Ag–N}_{\text{imid}}$ angle of $154.93(10)^\circ$. This is due to an additional weak $\text{CN}\cdots\text{Ag}$ interaction ($d_{\text{NCN–Ag}} = 2.627(3)$ Å) with the nitrile group of the acacCN capping ligand of a neighboring complex (Figure 9). This leads to the formation of one-dimensional chains of trinuclear species. Since only one of the two complexes **9** interact with the silver ion, the resulting chain possesses a comb shape. The consecutive comb shape arrangements are interdigitated with a face-to-face organization of the copper complexes. The space between combs is occupied by *o*-xylene molecules.

Conclusion

Two novel imidazole and pyrazole 5-phenyl-dipyrrins have been prepared and used as ligands for the formation of a series of heteroleptic (acacR)Cu(dpm) complexes (R = H, CN). The two (acacCN)Cu(dpm) complexes **9** and **10**

self-assemble into one-dimensional chains but with different connectivity patterns. In the case of the imidazole appended complex **9**, the diazole is coordinated to the copper atom in a square pyramidal coordination environment. Rather interestingly, in the case of the pyrazole analogue, **10**, the peripheral nitrile group of the acacCN capping ligand is weakly coordinated to a copper atom. Upon self-assembly of the imidazole functionalized complexes **7** and **9** with silver salts, trinuclear species are formed. While, in the case of **7**, the absence of peripheral coordinating nitrile groups prevents any self-assembly based on coordination processes leading to extended architectures, for **9**, the trinuclear complexes form one-dimensional polymers. In the presence of a weakly coordinating anion such as BF_4^- or PF_6^- , the CN groups weakly interact with the copper atoms of another trinuclear unit. In the case of the coordinating OTf^- anion, the axial position on the copper center is occupied and thus not available. Consequently, the interaction of the nitrile group takes place with the silver ion of another trinuclear unit. These results illustrate that proper functionalization of heteroleptic complexes can lead to the formation of extended heterometallic architectures upon association with another metal center. This approach seems promising for the development of novel heteronuclear networks. Such work is currently underway in our laboratory with the development of new $(\text{acacCN})_x\text{M}(\text{dpm})_y$ complexes and the study of their self-assembly using other metal centers.

Acknowledgment. We thank the Université de Strasbourg, the Institut Universitaire de France, the Ministry of Education and Research, the CNRS, and Marie Curie Est Actions FUMASSEC Network (Contract No. MEST-CET-2005-020992) for financial support.

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.