Design and Structural Analysis of Metallamacrocycles Based on Zinc Halides and a V-Shaped Bismonodentate Ligand of the Cyclophane Type

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Keywords: Cyclophanes / Pyridine / Zinc / Metallacycles

The ligand **1**, based on the [1,1,1,1]cyclophane skeleton and bearing two pyridine units as monodentate coordination sites on the same face of the backbone, leads, in the presence of ZnX_2 (X = Cl, Br or I) complexes, to three isostructural neutral metallamacrocycles with an M/L ratio of 2:2. All three binuclear complexes have been characterised in the solid state by single-crystal X-ray diffraction. All three metallamacrocycles possess a roof-shaped geometry affording a pocket with a single opening. The latter is occupied by solvent molecules in the solid state. A correlation between the size of the halide and dimensions of the pocket is described.

Introduction

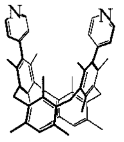
Over the last decade considerable efforts have been invested in the design and synthesis of macro(poly)cyclic structures of the metallamacrocycle type.[1−9] These molecules are based on the interconnection of organic fragments (L) bearing coordination sites and metal centres (M). The topology (macrocyclic, macrobicyclic etc.) and the nuclearity (M/L ratio) of such complexes have been shown to be dependent on both the structural and coordination features of the organic ligand (number of coordination sites, denticity of the coordination units and their spatial arrangement) and on the stereochemical demands of the metal centre (coordination geometry, number of available coordination sites and their disposition within the coordination sphere of the metal).

In a continuation of our investigations on the design and formation of metallamacrocycles,[10−15] we designed the V-shaped ligand **1** and explored its ability to form metallamacrocycles with an imposed 2:2 nuclearity.

We report here the formation of a homologous series of metallamacrocycles based on ZnX_2 (X = Cl, Br, I) and the V-shaped ligand **1**, and their solid state structures.

Results and Discussion

The design of the ligand **1** is based on the [1.1.1.1]metacyclophane skeleton (Scheme 1), which adopts the thermally stable 1,3-alternate conformation.[16] The functionalisation of the two distal aromatic moieties by two pyridine derivatives leads to ligand **1**, for which the two monodentate coordination sites are located on the same face of the backbone. The connection between the cyclophane skeleton and pyridines was achieved through C−C bonds at the *para* position of the pyridine ring.



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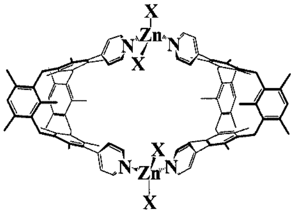

2: X = Cl
3: X = Br
4: X = I

Scheme 1

Due to the rather rigid nature of the ligand **1** and its V-shaped geometry (angle of 30−40° between the pyridine rings), it appeared interesting to explore the possibility of preparing metallamacrocycles using this ligand. The majority of metallamacrocycles reported to date are based on square-planar protected Pd^{II} and Pt^{II} complexes,[2−4] however, based on the geometry of **1** and the orientation of the two pyridines, metal centres adopting a tetrahedral coordination geometry appeared to be the most interesting ones

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for the formation of metallamacrocycles. Thus, three zinc halides (ZnX_2, X = Cl, Br, I) were used. The rationale behind the choice of this type of complex was based on the fact that, taking into account the neutral nature of the ligand **1** and the rather strong biding ability of halides towards Zn^{2+} dication, the combination of **1** and ZnX_2 would lead to neutral metallamacrocycles **2**−**4**. In other words, for a neutral ZnX_2 complex adopting a tetrahedral coordination geometry, two vertices would be occupied by two halides and thus the remaining two coordination positions would be available for coordination to two molecules of **1** through their pyridines. It is perhaps interesting to note that the majority of metallamacrocycles are obtained using *cis*-protected square-planar metal complexes such as diphosphane or ethylenediamine complexes of Pd^{II} and Pt^{II}, whereas in the present case, the connecting metal cation adopts a tetrahedral coordination geometry. This aspect has been recently demonstrated by Braga et al.[7] Furthermore, it was believed that by changing the steric demand of the halogen, one could tailor the geometric features of the metallamacrocycles. Indeed, the increase in the size of the halogen from chloride to bromide and finally to iodide must induce a strong deformation of the tetrahedral Zn complex by increasing the X−Zn−X angle and, consequently, would lead to a decrease in the N−Zn−N angle.

Dealing with the synthesis of metallamacrocycles, an important issue is the control of the nuclearity (Figure 1), i.e. the M/L ratio. Indeed, using rigid and linear organic bismonodentate ligands, depending on the metal cation used, a variety of cyclic compounds such as [2.2]- (Figure 1a), [3.3]- (Figure 1b), [4.4]- (Figure 1c), [5.5]- (Figure 1d) and [6.6]metallamacrocycles (Figure 1e) may be obtained. Based on the angular characteristics of the ligand **1**, we believed that use of ZnX_2 complexes as connecting centres would favour the formation of the [2,2]metallamacrocycle (Figure 1a).

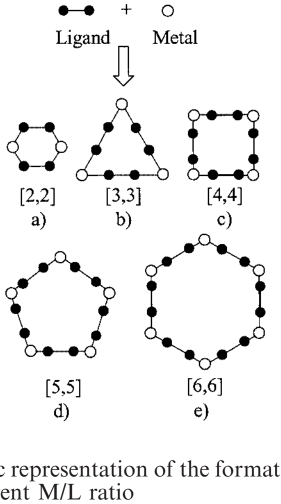

Figure 1. Schematic representation of the formation of metallamacrocycles with different M/L ratio

Metallamacrocycles **2** and **3** were obtained in quantitative yield by mixing the ligand **1** and ZnX_2 (X = Cl or Br) in CH_2Cl_2 at room temperature and then evaporating the solvent. Both binuclear complexes are soluble in $CHCl_3$. They were characterised in solution by ^1H and ^{13}C NMR spectroscopy, and by X-diffraction studies on single crystals in the solid state.

In solution, the ^1H NMR investigations in $CDCl_3$ at 25 °C revealed that the signals corresponding to H atoms belonging to the pyridine units are significantly downfield shifted for both complexes **2** and **3** with respect to the free ligand **1** (Figure 2). Interestingly, addition of an excess of $ZnCl_2$ or $ZnBr_2$ to a solution containing **2** and **3**, respectively, has no effect on the line-widths and chemical shifts of the signals, indicating that the species present in solution are the metallamacrocycles **2** and **3** with a well-defined 2M/2 L ratio.

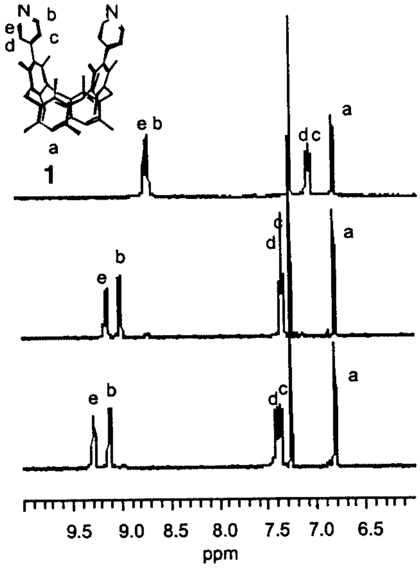

Figure 2. ^1H NMR (300 MHz, $CDCl_3$) studies at room temperature of the free ligand **1** (top) and metallamacrocycles **2** (middle) and **3** (bottom); only signals corresponding to protons belonging to pyridine units are presented

Compound **4**, due to its insolubility in $CHCl_3$, was not characterised in solution under the same conditions but only in the solid state by single-crystal X-ray diffraction.

In the solid state, the X-ray diffraction investigations revealed that, for all three compounds, neutral metallamacrocycles of the [2,2]-type are formed.

In the case of **2** (Figure 3a), the crystal is composed of $(\mathbf{1}\cdot ZnCl_2)_2$, and one ethanol and eight chlorobenzene molecules. The coordination sphere around the metal centre is composed of two Cl^- anions and two N atoms belonging to two pyridine units of two ligands **1**, with Zn−N and Zn−Cl bond lengths in the range 2.03−2.07 Å and 2.19−2.23 Å, respectively. The metal centre adopts a distorted tetrahedral coordination geometry with N−Zn−N and Cl−Zn−Cl angles of 101.3−101.7°, and 122.0−126.0°, respectively. Due to the rigidity of **1** and the tetrahedral geometry around the zinc(II) cation, the metallamacrocycle adopts a roof-type conformation with an average angle between the two main cyclophane axes of 110° and a Zn−Zn separation of 11.37 Å. Due to the peculiar arrangement of the two cyclophane units **1**, a pocket-type cavity possessing a single opening is formed; this is occupied by one chlorobenzene molecule.

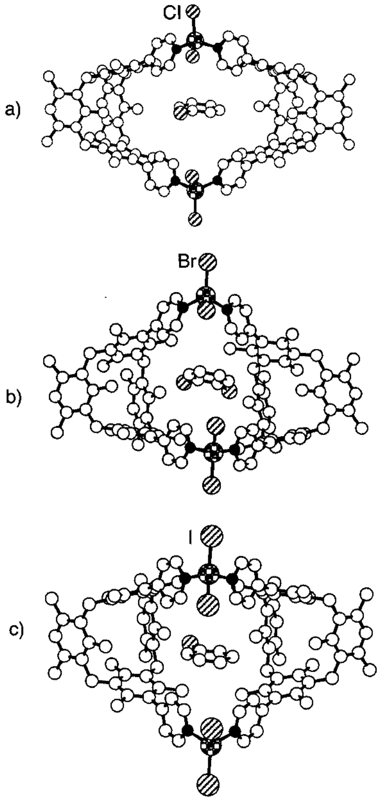

Figure 3. The solid-state structures of the metallamacrocycles **2** (a), **3** (b) and **4** (c); non-included solvent molecules and H atoms are omitted for clarity; see text for bond lengths and angles

In the case of **3** (Figure 3b), the crystal is composed of a (**1**·$ZnBr_2$)$_2$ metallamacrocycle and nine 1,2-dichlorobenzene molecules. Again, the coordination sphere around the metal centre is composed of a set of two Br^- anions and two N atoms with average Zn−N and Zn−Br bond lengths of 2.07 Å and 2.34 Å, respectively. The Zn^{2+} cation adopts a more distorted tetrahedral coordination geometry, with N−Zn−N and Br−Zn−Br angles of 93.7°, and 123.4°, respectively. Once again, the metallamacrocycle **3** adopts a roof-type conformation, as expected, with an average angle between the two main cyclophane axes of 82° and a Zn−Zn separation of 10.92 Å. The pocket-type cavity is occupied by a 1,2-dichlorobenzene molecule.

In the case of **4** (Figure 3c), the crystal is composed of a (**1**·ZnI_2)$_2$ metallamacrocycle and three chlorobenzene molecules. The latter were found to be disordered over two positions. Again, the coordination sphere around the metal centre is composed of a set of two I^- anions and two N atoms with average Zn−N and Zn−I bond lengths of 2.07 Å and 2.54 Å, respectively. The Zn^{2+} cation adopts an even more distorted tetrahedral coordination geometry with N−Zn−N and I−Zn−I angles of 92.6° and 121.6°, respectively. Once again, the metallamacrocycle **4** adopts a roof-type conformation, as expected, with an average angle between the two main cyclophane axes of 77.0° and a Zn−Zn separation of 11.21 Å. The pocket-type cavity is occupied by a disordered chlorobenzene molecule.

For all metallamacrocycles **2**−**4**, except for a few van der Waals contacts, no particular host-guest type interactions can be identified.

In $CDCl_3$ solution, no trace of the inclusion complexes of **2** and **3** could be observed by H-H NOESY investigations.

In summary, owing to the rigidity of the V-shaped bismonodentate ligand **1** and the orientation of the pyridine units, three isostructural neutral metallamacrocycles **2**−**4** of the 2M/2 L-type have been obtained in the presence of ZnX_2 (X = Cl, Br or I). All three metallamacrocycles have been characterised in the solid state by single-crystal X-ray diffraction. Due to the geometry of the ligand, the binuclear metallamacrocycles contain a pocket-type cavity possessing a single opening. The dimension of the cavity is determined by the size of the halide. In all three cases, the cavity is occupied by solvent molecules. Using the ligand **1**, the formation of other types of finite metallamacrocycles using other metal centres and the generation of infinite coordination networks are currently under investigations.

Experimental Section

Synthesis of Metallamacrocycles 2−4

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.

(1·ZnCl$_2$)$_2$ 2: A mixture of ligand **1**[16] (20 mg, 0.029 mmol) and $ZnCl_2$ (3.9 mg, 0.029 mmol) in CH_2Cl_2 (7 mL) was stirred at room temp. for 2 hours. Subsequent evaporation of the solvent gave the pure complex **2** as a white powder in quantitative yield (23 mg). $C_{100}H_{108}Cl_4N_4Zn_2 \cdot 0.5CH_2Cl_2$ (1681.1): calcd. C 71.80, H 6.53, N 3.33; found C 71.78, H 6.55, N 3.27. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 1.19 (s, 12 H, *p*-CH_3), 1.28 (s, 12 H, *p*-CH_3), 1.99 (s, 24 H, *o*-CH_3), 2.34 (s, 24 H, *o*-CH_3), 3.90 et 3.98 (AB, 2d, 16 H, *J* = 17 Hz, Ar-CH_2-Ar), 6.81 (s, 4 H, H-Ar), 7.34 (d, *J* = 5 Hz, 4 H, H-Py), 7.36 (d, *J* = 5 Hz, 4 H, H-Py), 9.00 (d, *J* = 5 Hz, 4 H, H-Py), 9.15 (d, *J* = 5 Hz, 4 H, H-Py) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz, 25 °C): δ = 17.5, 18.1, 19.5, 21.4, 32.2, 126.4, 127.6, 130.1, 130.6, 144.4, 135.4, 136.8, 137.4, 138.2, 148.9, 149.1 ppm.

(1·ZnBr$_2$)$_2$ 3: A mixture of ligand **1**[16] (20 mg, 0.029 mmol) and $ZnCl_2$ (6.5 mg, 0.029 mmol) in CH_2Cl_2 (7 mL) was stirred at room temp. for 2 hours. Subsequent evaporation of the solvent gave the pure complex **3** as a white powder in quantitative yield (26 mg). $C_{100}H_{108}Br_4N_4Zn_2 \cdot 2CH_2Cl_2$ (1986.3): calcd. C 61.68, H 5.68, N 2.82; found C 61.84, H 5.62, N 2.80. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 1.19 (s, 12 H, *p*-CH_3), 1.28 (s, 12 H, *p*-CH_3), 1.98 (s, 24 H, *o*-CH_3), 2.34 (s, 24 H, *o*-CH_3), 3.89 et 3.98 (AB, 2d, 16 H, *J* = 17 Hz, Ar-CH_2-Ar), 6.81 (s, 4 H, H-Ar), 7.37 (d, *J* = 5.5 Hz, 4 H, H-Py), 7.41 (d, *J* = 5.5 Hz, 4 H, H-Py), 9.12 (d, *J* = 5.5 Hz, 4 H, H-Py), 9.29 (d, *J* = 5.5 Hz, 4 H, H-Py) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz, 25°C): δ = 17.5, 18.1, 19.5, 21.3, 32.1, 126.5, 127.8, 130.1, 130.5, 133.4, 135.3, 136.6, 136.9, 137.3, 138.2, 148.9, 149.0, 153.4, 157.1 ppm.

(1·ZnI$_2$)$_2$ 4: Due to the insolubility of complex **4** in CH_2Cl_2, this metallamacrocycle was generated directly as crystals in a crystallising tube upon slow diffusion of an ethanol solution (0.75 mL) of ZnI_2 (5.7 mg, 0.018 mmol) into a chlorobenzene (0.5 mL) solution of ligand **1**[16] (5 mg, 0.0073 mmol).

Crystallisation Conditions

Metallamacrocycles 2 and 3: An EtOH solution (1 mL) of ZnX_2 (4.4 mg for X = Cl, 7.2 mg for X = Br) was added dropwise to a stirred solution (5 mL) of **1** (20 mg, 0.029 mmol) in chlorobenzene (X = Cl) or 1,2-dichlorobenzene (X = Br). After stirring at room temperature for two hours, EtOH (3 mL) was diffused into the solution. Complexes **2** and **3** were obtained as colourless crystals after about a week.

Single crystals of the binuclear metallamacrocycle **4** were obtained as described above.

Crystal Structure Characterisation: X-ray diffraction data collection was carried out on a Kappa CCD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using graphite-monochromated Mo-K_α radiation. For all structures, diffraction data were corrected for absorption and analysed with the OpenMolen package.[17] All non-H atoms were refined anisotropically.
Crystal Data for 2 ($(1\cdot ZnCl_2)_2$): Colourless crystals, 173 K, $C_{200}H_{216}Cl_8N_8Zn_4\cdot 8C_6H_5Cl\cdot C_2H_5OH$, M = 4223.66, triclinic, space group $P\bar{1}$, $a = 12.4464(2)$, $b = 21.8475(2)$, $c = 22.8606(3)$ Å, $\alpha = 112.173(5)°$, $\beta = 90.786(5)°$, $\gamma = 92.262(5)°$, $V = 5749.4(1)$ Å^3, $Z = 1$, $D_c = 1.22$ g cm^{-3}, $\mu = 0.653$ mm^{-1}, 14989 data with $I > 3\sigma(I)$, $R = 0.117$, $Rw = 0.142$.
Crystal Data for 3 ($(1\cdot ZnBr_2)_2$): Colourless crystals, 173 K, $C_{50}H_{52}Br_2N_2Zn\cdot 4.5C_6H_4Cl_2$, M = 1567.69, monoclinic, space group $C2/c$, $a = 36.3141(4)$, $b = 11.4622(1)$, $c = 36.2867(4)$ Å, $\beta = 107.446(5)°$, $V = 14409.2(3)$ Å^3, $Z = 8$, $D_c = 1.45$ g cm^{-3}, $\mu = 1.828$ mm^{-1}, 8040 data with $I > 3\sigma(I)$, $R = 0.053$, $Rw = 0.080$.
Crystal data for 4 ($(1\cdot ZnI_2)_2$): Colourless crystals, 173 K, $C_{50}H_{54}I_2N_2Zn\cdot 3C_6H_5Cl$, M = 1337.84, monoclinic, space group $C2/c$, $a = 34.2298(5)$, $b = 11.7252(2)$, $c = 34.6599(7)$ Å, $\beta = 117.237(5)°$, $V = 12368.4(6)$ Å^3, $Z = 8$, $D_c = 1.44$ g cm^{-3}, $\mu = 1.566$ mm^{-1}, 8235 data with $I > 3\sigma(I)$, $R = 0.078$, $Rw = 0.091$.
CCDC 199799−199801 (**2**−**4**) 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.

Acknowledgments

We would like to thank the Université Louis Pasteur and the Ministry of Research and Technology for financial support and a scholarship to C. K.

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Received December 17, 2002
[I02682]