

Design and Structural Analysis of Metallamacrocycles Based on a Combination of Ethylene Glycol Bearing Pyridine Units with Zinc, Cobalt and Mercury

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In the presence of MX_2 salts, ligand **1** (in a M/L ratio of 2:2, $\text{M} = \text{Zn, Hg, Co}$, $\text{X} = \text{Cl or I}$), based on the ethylene glycol fragment bearing two pyridine units as monodentate coordination sites, leads to isostructural square-shaped neutral metallamacrocycles as demonstrated by X-ray diffraction on single crystals. For all dinuclear complexes generated, the dicationic metal centre adopts a distorted tetrahedral coordination geometry and its coordination sphere is composed of the X_2N_2 set of coordinating atoms. For all complexes, the

parallel packing of the cyclic structures generates channels which are occupied by solvent molecules. The solvent molecules, which behave as substrates, are positioned within the cavity of the metallamacrocycles. Control of the dimension of the macrocycles, by varying the size of the connecting metal centre, has also been demonstrated.

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Introduction

Metallamacrocycles are finite entities composed of organic fragments and endocyclic metal centres.^[1–11] These species may be described as cyclic structures either resulting from the bridging of metal centres by organic ligands that possess at least two coordinating sites or from the interconnection of organic ligands by the metal centres. For the design of metallamacrocycles, one must take into account the characteristics of the organic ligand (shape, rigidity, number and disposition of the coordinating sites) as well as the stereochemical requirements of the metal centre (oxidation state, geometry, number and disposition of free coordination sites).^[3]

The majority of metallamacrocycles reported to date are based on the combination of *cis*-protected cationic square-planar metal units such as diphosphane or ethylenediamine complexes of Pd^{II} and Pt^{II} and often bis(pyridine) neutral ligands.^[2–4] For these cases, due to the neutral nature of the ligands used, the metallamacrocycles formed are cationic in nature and thus are associated with anions for charge neutrality purposes. In order to generate uncharged metallamacrocycles, one may consider a combination of neutral

metal complexes and organic ligands. This has been previously demonstrated with metal halide complexes.^[11,12] Indeed, in that case, the coordinating halide centres not only neutralise the cationic charge of the metal cation, but also, by occupying some of the coordination sites within the first coordination sphere around the metal, allow the disposition of the remaining unoccupied sites to be controlled. This aspect has been demonstrated by us both in the case of discrete metallamacrocycles^[12] and for coordination networks.^[13–20]

Another important issue associated with the metallamacrocycles is the control of the nuclearity (i.e. the metal to ligand ratio). Indeed, depending on the nature of the bis(monodentate) ligand (rigidity, positioning of the coordinating sites) and the metal cation used (number and disposition of coordination sites), different cyclic structures such as [1.1] I, [2.2] II, [3.3] III, [4.4] IV etc. may be expected (Figure 1).^[3,21]

Here, in the continuation of our investigations on the design of metallamacrocycles,^[12,21–27] we describe the formation of four new neutral metallamacrocycles based on the use of the bis(monodentate) ligand **1** and neutral metal halide complexes (MX_2 ; $\text{M} = \text{Zn, Hg, Co}$; $\text{X} = \text{Cl or I}$).

Results and Discussion

The design of ligand **1** (Scheme 1) is based on the ethylene glycol fragment **2** as a spacer connecting two monodentate pyridine derivatives. The connection between the two

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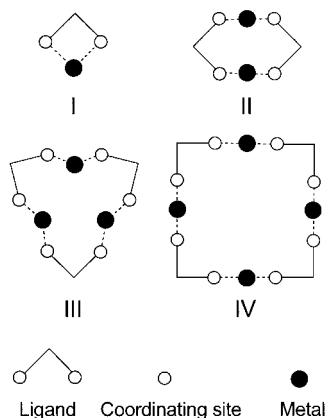
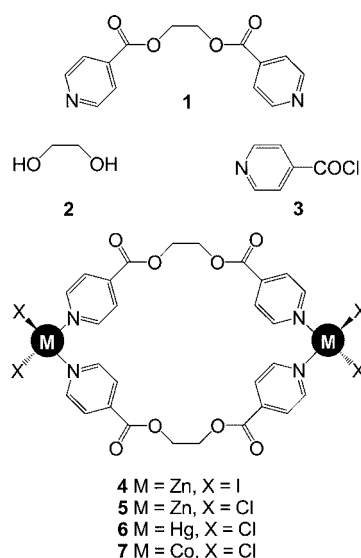


Figure 1. Schematic representations of the formation of metallamacrocycles of different nuclearity between a bis-monodentate fragment and a metal centre possessing two free coordination sites



Scheme 1

units is achieved through an ester group at the 4-position of the pyridine ring. Although the straight forward synthesis of **1** has been reported,^[28] we used our own methodology consisting of the condensation of ethylene glycol **2** with **3** in dry THF and in the presence of Et_3N (see Exp. Sect.).

Compound **1**, which is of the bis(monodentate) type, may either behave as a ligand and thus lead to metallamacrocyclic complexes or act as a tecton and generate coordination networks in the presence of appropriate metal centres.^[29,30] We have previously demonstrated the latter case using analogous oligoethylene glycol based tectons, which lead to the formation of double-helical infinite networks when combined with silver cations.^[31,32] Ligand **1** has also been used for the formation of 1D coordination networks in the presence of copper bromide.^[33] The formation of coordination networks based on an analogous compound for which the ethylene glycol unit is replaced by an ethylene diamine fragment has also been reported.^[34]

For the generation of metallamacrocycles under self-assembly processes, the choice of the coordinating heteroatoms and the cationic metal centre is crucial. Indeed, the self-assembly phenomena requires reversible coordination bond formation. Since ligand **1** contains two pyridine units as coordinating sites, zinc(II), mercury(II) and cobalt(II) halides have been chosen because the binding of pyridine to these metals in the oxidation state II is reversible. Thus, although many different species may be formed in solution, the selection of a metallamacrocyclic with a given nuclearity may be achieved by the crystallisation process. In the present investigation, zinc(II), mercury(II) and cobalt(II) halides were combined with ligand **1** under crystallisation conditions leading exclusively to four new metallamacrocycles **4–7**, which were characterised by elemental analysis and X-ray diffraction on single crystals (Table 1). All four metallamacrocycles were found to be insoluble in common solvents such as CH_2Cl_2 , CHCl_3 , MeOH, EtOH, THF, CH_3CN and dioxane and for that reason they could not be characterised by NMR spectroscopy. The metallamacrocycles **4–7** were slightly soluble in DMF and readily soluble in DMSO. However, the ^1H NMR solution study in DMSO revealed that the chemical shifts observed for all signals were identical to those observed for the free ligand in the same solvent, probably implying that the metallamacrocycles are degraded in DMSO.

Treatment of ligand **1** with ZnI_2 , produced slightly yellowish single crystals upon slow diffusion of a solution of ZnI_2 in EtOH into a solution of **1** in CHCl_3 . The X-ray diffraction study of **4** (Table 1) revealed that the crystal (triclinic, $P\bar{1}$) is composed of one ZnI_2 dinuclear [2.2] complex **4** (Type II; Figure 1) and one disordered CHCl_3 solvent molecule. The solvent molecule is located within the cavity of the metallamacrocyclic of the cyclophane (there are four edges, each defined by one pyridine unit), which leads to an inclusive complex in the crystalline phase (Figure 2).

The shape of the metallamacrocyclic is a very slightly distorted square ($8.65 \text{ \AA} \times 8.72 \text{ \AA}$) with the two ZnI_2 units occupying diagonal corners ($\text{Zn}\cdots\text{Zn}$ distance $12.25 \text{ \AA}$). For ligand **1**, the ethylene glycol fragment adopts a gauche conformation with the $\text{O}-\text{C}-\text{C}-\text{O}$ dihedral angles of -80.2° and $+80.3^\circ$. The plane of the two ester groups (average $\text{C}-\text{O}$ and $\text{C}=\text{O}$ distances are approximately $1.32 \text{ \AA}$ and $1.19 \text{ \AA}$, respectively; the $\text{O}-\text{C}-\text{O}$ angle lies between 123.6° and 125.0°) is slightly tilted with respect to the connected pyridine unit ($\text{C}-\text{C}-\text{C}-\text{O}$ dihedral angles of 2.3° and 6.2°). The coordination sphere around the metal is composed of two I^- anions and two N atoms belonging to two pyridine units of two different ligands (**1**) with average $\text{Zn}-\text{N}$ and $\text{Zn}-\text{I}$ bond lengths of approximately $2.06 \text{ \AA}$ and $2.54 \text{ \AA}$, respectively (Figure 2). The metal centre adopts a distorted tetrahedral coordination geometry with $\text{N}-\text{Zn}-\text{N}$ and $\text{I}-\text{Zn}-\text{I}$ angles of 102.8° and 121.0° , respectively. The $\text{N}-\text{Zn}-\text{I}$ angle varies between 106.4° and 107.4° . The slightly distorted square metallamacrocycles are packed in a parallel fashion thus generating channels occupied by solvent molecules. In one direction of space, the metallamacrocycles probably interact through stacking be-

Table 1. X-ray data for metallamacrocycles **4**–**7** formed between ligand **1** and metal halides

	4 :1-ZnI ₂	5 :1-ZnCl ₂	6 :1-HgCl ₂	7 :1-CoCl ₂
Chemical Formula	C ₂₉ H ₂₅ Cl ₃ I ₄ N ₄ O ₈ Zn ₂	C ₂₉ H ₂₄ Cl ₇ N ₄ O ₈ Zn ₂	C ₁₅ H ₁₃ Cl ₄ HgN ₂ O ₄	C ₁₅ H ₁₃ Cl ₄ CoN ₂ O ₄
Molecular mass	1302.23	935.45	627.68	486.024
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	9.860(2)	9.6818(4)	10.0469(2)	10.030(2)
<i>b</i> (Å)	10.042(3)	18.9516(13)	19.3318(4)	18.899(5)
<i>c</i> (Å)	10.228(3)	10.2085(7)	10.3355(2)	10.112(2)
α (°)	81.30(2)	90.00	90.00	90.00
β (°)	81.81(2)	98.198(5)	98.814(5)	98.85(3)
γ (°)	86.97(2)	90.00	90.00	90.00
<i>V</i> (Å ³)	990.4(4)	1854.0(2)	1983.70(7)	1894.0(8)
<i>D</i> _{calcd.} (gcm ^{−3})	2.184	1.676	2.10	1.70
<i>Z</i>	1	2	4	4
Colour	colourless	colourless	colourless	blue
Crystal size (mm)	0.37 × 0.21 × 0.08	0.40 × 0.20 × 0.15	0.20 × 0.15 × 0.06	0.15 × 0.07 × 0.01
μ (Mo- <i>K</i> _α) (mm ^{−1})	4.580	1.850	8.320	1.494
<i>T</i> (K)	173	173	173	173
Data collected	5760	5399	10139	34078
Obsd. data [<i>I</i> > 3σ(<i>I</i>)]	4916	3785	3570	3341
<i>R</i> 1	0.039	0.050	0.029	0.043
<i>wR</i> 2	0.129	0.113	0.046	0.156
GooF	1.116	1.035	1.008	1.114
CCDC No	216069	216070	216071	216073

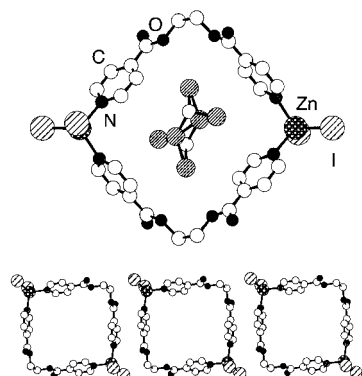


Figure 2. Solid-state structure of the dinuclear zinc metallamacrocycle **4** obtained upon reacting ligand **1** with ZnI₂; the cavity of the square macrocycle is occupied by a disordered CHCl₃ molecule (top) and in one direction of space; the metallamacrocycles interact through stacking between pyridine units (bottom); H atoms are not represented for clarity; for bond lengths and angles see text

tween pyridine units disposed in an anti-parallel manner (shortest distance between carbon atoms of two pyridines belonging to two consecutive metallamacrocycles is ca. 3.80 Å).

As expected, when ZnI₂ was replaced by ZnCl₂ under the same conditions, the X-ray diffraction study (Table 1) again revealed a similar metallamacrocycle **5** (Figure 3). The crystal structure (monoclinic, *P*2₁/*c*) is again composed of one ZnCl₂ dinuclear complex **5** and one disordered CHCl₃ solvent molecule. The latter, as mentioned above, is located within the cavity of the metallamacrocycle (Figure 3). The metallamacrocycle adopts a similarly distorted square form as above with almost identical dimensions (8.64 Å × 8.73 Å, Zn···Zn distance is 12.36 Å). Ligand **1** presents the same characteristics as those observed for the ZnI₂ complex **4**,

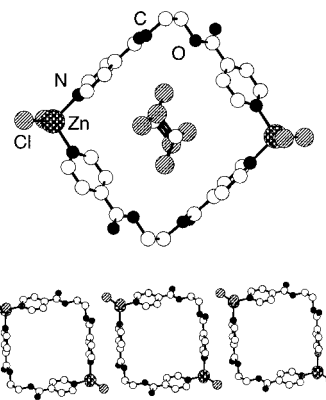


Figure 3. The solid-state structure of the dinuclear zinc metallamacrocycle **5** (top) obtained upon reacting ligand **1** with ZnCl₂; the square macrocycle forms an inclusive complex with a CHCl₃ molecule (disordered) and the packing of consecutive units (bottom); H atoms are not represented for clarity; for bond lengths and angles see text

that is, gauche conformation of the ethylene glycol fragment (O–C–C–O dihedral angles -77.2° and $+77.2^\circ$). The plane of the two ester groups (average C–O and C=O distances are ca. 1.32 Å and 1.19 Å, respectively; the O–C–O angle lies between 124.6° and 125.2°) is again slightly tilted with respect to the connected pyridine unit (C–C–C–O dihedral angles of -0.8° and $+10.2^\circ$). The coordination sphere around the metal centre is composed of two Cl[−] anions and two N atoms belonging to two pyridine units of two different ligands (**1**) with Zn–N and Zn–Cl average bond lengths of approximately 2.05 Å and 2.21 Å, respectively (Figure 2). The metal centre adopts a distorted tetrahedral coordination geometry with N–Zn–N and Cl–Zn–Cl angles of 101.6° and 121.5° , respectively. The

N–Zn–Cl angle varies between 105.9° and 111.4° . Again, as for the previous case mentioned above, the square metallamacrocycles are packed in a parallel fashion generating channels. Also, in one direction of space, the metallamacrocycles probably interacts through stacking between pyridine units disposed in an anti-parallel fashion (shortest distance between carbon atoms of two pyridines belonging to two consecutive metallamacrocycles is ca. $3.67 \text{ \AA}$). Comparison of structures **4** and **5** shows that changing the steric demand of the halogen atoms coordinated to the metal centre has almost no effect on the size of the metallamacrocycle.

In order to increase the dimensions of the metallamacrocycle, that is, the size of the endocyclic cavity, it may be possible to increase the size of the metal centre. For that reason, ligand **1** was treated with HgCl_2 . Upon slow diffusion of a solution of HgCl_2 in EtOH into a solution of **1** in $\text{C}_2\text{H}_2\text{Cl}_4$, colourless crystals were obtained (Table 1). The crystal structure (monoclinic, $P2_1/c$) is composed of one neutral metallamacrocycle **6** and one tetrachloroethane solvent molecule. The solvent molecule is again located within the cavity of the metallamacrocycle **6** (Figure 4). The structure again adopts a slightly distorted square form with larger dimensions, as expected ($8.98 \text{ \AA} \times 9.05 \text{ \AA}$, the $\text{Hg}\cdots\text{Hg}$ distance is $13.29 \text{ \AA}$). Ligand **1** presents the same characteristics as those observed for the dinuclear metallamacrocycles **4** and **5** obtained with zinc, that is, gauche conformation of the ethylene glycol fragment ($\text{O}-\text{C}-\text{C}-\text{O}$ dihedral angles -81.8° and $+81.8^\circ$). The plane of the two ester groups (average $\text{C}-\text{O}$ and $\text{C}=\text{O}$ distances are ca. $1.33 \text{ \AA}$ and $1.19 \text{ \AA}$, respectively, the $\text{O}-\text{C}-\text{O}$ angle lies between 123.6° and 123.8°) is again slightly tilted with respect to the connected pyridine unit ($\text{C}-\text{C}-\text{C}-\text{O}$ dihedral angles of -1.2° and -8.9°). The coordination sphere around the Hg^{2+} cation is composed of two Cl^- anions and two N atoms belonging to two pyridine units of two different ligands (**1**) with $\text{Hg}-\text{N}$ and $\text{Hg}-\text{Cl}$ average bond lengths of approximately $2.39 \text{ \AA}$ and $2.36 \text{ \AA}$, respectively. The metal centre adopts a distorted tetrahedral coordination geometry with $\text{N}-\text{Hg}-\text{N}$ and $\text{Cl}-\text{Hg}-\text{Cl}$ angles of 97.0° and 141.7° ,

respectively. The $\text{N}-\text{Hg}-\text{Cl}$ angle varies between 97.0° and 104.7° . As for the previous cases mentioned above, the square metallamacrocycles are packed in a parallel fashion with stacking interactions (shortest distance between carbon atoms of two pyridines belonging to two consecutive metallamacrocycles ca. $3.60 \text{ \AA}$) in one direction of space between consecutive metallamacrocycles **6** (Figure 4).

Finally, ligand **1** was allowed to react with CoCl_2 under crystallisation conditions. The slow diffusion of a solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in EtOH into a solution of **1** in $\text{C}_2\text{H}_2\text{Cl}_4$ afforded blue crystals (Table 1). The crystal structure (monoclinic, $P2_1/c$) is composed of one CoCl_2 dinuclear complex **7** and one tetrachloroethane solvent molecule. Again the solvent molecule is located within the cavity of the metallamacrocycle **7** (Figure 5), which adopts a slightly distorted square shape with similar dimensions ($8.63 \text{ \AA} \times 8.71 \text{ \AA}$, $\text{Co}\cdots\text{Co}$ distance is ca. $12.22 \text{ \AA}$) close to those observed for the Zn complexes **4** and **5**. Ligand **1** presents the same characteristics as those observed for the dinuclear metallamacrocycles **4–6** which were obtained with zinc and mercury, that is, gauche conformation of the ethylene glycol fragment ($\text{O}-\text{C}-\text{C}-\text{O}$ dihedral angles -77.8° and $+77.9^\circ$). The plane of the two ester groups (average $\text{C}-\text{O}$ and $\text{C}=\text{O}$ distances are ca. $1.33 \text{ \AA}$ and $1.19 \text{ \AA}$, respectively; $\text{O}-\text{C}-\text{O}$ angles lie between 124.2° and 125.0°) is again tilted with respect to the connected pyridine unit ($\text{C}-\text{C}-\text{C}-\text{O}$ dihedral angles of -1.5° and $+9.9^\circ$). Interestingly, the coordination sphere around the Co^{2+} cation is only composed of two Cl^- anions and two N atoms belonging to two pyridine units of two different ligands (**1**) with $\text{Co}-\text{N}$ and $\text{Co}-\text{Cl}$ average bond lengths of approximately $2.04 \text{ \AA}$ and $2.22 \text{ \AA}$, respectively. The metal centre adopts a distorted tetrahedral coordination geometry with $\text{N}-\text{Co}-\text{N}$ and $\text{Cl}-\text{Co}-\text{Cl}$ angles of 105.7° and 120.4° , respectively. The $\text{N}-\text{Co}-\text{Cl}$ angle varies between 105.4° and 110.2° . This coordination geometry around Co^{II} with the (X_2N_2) set of coordinating centres differs from the previously observed octahedral geometry with the same type of donor sites (pyridine and Cl^-).^[13–18] Once again, as for

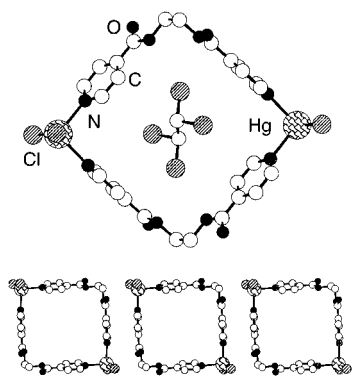


Figure 4. The solid-state structure of the dinuclear mercury metallamacrocycle **6** (top) obtained upon reacting ligand **1** with HgCl_2 ; the square macrocycle forms an inclusive complex with tetrachloroethane molecule; the packing of consecutive units generates channels (bottom); H atoms are not represented for clarity; for bond lengths and angles see text

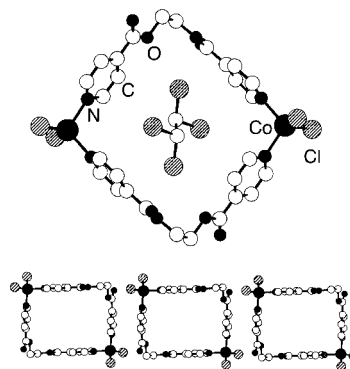


Figure 5. The solid-state structure of the dinuclear cobalt metallamacrocycle **7** (top) obtained upon reacting ligand **1** with CoCl_2 ; the Co^{II} centre adopts a distorted tetrahedral coordination geometry; the square macrocycle forms an inclusive complex with tetrachloroethane molecule; the packing of consecutive units generates channels (bottom); H atoms are not represented for clarity; for bond lengths and angles see text

the previous cases mentioned above, the slightly distorted square metallamacrocycles are packed in a parallel fashion with stacking interactions (shortest distance between carbon atoms of two pyridines belonging to two consecutive metallamacrocycles is ca. 3.60 Å) are in one direction of space between consecutive metallamacrocycles of **7**.

In summary, the rather simple ligand **1**, composed of an ethylene glycol unit bearing two pyridines as monodentate coordination sites, leads in the presence of metal halides (MX_2 : $\text{M} = \text{Zn, Hg, Co}$; $\text{X} = \text{Cl or I}$) in a M/L ratio of 2:2 to isostructural square-shape neutral metallamacrocycles. The metallamacrocyclic structures offer rather large cavities of the cyclophane type which are occupied by solvent molecules. In the crystal, the square-cyclic units are packed in a parallel fashion, thus generating channels occupied by solvent molecules. In one direction of space, the metallamacrocycles probably interact with each other through stacking of the pyridine units belonging to consecutive units and are disposed in an anti-parallel manner. Since the solvent molecules included in the cavity of the metallamacrocycles may play a template role and thus define the nuclearity of the complex, we are currently evaluating this aspect. The formation of other types of finite metallamacrocycles using ligand **1**, other metal centres and the generation of infinite coordination networks are currently under investigation. The ability of the analogous ligand for which the pyridine units are connected at the 3-position to generate metallamacrocycles and/or coordination networks with a variety of metal complexes is also currently being investigated.

Experimental Section

General: All commercially available reagents were purchased and used without further purification. ^1H and ^{13}C NMR spectra were recorded on Bruker spectrometers at 400 and 300 MHz and at 50 MHz, respectively. Microanalyses were performed by the Service de Microanalyses de la Fédération de Recherche Chimie, Université Louis Pasteur, Strasbourg.

Synthesis of Ligand 1: A solution of **3** as its hydrochloride salt (2.15 g, 12 mmol) in dry THF (30 mL) was added to ethylene glycol **2** (0.3 g, 4.8 mmol) under argon. The mixture was stirred before Et_3N (5 mL) was added and stirred at room temperature for a further 12 hours. The brownish solution was evaporated to dryness under reduced pressure. A saturated aqueous hydrogenocarbonate solution (50 mL) was added to the residue and the mixture was extracted with CH_2Cl_2 (3×50 mL). The organic solvent was removed and the residue purified by column chromatography (SiO_2 , CH_2Cl_2 -0.2 % MeOH) affording the pure compound **1** (0.66 g, 51 %) as a slightly yellowish oil. $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_4$ (272.26): calcd. C 61.76, H 4.44, N 10.29; found C 61.59, H 4.53, N 9.96. ^1H NMR (CDCl_3 , 300 MHz, 25 °C): δ = 4.71 (s, 4 H, CH_2O), 7.84 (dd, 4 H, J = 1.65 and 4.41 Hz), 8.79 (dd, J = 1.6, 4.4 Hz, 4 H) ppm. ^{13}C NMR (CDCl_3 ; 300 MHz; 25 °C): δ = 63.2, 122.8, 136.7, 150.7, 164.9 ppm.

Synthesis of Metallamacrocycles 4–7: Single crystals of suitable quality for X-ray diffraction investigations were obtained within 2–4 days at room temperature, upon slow diffusion of a CHCl_3 or

$\text{C}_2\text{H}_2\text{Cl}_4$ solution (1 mL) of **1** (5 mg) into a EtOH (2 mL) solution of ZnI_2 , ZnCl_2 , HgCl_2 or $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (1.5 mg); **4**: $\text{C}_{14}\text{H}_{12}\text{O}_4\text{N}_2 \cdot \text{ZnI}_2$ (591.45): calcd. C 28.43, H 2.05, N 4.74; found C 28.38, H 2.12, N 4.68; **5**: $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_4 \cdot \text{ZnCl}_2$ (408.55): calcd. C 41.16, H 2.96, N 6.86; found C 41.33, H 3.08, N 6.90; **6**: $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_4 \cdot \text{HgCl}_2$ (543.76): calcd. C 30.92, H 2.22, N 5.15; found C 30.89, H 2.32, N 5.46; **7**: $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_4 \cdot \text{CoCl}_2$ (410.10): calcd. C 41.82, H 3.10, N 6.97; found C 41.88, H 3.06, N 6.99.

Crystal Structure Characterisation: X-ray diffraction data was carried out on a Kappa CCD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, with graphite-monochromated Mo-K_α radiation (Table 1). In the case of **6**, diffraction data were corrected for absorption and analysed using the OpenMolen package,^[35] whereas for the other three metallamacrocycles **4**, **5** and **7**, Nonius–Maxus Package 4.3 was used. All non-H atoms were refined anisotropically. CCDC-216069 to -216071 and -216073 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk.

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