Inorganic Chemistry Article

Inorg. Chem. 2010, 49, 11231–11239 11231
DOI: 10.1021/ic1019235

Heterometallic Architectures Based on the Combination of Heteroleptic Copper and Cobalt Complexes with Silver Salts

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Received September 20, 2010

A strategy for the formation of heterometallic coordination polymers based on novel copper(II) and cobalt(III) heteroleptic complexes (acacCN)Cu(dpm) and (acacCN)Co(dpm)$_2$ (acacCN=3-cyanoacetylacetonate; dpm=dipyrrin) is presented. Using dipyrrins appended with a *p*- or *m*-pyridyl group, dpm-4py and dpm-3py, four novel copper and cobalt complexes were prepared and characterized both in solution and in the solid state. These two classes of complexes show different electrochemical properties upon investigation by cyclic voltammetry in CH_2Cl_2. While the copper complexes show only irreversible reduction processes, the voltammogram of the cobalt species reveals the presence of two quasi-reversible reductions. In the solid state, the copper(II) compounds self-assemble to form one-dimensional architectures upon coordination of the peripheral pyridyl group to the copper center, as characterized by single-crystal X-ray diffraction. Owing to the filled coordination sphere of the octahedral cobalt centers, the (acacCN)Co(dpm-py)$_2$ compounds crystallize as isolated molecules. Upon reaction with silver salts, these complexes form crystalline heterometallic architectures with different organization and dimensionality, depending on the nature of the metal center and the position of the nitrogen atom in the pyridyl group. The two copper complexes lead to the formation of trinuclear species, $\{[(\text{acacCN})\text{Cu}(\text{dpm-py})]_2\text{Ag}\}^+$, resulting from coordination of the pyridyl groups to the silver cations. However, while meta-functionalized complexes self-assemble into an extended architecture via weak interaction of the peripheral nitrile of the acacCN ligand to the Ag^+ cation, this interaction is not present in the para-functionalized analogue. In both networks based on the Ag(BF$_4$) salt, coordination of the tetrafluoroborate anion to the silver center in the rather rare chelate mode is observed. Upon assembly of the cobalt metallatectons with silver salts, two-dimensional (2D) coordination polymers are obtained in crystalline form, resulting, however, from different sets of interactions. Indeed, no coordination of the peripheral nitrile of the acacCN ligand is observed in the network incorporating the *m*-pyridyl-appended dpm; coordination of the pyridyl groups to the silver center and $d^{10}-d^{10}$ interactions lead to a 2D architecture. In the case of the para analogue, a 2D honeycomb network is observed owing to coordination of the Ag^I ion to two pyridyl nitrogen atoms and to one peripheral nitrile group of a acacCN ligand. This latter polymer represents a geometrical hybrid of the networks reported in the literature based on homoleptic Co(dpm-4py)$_3$ and Cr(acacCN)$_3$ complexes.

Introduction

In the field of coordination polymers or metal−organic frameworks, heterometallic architectures hold a unique place.[1] Indeed, their heterometallic nature is likely to prompt structural variation as well as modulation of the physical properties of solid-state materials composed of such periodic arrangements. Their synthesis is, however, not straightforward because control over the relative arrangement of the different metal centers remains difficult. To address this issue, a stepwise approach based on ligands appended with differentiated coordination sites can be followed.[2] Upon reaction of an organic ligand bearing additional peripheral coordination sites with a first

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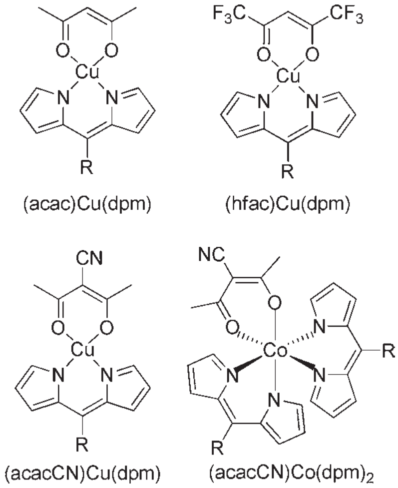
Scheme 1



metal center, discrete complexes or metallatectons bearing peripheral coordination sites can be formed.[3] Subsequent association of the latter with a second metal cation using the free peripheral sites thus leads to heterometallic architectures. This process can be iterated depending on the number of available peripheral coordination sites. While various ligands can be considered for the application of such a strategy, dipyrrins (dpm)[4] have been shown to be particularly well-suited owing to their easy synthesis and functionalization.[5] Derivatives appended with pyridyl, carboxylic acid, nitrile, or imidazolyl groups have been indeed employed for the stepwise construction of crystalline heterometallic architectures.[6,7] While a particular emphasis has been put on the use of homoleptic metal dipyrrin complexes,[6] heteroleptic species can also be successfully used for such a purpose.[7]

In this respect, the family of copper complexes of the (L)Cu(dpm) type, where L = acac, hfac, or acacCN, is particularly interesting (acac = acetylacetonate; hfac = hexafluoroacetylacetonate; acacCN = 3-cyanoacetylacetonate; Scheme 1).[7c,8] First, the species incorporating a dipyrrin ligand appended with a pyridyl (dpm-py), quinoline, imidazolyl (dpm-imid), or thioether group have been shown to form homometallic coordination polymers under self-assembly conditions, leading to pentacoordinated $\mathrm{Cu^{II}}$ centers, as presented Figure 1a.[7c,8] Moreover, we have recently reported that the (acacCN)Cu(dpm-imid) complex forms trinuclear species when associated with silver salts upon coordination of the imidazolyl peripheral group connected to the dpm ligand (Figure 1b).[7c] These trinuclear compounds can self-assemble via coordination of the peripheral nitrile groups present on the acacCN ligands to either $\mathrm{Cu^{II}}$ or $\mathrm{Ag^{I}}$ ions.

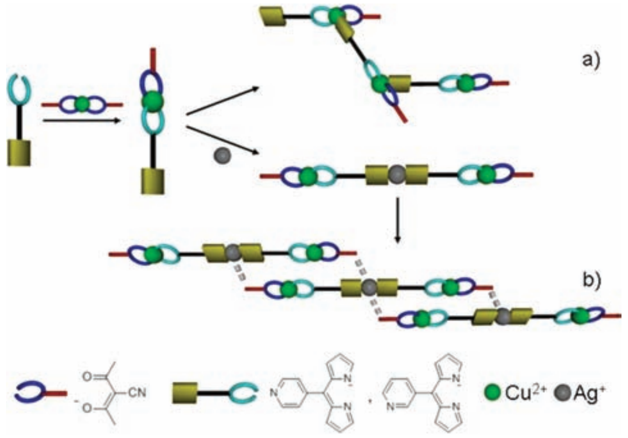


Figure 1. Heteroleptic (acacCN)Cu(dpm-py) complexes which are prone to self-assembly into homometallic architectures (a) and can form heterometallic coordination polymers upon reaction with silver(I) salts (b). Note that the (acacCN)Cu(dpm-imid) complex has been demonstrated to also be prone to forming analogous architectures.[7c].

Given these results and in light of the many $\mathrm{(acacCN)_xM}$ complexes as well as heteroleptic analogues reported,[9–11] it was believed that extension of this approach to novel heteroleptic complexes of the $\mathrm{(acacCN)_xM(dpm)_y}$ type, besides the above-mentioned (acacR)Cu(dpm), should lead to the formation of novel heterometallic architectures. Our targets were the novel $\mathrm{(acacCN)Co^{III}(dpm)_2}$ complexes (Scheme 1). Indeed, other cobalt(III) heteroleptic complexes such as (salen)Co(dpm) [salen = *N*,*N*′-bis(salicylidene)ethylenediamine] have been reported.[7b,12] Furthermore, while this species bears one acacCN capping ligand, such as for the (acacCN)-Cu(dpm-imid) compound, the presence of an additional dipyrrin should have an influence on the dimensionality of the final heterometallic architectures (Figure 2). It is also important to note that, in contrast with this latter family of complexes, the $\mathrm{Co^{III}}$ centers feature an octahedral coordination sphere without any available coordination site. Therefore, the self-assembly of this mononuclear species into coordination polymers cannot be envisioned. We report

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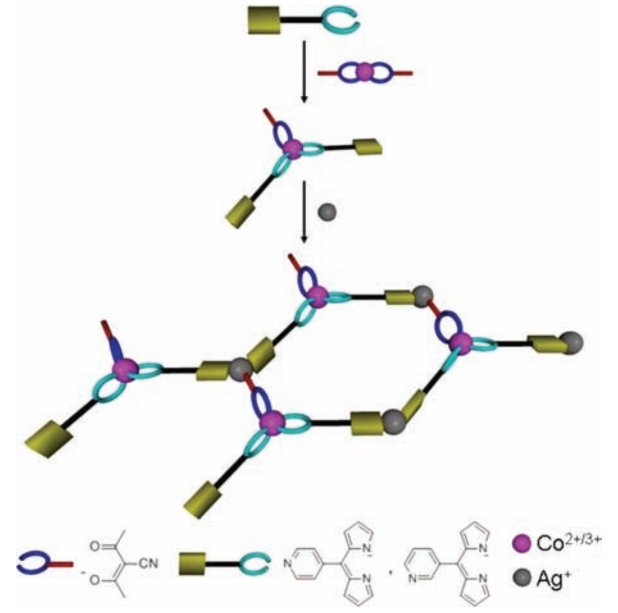

Figure 2. Formation of heterometallic networks of higher dimensionality based on the self-assembly of octahedral (acacCN)Co(dpm-py)$_2$ species with silver salts.

herein the synthesis of four novel heteroleptic (acacCN)-Cu(dpm-py) and (acacCN)Co(dpm-py)$_2$ complexes incorporating *m*- and *p*-pyridyl-appended dipyrrins, and their assembly with silver salts to form heterometallic coordination polymers.

Experimental Section

Synthesis. The starting Cu(acacCN)$_2$(H$_2$O) and Co(acacCN)$_2$ complexes were prepared as described.[9] Dipyrrins **1** and **2** were synthesized following the reported procedure.[13] Pyrrole was purified over an alumina column before use. All other reagents were obtained commercially and used without further purification. Solvents were of analytical grade. ^{1}H and ^{13}C NMR spectra were acquired at 25 °C on a Bruker AV 300 (300 MHz) with the deuterated solvent as the lock and the residual solvent as the internal reference. NMR chemical shifts are given in parts per million, and *J* values are given in hertz.

Complex 3. A tetrahydrofuran (THF) solution (30 mL) of **1** (100 mg, 0.45 mmol) was added to a THF solution (20 mL) of Cu(acacCN)$_2$(H$_2$O) (150 mg, 0.45 mmol). The mixture immediately turned red and was stirred for 1 h. It was evaporated to dryness, and the residue was purified by column chromatography (SiO$_2$, 90/10 CHCl$_3$/EtOAc, $R_f = 0.30$) to afford **3** as a dichroic red−green solid (178 mg, 96%). Dichroic red−green crystals were grown by the slow diffusion of *n*-pentane into a CHCl$_3$ solution of the complex. UV−vis [CH$_2$Cl$_2$; λ_{max}, nm (ε, L·mol^{-1}·cm^{-1})]: 229 (14 000), 296 (14 000), 342 (5000), 474 (23 000), 491 (36 000). IR (ATR, cm^{-1}): ν_{CN} 2206. HRMS (ESI). Calcd for $C_{20}H_{17}CuN_4O_2$ ([M + H]$^+$): *m*/*z* 408.064. Found: *m*/*z* 408.064. Anal. Calcd for $C_{20}H_{16}CuN_4O_2$: C, 58.89; N, 13.73; H, 3.95. Found: C, 58.39; N, 13.71; H, 4.26.

Complex 4. A THF solution (10 mL) of **2** (30 mg, 0.13 mmol) was added to a THF solution (10 mL) of Cu(acacCN)$_2$(H$_2$O) (44 mg, 0.13 mmol). The solution immediately turned red and was stirred for 30 min. It was evaporated to dryness, and the residue was purified by column chromatography (SiO$_2$, 99/1 CH$_2$Cl$_2$/MeOH, $R_f = 0.68$) to afford **4** as a dichroic red−green solid (53 mg, 96%). Dichroic red−green crystals were grown by the slow evaporation of a dioxane solution of the complex. UV−vis [CH$_2$Cl$_2$; λ_{max}, nm (ε, L·mol^{-1}·cm^{-1})]: 228 (27 000), 293 (16 000), 357 (5000), 468 (18 000), 492 (36 000). IR (ATR, cm^{-1}): ν_{CN} 2203. HRMS (ESI). Calcd for $C_{20}H_{17}CuN_4O_2$ ([M + H]$^+$): *m*/*z* 408.064. Found: *m*/*z* 408.059. Anal. Calcd for $C_{20}H_{16}CuN_4O_2$: C, 58.89; N, 13.73; H, 3.95. Found: C, 58.53; N, 13.86; H, 4.12.

Complex 5. A CHCl$_3$ solution (30 mL) of **1** (100 mg, 0.45 mmol) was added to a MeOH solution (20 mL) of Co(acacCN)$_2$ (66 mg, 0.21 mmol). The solution immediately turned red and was stirred overnight. After evaporation to dryness, the red solid residue was purified by column chromatography (SiO$_2$, 99/1 CHCl$_3$/MeOH, $R_f = 0.31$) to afford **5** as a dichroic red−green solid (80 mg, 59%). Dichroic red−green crystals were grown by the slow diffusion of *n*-pentane into a CHCl$_3$ solution of the complex. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.82 (m, 4H), 7.87 (d, $J = 7.6$ Hz, 2H), 7.48 (dd, $J^1 = 7.5$ Hz, $J^2 = 4.5$ Hz, 2H), 7.41 (t, $J = 1.4$ Hz, 2H), 6.90 (dd, $J^1 = 4.3$ Hz, $J^2 = 1.2$ Hz, 2H), 6.71 (t, $J = 1.5$ Hz, 2H), 6.67 (dd, $J^1 = 4.3$ Hz, $J^2 = 1.4$ Hz, 2H), 6.62 (dd, $J^1 = 4.3$ Hz, $J^2 = 1.5$ Hz, 2H), 6.28 (dd, $J^1 = 4.5$ Hz, $J^2 = 1.5$ Hz, 2H), 2.28 (s, 6H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 193.6, 155.5, 150.4, 150.3, 150.1, 142.4, 142.3, 137.6, 135.8, 135.7, 133.8, 133.5, 132.8, 122.7, 120.0, 119.5, 88.5, 27.7. UV−vis [CH$_2$Cl$_2$; λ_{max}, nm (ε, L·mol^{-1}·cm^{-1})]: 227 (36 000), 311 (13 000), 395 (8000), 483 (33 000). IR (ATR, cm^{-1}): ν_{CN} 2207. HRMS (ESI). Calcd for $C_{34}H_{27}CoN_7O_2$ ([M + H]$^+$): *m*/*z* 624.155. Found: *m*/*z* 624.157.

Complex 6. A CHCl$_3$ solution (20 mL) of **2** (80 mg, 0.36 mmol) was added to a MeOH solution (20 mL) of Co(acacCN)$_2$ (55 mg, 0.18 mmol). The solution immediately turned red and was stirred overnight. After evaporation to dryness, the red solid residue was purified by column chromatography (SiO$_2$, 99/1 CHCl$_3$/MeOH, $R_f = 0.28$) to afford the product as a dichroic red−green solid (60 mg, 54%). Dichroic red−green crystals were grown by the slow diffusion of *n*-pentane into a dioxane solution of the complex. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.77 (d, $J = 5.5$ Hz, 4H), 7.46 (d, $J = 5.8$ Hz, 4H), 7.39 (t, $J = 1.3$ Hz, 2H), 6.88 (dd, $J^1 = 4.6$ Hz, $J^2 = 1.4$ Hz, 2H), 6.68 (t, $J = 1.4$ Hz, 2H), 6.65 (dd. $J^1 = 4.3$ Hz, $J^2 = 1.6$ Hz, 2H), 6.61 (dd, $J^1 = 4.2$ Hz, $J^2 = 1.7$ Hz, 2H), 6.27 (dd, $J^1 = 4.2$ Hz, $J^2 = 1.5$ Hz, 2H), 2.28 (s, 6H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 193.6, 155.6, 150.5, 149.3, 145.3, 142.3, 134.8, 134.7, 133.7, 132.7, 125.0, 119.9, 119.6, 119.5, 88.5, 27.7. UV−vis [CH$_2$Cl$_2$; λ_{max}, nm (ε, L·mol^{-1}·cm^{-1})]: 233 (78 000), 302 (17 000), 393 (10 000), 485 (41 000). IR (ATR, cm^{-1}): ν_{CN} 2209. HRMS (ESI). Calcd for $C_{34}H_{27}CoN_7O_2$ ([M + H]$^+$): *m*/*z* 624.155. Found: *m*/*z* 624.157.

Coordination Polymer 7. To a solution of **3** (15 mg, 0.037 mmol) in *o*-xylene (5 mL) was added a solution of AgOTf (9.42 mg, 0.037 mmol) in *o*-xylene (2 mL), causing the immediate precipitation of a red solid. MeCN was added until complete redissolution. The mixture was left for slow evaporation in the absence of light. Crystals appeared after a few days (8.1 mg, 41%). IR (ATR, cm^{-1}): ν_{CN} 2213. Anal. Calcd for $C_{41}H_{32}AgCu_2F_3N_8O_7S$: C, 45.90; N, 10.44; H, 3.00. Found: C, 45.07; N, 8.66; H, 3.46.

Coordination Polymer 8. To a solution of **3** (15 mg, 0.037 mmol) in benzene (5 mL) was added a solution of AgBF$_4$ (7.14 mg, 0.037 mmol) in benzene (2 mL), causing the immediate precipitation of a red solid. MeCN was added until complete redissolution. The mixture was left for slow evaporation in the absence of light. Crystals appeared after a few days (4.5 mg, 24%). IR (ATR, cm^{-1}): ν_{CN} 2219. Anal. Calcd for $C_{40}H_{32}AgBCu_2F_4N_8O_4$: C, 47.54; N, 11.09; H, 3.19. Found: C, 47.48; N, 11.42; H, 3.53.

Coordination Polymer 9. To a solution of **4** (15 mg, 0.037 mmol) in *o*-xylene (5 mL) was added a solution of AgBF$_4$ (7.14 mg, 0.037 mmol) in *o*-xylene (2 mL), causing the immediate precipitation of a red solid. MeCN was added until complete redissolution. The mixture was left for slow evaporation in the absence of light. Crystals appeared after a few days (11.0 mg, 59%). IR (ATR, cm^{-1}): ν_{CN} 2212. Anal. Calcd for $C_{40}H_{32}AgBCu_2F_4N_8O_4$: C, 47.54; N, 11.09; H, 3.19. Found: C, 47.66; N, 11.18; H, 3.50.

Coordination Polymer 10. To a solution of **5** (15 mg, 0.024 mmol) in *o*-xylene (5 mL) was added a solution of AgOTf (5.9 mg,

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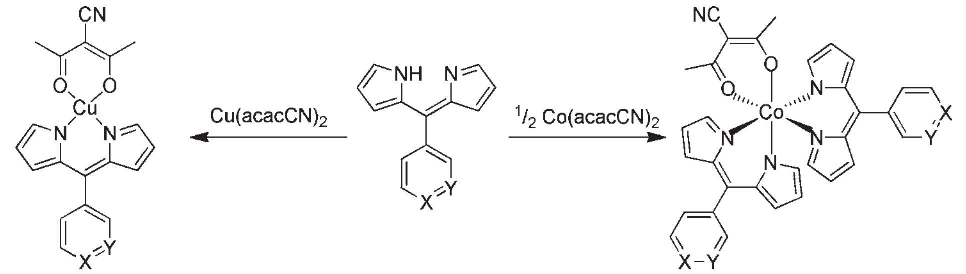
Table 1. Crystallographic Data for Compounds **3**−**6**

	3	**4**	(**5**)$_2$(CHCl$_3$)	**6**(C$_4$H$_8$O$_2$)$_{1.5}$	**7**
formula	$C_{20}H_{16}CuN_4O_2$	$C_{20}H_{16}CuN_4O_2$	$C_{69}H_{53}Cl_3Co_2N_{14}O_4$	$C_{40}H_{38}CoN_7O_5$	$C_{41}H_{32}AgCu_2F_3N_8O_7S$
fw	407.91	407.92	1366.46	755.70	1072.76
cryst syst	monoclinic	monoclinic	triclinic	triclinic	triclinic
space group	$P2_1/c$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	20.4333(10)	22.1808(8)	8.0265(2)	8.7518(2)	7.9711(2)
b, Å	8.5181(4)	11.7623(5)	9.5883(2)	14.3595(3)	9.1922(2)
c, Å	21.5238(10)	15.1987(6)	20.0801(5)	15.0712(3)	14.6259(4)
α, deg			99.6540(10)	91.4900(10)	101.2980(10)
β, deg	99.825(2)	108.2100(10)	90.6380(10)	106.4220(10)	93.9740(10)
γ, deg			96.9870(10)	98.6120(10)	102.1420(10)
V, Å^3	3691.3(3)	3766.7(3)	1511.39(6)	1791.60(7)	1020.54(4)
Z	8	8	1	2	1
T, K	173(2)	173(2)	173(2)	173(2)	173(2)
μ, mm^{-1}	1.206	1.182	0.747	0.535	1.635
reflns collected	29 635	12 133	18 888	22 084	15 337
indep reflns (R_{int})	8451 (0.0349)	4314 (0.0353)	6968 (0.0260)	8122 (0.0253)	4624 (0.0256)
R1 [$I > 2\sigma(I)$]^a	0.0537	0.0424	0.0486	0.0406	0.0648
wR2 [$I > 2\sigma(I)$]^a	0.1378	0.0921	0.1327	0.1121	0.1561
R1 (all data)^a	0.0741	0.0539	0.0544	0.0489	0.0658
wR2 (all data)^a	0.1464	0.0977	0.1368	0.1264	0.1569
GOF	1.093	1.086	1.044	1.074	1.388

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

Scheme 2. Synthesis of Complexes **3**−**6**



X = CH, Y = N, **3**
X = N, Y = CH, **4**

X = CH, Y = N, **1**
X = N, Y = CH, **2**

X = CH, Y = N, **5**
X = N, Y = CH, **6**

0.024 mmol) in *o*-xylene (2 mL), causing the immediate precipitation of a red solid. MeCN was added until complete redissolution. The mixture was left for slow evaporation in the absence of light. Crystals appeared after a few days (10.3 mg, 46%). IR (ATR, cm^{-1}): ν_{CN} 2212. Anal. Calcd for $C_{35}H_{26}AgCoF_3N_7O_5S \cdot CH_3CN$: C, 48.22; H, 3.17; N, 12.16. Found: C, 47.98; H, 3.48; N, 11.82.

Coordination Polymer 11. To a solution of **6** (15 mg, 0.024 mmol) in benzene (5 mL) was added a solution of AgBF$_4$ (4.5 mg, 0.024 mmol) in benzene (2 mL), causing the immediate precipitation of a red solid. MeCN was added until complete redissolution. The mixture was left for slow evaporation in the absence of light. Crystals of **11** appeared after a few days (13.3 mg, 56%). IR (ATR, cm^{-1}): ν_{CN} 2197. Anal. Calcd for $C_{43}H_{38}AgBCoF_4N_{10}O_2$: C, 52.67; N, 14.28; H, 3.91. Found: C, 50.65; N, 13.07; H, 3.78.

X-ray Crystallography. Data (Tables 1 and 2) were collected on a Bruker SMART CCD diffractometer with Mo Kα 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.[14] The hydrogen atoms were introduced at calculated positions and not refined (riding model).

CCDC 793850−793858 and 797959 contain the supplementary crystallographic data for compounds **3**−**11**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Synthesis and Characterization in Solution. The reaction of dipyrrins **1** and **2**, prepared as described,[13] with 1 equiv of Cu(acacCN)$_2$(H$_2$O) afforded in 96% the corresponding complexes (acacCN)Cu(dpm), **3** and **4**, respectively (Scheme 2). An analogous reaction of 2 equiv of **1** or **2** with 1 equiv of Co(acacCN)$_2$ afforded the complexes (acacCN)Co(dpm)$_2$, **5** and **6**, in 59 and 54%, respectively (Scheme 2). We should note that, during the reaction, Co^{II} is oxidized to Co^{III}, as is usually observed in the preparation of the homoleptic Co(dpm)$_3$[6,15] as well as the heteroleptic (salen)Co(dpm)[12] complexes and is in agreement with the electrochemical properties of these species (vide infra). It is also interesting to note that, unlike for the copper case,[8] the reaction with 3 equiv of dpm does not lead to the homoleptic Co(dpm)$_3$ compounds. Furthermore, the reaction of **5** and **6** with another dipyrrin does not lead to substitution of the remaining acacCN capping ligands.

The absorption spectra of **3** and **4** in CH$_2$Cl$_2$ show intense bands around 490 nm, as observed for analogous

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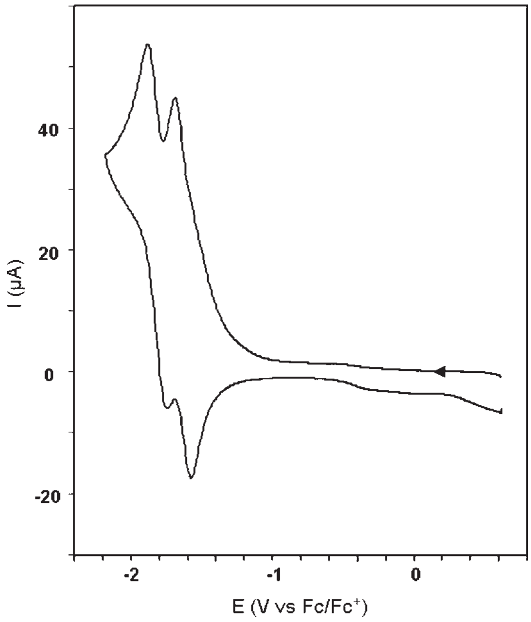

Figure 3. Cyclic voltammogram of **6** in CH_2Cl_2 [0.1 M (n-Bu_4N)PF_6; scan rate 100 $mV \cdot s^{-1}$].

complexes.[8] Complexes **5** and **6** feature absorption maxima at 395 and 483 nm with an additional shoulder at lower energy (around 510 nm) in CH_2Cl_2. This parallels the absorption spectra reported for the homoleptic analogues and the (salen)Co(dpm) complexes.[12,15] These bands have been assigned to ligand-to-metal charge transfer and $\pi-\pi^*$ transition of the dipyrrin chelate.[4−8,15,16]

In spite of the large number of metal dipyrrin complexes reported in the literature, only a few have been characterized by cyclic voltammetry.[16] The electrochemical behavior of **3**−**6** was, therefore, investigated. For the copper complexes **3** and **4**, cyclic voltammetry revealed only irreversible poorly defined reduction waves in CH_2Cl_2. Interestingly, the cobalt species **5** and **6** show two quasi-reversible reduction processes at −1.66 V vs Fc^0/Fc^+ ($\Delta E = 0.08$ V) and −1.87 V vs Fc^0/Fc^+ ($\Delta E = 0.10$ V) (for **6**, see Figure 3). The low reduction potential of these species is in agreement with a spontaneous oxidation of the cobalt center during the synthesis. No oxidation processes of these compounds could be observed in the CH_2Cl_2 electrochemical window. Both **5** and **6** display almost identical cyclic voltammograms, indicating that the position of the nitrogen in the pyridyl ring has no incidence on the electrochemical characteristics.

Crystal Structure of the Mononuclear Complexes. Crystals of **3** and **4** were obtained by n-pentane vapor diffusion into a $CHCl_3$ solution of the complexes. Complex **3** crystallizes in the monoclinic space group $P2_1/c$ with two molecules in general positions. The copper atoms are in a square-pyramidal environment, owing to coordination to the dpm and acacCN chelates as well as to the peripheral pyridyl nitrogen atom of a neighboring complex. This leads to the formation of a helix (Figure 4), whereas zigzag chains have been observed in the reported crystal structure of the parent (acac)Cu(**1**) complex.[8a] The main difference between the two crystallographically independent molecules in the unit cell lies in the slight torsion between the two chelates (4.5°) observed for one of them.

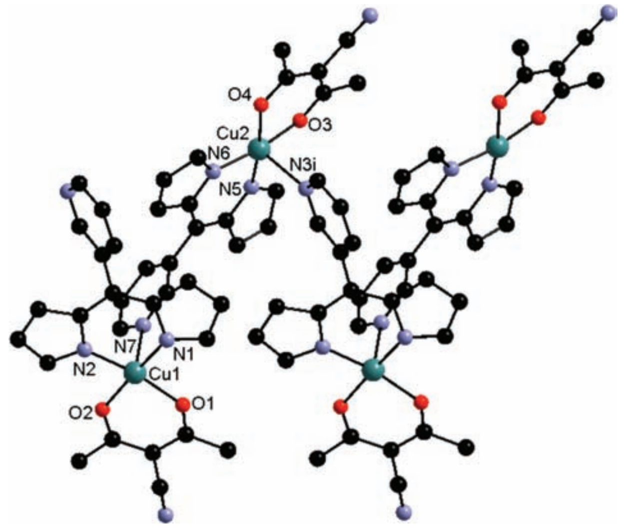

Figure 4. Helix in the structure of **3**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Cu1−O1, 1.972(3); Cu1−O2, 1.949(3); Cu1−N1, 1.958(3); Cu1−N2, 1.949(3); Cu1−N7, 2.346(3); Cu2−O3, 1.964(3); Cu2−O4, 1.966(3); Cu2−N5, 1.964(3); Cu2−N6, 1.956(3); Cu2−N3i, 2.322(3). Symmetry code: i, x, $1 + y$, z.

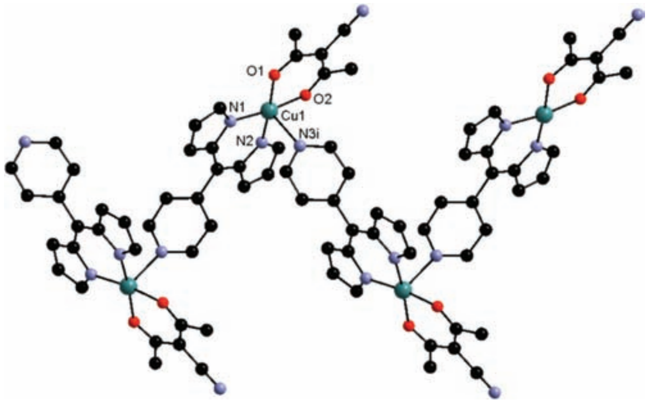

Figure 5. 1D network in the crystal structure of complex **4**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Cu1−O1, 1.9590(18); Cu1−O2, 1.9705(18); Cu1−N1, 1.955(2); Cu1−N2, 1.962(2); Cu1−N3i, 2.376(2). Symmetry code: i, $^1/_2 - x$, $^1/_2 + y$, $^1/_2 - z$.

Complex **4** crystallizes in the monoclinic space group $C2/c$ with one molecule in the general position. As in the case of **3**, the copper atom, in a square-pyramidal environment, is coordinated to the dpm and acacCN chelates and the nitrogen atom of the pyridyl group of a neighboring complex (Figure 5), with bond distances in the same range as that observed for analogous species.[8] This gives rise to one-dimensional (1D) zigzag chains as observed in the crystal structure of the parent (acac)Cu(**2**) complex.[8a]

Crystals of **5** and **6** were obtained upon the slow diffusion of n-pentane vapors in a concentrated $CHCl_3$ or dioxane solution of the complexes, respectively. They both

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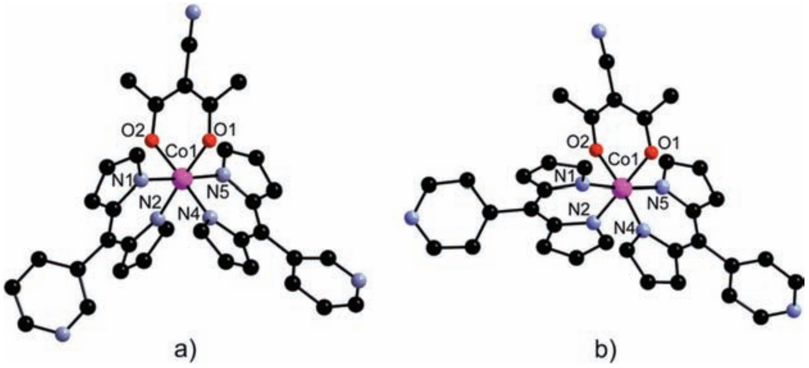

Figure 6. Crystal structures of cobalt complexes **5** and **6**. Hydrogen atoms and solvent molecules have been omitted for clarity. Only the Λ isomers are presented. Selected bond lengths (Å): for **5**, Co1−N1, 1.9327(19); Co1−N2, 1.9176(19); Co1−N4, 1.9175(19); Co1−N5, 1.9356(19); Co1−O1, 1.9150(16); Co1−O2, 1.9195(16); for **6**, Co1−N1, 1.9276(16); Co1−N2, 1.9028(16); Co1−N4, 1.9210(16); Co1−N5, 1.9317(16); Co1−O1, 1.9232(13); Co1−O2, 1.9061(13).

Table 2. Crystallographic Data for Compounds **7**−**11**

	7$(CH_3CN)_2$	**8** (C_6H_6)	**9**	**10**(CH_3CN)	**11**$(C_6H_6)_{0.5}(CH_3CN)_3$
formula	$C_{45}H_{38}AgCu_2F_3N_{10}O_7S$	$C_{46}H_{38}AgBCu_2F_4N_8O_4$	$C_{40}H_{32}AgBCu_2F_4N_8O_4$	$C_{37}H_{29}AgCoF_3N_8O_5S$	$C_{43}H_{38}AgBCoF_4N_{10}O_2$
fw	1072.76	1088.63	1010.50	921.54	980.44
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$C2/c$	$C2/c$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a, Å	21.2562(12)	21.0203(7)	7.2622(2)	11.4601(2)	9.9369(3)
b, Å	20.3813(14)	19.2974(7)	21.5157(6)	25.0292(6)	11.1115(3)
c, Å	14.5279(9)	14.3301(5)	12.3601(4)	13.8946(3)	15.8223(4)
α, deg					73.8980(10)
β, deg	131.2770(10)	131.0430(10)	91.519(2)	109.0160(10)	86.2550(10)
γ, deg					89.2360(10)
V, $Å^3$	4730.0(5)	4384.1(3)	1930.60(10)	3767.99(14)	2127.06(10)
Z	4	4	2	4	2
T, K	173(2)	173(2)	173(2)	173(2)	173(2)
μ, mm^{-1}	1.622	1.476	1.668	1.085	0.918
reflns collected	21 220	14 782	35 838	27 714	30 834
indep reflns (R_{int})	5401 (0.0327)	5021 (0.0293)	4413 (0.0279)	8608 (0.0352)	9685 (0.0313)
R1 $[I > 2\sigma(I)]$[a]	0.0628	0.0371	0.0426	0.0579	0.0486
wR2 $[I > 2\sigma(I)]$[a]	0.1715	0.0992	0.1085	0.1453	0.1168
R1 (all data)[a]	0.0799	0.0491	0.0460	0.0736	0.0610
wR2 (all data)[a]	0.1868	0.1231	0.1114	0.1630	0.1289
GOF	1.025	1.125	1.114	1.111	1.121

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

crystallize in the triclinic space group $P\bar{1}$. In the unit cell of $(\mathbf{5})_2CHCl_3$, a complex in the general position and a $CHCl_3$ solvate molecule on an inversion center are observed. In $(\mathbf{6})(C_4H_8O_2)_{1.5}$, a complex and a dioxane molecule are in general positions and an additional dioxane molecule lies on an inversion center. In both complexes, the Co^{III} cation is in an octahedral coordination environment with Co−O and Co−N bond distances in agreement with reported values for $Co(dpm)_3$ and (salen)Co(dpm) complexes (Figure 6).[6,7,12,15] Interestingly, in the structure of **6**, one dpm ligand shows a slight rotation around the NN hinge with the Co cation at a 0.477 Å distance to the chelate plane (Figure 6b). Note that both Δ and Λ enantiomers are present within the crystal, forming thus a racemate. As is expected for such species incorporating a metal center with a filled coordination sphere, no intermolecular interactions leading to a coordination polymer are present here; consequently, a discrete species is observed in the solid state.

Heterometallic Architectures. Upon slow evaporation in the dark, combinations of complexes **3**−**6** with silver salts in benzene/MeCN or *o*-xylene/MeCN mixtures lead to the formation of crystals composed of heterometallic coordination polymers **7**−**11**.

Upon the reaction of 2 equiv of complex **3** with 1 equiv of Ag(OTf) or $Ag(BF_4)$, crystals of the heterometallic coordination polymers $[(\mathbf{3})_2Ag(OTf)]$ (**7**), $[(\mathbf{3})_2Ag(OTf)](CH_3CN)_2$ [**7**$(CH_3CN)_2$], and $[(\mathbf{3})_2Ag(BF_4)](C_6H_6)$ [**8**(C_6H_6)] were obtained. Note that while trying to reprepare crystals of the nonsolvated polymer **7**, the acetonitrile solvate **7**$(CH_3CN)_2$ was obtained and shown by powder X-ray diffraction to be a single phase. Whereas the unsolvated material crystallizes in the triclinic space group $P\bar{1}$ with one silver cation disordered around an inversion center and a triflate anion on an inversion center and one complex **3** in general position, for the CH_3CN solvate, the space group is monoclinic ($C2/c$). Interestingly, in spite of the different anions and solvent molecules, **7**$(CH_3CN)_2$ and **8**(C_6H_6) are isomorphous with rather different b parameters (see Table 2). Therefore, only **8**(C_6H_6) is presented in detail. They both crystallize in the monoclinic space group $C2/c$ with one silver cation and an anion on a 2-fold axis, one complex **3** in the general position, and either a disordered acetonitrile in the general position or a

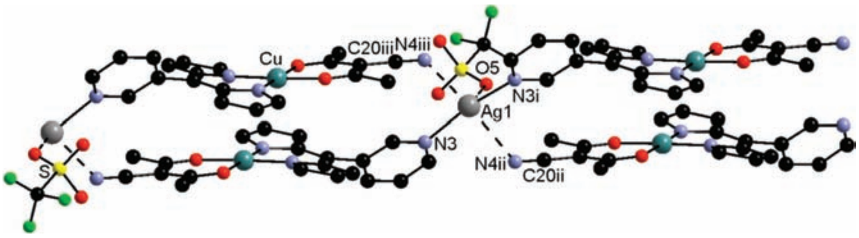

Figure 7. 1D network in the crystal structure of **7**. Hydrogen atoms have been omitted for clarity. Only one of the two positions of the silver cation and OTf^- anion is presented. Selected bond lengths (Å) and angles (deg): Ag1−N3, 2.191(5); Ag1−N3i, 2.204(5); Ag1−N4ii, 2.786(6); Ag1−N4iii, 2.666(6); Ag1−O5, 2.590(16); N3−Ag1−N3i, 164.85(5); N3−Ag1−N4i, 86.5(2); N3−Ag1−O5, 98.3(5); N4ii−Ag1−N4iii, 168.1(2); C20ii−N4ii−Ag1, 128.5(5); C20iii−N4iii−Ag1, 134.2(5). Symmetry codes: i, $-1 + x$, $2 - y$, $-z$; ii, $-1 + x$, y, $-1 + z$, iii, $-x$, $2 - y$, $1 - z$.

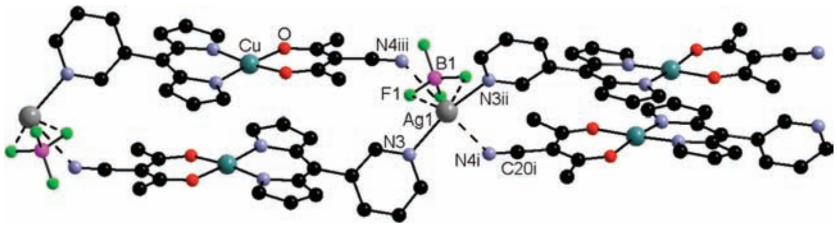

Figure 8. 1D network in **8**. Hydrogen atoms and benzene solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ag1−N3, 2.216(2); Ag1−N4i, 2.668(4); Ag1−F1, 2.838(3); N3−Ag1−N3ii, 147.23(13); N3−Ag1−N4i, 89.45(11); N3−Ag1−F1, 85.33(9); N4i−Ag1−N4iii, 162.18(10); N4i−Ag1−F1, 90.82(8); C20i−N4i−Ag1, 134.5(3); B1−F1−Ag1, 102.1(1). Symmetry code: i, $^1/_2 + x$, $^3/_2 - y$, $-^1/_2 + z$; ii, $1 - x$, y, $^1/_2 - z$; iii, $^1/_2 - x$, $^1/_2 - y$, $1 - z$.

benzene molecule on an inversion center, respectively. In the three structures, the copper center is coordinated, in a square-planar fashion, to the dpm and acacCN chelates. The three polymers are based on the self-assembly of trinuclear species $[(\mathbf{3})_2Ag]^+$ formed upon coordination of the pyridyl group of two molecules of **3** to the silver cation (Figures 7 and 8). Owing to weak interactions between the peripheral nitrile group of the acacCN moiety of **3** with the silver cation, the trinuclear complexes are interconnected with $Ag-N_{acacCN}$ distances of 2.666(6) and 2.786(6) Å for **7**, 2.868(8) Å for $\mathbf{7}(CH_3CN)_2$, and 2.668(4) Å for **8**, as was observed previously for the imidazole analogues.[7c] It is worth noting that no influence of the nature of the anion on the mode of organization of these trinuclear species is observed here, in contrast with what has been recently reported with imidazolyl-based ligands.[7c]

It is interesting to note that, in the three structures, the anion interacts with the Ag^+ cation. In particular, in **8**, the BF_4^- anion interacts with the silver ion in a chelate fashion with an Ag−F distance of 2.838(4) Å (Figure 8). Such an organization is rather scarce because the BF_4^- anion is generally considered a weakly coordinating species.[17] Nonetheless, such chelates have been reported in the literature with similar coordination distances.[18]

An analogous reaction of **4** with $Ag(BF_4)$ leads to the formation of $[(\mathbf{4})_2Ag(BF_4)]$ (**9**) crystallizing in the monoclinic space group $P2_1/n$, with one complex **4** in the general position, a silver ion on an inversion center, and a tetrafluoroborate anion disordered around an inversion center. Here again, trinuclear species of the $[(\mathbf{4})_2Ag]^+$ type are formed,

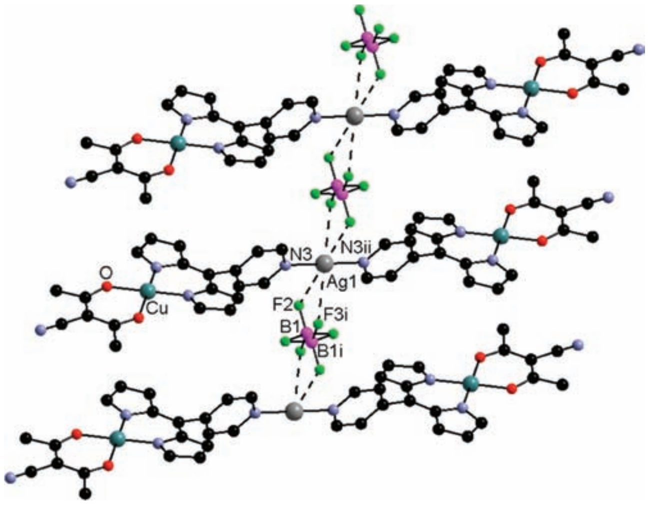

Figure 9. 1D network in **9**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ag1−N3, 2.137(3); Ag1−F2, 2.827(5); Ag1−F3i, 2.844(6); N3−Ag1−N3ii, 180.0; N3−Ag1−F2, 86.42(11); N3−Ag1−F3i, 70.30(15); B1−F2−Ag1, 110.5(5); B1i−F3i−Ag1, 121.2(5). Symmetry code: i, $-x$, $-y$, $-z$; ii, $1 - x$, $-y$, $-z$.

owing to the linear coordination of two pyridyl groups to the Ag^+ cation (Figure 9) with Ag−N distances in the range of what was observed for other heterometallic architectures based on dipyrrin **2**.[6] Unlike for **7** and **8**, the peripheral nitrile group is not involved in any coordination in this structure. However, the BF_4^- anion is weakly coordinated to the silver cation with Ag−F distances of 2.827(5) and 2.844(6) Å as observed in the case of **8**, leading to a 1D organization (Figure 9). Unfortunately, the reaction of **4** with other silver salts did not afford crystalline materials. It would indeed have been interesting to investigate the effect of the anion on the coordination of the peripheral nitrile group.

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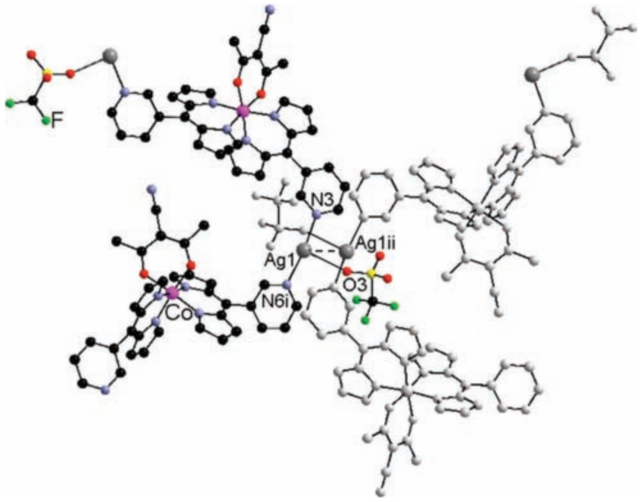

Figure 10. 2D arrangement in **10** resulting from $d^{10}-d^{10}$ interactions between 1D networks. One of the 1D chains has been faded for clarity. Hydrogen atoms and solvent molecules are not shown for clarity. Selected bond lengths (Å) and angles (deg): Ag1−N3, 2.154(4); Ag1−N6i, 2.148(4); Ag1−O3, 2.665(5); Ag1−Ag1ii, 3.2244(8); N3−Ag1−N6i, 171.09(14); N3−Ag1−O3, 94.38(16); N6i−Ag1−O3, 91.92(15). Symmetry code: i, $^1/_2 + x$, $^1/_2 - y$, $-^1/_2 + z$; ii, $2 - x$, $-y$, $-z$.

The reaction of complex **5** with Ag(OTf) in a *o*-xylene/MeCN mixture leads to the formation of the 1D coordination polymer [**5**Ag(OTf)](CH_3CN) [**10**(CH_3CN)] crystallizing in the monoclinic space group $P2_1/n$ with one complex **5**, one silver cation, one triflate anion, and a CH_3CN solvate molecule in general positions (Figure 10). The coordination environment around the cobalt center is similar to what has been observed in the structure of **5**. The Ag^+ cation is linearly coordinated to the pyridyl nitrogen atoms of two cobalt complexes **5** and interacts weakly with a triflate anion, leading to a T-shaped coordination environment. Surprisingly again, the peripheral nitrile is not involved in any coordination interaction. When taking into account $d^{10}-d^{10}$ interactions[19] between chains as observed in $[(dpm)Ag]_2^{2+}$ macrocycles,[20] the overall architecture is a two-dimensional (2D) network (Figure 10).

Upon the reaction of complex **6**, bearing pyridyl groups in the para position, with $Ag(BF_4)$ in a benzene/MeCN mixture, crystals of [**6**Ag](BF_4)$(C_6H_6)_{0.5}(CH_3CN)_3$, **11**$(C_6H_6)_{0.5}(CH_3CN)_3$, are obtained. The latter crystallizes in the triclinic space group $P\overline{1}$ with one complex **6**, one silver cation, one tetrafluoroborate anion, and three MeCN solvate molecules in general positions and one benzene molecule located on an inversion center. In this structure, the Ag^+ center adopts a trigonal coordination geometry with its coordination composed of two pyridyl nitrogen atoms belonging to two cobalt complexes and to the nitrile group of the capping acacCN ligand of a third cobalt complex. Consequently, a honeycomb 2D arrangement is obtained (Figure 11a). The hexagonal cavities are filled with solvent molecules and anions. While the $Ag-N_{py}$ distances are similar to what was observed in other heterometallic architectures based on dipyrrin **2**[6] and in **7**−**10**, the $Ag-N_{acacCN}$ distance of 2.277(3) Å is considerably shorter than the ones in **7**−**10** and in the imidazole-based analogues.[7c] This latter distance is, however, in agreement with reported heterometallic architectures based on the acacCN ligand.[10] Interestingly, each 2D layer is homochiral, containing either the Λ or Δ enantiomer of **6**. These layers stack in an alternate ΛΔΛ fashion (Figure 11b). The Ag−Ag distance between consecutive layers is 4.705(2) Å. This coordination polymer with (6,3) topology is reminiscent of the ones based on the homoleptic complexes Fe(**2**)$_3$ and Co(**2**)$_3$ with $Ag(MF_6)$ (M = P, Sb) and on $Cr(acacCN)_3$ with Ag(OTf) and $Ag(BF_4)$.[6,10b] As a result of the heteroleptic nature of **6**, the 2D network is a hybrid of these two families of polymers. Indeed, the Co−Ag distances are 9.882(4) and 9.863(5) Å when bridged by **4** and 8.021(3) Å when bridged by the acacCN ligand. These parameters are similar to the ones observed for the two classes of networks, respectively.[6,10b]

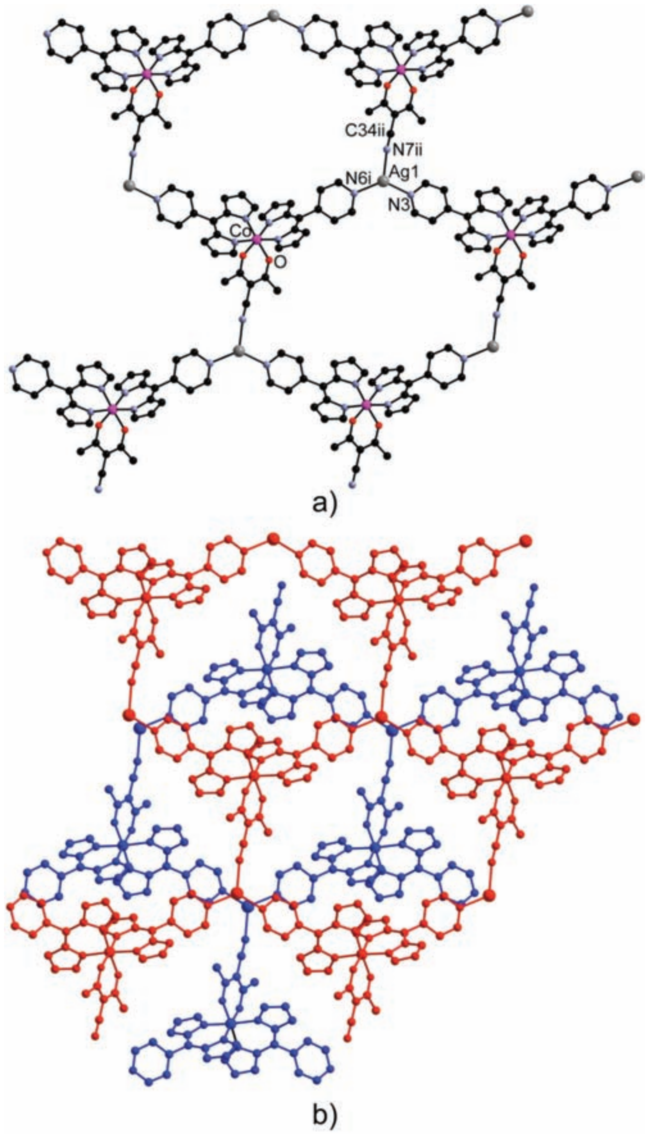

Figure 11. Honeycomb network in **11** (a) and stacking of two consecutive homochiral networks with opposite chirality based on different enantiomers of **6** (b). Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ag1−N3, 2.253(3); Ag1−N6i, 2.236(3); Ag1−N7ii, 2.277(3); N3−Ag1−N6i, 129.81(11); N3−Ag1−N7ii, 107.66(13); N6i−Ag1−N7ii, 118.90(13); C34ii−N7ii−Ag1, 167.7(3). Symmetry code: i, x, $1 + y$, $-1 + z$; ii, x, $1 + y$, z.

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Conclusion

Four novel copper(II) and cobalt(III) heteroleptic complexes incorporating the acacCN and pyridyl-appended dipyrrins **1** and **2** have been prepared. These two classes of complexes, (acacCN)Cu(dpm-py) and (acacCN)Co(dpm-py)$_2$, show different electrochemical properties, as revealed by cyclic voltammetry in CH_2Cl_2. While the copper complexes **3** and **4** show only irreversible reduction processes, two quasi-reversible reduction waves have been observed for the cobalt species **5** and **6**. In the solid state, as a result of coordination of the peripheral pyridyl group to the copper center, the copper(II) compounds self-assemble into either a helical architecture for **3** bearing a pyridyl in the meta position or a zigzag chain for **4** featuring functionalization in the para position. Owing to the filled coordination sphere of the octahedral cobalt centers, compounds **5** and **6** crystallize as isolated molecules. Upon reaction with silver salts, depending on the nature of the metal center and the position of the pyridyl nitrogen atom, the four complexes **3**–**6** lead to the formation of crystalline heterometallic architectures with different organization and dimensionality. Both **3** and **4** lead to the formation of trinuclear species, $\{[(acacCN)Cu(dpm\text{-}py)]_2Ag\}^+$, resulting from the coordination of two copper complexes to a silver center. However, while the latter species self-organize into an extended architecture owing to the presence of weak interaction of the peripheral nitrile of the acacCN moiety to the Ag^+ cation in **7** and **8**, this interaction is not present in **9** incorporating complex **4**. In both networks based on the use of $Ag(BF_4)$ salt, **8**, and **9**, the tetrafluoroborate anion interacts with the silver center. The influence of the position of the nitrogen atom of the pyridyl group is reversed in the cobalt-based networks **10** and **11**. Indeed, in **10**, based on **5** bearing a pyridyl in the meta position, the peripheral nitrile group does not coordinate the Ag^+ ion. However, a 2D network is observed to result from coordination of the pyridyl groups to the silver center and d^{10}–d^{10} interactions. The coordination polymer **11** is a 2D network owing to coordination of the Ag^I ion to the pyridyl nitrogen atoms in the para position and the peripheral nitrile of the acacCN ligand. This latter polymer represents a geometrical hybrid of the networks reported in the literature based on homoleptic Co(**2**)$_3$ and Cr(acacCN)$_3$ complexes. These results show that these heteroleptic complexes can be used as metallatectons for the sequential formation of heterometallic networks as their homoleptic analogues. The presence of two differentiated coordination poles at the periphery of these building blocks is currently being exploited for the preparation of heterotrimetallic architectures.

Acknowledgment. We thank the University of Strasbourg, the Institut Universitaire de France, the Ministry of Education and Research, the CNRS, the Marie Curie Est Actions FUMASSEC Network (Contract MEST-CET-2005-020992), and the REU program (fellowship to B.K.) 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.