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ARTICLE

Rigid yet flexible heteroleptic Co(III) dipyrin complexes for the construction of heterometallic 1- and 2-D coordination polymers

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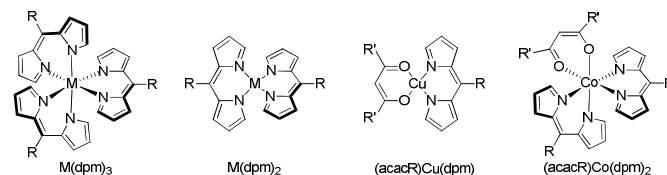
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A series of four discrete complexes of the (acac)Co(dpm)₂ or (hfac)Co(dpm)₂ type incorporating either the 3- or 4-pyridyl appended dipyrin (dpm) ligand has been prepared, characterized and employed as metallatectons for the construction of heterometallic coordination polymers (CPs) upon combination with CdX₂ salts (X = Br, Cl). For these species, the Co(III) center, in an octahedral environment, is coordinated to two dpm chelates and an acetylacetonate based capping ligand (acac or hfac). For both the metallatectons and the infinite CPs, a rotation around the N-N chelate hinge is responsible for different shapes adopted by the dpm moiety and hence different orientations of the peripheral pyridyl units. This behaviour does not seem to arise from the nature of the capping ligand (acac or hfac), the position of the peripheral pyridyl unit (3- or 4-) nor the nuclearity of the CdX₂ nodes. Depending on the shape of the metallatecton and the orientation of the coordinating sites, 1D networks composed of metallamacrocyclic moieties and 2D grid type coordination polymers are obtained.

Introduction

The bis-pyrrolic ligands of the dipyrin type (dpm),¹ known since the 1920s,² have recently received a revived interest. Indeed, not only they can be readily functionalized both at the 5 and pyrrolic positions, they also behave as monoanionic chelates under mild basic conditions leading to a variety of metal complexes. Both homo- and hetero-leptic species have thus been investigated for their catalytic³ or photophysical⁴ properties and for their ability to form infinite periodic architectures such as coordination polymers (CPs) or Metal-Organic Frameworks (MOFs).⁵ Introduction of peripheral coordinating sites on the dpm backbone leads to a differentiated ligand that forms, upon reaction with a first metal centre, metallatectons.⁶ The latter can be employed for the sequential construction of heterometallic CPs upon combination with a second metal cation.⁷ Following this approach, four main types of metallatectons have been employed (Scheme 1): homoleptic species of the M(dpm)₂ and M(dpm)₃ type or heteroleptic derivatives of either the (acacR)Cu(dpm) or the (acacR)Co(dpm)₂ kind (acacR = functionalized acetylacetonate ligand).⁸⁻¹⁰ Assembly of these complexes with Ag(I) salts has been particularly investigated, revealing in several cases the presence of Ag-π interactions with the pyrrolic system, thus limiting the structural predictability.⁹ In order to circumvent this issue, we have recently reported that heterometallic CPs

can also be obtained upon combining homoleptic M(dpm)₂ derivatives (Scheme 1) bearing either a 4-pyridyl or phenyl-imidazolyl peripheral group with CdCl₂.¹⁰ The resulting two-dimensional architectures are of the grid type with four peripheral coordinating sites of the metallatecton located at the square base of the octahedral Cd(II) cation and the remaining two apical positions occupied by chloride anions. Following these results, it appeared interesting to investigate the substitution of (acacR)Co(dpm)₂ metallatectons for the M(dpm)₂ complexes. Although these compounds also incorporate two dpm ligands, the octahedral environment around the Co(III) cation should induce a different relative arrangement of the peripheral coordinating units, and hence one may expect other types of organization for the CPs than the grid one.



Scheme 1. Dipyrin based metallatectons described to afford heterometallic CPs in the literature.

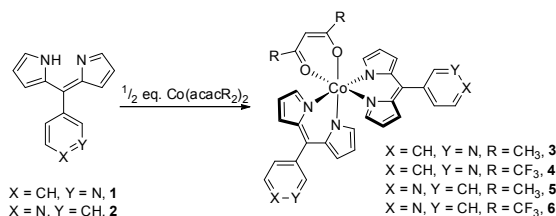
We report herein the systematic investigation of the assembly of novel heteroleptic (acacR)Co(dpm)₂ complexes (Scheme 2)

with CdCl_2 or CdBr_2 for the formation of heterometallic CPs with diverse orientation of the peripheral coordinating groups. Acetylacetonate (acac) and hexafluoroacetylacetonate (hfac) have been employed to study the effect of the capping ligand on the structural arrangement. Regarding the dpm derivatives, ligands **1** and **2** bearing a 3- or a 4-pyridyl peripheral coordinating site have been chosen, since this type of nitrogen based units has already demonstrated its ability to lead to CPs with CdX_2 salts.¹¹⁻¹² It is worth noting that, whereas for the 4-pyridyl based ligand **2**, the rotation around the $\text{C}_{\text{dpm}}\text{-C}_{\text{py}}$ bond does not affect the orientation of the coordinating nitrogen atoms, in marked contrast, for the ligand **1**, different rotamers leading to different connectivity patterns may be expected.

Results and discussion

Synthesis and characterization of the metallatectons

Reaction of two equivalents of dpm based ligands **1** and **2**, prepared as described,^{8d,13} with one equivalent of $(\text{acac})_2\text{Co}$ or $(\text{hfac})_2\text{Co}$ led to the formation of complexes **3-6** (Scheme 2) in 19 to 67 % yield. It is worth noting that, during the course of the reaction, oxidation of Co(II) to Co(III) by aerial oxygen occurs. As reported for analogous species,^{9d,9e,14} an intense absorption band at 488 nm is observed in the UV-Visible spectrum of **3-6**, that can be attributed to $\pi\text{-}\pi^*$ ligand centred transition of the dpm.



Scheme 2. Synthesis of complexes **3-6**.

The crystal structure of all four discrete complexes has been determined by single-crystal X-Ray diffraction (Table 2). For compounds **3-6** (Fig. 1), the Co(III) cation, in an octahedral environment, is coordinated to two dpm chelates and either an acac or hfac capping ligand with Co-N and Co-O (Table 1) in agreement with reported structures for this type of complexes.^{9d,9e,14} It should be noted that for **3-4** and **6**, both Λ and Δ enantiomers are present while, in the analysed crystal of **5**, only the Λ enantiomer is observed. However, the batch of crystals should be a racemate as both enantiomers are present in the CPs obtained from this compound (*vide infra*).

The main difference between these four compounds lies in the deviation of the plane of the dpm from the corresponding CoN_3O basal plane of the octahedral coordination sphere of the metal centre, owing to a rotation around the N-N hinge of the chelate (Fig. 1). Interestingly, while the dpm chelates are compressed towards each other for complex **3**, they are folded in opposite directions for **4-6**, leading to an arrangement analogous to what is observed for $\text{M}(\text{dpm})_2$ complexes (Table 1).¹⁰ A closer look at the reported crystal structures of

$(\text{acacR})\text{Co}(\text{dpm})_2$ derivatives reveals also a broad range of relative orientations of the peripheral binding sites.^{9d,9e,14c} The different orientations of the ligands for these complexes may be due to packing effects, in light of the other arrangements of the dpm in the corresponding CPs (*vide infra*).

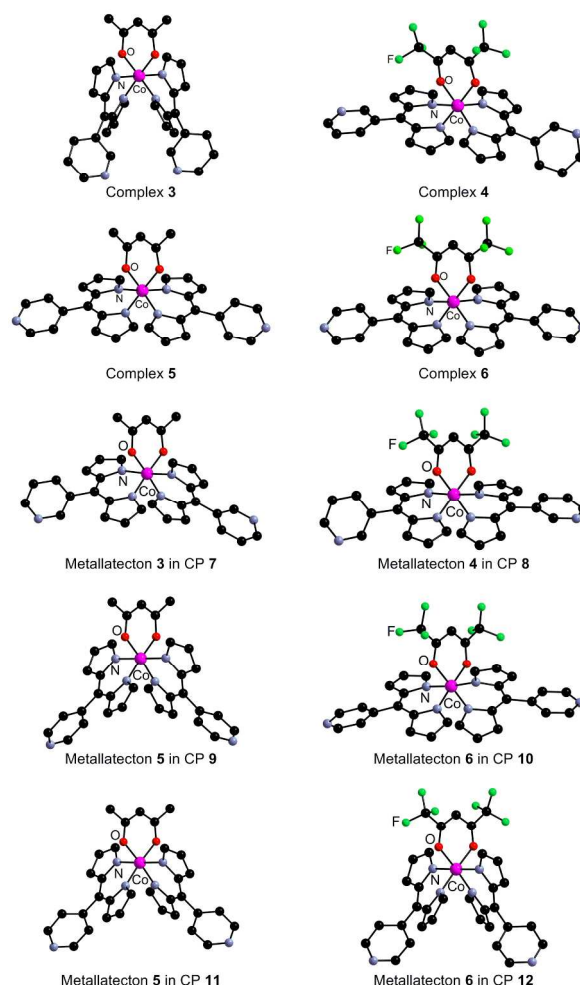


Fig. 1 Crystal structures of complexes **3-6** and as fragments present in CPs **7-12**, highlighting the different organizations of the dpm around the Co(III) center. Hydrogen atoms and solvent molecules have been omitted for clarity. Only the Λ enantiomers are shown.

Table 1. Selected average bond distances (Å) and angles between the dpm chelate and the corresponding CoN_3O basal plane (°).

	Co-N	Co-O	Cd-N	Cd-X	$\alpha_{\text{dpm-CoN}_3\text{O}}$
3	1.926	1.903			-32.7
4	1.916	1.934			+8.6, +27.9
5	1.920	1.904			+19.1, +22.6
6	1.909	1.934			+25.0
7	1.926	1.908	2.412	2.551	+1.3, +16.0
8	1.906	1.930	2.421	2.548	+25.0, +29.3, +18.7, +26.2
9	1.928	1.910	2.407	2.590	-19.4, -20.1, -19.6, -20.4
10	1.903	1.933	2.415	2.531	+21.5, +24.2
11	1.933	1.907	2.368	2.758	-16.9, -17.7, -15.5, -17.1
12	1.918	1.932	2.370	2.615	-25.1, -26.4, -27.0, -27.8

Heterometallic coordination polymers

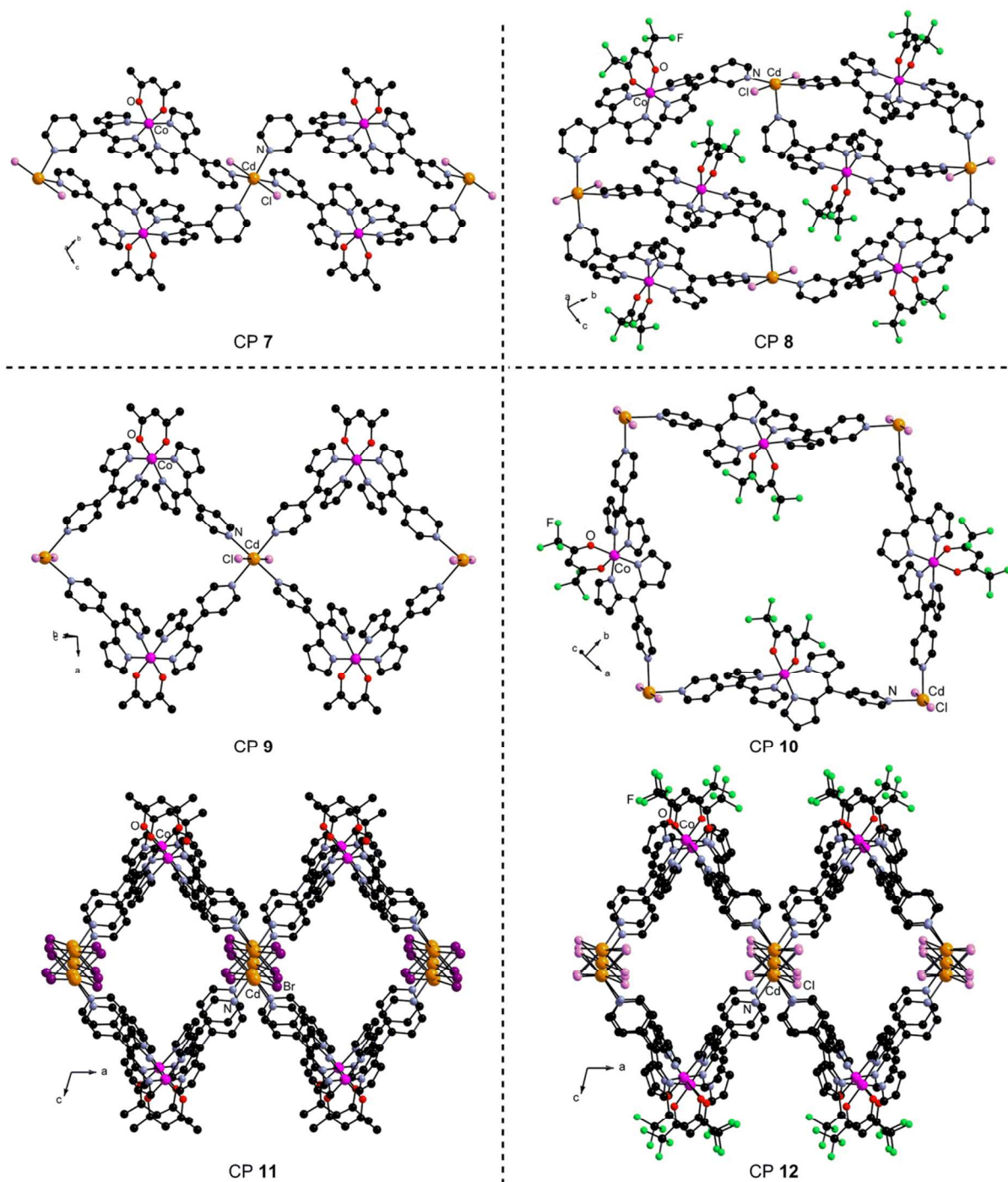


Fig. 2 Portions of the crystal structures of CPs 7-12. Hydrogen atoms and solvent molecules have been omitted for clarity.

Heterometallic CPs 7-12 were obtained by layering a DMF solution of complexes 3-6 with a 1/1 DMF/MeOH buffer, topped with a MeOH solution of CdX_2 ($X = \text{Cl}, \text{Br}$). In some cases, upon complete mixing of the layers, crystals appeared

only after Et_2O vapour diffusion into the mixture. It should be noted that the crystallization yields for the preparation of the CPs are rather low affording only few crystals. In addition, desolvation upon removal from the mother liquor leads to the

loss of crystallinity. This prevents further investigations by X-Ray powder diffraction and porosity studies.

Crystals of CPs **7-10** (Tables 2 and 3), formulated $[(\text{metallatecton})_2\text{CdCl}_2](\text{solvent})_x$, were obtained from CdCl_2 and complexes **3-6**, respectively. For all four compounds, the Cd(II) cation, in an octahedral environment, is coordinated to pyridyl groups belonging to four different Co(III) metallatectons and to two chloride anions in axial positions, as for the reported 2D grids based on $\text{M}(\text{dpm})_2$ species with similar Cd-N and C-Cl distances (Table 1).¹⁰ The organization of this motif and thus the connectivity pattern in the crystal depends on the position of the pyridyl group as well as on the nature of the capping ligand. For CP **7** ($[(\mathbf{3})_2\text{CdCl}_2]$), [2+2] metallamacrocycles are formed leading to a 1D arrangement (Fig. 2). It is worth noting that, in this structure, the two dpm chelates are not as compressed towards each other as in the structure of the starting Co(III) complex **3** (Table 1, Fig. 1). For CP **8**, $[(\mathbf{4})_2\text{CdCl}_2](\text{DMF})$, again a 1D network is observed. However, the [2+2] tetranuclear metallamacrocycles are, in this case, bridged by two metallatectons **4** along the *b* axis (Fig. 2). The relative arrangement of the two dpm chelates (Table 1, Fig. 1) does not differ strikingly from what is observed for **4**. A 1D network, similar to the one observed in **7**, is obtained for CP **9**, $[(\mathbf{5})_2\text{CdCl}_2](\text{DMF})$ (Fig. 2) also based on a $(\text{acac})\text{Co}(\text{dpm})_2$ species. In this case, the dpm chelates are more compressed in the infinite architecture than in the structure of the starting complex (Table 1, Fig. 1).

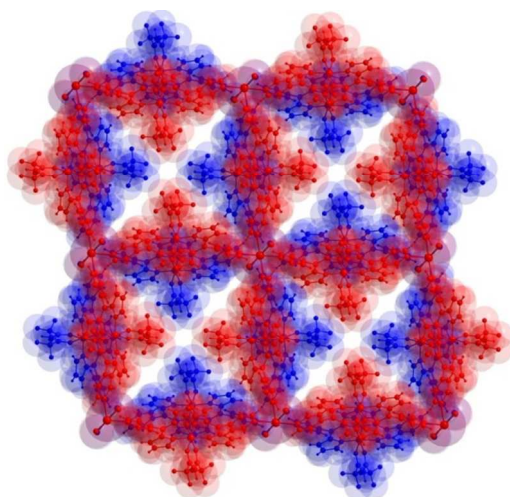


Fig. 3 Stacking of consecutive 2D grid layers in the structure of CP **10**.

In contrast, for CP **10** ($[(\mathbf{6})_2\text{CdCl}_2]$), instead of [2+2] metallamacrocycle, the formation of a [4+4] metallamacrocycle is observed. This results from the almost linear arrangement of the dpm ligands within the hfac based metallatecton. A 2D grid network is thus observed (Fig. 1) with Cd cations distant of 19.588(4) Å, reminiscent of the ones reported for the architectures based on $\text{M}(\text{dpm})_2$ complexes.¹⁰ However, in this case, two of the four hfac capping ligands point towards the square-grid cavity. In the crystal, consecutive grids are rotated by 90° and the CdCl_2 units are arranged in an eclipsed manner

(Fig. 3). It should be noted that, owing to high positional disorder of the solvent molecules (DMF, MeOH, Et₂O) present in the crystal, the SQUEEZE command was used to remove the corresponding electron density.¹⁵

Interestingly and unexpectedly, combinations of metallatectons **5** and **6** with CdX_2 (X = Cl, Br) also led to the formation of heterometallic CPs **11** and **12** based on an inorganic polymeric pillar instead of the mononuclear CdCl_2 node as observed before. Even though they incorporate complexes with different capping ligands, the two CPs formulated as $[(\text{metallatecton})_2\text{Cd}_5\text{X}_{10}(\text{MeOH})_2](\text{solvent})_x$ are isomorphous (Table 3). Within the inorganic unit, the three crystallographically independent Cd(II) cations are in an octahedral coordination environment and bound to four bridging chloride anions but the two remaining ligands differ in nature and position. Two Cd(II) cations are coordinated to two pyridyl groups, either in *cis* or *trans* orientation, whereas the third Cd(II) center is bound to one pyridyl group and one MeOH molecule in *cis* arrangement (Fig. 4). The latter is hydrogen bonded to a DMF molecule (O...O = 2.798(7) Å for **9**, 2.737(6) Å for **10**) (Fig. 4). As for CPs **7** and **9**, [2+2] metallamacrocycles are formed. In **11** and **12**, they bridge the inorganic pillars leading to a 2D network, featuring 1D channels. In these channels, DMF molecules are incorporated. For CP **11**, the two dpm chelates of the metallatecton **5** have an arrangement similar to what is observed in **9**, whereas, for CP **12**, the nitrogen based chelates are strikingly more compressed than in the structures of the parent complex **6** and of CP **10** (Table 1, Fig. 1)

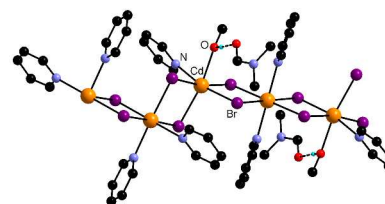


Fig. 4 Portion of the polymeric inorganic pillar in CP **11**. Only the pyridyl groups coordinated to the Cd(II) cations have been presented for clarity.

The changes in the shape of the individual metallatectons **3-6** and in the infinite coordination polymers CPs **7-12** are highlighted in Figure 1. Although **3** and **4** both incorporate the 3-pyridyl appended dpm **1**, they differ by the nature of the capping ligand (acac for **3** and hfac for **4**). The metallatecton **3** displays a more compressed arrangement as an individual complex than in CP **7**. For compound **4**, no significant modification is observed upon coordination to CdCl_2 and the metallatecton remains in a more stretched conformation. For the species based on the 4-pyridyl appended ligand **2**, again both metallatectons **5** and **6** have been crystallized allowing thus to compare their shapes with the ones adopted in corresponding CPs comprising a mono- or poly-nuclear CdX_2 node. Upon coordination to Cd(II) centers, metallatecton **5** features a more compressed arrangement of the dpm chelates than for the starting species (Fig. 1). However, the organisation in CPs **9** and **11** are similar. Contrastingly, depending on the

nuclearity of the Cd(II) node, hfac-based metallatecton **6** presents different arrangements of the dpms. Indeed, in CP **10**, a stretched arrangement leads to a complex paralleling $M(\text{dpm})_2$ species, which upon combination with the CdCl_2 mononuclear nodes affords 2D grid-type networks similar to the reported ones.¹⁰ In CP **12**, built on an infinite 1D inorganic pillar, the dpm chelates of the metallatectons are more compressed. Based on the observations mentioned above, no clear trend on the tendency to adopt a compressed or stretched arrangement depending on the nature of the capping ligand (hfac vs acac) or on the position of the peripheral coordinating nitrogen atom (3- vs. 4-pyridyl group) may be formulated. However, it may be worth noting that, although one might consider all four metallatectons **3-6**, based on conjugated ligands and incorporating all a Co(III) cation in an octahedral environment, as rigid entities, in fact they are rather flexible owing to the possible rotation around the N-N hinge within the dpm moiety.

Conclusions

A series of four complexes of the $(\text{acac})\text{Co}(\text{dpm})_2$ or $(\text{hfac})\text{Co}(\text{dpm})_2$ type incorporating either the 3- or 4-pyridyl appended dipyrin ligand has been prepared and characterized. In these species, the Co(III) center, in an octahedral environment, is coordinated to two dpm chelates and to an acetylacetonate based capping ligand (acac or hfac). The crystal structures of these compounds reveal that a rotation around the N-N chelate hinge leading to different arrangements of the dpms and hence of the peripheral pyridyl units is observed.

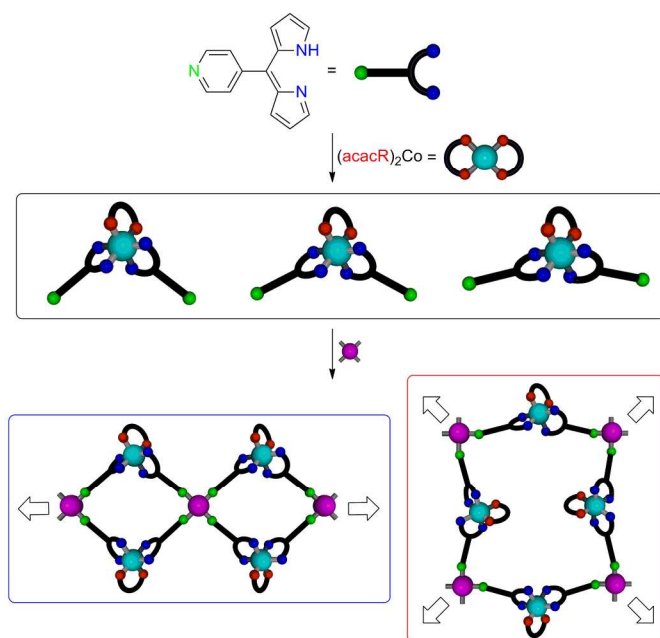


Fig. 5 Schematic representations, featuring different possible arrangements of the dpms moiety, of the formation of heterometallic CPs based on Co(III) metallatectons.

Combinations of metallatectons **3-6** with CdX_2 salts as a neutral connecting node afford a series of heterometallic CPs. Within

the infinite architectures, probably due to packing, the shape of metallatectons differs. Furthermore, depending on the nuclearity of the secondary metallic node, the conformation of the metallatecton varies. With the above mentioned observations in hand, unfortunately, no clear trend correlating the nature of the capping ligand (acac/hfac), the position of the peripheral binding unit (3- or 4-pyridyl) or the nuclearity of the CdX_2 connecting node can be drawn. This lack of correlation is probably due to the flexible nature of the metallatecton and to packing processes. Indeed, owing to the possible rotation around the N-N hinge within the dpm unit, metallatectons display different shapes (Fig. 5) leading to different connectivity patterns ranging from 1D to 2D networks (Fig. 5). We are currently exploring the possibility of generating other types of coordination networks using other heteroleptic metallatectons.

Experimental section

SYNTHESIS

Ligands **1** and **2** were synthesized as described.^{8d,13} All other reagents and solvents were obtained from commercial sources and used as received. ¹H- and ¹³C-NMR spectra were recorded at 25 °C on a Bruker AV 300 (300 MHz) spectrometer in deuterated solvents using the residual non deuterated solvent signal as the internal reference. NMR chemical shifts and *J* values are given in ppm and Hz respectively.

Complex 3. A solution of dpm **1** (265 mg, 1.20 mmol) in CHCl_3 (50 mL) was added dropwise to a solution of $\text{Co}(\text{acac})_2$ (154 mg, 0.60 mmol) in MeOH (50 mL). The red mixture was stirred at room temperature for 18h. After removal of the solvent under vacuum, the residue was purified by column chromatography (SiO_2 , $\text{CHCl}_3/\text{MeOH}$ 99/1) to afford complex **3** (170 mg, 0.28 mmol, 47%) as a red solid. $\lambda_{\text{max}}(\text{CHCl}_3)/\text{nm}$ ($\epsilon/\text{mol}^{-1} \text{L cm}^{-1}$): 302 (16700), 404 (9700), 488 (39000). δ_{H} (400 MHz, CDCl_3) 1.97 (s, 1H), 5.40 (s, 1H), 6.26 (dd, $J = 1.2$ and 4.3 Hz, 2H), 6.58 (dd, $J = 1.6$ and 4.3 Hz, 2H), 6.61 (dd, $J = 1.3$ and 4.4 Hz, 2H), 6.68-6.69 (m, 2H), 6.84 (dd, $J = 1.0$ and 4.2 Hz, 2H), 7.44(br s, 2H), 7.55 (t, $J = 1.4$ Hz), 7.85 (br s, 2H), 8.72 (br s, 4H). δ_{C} (125 MHz, CDCl_3) 26.8, 97.8, 118.6, 118.8, 122.5, 132.2, 132.9, 135.8, 136.1, 137.6, 141.8, 149.8, 150.4, 150.7, 154.8, 188.2. HRMS (ESI), m/z : $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_{33}\text{H}_{28}\text{CoN}_6\text{O}_2$: 599.160, found 599.162. Single crystals were obtained by Et_2O vapour diffusion into a CHCl_3 solution of **3**.

Complex 4. To a solution of $\text{Co}(\text{hfac})_2$ (273 mg, 0.58 mmol) in MeOH (20 mL), a solution of dpm **1** (255 mg, 1.15 mmol) in CHCl_3 (20 mL) was added dropwise. The mixture was stirred for 18h and the solvent was removed under vacuum. The residue was purified by column chromatography (SiO_2 , $\text{AcOEt}/\text{Pentane}$) to afford compound **4** (80 mg, 0.13 mmol, 19%) as a red solid. $\lambda_{\text{max}}(\text{CHCl}_3)/\text{nm}$ ($\epsilon/\text{mol}^{-1} \text{L cm}^{-1}$): 311 (18900), 383 (9500), 488 (39400). δ_{H} (400 MHz, CDCl_3) 6.00 (s, 1H), 6.31 (d, $J = 3.5$ Hz, 2H), 6.63 (d, $J = 3.5$ Hz, 2H), 6.72 (d, $J = 3.8$ Hz, 2H), 6.89 (s, 2H), 6.94 (d, $J = 3.8$ Hz, 2H), 7.46-7.49 (m, 2H), 7.89 (d, $J = 5.6$ Hz, 4H), 8.78-8.80 (m, 4H). HRMS (ESI), m/z : $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_{33}\text{H}_{22}\text{CoF}_6\text{N}_6\text{O}_2$: 707.103, found 707.106. Single crystals were obtained by *n*-pentane vapour diffusion into a CHCl_3 solution of **4**.

Complex 5. A solution of dpm **2** (300 mg, 1.35 mmol) in CHCl_3 (75mL) was added dropwise to a solution of $\text{Co}(\text{acac})_2$ (174 mg, 0.68 mmol) in MeOH (75 mL). The mixture was stirred overnight and the solvent was removed under vacuum.

The residue was purified by column chromatography (SiO₂, CH₂Cl₂/MeOH 95/5) yielding complex **5** (255 mg, 0.43 mmol, 60%) as a red solid. $\lambda_{\text{max}}(\text{CHCl}_3)/\text{nm}$ ($\epsilon/\text{mol}^{-1} \text{ L cm}^{-1}$): 299 (12200), 404 (9200), 488 (37600). δ_{H} (300 MHz, CDCl₃) 1.97 (s, 6H), 5.40 (s, 1H), 6.25 (dd, $J = 1.5$ and 4.4 Hz, 2H), 6.56-6.60 (m, 4H), 6.65-6.66 (m, 2H), 6.82 (dd, $J = 1.2$ and 4.4 Hz, 2H), 7.48 (br, 4H), 7.53-7.54 (m, 2H), 8.79 (br, 4H). δ_{C} (125 MHz, CDCl₃) 29.8, 89.6, 114.0, 116.3, 119.7, 120.3, 125.0, 133.2, 134.1, 135.1, 135.1, 143.4, 145.2, 149.4, 151.2, 156.3. HRMS (ESI), m/z : $[\text{M} + \text{H}]^+$ calcd. for C₃₃H₂₈CoN₆O₂: 599.160, found 599.162. Single crystals were obtained by *n*-pentane vapour diffusion into a THF solution of **5**.

Complex 6. To a MeOH (75 mL) solution of Co(hfac)₂ (320 mg, 0.68 mmol), a CHCl₃ (75 mL) solution of dpm **2** (300 mg, 1.35 mmol) was added dropwise. The mixture was stirred overnight and the solvent was removed under vacuum. Purification by column chromatography (SiO₂, CH₂Cl₂/MeOH 95/5) afforded compound **6** (323 mg, 0.46 mmol, 67%) as a red solid. $\lambda_{\text{max}}(\text{CHCl}_3)/\text{nm}$ ($\epsilon/\text{mol}^{-1} \text{ L cm}^{-1}$): 305 (12600), 384 (10100), 488 (41300). δ_{H} (400 MHz, CDCl₃) 6.01 (s, 1H), 6.30 (dd, $J = 1.5$ and 4.4 Hz, 2H), 6.62 (dd, $J = 1.5$ and 4.3 Hz, 2H), 6.71 (d, $J = 4.1$ Hz, 2H), 6.92 (d, $J = 4.1$ Hz, 2H), 7.46 (s, 2H), 7.49 (s, 4H), 8.82 (s, 4H). δ_{C} (125 MHz, CDCl₃) 89.6, 111.7, 114.0, 116.3, 118.5, 119.7, 120.3, 125.0, 132.0, 134.1, 135.1, 135.1, 143.4, 145.2, 149.4, 151.2, 156.3, 177.0. HRMS (ESI), m/z : $[\text{M} + \text{H}]^+$ calcd. for C₃₃H₂₂CoF₆N₆O₂: 707.103, found 707.102. Single crystals were obtained by *n*-pentane vapour diffusion into a CHCl₃ solution of **6**.

CP 7. In a screw-cap vial ($\varnothing \times h = 16.6 \times 61$ mm), a DMF (3 mL) solution of complex **3** (17.2 mg, 0.029 mmol) was layered with a DMF/MeOH (1/1, 2 mL) buffer and then topped with a MeOH (3 mL) solution of CdCl₂ (18 mg, 0.010 mmol). Red single crystals were obtained after few days (17.8 mg, 0.012 mmol, 82%).

CP 8. In a screw-cap vial ($\varnothing \times h = 16.6 \times 61$ mm), a DMF (1 mL) solution of complex **4** (5 mg, 0.007 mmol) was layered with a DMF/MeOH (1/1, 2 mL) buffer and then a MeOH (1 mL) solution of CdCl₂ (10 mg, 0.05 mmol). Upon complete mixing of the layers, the solution was left to slowly evaporate in air over several weeks to afford few crystals of **8**.

CP 9. In a vial ($\varnothing \times h = 22 \times 65$ mm), a DMF (1.5 mL) solution of **5** (20 mg, 0.035 mmol) was layered with a DMF/MeOH (1/1, 2 mL) buffer and then topped with a MeOH (2 mL) solution of CdCl₂ (4 mg, 0.022 mmol). After the mixing of the layers, upon vapour diffusion of Et₂O, single crystals were obtained (6.5 mg).

CP 10 and CP 12. In a vial ($\varnothing \times h = 22 \times 65$ mm), a DMF (2 mL) solution of **6** (22.0 mg, 0.031 mmol) was layered with a DMF/MeOH (1/1, 2 mL) buffer and then topped with a MeOH (4 mL) solution of CdCl₂ (4.2 mg, 0.02 mmol). Vapour diffusion of Et₂O on this mixture afforded red single crystals (13.8 mg). Both compounds were obtained under the same experimental conditions.

CP 11. In a vial ($\varnothing \times h = 22 \times 65$ mm), a DMF (2 mL) solution of **5** (20 mg, 0.035 mmol) was layered with a DMF/MeOH (1/1, 2 mL) buffer and then topped with a MeOH (2 mL) solution of CdBr₂ (20 mg, 0.073 mmol). Upon vapor diffusion of Et₂O on this mixture, red crystals were formed (6.8 mg, 0.0015 mmol, 17%).

X-RAY DIFFRACTION

Data (Tables 2 and 3) were collected on a Bruker SMART CCD diffractometer with Mo-K α 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.¹⁶ Hydrogen atoms were introduced at calculated positions and not refined (riding model). For complex **4**, the CF₃ groups are disordered over two positions. For CPs **9**, **10** and **12**, solvent molecules present in the structures show high positional disorder. To account for the corresponding electron density, the SQUEEZE command was used.¹⁵

CCDC 984811-984820 contain the supplementary crystallographic data for compounds **3-12**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

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Notes and references

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Table 2 Crystallographic data for 3-7.

	3	4	5 (THF)	6	7
Formula	C ₃₃ H ₂₇ CoN ₆ O ₂	C ₃₃ H ₂₁ CoF ₆ N ₆ O ₂	C ₃₇ H ₃₅ CoN ₆ O ₃	C ₃₃ H ₂₁ CoF ₆ N ₆ O ₂	C ₆₈ H ₆₂ CdCl ₂ Co ₂ N ₁₂ O ₆
FW	594.54	706.49	670.64	706.49	1444.46
Crystal system	Monoclinic	Triclinic	Orthorhombic	Monoclinic	Triclinic
Space group	C2/c	P-1	P2 ₁ 2 ₁ 2 ₁	C2/c	P-1
<i>a</i> / Å	17.4918(3)	10.0207(1)	13.2927(15)	13.3859(5)	9.4261(2)
<i>b</i> / Å	10.4582(2)	10.1954(1)	14.5956(16)	13.5080(5)	13.4558(2)
<i>c</i> / Å	14.8252(3)	15.5113(2)	17.1231(17)	17.1308(7)	13.9409(2)
<i>α</i> / °		106.4490(10)			106.570(1)
<i>β</i> / °	97.1970(10)	92.1220(10)		96.215(2)	106.717(1)
<i>γ</i> / °		103.1410(10)			98.602(1)
<i>V</i> / Å ³	2690.65(9)	1471.30(3)	3322.2(6)	3079.3(2)	1573.0(5)
<i>Z</i>	4	2	4	4	1
<i>T</i> / K	173(2)	173(2)	173(2)	173(2)	173(2)
<i>μ</i> / mm ⁻¹	0.682	0.665	0.563	0.636	1.005
Refls. coll.	22018	29205	23046	10207	24944
Ind. refls. (<i>R</i> _{int})	3676 (0.0220)	7856 (0.0332)	6984 (0.0493)	3492 (0.0391)	8347 (0.0194)
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>)) ^a	0.0326	0.0463	0.0416	0.0598	0.0322
<i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>)) ^a	0.0866	0.1130	0.0991	0.1441	0.0841
<i>R</i> ₁ (all data) ^a	0.0365	0.0654	0.0735	0.0743	0.0389
<i>wR</i> ₂ (all data) ^a	0.0899	0.1240	0.1147	0.1569	0.0885
<i>GOF</i>	0.897	1.040	1.039	1.043	1.057

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

Table 3 Crystallographic data for 8-12.

	8	9	10	11	12
Formula	C ₆₉ H ₄₉ CdCl ₂ Co ₂ F ₁₂ N ₁₃ O ₅	C ₆₉ H ₆₁ CdCl ₂ Co ₂ N ₁₃ O ₅	C ₆₆ H ₄₂ CdCl ₂ Co ₂ F ₁₂ N ₁₂ O ₄	C ₁₆₆ H ₁₈₄ Br ₁₀ Cd ₅ Co ₄ N ₃₄ O ₂₂	C ₁₅₆ H ₁₄₆ Cd ₅ Cl ₁₀ Co ₄ F ₂₄ N ₂₆ O ₁₆
FW	1669.37	1453.47	1596.28	4614.37	4249.21
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	P-1	P2 ₁ /n	C2/c	P-1	P-1
<i>a</i> / Å	8.7796(4)	21.3913(5)	23.1158(7)	12.1312(6)	11.3197(5)
<i>b</i> / Å	16.0109(7)	14.0119(3)	25.2786(8)	17.8056(8)	16.7537(9)
<i>c</i> / Å	25.1541(11)	26.0194(7)	15.2033(5)	22.2981(10)	24.2708(13)
<i>α</i> / °	83.011(2)			102.464(2)	99.224(2)
<i>β</i> / °	82.318(2)	97.703(1)	100.685(1)	105.322(2)	102.917(2)
<i>γ</i> / °	79.518(2)			94.702(2)	94.544(2)
<i>V</i> / Å ³	3428.4(3)	7728.5(3)	8729.8(5)	4486.1(4)	4396.6(4)
<i>Z</i>	2	4	4	1	1
<i>T</i> / K	173(2)	173(2)	173(2)	173(2)	173(2)
<i>μ</i> / mm ⁻¹	0.958	0.818	0.748	3.240	1.203
Refls. coll.	64851	87748	60417	136106	69501
Ind. refls. (<i>R</i> _{int})	18106 (0.0492)	22479 (0.0659)	9862 (0.0382)	23807 (0.0541)	23337 (0.0543)
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>)) ^a	0.0788	0.0592	0.0402	0.0529	0.0606
<i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>)) ^a	0.1975	0.1615	0.1182	0.1216	0.1524
<i>R</i> ₁ (all data) ^a	0.1146	0.0980	0.0554	0.1093	0.0877
<i>wR</i> ₂ (all data) ^a	0.2165	0.1750	0.1231	0.1409	0.1615
<i>GOF</i>	1.103	1.032	1.129	1.039	1.048

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

Graphical abstract

Acetylacetonate Co(III)-dipyrin complexes lead to flexible metallatectons displaying diverse shapes when combined with CdX_2 salts.

