Modular construction of a series of heteronuclear metallamacrocycles†

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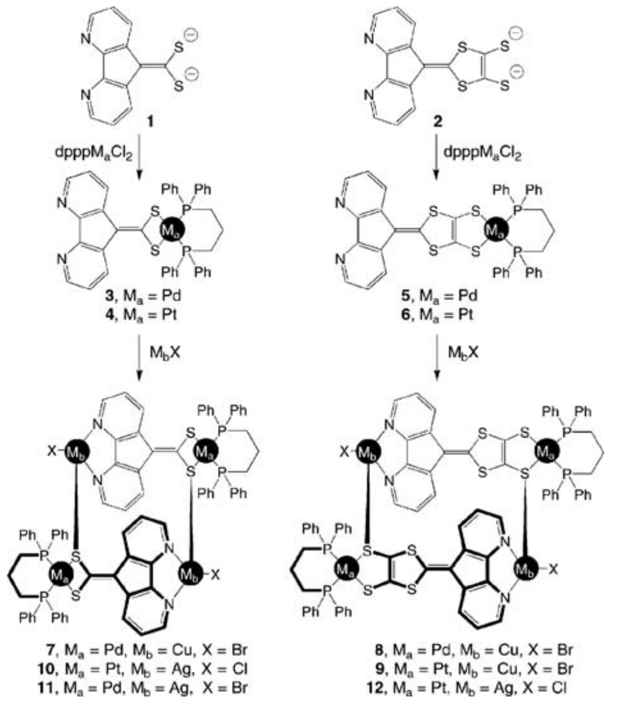
High modularity in a series of heteronuclear d^8–d^{10} metallamacrocycles built on differentiated ligands is demonstrated.

Metallo-organic cyclic architectures of the polygon type have received much attention owing to their inherent shape as well as potential applications in catalysis, optics or magnetism.[1] These discrete species are defined by the endocyclic role played by metal centres *i.e.* the closed structure results from the connection of the organic ligands by metal centres or complexes. Among the many structures reported, molecular rectangles are the most simple and illustrative examples of this class of molecules. It is interesting to note that the majority of cases reported so far deal with homometallic species obtained by self-assembly processes engaging one type of ligand and a unique metal centre or metal complex. Using a variety of ligands and metals, we have reported several metallamacrocycles of this type.[2] Heterometallic metallamacrocycles are of interest since they are based on the precise positioning of at least two different metal centres within a cyclic architecture. However, the preparation of such assembly is more complex and requires a stepwise construction approach. We have recently developed a sequential construction strategy based on organic ligands **1** and **2** (Scheme 1) bearing two differentiated coordination poles, a primary (enedithiolate) and a secondary one (4,5-diazafluorene).[3] As a result of this differentiation, upon reaction with a first metal complex (M_a) bearing an auxiliary ligand protecting some of the coordination sites, a discrete species is generated. The latter, possessing a secondary coordination pole at its periphery, leads to either homonuclear complexes in the presence of the same metal M_a or to heterometallic discrete or infinite network architectures in the presence of a different protected metal complex (M_b) or metal center, respectively.

Searching for other heterometallic species, we have pursued our approach using both ligands **1** and **2** and other metal centres and capped complexes. Unexpectedly, we discovered that this approach also leads to the formation of [2 + 2] heteronuclear metallamacrocycles resulting from the double interconnection of two heterobimetallic complexes in head-to tail fashion through sulfur–metal interactions (Fig. 1).

In order to explore the generality of this observation, we have varied each parameter (L, M_a and M_b and X) and wish to report herein on a systematic study of the formation of such species combining ligands **1** and **2** with two metal centres (M_a = Pd^{II} or Pt^{II} and M_b = Cu^I or Ag^I).



Scheme 1

Complexes **3** and **4** were prepared in 57 and 72% yield, respectively by reaction of *in situ* generated tetraethylammonium salt of **1**[3b] with one equivalent of dpppMCl$_2$ (Scheme 1).‡

Upon slow diffusion of a MeCN solution of CuBr(SMe$_2$) into a CH$_2$Cl$_2$ solution of **3**, bright orange crystals appeared after few days. X-Ray diffraction analysis on single crystal (monoclinic, $P2_1/c$) revealed the presence of the centrosymmetric metallamacrocycle **7** and two CH$_2$Cl$_2$ solvent molecules.§ The Cu(I) center is coordinated to the two nitrogen atoms of the 4,5-diazafluorene moiety and one Br$^-$ anion (Fig. 2). The unsymmetrical nature of the coordination of the two nitrogen atoms to the Cu(I) is analogous to what has been reported for other complexes with 4,5-diazafluorene derivatives.[4] Interestingly the formation of Cu–S contact

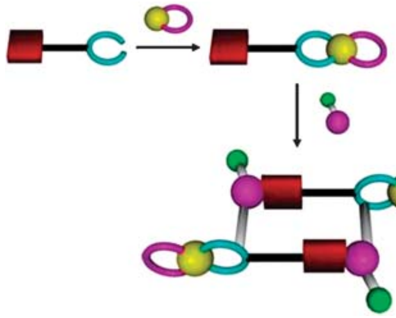


Fig. 1 Sequential construction of heteronuclear metallamacrocycles.

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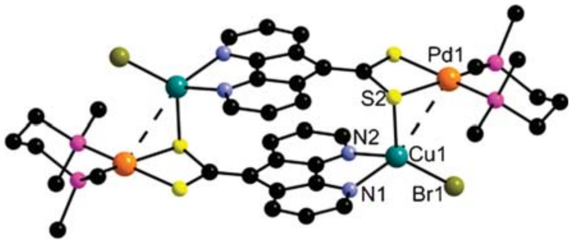

Fig. 2 View of the metallamacrocycle **7**. The phenyl rings of the dppp as well as the hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Cu1–N1, 2.278(5); Cu1–N2, 2.150(5); Cu1–Br1, 2.3581(9); Cu1–S2, 2.3425(14); Cu1–Pd1, 3.1211(8).

(2.3425(14) Å) interconnects the two heterometallic moieties **3** and thus leads to the formation of the cyclic structure. In addition to Cu–S contact, π–π stacking interactions (d = 3.33 Å) between the two 4,5-diazafluorene moieties are also present. Furthermore, a short Cu–Pd distance is also observed (3.1211(8) Å).

In order to investigate the role played by the ligand and the first metal center (M_a), the palladium and platinum complexes **5** and **6**, respectively were prepared in 87 and 52% yield, respectively and characterized by solution NMR, UV-vis, mass spectrometry and X-ray single crystal analysis (not presented here).‡ Reaction of **5** in $CHCl_3$ with one equivalent of $CuBr(SMe_2)$ in MeCN led to dark red crystals (triclinic, $P\bar{1}$).§ The latter is composed of **8** and six $CHCl_3$ solvent molecules (Fig. 3, top). The geometry around the metal center is rather similar to the one observed for **7** with a Cu–Pd distance of 2.9314(14) Å, shorter than the sum of the van der Waals radii, 3.03 Å,[5] suggesting the presence of d^8–d^{10} interactions[6] as previously observed for other dithiolate based complexes.[7] The main difference between the two metallamacrocycles **7** and **8** lies in their size, a direct result of the structure of the bridging ligands **1** and **2**. When using the platinum complex **6**, isomorphous crystals containing **9** and six $CHCl_3$ solvent molecules were obtained and analysed by XRD.§ As showed in Fig. 3 (bottom) the metallamacrocycle presents an analogous structure with a Cu–Pt distance of 2.909(2) Å shorter than the sum of the van der Waals radii (3.15 Å)[5] implying again the same type of d^8–d^{10} interactions.

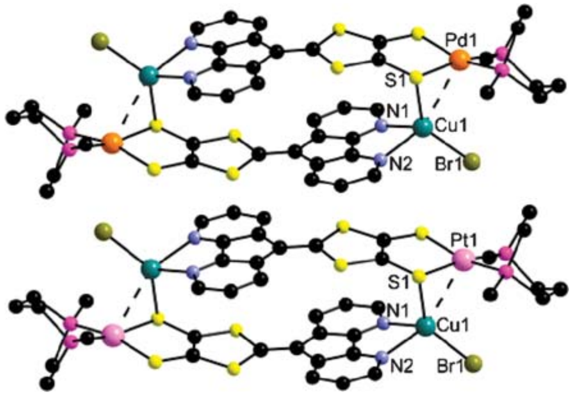

Fig. 3 View of the metallamacrocycles **8** (top) and **9** (bottom). The phenyl rings of the dppp as well as the hydrogen atoms are omitted for clarity. Selected bond lengths (Å): for **8**, Cu1–N1, 2.149(8); Cu1–N2, 2.331(8); Cu1–Br1, 2.3590(17); Cu1–S1, 2.349(3); Cu1–Pd1 2.9314(14). For **9**: Cu1–N1, 2.132(13); Cu1–N2, 2.351(15); Cu1–Br1, 2.372(3); Cu1–S1, 2.395(5); Cu1–Pt1, 2.909(2).

To study the role played by the second metal center (M_b), another d^{10} cation, silver(I), was used. A CH_2Cl_2 solution of **4** was reacted with a MeCN solution of $AgSbF_6$ forming small orange crystals (triclinic, $P\bar{1}$).§ The crystal contains **10** and one CH_2Cl_2 solvent molecule. Once again, the metallamacrocycle **10**, resulting from the face-to-face disposition of two **4** complexes interconnected by two Ag–S and one Ag–Pt contacts of 3.220(2), 3.242(2) and 2.9506(6) Å is obtained (Fig. 4, top). The later distance is shorter than the sum of the van der Waals radii (3.47 Å) for Pt and Ag.[5] Although $AgSbF_6$ was used, surprisingly, a chloride anion is found in the structure. We have noticed that when AgOTf was employed, the same chloride complex was also obtained. To assess whether the halide anion resulted from the solvent decomposition, the same reaction using CH_2Br_2 as solvent instead of CH_2Cl_2 afforded the analogous metallamacrocycle **11** incorporating two Br^- anions as a CH_2Br_2 and water solvate (Fig. 4, bottom). For the binding of Ag(I) by 4,5-diazafluorene, several coordination modes ranging from monodentate to bis monodentate have been reported.[8] Here, the Ag(I) cation is coordinated by both nitrogen atoms albeit in an unsymmetrical fashion, particularly in **10**. As for **7**, the 4,5-diazafluorene moieties overlap with a π–π stacking distance of 3.36 and 3.344 Å, in **10** and **11**, respectively.

In order to investigate the role played by the ligand, the complex **6** based on the ligand **2** was used, leading to the crystallization of the metallamacrocycle **12** (monoclinic $P2_1/c$) as a CH_2Cl_2 and CH_3CN double solvate.§ This macrocycle has an arrangement analogous to the one observed for **9**. A short Pt–Ag distance is detected (Fig. 5).

The stability of the metallamacrocycles in solution was probed by electrospray mass spectrometry for compounds **7**, **8**, **9** and **12**. In all cases, the metallamacrocycles could be identified. Unfortunately, owing to the very limited solubility of these compounds in common organic solvents, no solution NMR studies could be performed.

In conclusion, we have discovered a robust sequential strategy for the synthesis of new heteronuclear [2 + 2]

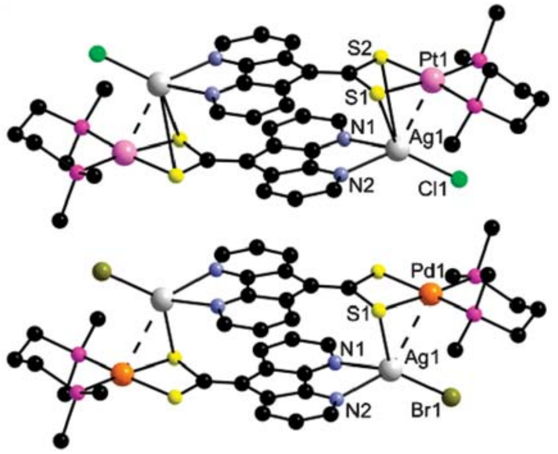

Fig. 4 View of the metallamacrocycles **10** (top) and **11** (bottom). The phenyl rings of the dppp as well as the hydrogen atoms are omitted for clarity. Selected bond lengths (Å): for **10**: Ag1–N1, 2.508(6); Ag1–N2, 2.357(6); Ag1–Cl1, 2.4495(15); Ag1–S1, 3.220(2); Ag1–S2, 3.242(2); Ag1–Pt1, 2.9506(6). For **11**: Ag1–N1, 2.423(9); Ag1–N2, 2.501 (9); Ag1–Br1, 2.5634(12); Ag1–S1, 2.746(2); Ag1–Pd1, 3.0424(11).

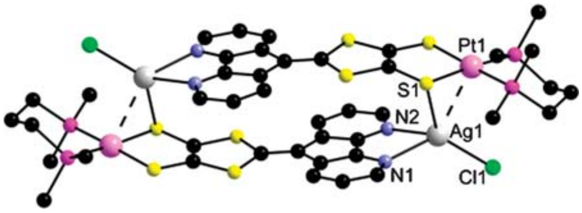

Fig. 5 View of the metallamacrocycle **12**. The phenyl rings of the dppp as well as the hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ag1–N1, 2.479(9); Ag1–N2, 2.478(8); Ag1–Cl1, 2.497(2); Ag1–S1, 2.914(2); Ag1–Pt1, 2.9396(8).

metallamacrocycles of the [(L, M_a, M_b, X)]$_2$ type. The systematic study revealed the possibility of combining Pd and Pt d^8 and Cu and Ag d^{10} cations with two different dithiolate and halide (Cl^-, Br^-) ligands. We have also demonstrated that the size of the cyclic structure may be modulated by the length of the ligand. Finally, the formation of the metallamacrocycles results from three types of interactions (S–M_b, π–π stacking and d^8–d^{10}). Extension to Au(I) as well as other extended sulfur based ligands and blocking phosphines is currently under way.

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Notes and references

‡ Analytical data for **3**: δ_H(300 MHz, $CDCl_3$) 8.78 (2H, dd, $J = 1.2$ and 8.1 Hz), 8.47 (2H, dd, $J = 1.2$ and 4.6 Hz), 7.62 (8H, m), 7.42 (12H, m), 7.11 (2H, dd, $J = 4.6$ and 8.1 Hz), 2.59 (4H, br m), 2.11 ppm (2H, br m); δ_P(121.5 MHz, $CDCl_3$) 9.22 ppm. ES-MS: 783.05 [**3** + Na]$^+$, 761.06 [**3** + H]$^+$. λ_{max}(CH_2Cl_2)/nm 319 (ε/dm^3 mol^{-1} cm^{-1}, 22 400), 370 (25 000, sh), 388 (37 400), 406 (37 300). Analytical data for **4**: δ_H(300 MHz, $CDCl_3$) 8.69 (2H, d, $J = 8.4$ Hz), 8.46 (2H, d, $J = 4.8$ Hz), 7.66 (8H, m), 7.42 (12H, m), 7.14 (2H, dd, $J = 8.4$ and 4.8 Hz), 2.68 (4H, br m), 2.15 ppm (2H, br m); δ_P(121.5 MHz, $CDCl_3$) −2.97 ppm (J_{PtP} = 2813 Hz). ES-MS: 873.10 [**4** + Na]$^+$, 850.11 [**4** + H]$^+$. λ_{max}(CH_2Cl_2)/nm 319 (ε/dm^3 mol^{-1} cm^{-1} 9800), 370 (20 000), 394 (32 700), 412 (35 700). Analytical data for **5**: δ_H(300 MHz, $CDCl_3$) 8.53 (2H, dd, $J = 1.3$ and 4.8 Hz), 7.97 (2H, dd, $J = 1.3$ and 8.1 Hz), 7.59 (8H, m), 7.39 (12H, m), 7.24 (2H, dd, $J = 4.8$ and 8.1Hz), 2.64 (4H, br m), 2.21 ppm (2H, br m); δ_P(121.5 MHz, $CDCl_3$) 3.99 ppm. ES-MS: 870.98 [**5** + Na]$^+$, 848.00 [**5** + H]$^+$. λ_{max}(CH_2Cl_2)/nm 292 (ε/dm^3 mol^{-1} cm^{-1} 42 500), 320 (29 900, sh), 442 (11 800, sh), 492 (26 400). Analytical data for **6**: δ_H(300 MHz, $CDCl_3$) 8.55 (2H, dd, $J = 1.5$ and 4.8 Hz), 8.00 (2H, dd, $J = 1.5$ and 8.4 Hz), 7.60 (8H, m), 7.39 (12H, m), 7.25 (2H, dd, J = 4.8 and 8.4 Hz), 2.75 (4H, br m), 2.23 ppm (2H, br m); δ_P(121.5 MHz, $CDCl_3$) −5.29 ppm (J_{PtP} = 2692 Hz). ES-MS: 961.05 [**6** + Na]$^+$, 938.07 [**6** + H]$^+$. λ_{max}(CH_2Cl_2)/nm 307 (ε/dm^3 mol^{-1} cm^{-1} 23 900), 321 (25 900), 334 (20 000, sh), 488 (24 100). Analytical data for **7**: ES-MS: 1729.39 [(**3**)$_2$Cu$_2$Br]$^+$, 1585.44 [(**3**)$_2$Cu]$^+$. Analytical data for **8**: ES-MS: 1904.69 [(**5**)$_2$Cu$_2$Br]$^+$, 1761.85 [(**5**)$_2$Cu]$^+$. Analytical data for **9**: ES-MS: 2081.94 [(**6**)$_2$Cu$_2$Br]$^+$, 1939.10 [(**6**)$_2$Cu]$^+$. Analytical data for **12**: ES-MS: 1883.18 [(**6**)$_2$Ag]$^+$.

§ Crystal data for [(**3**)CuBr]$_2$(CH_2Cl_2)$_2$, **7**: $C_{80}H_{68}Br_2Cl_4Cu_2N_4P_4Pd_2S_4$, M = 1979.00, monoclinic, space group $P2_1/c$ (No. 14), a = 16.2955(4), b = 9.4183(2), c = 26.7138(7) Å, β = 103.598(2)°, V = 3985.00(17) Å^3, T = 173(2) K, Z = 2, D_c = 1.649 g cm^{-3}, μ = 2.339 mm^{-1}, 57 135 collected reflections, 9202 independent (R_{int} = 0.0682), *GooF* = 1.078, R_1 = 0.0496, wR_2 = 0.1361 for $I > 2\sigma(I)$ and R_1 = 0.0844, wR_2 = 0.1612 for all data. Crystal data for [(**5**)CuBr]$_2$($CHCl_3$)$_6$, **8**: $C_{88}H_{70}Br_2Cl_{18}Cu_2N_4P_4Pd_2S_8$, M = 2701.64, triclinic, space group $P\bar{1}$ (No. 2), a = 13.5736(5), b = 13.6129(6), c = 14.8510(6) Å, α = 69.876(2), β = 87.186(2), γ = 82.441(2)°, V = 2554.17(18) Å^3, T = 173(2) K, Z = 1, D_c= 1.756 g cm^{-3}, μ = 2.283 mm^{-1}, 29 900 collected reflections, 11 264 independent (R_{int} = 0.0593), *GooF* = 1.130, R_1 = 0.0961, wR_2 = 0.2409 for $I > 2\sigma(I)$ and R_1 = 0.1289, wR_2 = 0.2714 for all data. Crystal data for [(**6**)CuBr]$_2$($CHCl_3$)$_6$, **9**: $C_{88}H_{70}Br_2Cl_{18}Cu_2N_4P_4Pt_2S_8$, M = 2879.02, triclinic, space group $P\bar{1}$ (No. 2), a = 13.5454(13), b = 13.6020(13), c = 14.9359(15) Å, α = 70.051(6), β = 87.390(6), γ = 82.447(6)°, V = 2564.3(4) Å^3, T = 173(2) K, Z = 1, D_c = 1.864 g cm^{-3}, μ = 4.648 mm^{-1}, 16 484 collected reflections, 10 180 independent (R_{int} = 0.0834), *GooF* = 0.983, R_1 = 0.0934, wR_2 = 0.2233 for $I > 2\sigma(I)$ and R_1 = 0.1807, wR_2 = 0.2944 for all data. Crystal data for Crystal data for [(**4**)AgCl]$_2$(CH_2Cl_2), **10**: $C_{79}H_{66}Ag_2Cl_4N_4P_4Pt_2S_4$, M = 2071.20, triclinic, space group $P\bar{1}$ (No. 2), a = 9.9781(2), b = 12.6890(3), c = 17.2016(4) Å, α = 101.3700(10), β = 96.1060(10), γ = 109.7470(10)°, V = 1974.00(8) Å^3, T = 173(2) K, Z = 1, D_c = 1.742 g cm^{-3}, μ = 4.388 mm^{-1}, 28 772 collected reflections, 8915 independent (R_{int} = 0.0449), *GooF* = 1.070, R_1 = 0.0361, wR_2 = 0.0981 for $I > 2\sigma(I)$ and R_1 = 0.0539, wR_2 = 0.1140 for all data. Crystal data for [(**3**)AgBr]$_2$(CH_2Br_2)(H_2O), **11**: $C_{79}H_{68}Ag_2Br_4N_4OP_4Pd_2S_4$, M = 2089.67, triclinic, space group $P\bar{1}$ (No. 2), a = 10.2098(3), b = 12.0948(4), c = 17.5469(6) Å, α = 101.960(2), β = 95.545(2), γ = 104.022(2)°, V = 2031.83(11) Å^3, T = 173(2) K, Z = 1, D_c = 1.708 g cm^{-3}, μ = 3.104 mm^{-1}, 26 156 collected reflections, 9324 independent (R_{int} = 0.0467), *GooF* = 1.073, R_1 = 0.0794, wR_2 = 0.2239 for $I > 2\sigma(I)$ and R_1 = 0.1168, wR_2 = 0.2579 for all data. Crystal data for [(**6**)AgCl]$_2$(CH_2Cl_2)$_2$(CH_3CN)$_2$, **12**: $C_{88}H_{74}Ag_2Cl_6N_6P_4Pt_2S_8$, M = 2414.51, monoclinic, space group $P2_1/c$ (No. 14), a = 9.8721(2), b = 16.2902(4), c = 27.9170(7) Å, β = 100.0700(10)°, V = 4420.41(18) Å^3, T = 173(2) K, Z = 2, D_c = 1.814 g cm^{-3}, μ = 4.084 mm^{-1}, 34 440 collected reflections, 10 142 independent (R_{int} = 0.0600), *GooF* = 1.046, R_1 = 0.0549, wR_2 = 0.1507 for $I > 2\sigma(I)$ and R_1 = 0.0905, wR_2 = 0.1798 for all data.

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