Porphyrin based metallamacrocycles†

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Upon combining 5,10-dipyridyl-15,20-diphenylporphyrin **1** or its copper metallated complex **2** with metal halides (MX_2: M = Zn, Cd, Hg; X = I or Br) five [2 + 2] metallamacrocycles of the square type were obtained and structurally characterised in the crystalline phase by X-ray diffraction methods. Whereas the free porphyrin **1** leads to the formation of homobinuclear metallamacrocycles with both CdI_2 and HgI_2, a homotetranuclear metallamacrocycle resulting from the metallation of the porphyrin core is obtained in the presence of ZnI_2. When using the premetallated copper complex **2**, two heterotetranuclear metallamacrocycles are generated in the presence of CdI_2 and $HgBr_2$.

Introduction

Metallamacrocycles are finite cyclic architectures composed of organic fragments and metal centres. For these entities, the metal centre connects the organic ligands through coordination bonds and thus occupies endocyclic positions. The stoichiometry as well as the shape of metallamacrocycles may be finely tuned through the coordination geometry of the metal centre and structural features of the organic ligand.[1–3]

Concerning the organic ligand, the porphyrin core is an interesting unit for the construction of molecular architectures.[4] Indeed, through the functionalisation of either the β-pyrrolic or *meso* positions, one may introduce further peripheral coordination sites, with respect to the four N atoms of the porphyrin core, and tune both their disposition and their orientation. Furthermore, one may either use the free functionalised porphyrin derivatives as free ligands or, by metallation of the porphyrin core by various metal centres, use the metallaporphyrins as construction units. Porphyrin derivatives bearing peripheral pyridine groups as additional coordination sites have been used for the formation of both discrete architectures[5–13] and infinite coordination polymers.[14–21] In particular, the 5,10-dipyridylporphyrin **1** or its metallated analogue **2** (Scheme 1) possessing two peripheral monodentate sites with 90° angle between them may be used as molecular corners for the formation of metallamacrocycles. Pursuing our studies on the formation of metallamacrocycles,[22] we have initiated a systematic investigation combining both compounds **1** and **2** with metal halides.

Here we report on the formation of five new metallamacrocycles (**3–7**) generated upon combining either the free porphyrin derivative **1** with CdI_2, HgI_2 or ZnI_2 or its copper complex with CdI_2 or $HgBr_2$.

Results and discussion

In principle, owing to the divergent disposition of the two peripheral coordinating sites, the combination of both compounds **1** and **2** with metal centres presenting at least two free coordination sites may either lead to the formation of discrete metallamacrocycles with various nuclearity such as for example [2 + 2] (Fig. 1a–c) and [4 + 4] (Fig. 1d–f) types or to infinite coordination networks[6,8,23] of the stair (Fig. 1g–i) or zigzag (j–l) types. Regarding the [2 + 2]- and [4 + 4]-metallamacrocycles, with the free porphyrin derivative **1** one would expect either homobinuclear (Fig. 1a) or homotetranuclear (Fig. 1d) complexes if the central porphyrin core remained uncomplexed or homotetranuclear (Fig. 1c) or homooctanuclear (Fig. 1f) species if both the porphyrin core and the peripheral pyridine units were engaged in the binding of the metal centre. Interestingly, using a premetallated porphyrin such as **2**, one may sequentially construct heterotetranuclear [2 + 2]-(Fig. 1b) or heterooctanuclear [4 + 4]-metallamacrocycles (Fig. 1e). Concerning the formation of infinite 1-D coordination networks, again one may envisage the formation of either homonuclear (Fig. 1g and 1i) and heteronuclear (Fig. 1h) stair type polymers or homonuclear (Fig. 1j and 1l) and heteronuclear (Fig. 1k) zigzag type polymers. It is worth noting that the formation of metallamacrocycles and coordination networks takes place by self-assembly processes.[24–26] Although strategically it would be of interest to be able to direct the processes towards either the discrete species or the polymeric assemblies, this is not possible with our current level of knowledge. However, interestingly, we found experimentally that both compounds **1** and **2** when associated with metal halides offering the tetrahedral coordination geometry, lead exclusively to the formation of metallamacrocycles of the [2 + 2] type.

Both the porphyrin **1**, prepared according to published procedure,[27] and metallaporphyrin **2**, prepared upon metallation of **1** by copper acetate (see experimental section), are neutral construction units. In order to avoid the presence of unbound anions and to control the coordination sphere around the metal centre, both units were combined with

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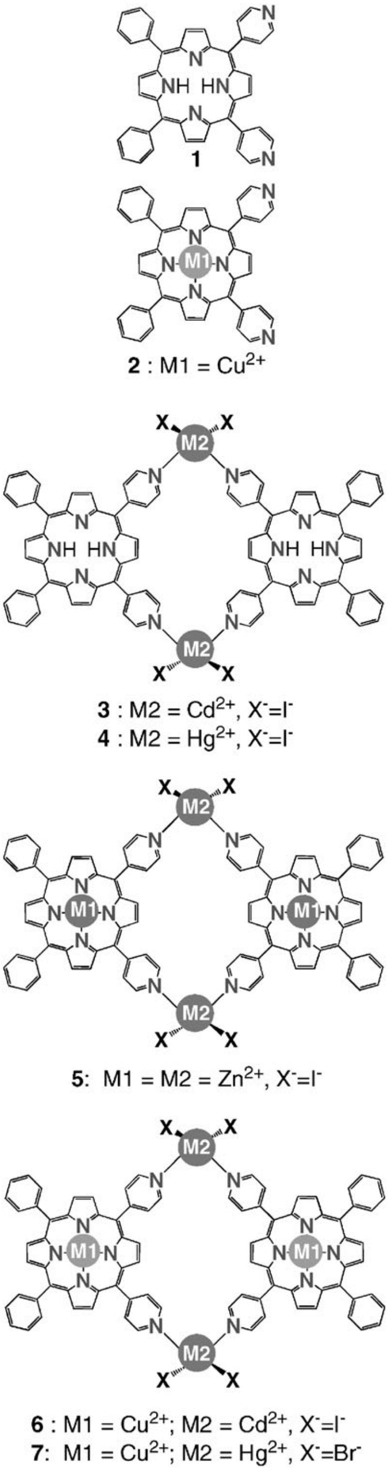
† The HTML version of this article has been enhanced with colour images.



1

2 : M1 = Cu^{2+}

3 : M2 = Cd^{2+}, X^-=I^-
4 : M2 = Hg^{2+}, X^-=I^-

5: M1 = M2 = Zn^{2+}, X^-=I^-

6 : M1 = Cu^{2+}; M2 = Cd^{2+}, X^-=I^-
7: M1 = Cu^{2+}; M2 = Hg^{2+}, X^-=Br^-

Scheme 1

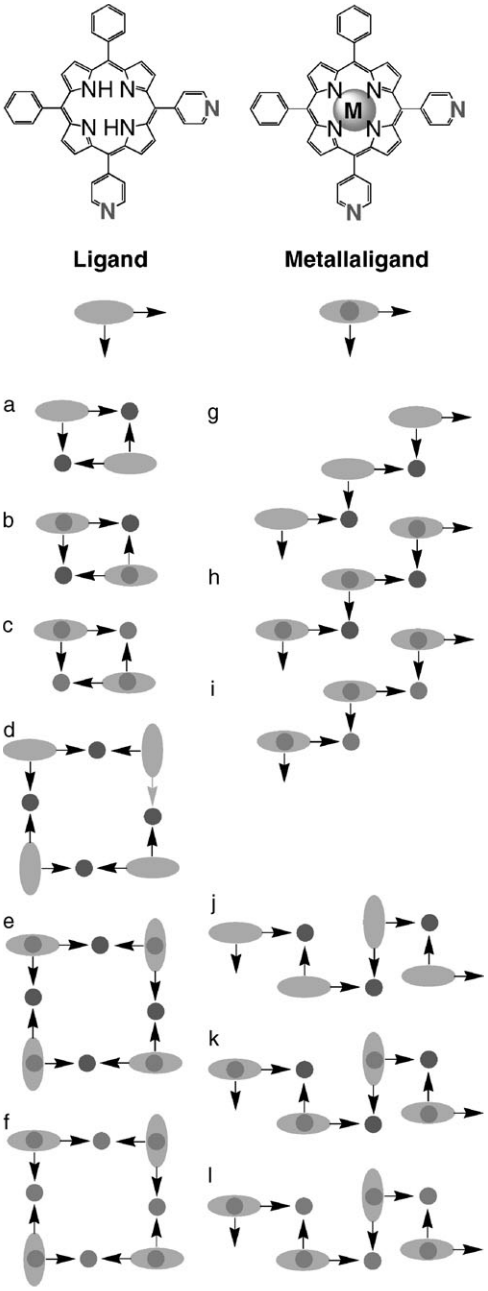


Fig. 1 Schematic representation of discrete [2,2] (a–c), [4,4] (d–f) metallamacrocycles and infinite 1-D coordination networks of the stair (g–i) and zigzag (j–l) types which may be formed by ligand (porphyrin **1**) and metallaligand (metallaporphyrin **2**) bearing two bismonodentate coordinating sites with 90° angle between them and metal centres possessing two free coordination sites.

neutral metal halides MX_2 (M = Cd, Zn, Hg; X = I or Br) which in principle might behave as tetrahedral connectors. Although the formation of metallamacrocycles using porphyrin derivatives is well documented,[6,8] most of the [2 + 2] metallamacrocycles reported for the porphyrin **1** are based on metal centres presenting two free coordination sites in *cis* disposition and adopting either square planar or octahedral coordination geometries.

Metallamacrocycles **3** and **4** were obtained as crystalline materials upon slow diffusion of a $CHCl_3$ solution of **1** into a MeOH solution of either CdI_2 (**3**) or HgI_2 (**4**). The homotetranuclear zinc metallamacrocycle **5** was obtained upon slow diffusion of a $CHCl_3$ solution of **1** into a MeOH solution of ZnI_2. Heterotetranuclear metallamacrocycles **6** and **7** were obtained as crystalline materials upon slow diffusion of a $CHCl_3$ solution of **2** into a MeOH solution of either CdI_2

Table 1 Data collection and refinements for **3**–**7**. Data were collected on a Bruker SMART CCD

Compound	**3**	**4**	**5**	**6**	**7**
Chemical Formula	$C_{86}H_{58}Cd_2Cl_6I_4N_{12}$	$C_{86}H_{58}Cl_6Hg_2I_4N_{12}$	$C_{85}H_{52}I_4N_{12}O_4Zn_4$	$C_{86}H_{54}Cd_2Cl_6Cu_2I_4N_{12}$	$C_{86}H_{54}Br_4Cl_6Cu_2Hg_2N_{12}$
Formula weight	2204.53	2380.92	2074.55	2327.59	2316.01
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	9.8032(3)	9.8204(3)	9.6797(3)	9.7586(5)	9.5541(4)
b (Å)	12.5002(4)	12.4299(3)	12.6462(4)	12.4722(5)	12.5202(5)
c (Å)	17.7426(5)	17.7025(5)	17.6494(6)	17.6672(7)	17.6342(6)
α (°)	86.910(2)	86.5920(10)	87.281(2)	87.060(2)	86.332(2)
β (°)	75.7380(10)	75.9920(10)	75.648(2)	75.477(2)	76.009(2)
γ (°)	86.087(2)	85.8720(10)	87.824(2)	85.986(2)	87.361(2)
V (Å^3)	2100.74(11)	2089.2	2089.94(12)	2075.21(16)	2041.60(14)
D_{calc} (Mg m^{-3})	1.743	1.892	1.648	1.862	1.884
Z	1	1	1	1	1
Crystal Size (mm^3)	0.25 × 0.18 × 0.05	0.20 × 0.19 × 0.11	0.20 × 0.15 × 0.10	0.08 × 0.06 × 0.03	0.13 × 0.08 × 0.03
μ(Mo-Kα) mm^{-1}	2.219	5.392	2.667	2.745	6.470
T (K)	173(2)	173(2)	173(2)	173(2)	173(2)
Reflections collected	42 885	32 404	99 428	26 517	21 296
Data/restraints/parameters	12097/6/490	9545/0/496	11233/0/495	9381/12/499	9317/12/506
R_{int}	0.0370	0.0496	0.0558	0.0720	0.0436
$R1$	0.0451	0.0461	0.0569	0.0509	0.0479
w$R2$	0.1435	0.1140	0.1722	0.1025	0.1063
Goodness-of-fit on $F2$	1.041	1.080	1.260	0.973	1.006

(**6**) or $HgBr_2$ (**7**). (For details see experimental section.) All metallamacrocycles **3**–**7** exhibit extremely low solubility in all common solvents thus preventing their study in solution.

The solid state structure of the single-crystals of **3**, obtained by the reaction of **1** with CdI_2, was investigated by X-ray diffraction studies (Table 1) which revealed that the crystal was composed of **1**, CdI_2 and a disordered $CHCl_3$ molecule. Two free porphyrin units are interconnected by two CdI_2 units leading thus to the formation of the homobinuclear centrosymmetric metallacycle **3** of [2 + 2] type (Fig. 2a). The Cd^{2+} cation adopts a distorted tetrahedral geometry (N–Cd–N and I–Cd–I angles of *ca.* 95.96° and 129.68°, respectively) and its coordination sphere is composed of two I^- anions ($d_{Cd–I}$ = 2.70 Å) and two pyridyl nitrogen atoms belonging to two ligands **1** ($d_{Cd–N}$ = 2.30 Å). The two pyridine units are tilted with respect to the porphyrin mean plane by 55.0 and 76.4°. The porphyrin macrocycle adopts a saddle-shape type deformation with an average displacement of 0.39 Å for the C_β atom. The metallacycle is slightly rectangular. Within the metallacycle **3**, the Cd–Cd distance is 14.00 Å. The centroids of two porphyrin rings are separated by *ca.* 14.22 Å. The two porphyrin moieties are parallel but not coplanar (separation of 0.570 Å of the two porphyrin mean planes). The packing of the metallacycles leads to the formation of channels along the *a* axis which are filled with disordered $CHCl_3$ molecules. The latter are located between cyclic units and not within their cavity. No specific interactions such as π–π interactions are observed between adjacent metallacycles.

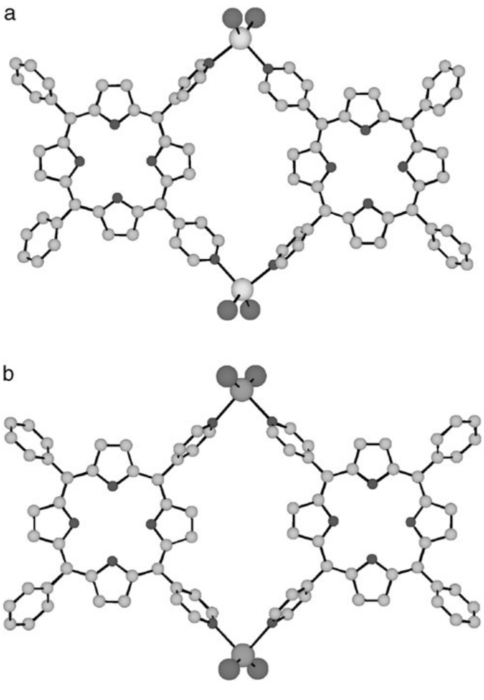


Fig. 2 Solid state structures of metallamacrocycles **3** and **4** formed upon treatment of **1** by CdI_2 (a) and HgI_2 (b). H atoms are not presented for sake of clarity. For bond distances and angles see text.

For the metallacycle **4** obtained when **1** was associated with HgI_2, a rather similar structure as the one described above for **3** was observed (Fig. 2b). Again the crystal was composed of **1**, HgI_2 and a disordered $CHCl_3$ molecule. The homobinuclear metallacycle **4**, again centrosymmetric, is generated by the bridging of two porphyrins **1** by two HgI_2 units. The mercury cation adopts a rather distorted tetrahedral geometry (N–Hg–N and I–Hg–I angles of *ca.* 89.07° and 141.78°, respectively) and is surrounded by two I^- anions ($d_{Hg–I}$ = 2.66 Å) and two pyridyl nitrogen atoms belonging to two ligands **1** ($d_{Hg–N}$ = 2.43 Å). The porphyrin moiety again adopts a saddle-shape type deformation with an average displacement of 0.39 Å of the C_β atom. Within the metallacycle **4**, of an almost perfect square shape, the Hg–Hg distance is 14.43 Å. The centroids of two porphyrin rings are separated by *ca.* 14.28 Å. The two porphyrins mean planes are parallel but not coplanar with 0.476 Å separation between them. The

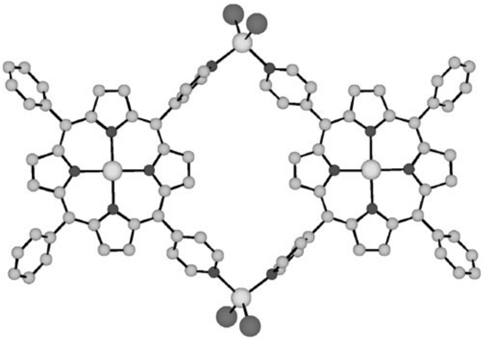


Fig. 3 Solid state structures of the metallamacrocycle **5** formed upon treatment of **1** by ZnI_2. For the sake of clarity disordered MeOH molecules bound to the Zn centre and H atoms are not presented. For bond distances and angles see text.

packing of the metallacycles leads again to the formation of channels along the *a* axis which are filled with disordered $CHCl_3$ molecules. The latter are located between cyclic units and not within their cavity. No specific interactions such as π–π interactions are observed between adjacent metallacycles.

The X-ray diffraction study of **5** (Table 1) revealed that the porphyrin core has been metallated during the crystallisation process by diffusion. The crystal contains the metallated porphyrin, ZnI_2 and two disordered MeOH and one disordered H_2O solvent molecules. Two zinc metallaporphyrins are bridged by two ZnI_2 units leading thus to the [2 + 2] metallamacrocycle **5** (Fig. 3). The latter is centrosymmetric in the solid state and the two zinc atoms are equivalent. Among the two disordered MeOH molecules (partial occupancy of 0.5) one is bound to the metal centre located within the core of the porphyrin unit and the other is located between metallacycles and H-bonded to the water molecule ($d_{OH\cdots O}$ = 2.64 Å). For the Zn-porphyrin moiety, the metal centre, displaced by 0.06 Å out of the porphyrin mean plane, is complexed by the four N atoms of the porphyrin (d_{Zn-N} = 2.09 Å) and further bound to a disordered (partial occupancy of 0.5) MeOH molecule (d_{Zn-O} = 2.36 Å). The porphyrin ring adopts a saddle-shape deformation with an average displacement for the C_β atom of 0.35 Å. For the bridging ZnI_2 unit, the metal adopts a distorted tetrahedral coordination geometry (N–Zn–N and I–Zn–I angles of 101.29° and 121.30°, respectively) and its coordination sphere is composed of two I^- anions and two N atoms belonging to two pyridine units of two different porphyrins (average Zn–N and Zn–I bond lengths of *ca.* 2.06 Å and 2.56 Å, respectively).

Within the metallacycle **5**, the two ZnI_2 are separated by 13.47 Å while the distance between the two Zn^{2+} complexed by the porphyrin core is 14.22 Å. Again, the two porphyrin moieties are parallel but not coplanar with 0.641 Å separation between them. The metallacycles are packed in a parallel fashion thus generating a channel along the *a* axis. The disordered unbound MeOH and H_2O molecules are H-bonded and located within the channels between consecutive metallacycles and not within the cavity of the latter.

For the compound **6**, obtained when **2** was combined with CdI_2, the unit cell is composed of two Cu-porphyrins, two CdI_2 units and a disordered $CHCl_3$ molecule (Table 1). The interconnection of the two metallaporphyrins by CdI_2 leads to the formation of the centrosymmetric heterotetranuclear metallacycle **6** (Fig. 4a). The Cu(II) atom is coordinated to four nitrogen atoms of the porphyrin core (d_{Cu-N} of *ca.* 2.00 Å, and N–Cu–N angles of *ca.* 90° (*cis*) and 175–177° (*trans*)) and adopts a slightly distorted square planar geometry (displacement of 0.042 Å from the porphyrin mean plane). The porphyrin ring shows a saddle-shape type deformation with an average displacement of the C_β of 0.41 Å. The two cadmium centres, adopting a rather distorted tetrahedral geometry, connecting the two porphyrins are bound to two I^- anions (d_{Cd-I} = 2.70 Å) and two pyridine groups belonging to two compounds **2** (d_{Cd-N} = 2.29 Å) with N–Cd–N and I–Cd–I angles of 95.75° and 129.44°, respectively. The Cu–Cu and the Cd–Cd distances are 14.27 and 13.99 Å, respectively. The two porphyrins mean planes are parallel but not coplanar (separation of *ca.* 0.50 Å).

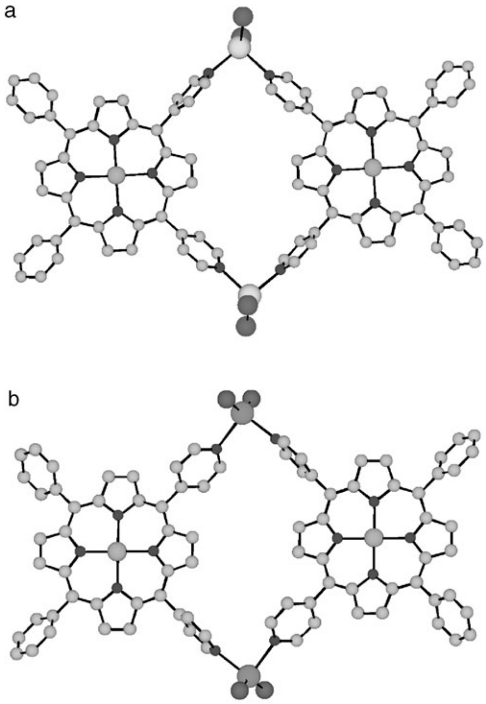


Fig. 4 Solid state structures of metallamacrocycles **6** and **7** formed upon treatment of **2** by CdI_2 (a) and $HgBr_2$ (b). H atoms are not presented for sake of clarity. For bond distances and angles see text.

For the heterotetrametallic compound **7**, a rather similar structure as the one observed for **6** is obtained. The unit cell is composed of two Cu-porphyrins, two $HgBr_2$ units and a disordered $CHCl_3$ molecule (Table 1). The interconnection of the two metallaporphyrins by $HgBr_2$ leads to the formation of the heterotetranuclear metallacycle (Fig. 4b). The Cu(II) centre, located inside the porphyrin cavity and coordinated to four nitrogen atoms (d_{Cu-N} of *ca.* 2.00 Å, and N–Cu–N angles of *ca.* 90° (*cis*) and 175–177° (*trans*)), adopts a slightly distorted square planar geometry (displacement of 0.036 from the porphyrin mean plan). The porphyrin ring exhibits a saddle-shape deformation with an average displacement of the C_β of 0.403 Å. The two mercury centres, adopting severely distorted tetrahedral geometry, connecting the two porphyrins are bound to two Br^- anions ($d_{Hg–Br}$ = 2.49 Å) and two pyridine groups belonging to two compounds **2** ($d_{Hg–N}$ = 2.40 Å) with N–Hg–N and Br–Hg–Br angles of 91.02° and 143.15°, respectively. The Cu–Cu and the Hg–Hg distances are 14.27 and 14.28 Å, respectively. Again, the two porphyrins mean plane are parallel but not coplanar (separation of *ca.* 0.77 Å).

Conclusion

5,10-Dipyridyl-15,20-diphenylporphyrin **1** or its copper metallated complex **2** bearing two peripheral pyridine sites are interesting molecular corners for the construction of either metallacycles or infinite coordination networks. We have shown that their combination with metal halides (MX_2: M = Zn, Cd, Hg; X = I or Br) adopting tetrahedral coordination geometry leads in all cases to the formation of centrosymmetric square type [2 + 2] metallamacrocycles. Interestingly, using the premetallated copper complex **2**, we have demonstrated the possibility of sequential construction of new heterotetranuclear metallamacrocycles based on either Cu(II)/Cd(II) or Cu(II)/Hg(II) couples. All five structures obtained are almost isostructural with the porphyrin core displaying almost identical structural features. Further work on the formation of heteropolymetallic assemblies based on analogues of porphyrin derivatives **1** and **2** is currently under progress.

Experimental section

General

All reagents were purchased from commercial sources and used without further purification except for pyrrole that was purified on an alumina pad. ^1H and ^{13}C spectra were recorded at room temperature on a Bruker (300 MHz) NMR spectrometer. UV–Vis absorption measurements were carried out on a UVIKON XL, Bio-Tek. spectrometer. Microanalyses were performed by the Service de Microanalyses de la Fédération de Recherche de Chimie, Université Louis Pasteur, Strasbourg or by Service de Microanalyse-Vernaison, CNRS, Lyon, France.

Synthesis of ligand 2

50 mg (8.0×10^{-2} mmol, 1 eq.) of **1**, prepared according to published procedure,[27] and 20 mg (1.1×10^{-1} mmol, 1,4 eq.) of $Cu(OAc)_2$ were dissolved in a mixture of $CHCl_3$ (50 ml) and glacial acetic acid (50 ml). This mixture was refluxed for 18 hours. After cooling the mixture to room temperature, the solvents were removed under reduced pressure. The residue was washed with MeOH (250 ml) and cyclohexane (100 ml). The desired copper complex **2**, dried under vacuum, was obtained as a purple red solid in 91% yield (50 mg). $C_{40}H_{26}N_6Cu \cdot CH_2Cl_2 \cdot 2H_2O$: calcd. (%) C 64.45, H 4.00, N 10.49, found (%) C 64.40, H 4.05, N 10.26. UV–Vis (CH_2Cl_2): λ_{max} (ε) = 410 (9.4×10^4 M^{-1} cm^{-1}), 527 (4.2×10^3 M^{-1} cm^{-1}) nm.

Synthesis of metallamacrocycles 3 and 4

Single crystals of suitable quality for X-ray diffraction investigations were obtained within 5–7 days at room temperature, upon slow diffusion of a $CHCl_3$ solution (0.5 ml) of **1** (1 mg, 1 eq.), prepared according to published procedure,[27] into a MeOH (2 ml) solution of CdI_2 (3.0 mg, 5 eq.) or HgI_2 (3.7 mg, 5 eq.), respectively. **3**: $C_{84}H_{56}N_{12}Cd_2I_4 \cdot 2CHCl_3$ (2204.53): calcd. (%) C 46.85, H 2.65, N 7.62, found (%) C 46.72, H 2.63, N 7.57; **4**: $C_{84}H_{56}N_{12}Hg_2I_4 \cdot 2CHCl_3$ (2381.00): calcd. (%) C 43.38, H 2.45, N 7.06, found (%) C 43.50, H 2.45, N 7.10.

Synthesis of metallamacrocycle 5

Single crystals of suitable quality for X-ray diffraction investigations were obtained within 5–7 days at room temperature, upon slow diffusion of a $CHCl_3$ solution (0.5 ml) of **1** (1 mg, 1 eq.), prepared according to published procedure,[27] into a MeOH (2 ml) solution of ZnI_2 (2.6 mg, 5 eq.). $C_{84}H_{52}N_{12}Zn_4I_4 \cdot 2CH_3OH \cdot H_2O$ (2080.56): calcd. (%) C 49.65, H 3.00, N 8.08, found (%) C 49.44, H 2.95, N 7.95.

Synthesis of metallamacrocycles 6 and 7

Single crystals of suitable quality for X-ray diffraction investigations were obtained within 5–7 days at room temperature, upon slow diffusion of a $CHCl_3$ solution (0.5 ml) of **2** (0.5 mg, 1 eq.) into a MeOH (2 ml) solution of $HgBr_2$ (1.3 mg, 5 eq.) or CdI_2 (1.4 mg, 5 eq.). **7**: $C_{84}H_{52}N_{12}Hg_2Cu_2Br_4 \cdot 2.5CHCl_3$ (2375.70): calcd. (%) C 43.73, H 2.31, N 7.07, found (%) C 43.69, H 2.25, N 7.04

Crystallography

Data were collected at 173(2) K on a Bruker APEX8 CCD Diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using graphite-monochromated Mo-Kα (λ = 0.71 073) radiation. For all structures, diffraction data were corrected for absorption and structural determination was achieved using the APEX (1.022) package. All hydrogen atoms have been calculated except those connected to disordered atoms.‡.

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‡ CCDC reference numbers CCDC 245804 and 611786–611789. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b606041m

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