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Design, synthesis and solid state structural characterisation of a metallacyclophane formed by a diazadioxamacrocycle bearing two pyridines and silver(I) cation

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Dedicated to F. Mathey on the occasion of his 60th birthday

Abstract

Upon functionalisation of 1,7-diaza-4,10-dioxacyclododecane **2** on both nitrogen atoms by two pyridine units using the *para*-position with respect to the nitrogen of the pyridine, the bismonodentate ligand **1** was obtained and structurally characterised in the solid state by X-ray diffraction on single-crystal. Under self-assembly condition, in the presence of $AgPF_6$, the above mentioned ligand **1** forms the macrotricyclic metallamacrocycle **4** composed of two ligands and two silver cations with linear coordination of both metal cations. The barrel type structure thus obtained was also characterised in the solid state by X-ray diffraction methods. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Pyridine; Silver; Metallamacrocycle; Self-assembly

1. Introduction

Over the last 10 years, the design of metallamacrocycles is a subject of intense interest [1–20]. Metallamacrocycles are cyclic entities obtained upon interconnection of organic ligands bearing coordination sites by metal cations. One may envisage the formation of metallamacrocycles using different strategies. In particular, they may be formed by conventional cyclisation processes using organic transformations based on molecular fragments containing metallic centres coordinated to organic moieties bearing at their extremities complementary reactive functionalities (Fig. 1a). However, so far, the strategy employed is based on cyclisation reactions using complexation processes between organic ligands bearing coordination sites at their extremities and appropriate metal cations (Fig. 1b).

Let us focus on metallamacrocycles containing two metallic centres adopting a linear coordination geometry. In that case, the design of the ligand may be based on two monodentate coordination sites interconnected by an organic moiety. When using flexible spacers connecting the two coordination sites, depending on the conformation of the connecting fragment, in the presence of metal cations, one may expect the formation of either discrete complexes of the metallamacrocycle type for the convergent disposition of the coordination sites (Fig. 2a) or infinite coordination networks for the

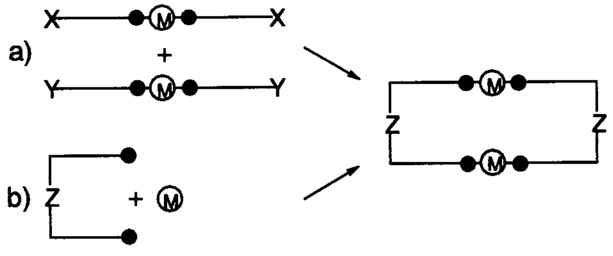

Fig. 1. Schematic representations of the formation of metallamacrocycles composed of two metal centres using either two linear coordination complex bearing at their extremities complementary reactive groups (a) or a bis monodentate ligand bearing at its both ends two coordination sites (b). Whereas for the first case, the metallamacrocycle is formed through an organic reaction, for the second case, the cyclic framework is obtained upon a complexation process.

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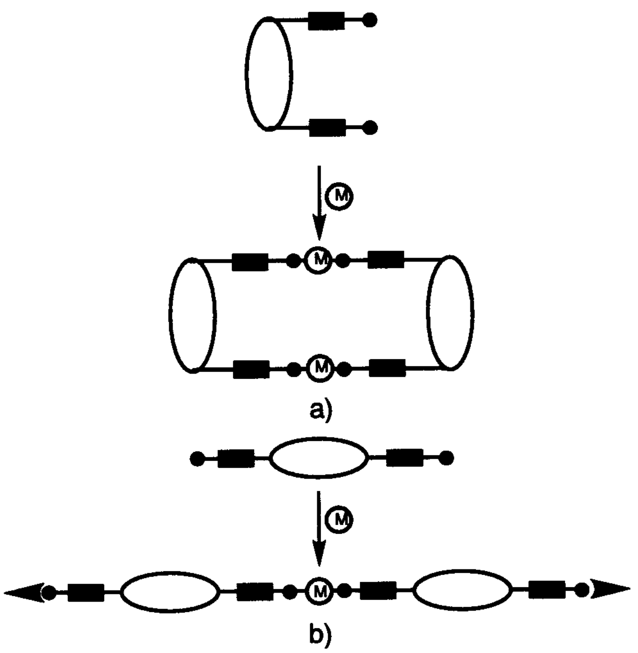


Fig. 2. Schematic representations of the formation of macrotricyclic metallacycles when using a macrocyclic backbone bearing two coordination sites oriented in a convergent fashion and a metal cation adopting a linear coordination geometry (a) or the formation of a 1-D coordination networks when using macrocyclic frameworks bearing two monodentate sites oriented in opposite directions and linearly coordinated metal centres (b).

divergent orientation of the monodentate sites (Fig. 2b).

The design of metallamacrocycle lies on the analysis of the nature of the coordination sites in conjunction with the type of metal cation envisaged on one hand, and structural and conformational features of the spacer connecting the coordination sites on the other hand.

Silver cation (Ag^+) appears to be a rather appealing metal cation since it undergoes reversible binding process with nitrogen containing coordination sites, and it may adopt a linear coordination geometry among a variety of other geometries such as trigonal, T-type, tetrahedral or octahedral. Dealing with the nature of the coordination site, pyridine, often used in the design of metallamacrocycles as well as coordination networks, seems to be an attractive candidate since not only it offers many possibilities in terms of connection to the spacer, i.e. connection at the *ortho*-, *meta*- or *para*-position, but it may also be electronically tuned by the use of appropriately disposed substituents with electron donor or acceptor abilities. Finally, concerning the spacer connecting the monodentate pyridine units, one may use flexible, rigid or a semi-rigid fragments with restricted conformational space. It has been recently demonstrated that a ligand containing two pyridines interconnected by a polyethylene glycol spacer self-assembles in the crystalline phase into a double stranded interwound infinite coordination network in the presence of silver cation [15]. On the other hand, using a cyclophane type derivative, a rigid backbone bearing four pyridines, the formation of a fourfold interpenetrated tridimensional coordination network in the presence of silver cation was demonstrated [16]. Dealing with metallamacrocycles, we have shown that pyridine containing ligands interconnected by medium size diaza macrocycles lead to the formation of metallamacrocycles in the presence of Ag^+ or a Pd(II) complex bearing an ethylenediamine moiety [17]. Finally, using the pyrazolyl units as coordinating centres, the formation of metallamacrocycles with silver(I) [18] or copper(II) [19] was demonstrated.

In the present contribution, we report on the design, synthesis and structural studies of the new ligands **1** based on two pyridine units interconnected by N_2O_2 diaza crown ether **2** and the formation, under self-assembly conditions, of the metallamacrocycle **4** when using Ag^+ cation.

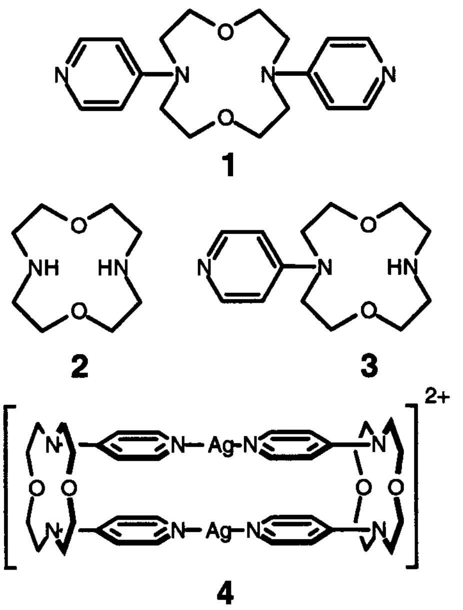
The design of the bis-monodentate ligand **1** was based on the use of two pyridine units as the coordination sites interconnected by the diazadioxa medium size macrocycle **2**. The connection between the pyridine units and the macrocycles was achieved using the two amine functionalities of the macrocycles. The connecting point on the pyridine ring was the *para*-position for electronic reasons. Indeed, ligand **1** may either be regarded as a derivative of the macrocycle **2** bearing two pyridine units or as two *p*-dialkylaminopyridines interconnected by two $-(CH_2)_2O(CH_2)_2-$ fragments. It is worth noting that the latter consideration implies an increase in the basicity as well as coordination ability of the pyridine units owing to the electronic delocalisation of the lone pair of the nitrogen atoms on the pyridine ring. In other terms, the nitrogen atom of the pyridine presents an anionic character with increased electron density [17].

The choice of macrocycles **2** was governed on one hand by the cyclic nature of **2** (medium size cycle) affording a restricted conformational space, and on the other hand, because of the presence of oxygen donor atoms within the backbone of the spacer, which may in addition offer the possibility of further interactions with metal cations.

2. Results and discussion

Compounds **1** (Scheme 1) was prepared by the condensation of 4-chloropyridine in excess with the lithium salt of **2** in dry THF. Compound **2** is commercially available. 4-Chloropyridine, a rather reactive specie, was purchased as its hydrochloride salt and was generated just before use by treatment with NaOH. The lithium salt of **2** was obtained upon treatment with

PhLi in dry THF at 4 °C. The condensation reaction in addition to the desired disubstituted ligands **1** (25% yield) afforded the monosubstituted compound **3** in 6% yield.



Scheme 1.

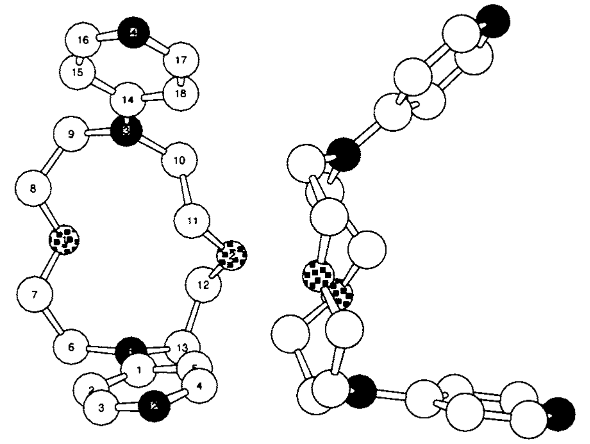


Fig. 3. The X-ray structure of the free ligand **1**. Top (left) and lateral (right) views showing the convergent orientation of the pyridines. H atoms are not presented for clarity. For bond distances and angles see text.

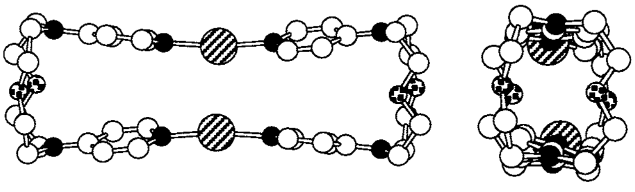


Fig. 4. The X-ray structure of metallamacrocycle **4** ($[\mathbf{1}_2Ag_2]^{2+}$) obtained upon reaction of the ligand **1** and $AgPF_6$. Lateral view (left) and a view along the axe of the barrel type architecture (right). The hexafluorophosphate anions are disordered. H atoms, anions and solvent molecules are not presented for clarity. For bond distances and angles, see text.

Compound **1**, in addition to classical methods, was further structurally characterised in the solid state by X-ray diffraction on single-crystal obtained upon slow evaporation of a $CHCl_3$ solution containing **1** (Fig. 3).

The X-ray study revealed the following relevant features. Compound **1** crystallises in monoclinic system with $P2/c$ as the space group. As predicted, the delocalisation of the lone pair of the nitrogen atoms on the pyridine ring resulted in a pronounced sp^2 character of N1 and N3 centres. Indeed, the N1–C1 and N3–C14 distances, in the range of ca. 1.37 Å, are considerably shorter than Ni ($i = 1$ or 3)–Cj ($j = 3$, 13, 9, 10) distances which are around 1.46 Å (Fig. 3 left). Furthermore, as expected, the average CNC angle for the endocyclic nitrogen atoms varies between 117 and 121°. The consequence of the delocalisation is also reflected by the CNCC dihedral angles between the pyridine rings and C–N1 or C–N3 bonds which are 8.0 and 18.2° for the pyridine ring containing the nitrogen N2 and 2.4 and 2.6° for the pyridine ring containing the nitrogen N4. Concerning the pyridine units, two rather short C–N distances varying between 1.33 and 1.35 Å are observed, whereas the C–C distances vary between ca. 1.37 and 1.40 Å. Dealing with the conformation of the macrocyclic moiety, interestingly, the two pyridine units are convergently oriented, predisposing thus the ligand to form metallamacrocyclic architectures of the barrel type (Fig. 3 right).

The formation of the metallamacrocycle **4** was achieved at 25 °C under self-assembly conditions using a 1/1 ratio of **1** and $AgPF_6$. Suitable single-crystals were obtained upon slow diffusion of a CH_3CN (2 ml) solution containing $AgPF_6$ (5 mg) into a $CHCl_3$ solution (2 ml) containing the ligand **1** (6 mg).

The structure of the metallamacrocycle **4**, of macrotricyclic type, was again investigated in the solid state by X-ray diffraction methods (Fig. 4). Compound **4** crystallises in monoclinic system with $P2/n$ as the space group. In the crystal, in addition to **4**, PF_6^- anions and CH_3CN solvent molecules are present. The crystal is formed by cationic and anionic stacks composed of **4** and PF_6^-, respectively, with CH_3CN molecules occupying the empty space. No specific interactions between cations, anions and solvent molecules are detected. The PF_6^- anionic component is disordered over two positions.

The binuclear metallamacrocycle **4** is formed by interconnection of two ligands **1** by two Ag^+ cations. Each silver cation is almost linearly coordinated to two N atoms belonging to two different ligands **1** with an average Ag^+–N distance of ca. 2.12 Å and NAgN angle of 170.9°. Both ligands **1** forming the cycle adopt almost the same conformation as the one observed for the free ligand with the two pyridine units oriented in a convergent fashion. The metric characteristics (bond distances and angles) are rather close to those observed for the free ligand **1**. As for the free ligand **1**, the nitrogen atoms belonging to the diazadioxa moiety present a pronounced sp^2 character with N–C distances in the range of ca. 1.36 Å and an average CNC angle varying between 116 and 122°.

The two pyridine rings belonging to **1** are almost parallel with a centroid to centroid distance of ca. 3.78 Å. The Ag^+–Ag^+ distance is 3.30 Å.

3. Conclusions

In conclusion, the synthesis of the ligand **1** based on the functionalisation of 1,7-diaza-4,10-dioxacyclododecane on both nitrogen atoms by two pyridine units using the *para*-position with respect to the nitrogen of the pyridine was achieved. The bismonodentate ligand **1**, which may be regarded as two *p*-dialkylaminopyridines interconnected by two $-(CH_2)_2O(CH_2)_2-$ fragments, was shown to form, in the presence of $AgPF_6$, the macrotricyclic metallamacrocycle **4** composed of two ligands and two silver cations with linear coordination of the metal cation. The formation of extended metallamacrocycles using other types of macrocyclic frameworks as the connectors between the two pyridine units and their use as receptor molecules is currently pursued.

4. Experimental

4.1. General details

When commercially available, all reagents were purchased and used without further purification. Reaction solvents were distilled prior to use using standard methods. All new compounds were purified by column chromatography using Kiessel gel 60 (Merck; 43–60 mesh). ^1H and ^{13}C-NMR spectra were recorded using Bruker spectrometers at 300 and 50 MHz, respectively. Microanalyses were performed by the 'Service de Microanalyses de l'Institut Charles Sadron, Strasbourg'.

4.2. Preparation of 4-chloropyridine

About 0.26 g (1.73 mmol) of the hydrochloride salt of 4-chloropyridine was dissolved in water (10 ml) and neutralised to pH 7 with 1 M NaOH. The aqueous phase was extracted with diethyl ether (3 × 20 ml). The organic layer was dried over $MgSO_4$ before it was evaporated to dryness affording thus the 4-chloropyridine as a yellowish liquid. The latter must be stored for a short period of time under argon and in the dark at 0 °C and used within 2–3 h.

4.3. Preparation of compound 1

To a dry THF solution (4 ml) of compound **2** (100 mg, 0.57 mmol) kept at 0 °C, a dry THF solution (4 ml) of phenyl lithium (1.23 mmol) also at 0 °C was added dropwise under argon over a period of 10 min. The mixture was further stirred at 0 °C for another 10 min before 4-chloropyridine (1.72 mmol), generated as mentioned above, was added under argon. The mixture was allowed to reach 25 °C and stirring was further continued for 15 h. To the mixture, water (2 ml) was carefully added while stirring. The mixture was evaporated to dryness affording a brownish solid which was dissolved in CH_2Cl_2 and purified by column chromatography (SiO_2, MeOH–NH_4OH: 98/2) affording the desired compound **1** as a slightly yellowish solid in 25% yield (47 mg) in addition to the monosubstituted compound **3** (6%, 9 mg) as an oil.

Compound **1** (328.42 g mol^{-1}): melting point (m.p.) = 245 °C; ^1H-NMR ($CDCl_3$, 300 MHz, 25 °C): δ (ppm): 3.53 (8H, t, $J = 4.6$ Hz, CH_2N), 3.71 (8H, t, $J = 4.6$ Hz, CH_2O), 6.47 (4H, d, $J = 6.6$ Hz, arom.), 8.17 (4H, d, $J = 6.6$ Hz, arom.); ^{13}C-NMR ($CDCl_3$, 50 MHz, 25 °C): δ (ppm): 52.55 (CH_2N), 68.14 (CH_2O), 107.32, 150.01, 152.87 (arom.); Anal. Calc. for $C_{18}H_{24}N_4O_2$. 0.5 CH_3OH: C 64.45, H 7.54, N 16.25, Found: C 64.77, H 7.35, N 16.58%.

Compound **3** (251.24 g mol^{-1}): ^1H-NMR ($CDCl_3$, 300 MHz, 25 °C): δ (ppm): 2.76 (4H, t, $J = 5.4$ Hz, CH_2NH), 3.56 (8H, m, CH_2N, CH_2O), 3.68 (4H, t, $J = 4.9$ Hz, CH_2O), 6.56 (2H, d, $J = 6.6$ Hz, arom.), 8.18 (2H, d, $J = 4.9$ Hz, arom.).

4.4. Crystal structure characterisation

For crystals of **1** and **4**, 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 both structures, diffraction data were corrected for absorption and analysed using OpenMolen package [20]. All non-H atoms were refined anisotropically.

Compound **1** (colourless, 294 K), $C_{18}H_{24}N_4O_2$, $M = 328.42$, monoclinic, $a = 11.5949(3)$, $b = 13.2755(4)$, $c = 11.6894(4)$ Å, $\beta = 114.118(5)$, $U = 1642.25(9)$ Å^3, $Z = 4$, crystal diameter (mm): 0.20 × 0.18 × 014, space group $P2/c$, DC = 1.33 g cm^{-3}, $\mu = 0.089$ mm^{-1}, 1668 data with $I > 3\sigma(I)$, $R = 0.039$, $R_w = 0.051$.

Compound **4** (colourless, 173 K), $C_{18}H_{24}N_4O_2$ $AgPF_6$ $3CH_3CN$, $M = 704.41$, monoclinic, $a = 13.3222(5)$, $b = 15.4484(4)$, $c = 14.8305(6)$ Å, $\beta = 96.113(8)$, $U = 3034.9(4)$ Å^3, $Z = 4$, crystal diameter (mm): 0.20 × 0.12 × 011, space group $P2/n$, DC = 1.54 g cm^{-3}, $\mu = 0.788$ mm^{-1}, 4809 data with $I > 3\sigma(I)$, $R = 0.033$, $R_w = 0.043$.

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