Exo-ligands based on two *p*-aminopyridine interconnection by tuneable alkyl chains: design, synthesis and structural analysis of silver and palladium metallamacrocycles

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Exo-ligands based on functionalisation of diazacyclic cores of variable size by two pyridines has been achieved; under self-assembly conditions, their ability to form metallamacrocycles in the presence of Pd^{II} or Ag^{II} was demonstrated by X-ray crystallography.

Since the pioneering investigations by Fujita et al.1 and by Saalfranck et al.² on metallamacrocycles considerable efforts have been focused on the design and synthesis of macrocyclic and macrobicyclic structures composed of metal centres connected by organic fragments.3 The majority of metallmacrocycles reported so far are based on bis-monodentate ligands such as 4,4'-bipyridine, pyrimidine, bipyrazine, 4,7-phenanthroline or bis-pyridines interconnected by rigid or flexible spacers.⁴ The same type of ligands has been also used for the formation of coordination networks.5 p-Dimethylaminopyridine (dmap) shows strong alkaline character. We thought that one could take advantage of its peculiar electronic distribution for the design of ligands capable of forming metallamacrocycles. In order to interconnect two or more metals into a cyclic framework, the ligand needs to be of the exo type, *i.e.* it should possess at least two coordination sites oriented in divergent fashion. We have previously reported exo-ligands based on 2,2'-bipyridine derivatives,⁶ catechol units⁷ or of mercaptocalixarene type.8 We now report the design, synthesis and structural analysis of exo-bis-monodentate ligands based on two dmap derivatives and of their binuclear silver and palladium metallamacrocycles.

The design of *exo*-ligands **4–6** (Scheme 1) was based on the interconnection of two *p*-aminopyridine substructures at the 4 position by two tuneable alkyl bridges. Ligands **4–6** may also be regarded as diazacycloalkanes⁹ **1–3** bearing two pyridines. We have previously used cyclic diamines for the design of cyclospermidines and cyclospermines¹⁰ and as backbones connecting donor and acceptor groups.¹¹ The design of **4–6** is rather versatile since, by controlling the size and thus the conformation of the medium size cyclic core and by choosing metals with specific coordination demands, one may investigate structural aspects in the formation of metallamacrocycles under self-assembly conditions.

The synthesis of **4**–**6** was achieved by treating under reflux a mixture of 4-chloropyridine, PhLi and compounds **1–3** in a 1:2.2:2.5 ratio in diethylether.¹² The yields reported are based on 4-chloropyridine. In all cases studied, in addition to **4–6**, the mono-substituted compounds **7–9** were also isolated. Thus,





treatment of 1, 2 or 3^{13} with 4-chloropyridine gave compounds 4 (20%) and 7 (22%), 5 (39%) and 8 (28%) or 6 (13%) and 9 (38%) respectively.

The formation of metallamacrocycles using PdII was achieved by mixing at room temp. an EtOH solution of ligands **4–6** with an aqueous solution of $[Pd(NO_3)_2(en)]$ (en = ethylenediamine). Upon addition of EtOH and Et₂O complexes were collected after several days as colourless crystalline materials. In addition to solution NMR spectroscopy, crystals were analysed by FAB⁺ spectrometry which revealed the formation of a trinuclear complex $\{[4_3\{Pd(en)\}_3(NO_3)_6]\}$ for the ligand 4 and binuclear complexes { $[L_2{Pd(en)}_2(NO_3)_4], L$ = 5 or 6} for ligands 5 and 6. For the $[6_2{Pd(en)}_2(NO_3)_4]$ complex the structure could be determined by X-ray crystallography which indeed revealed the formation of a PdII binuclear metallamacrocycle.‡ Although in the crystal H2O and EtOH molecules were present none of them nor NO₃⁻ anions were clathrated in the cavity of the macrocycle. In principle, owing to the non-symmetric nature of 6, two different isomeric complexes, one with C_{2v} and the other with D_{2h} ideal symmetry may be envisaged (Fig. 1). The difference between these two isomers originates from the mutual orientation of the cyclic cores. However in the solid state, only the complex with C_{2v} symmetry was observed (Fig. 2). The crystal structure showed the following features: (i) two ligands $\mathbf{6}$ bridge two Pd centres by adopting a bent conformation; (ii) as expected, both nitrogen atoms of the diaza core show a marked sp² character with an average C-N-C angle of ca. 120.3° and N-C distance of 1.37 Å demonstrating the delocalization of the nitrogen lone pairs on the pyridine rings; (iii) the coordination geometry around Pd atoms is almost square planar with the N-Pd-N angle varying from 83.7 to 93.5°; (iv) the average N–Pd distance is ca. 2.03 Å; (v) with Pd…Pd distance is 11.35 Å.



Fig. 1 Two possible isomeric structures D_{2h} (top) and C_{2v} (bottom) for the $[6_2{Pd(en)}_2]$ metallamacrocycle



Fig. 2 Crystal structure of the $[6_2{Pd(en)}_2 (NO_3)_4]$ metallamacrocycle (see text for bond angles and distances). Solvent molecules, anions and H atoms are not presented for sake of calrity.



Fig. 3 Two possible isomeric structures D_{2h} (top) and C_{2v} (bottom) for the [6₂Ag₂] metallamacrocycle



Fig. 4 A portion of the crystal structure of the $[6_2Ag_2(PF_6)_2]$ metallamacrocycle (see text for bond angles and distances) showing the formation of an infinite network formed by double Ag-aromatic interactions between consecutive units. Anions and H atoms are not presented for sake of clarity.

The formation of metallamacrocycles using Ag^I was investigated by diffusion at room temp. of a EtOH solution of ligand **6** with an aqueous solution of AgPF₆. After several days colourless crystals of the complex were filtered and further washed with Et₂O. The complex was characterised by NMR and by FAB spectrometry. Furthermore, in the solid state the structure of [**6**₂Ag₂(PF₆)₂] complex was elucidated by X-ray crystallography.‡ Again, as in the above mentioned Pd case, two different isomeric complexes may be envisagted (Fig. 3). Once again the complex with C_{2v} symmetry was observed (Fig. 4). The crystal analysis showed the following features: (*i*) the binuclear metallamacrocycle is formed through the bridging of two Ag^I atoms by two pyridine units belonging to two ligands **6** which adopt a bent conformation; (*ii*) as in the previous case, both nitrogen atoms of the diaza core show a marked sp² character with an average C–N–C angle of *ca*. 121.1° and N–C distance of 1.36 Å; (*iii*) the coordination geometry around Ag atoms is almost linear with an average N–Ag–N angle of *ca*. 175.8°; (*iv*) the average N–Ag distance is *ca*. 2.10 Å; (*v*) the Ag…Ag distance is 3.36 Å; (*vi*) quite interestingly, in the crystal the metallamacrocycles form a one dimensional network through four strong silver–aromatic (pyridine) interactions per unit with an average Ag–centroid distance of 3.43 Å (Fig. 4).

In conclusion, it has been demonstrated that a class of exo ligands based on the interconnection of two *p*-aminopyridines forms by self-assembly metallamacrocycles in the presence of Pd^{II} or Ag^I metals. A systematic investigation on the role of the conformation of the cyclic core is under current investigation.

Notes and References

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[‡] *Crystallographic data*: [6₂{Pd(en)}₂(NO₃)₄] (colorless, 173 K): C₁₉H₃₀N₆Pd·4NO₃·2C₂H₅OH·5H₂O, M = 1328.02, monoclininc, space group *P*2₁/*c*, a = 13.005(2) b = 16.532(2), c = 13.622(1) Å, U = 2927(1) Å³, $\beta = 91.603(9)^\circ$, Z = 2, $D_c = 1.34$ g cm⁻³, MACH3 Nonius, Mo-Kα, $\mu/\text{mm}^{-1} = 0.657$, 4549 data with $I > 3\sigma(I)$, R = 0.057, $R_w = 0.075$.

[**6**₂Ag₂(PF₆)₂] (colorless, 173 K): C₃₄H₄₄N₈Ag₂·2PF₆, M = 1070.45, monoclinic, space group $P2_1/c$, a = 7.6250(2), b = 23.5140(9), c = 10.9360(4) Å, $\beta = 93.105(7)^\circ$, U = 1957.9(2) Å³, Z = 2, $D_c = 1.82$ g cm⁻³, Nonius Kappa CCD, Mo-Kα, μ /mm⁻¹ = 1.164, 2958 data with $I > 3\sigma(I)$, R = 0.053, $R_w = 0.073$. CCDC 182/885.

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1626 Chem. Commun., 1998