Metallacyclophanes formed by a tetrapyrazolyl ligand and copper(II) cation

Abdelaziz Jouaiti, Marielle Loï, Mir Wais Hosseini* and André De Cian

Laboratoire de Chimie de Coordinaiton Organique, Université Louis Pasteur, F-67000 Strasbourg, France, UMR CNRS 7513. E-mail: hasseini@chimie.u-strasbg.fr

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Using a tetrakis(pyrazolyl)benzene ligand and $CuCl_2$ or $Cu(CF_3SO_3)_2$ salts, binuclear metallamacrocycles of cyclophane type have been exclusively obtained; structural characterisation by X-ray on single-crystal reveals that in both cases, chloride or triflate anions are coordinated to Cu metal centres adopting a square pyramial coordination geometry.

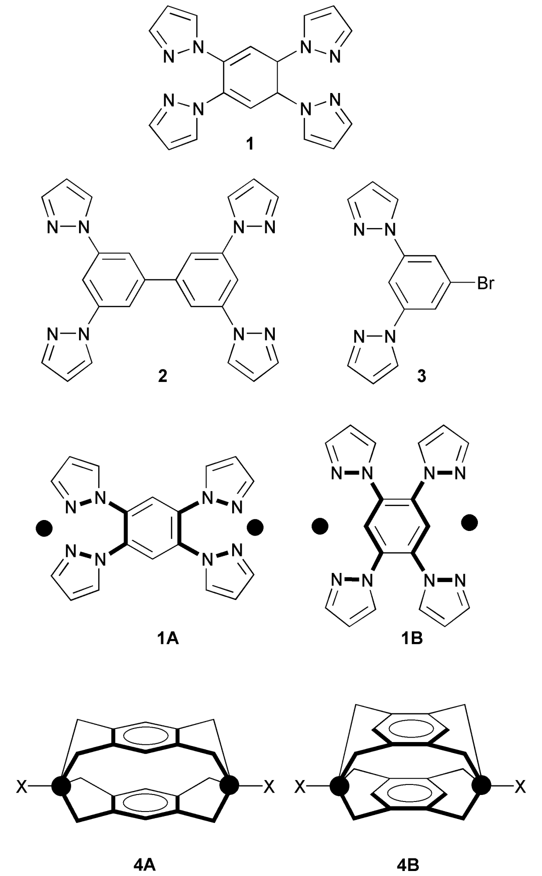
Metallamarocycles, macrocyclic frameworks based on interconnection of organic ligands by metal cations, have been attracting much attention over the past decade. Although the first examples were reported by Saalfrank *et al.*[1] and Fujita,[2] many other groups are now active in the design and synthesis of metallamacrocyles.[3] However, as connecting metallic centres the majority of examples reported so far are based on the use of diamagnetic transition metals such as Pd(II) and Pt(II) requiring square coordination geometry. Thus, using these metals, a variety of metallamacrocycles has been reported using ligands such as 4,4′-bipyridine, pyrimidine, bipyrazine, 4,7-phenanthroline or bis-pyridines interconnected by rigid or flexible spacers.[4] Using pyrazolyl based ligands, we have previously reported the formation of metallamacrocycles and metallatubulanes.[5]

Here, we report the design of new ligands based on pyrazolyl units as coordination sites and its self-assembly into binuclear metallamacrocycles using pentacoordinated paramagnetic Cu(II) cation.

Ligands **1** and **2** (Scheme 1), both based on aromatic cores (benzene or biphenyl) and bearing four pyrazolyl units, are designed to act as tetradentate ligands. For ligand **1**, two different arrangements of the coordination sites may be envisaged leading to either a seven (**1A**) or an eight membered ring cyclic system (**1B**) upon chelating to metal cations (Scheme 1). In both cases, owing to the disposition of the coordination sites ligand **1** may form metallamacrocyles in the presence of metals requiring square, octahedral or square pyramidal coordination geometry. For the latter case, the two possibilities (**4A** and **4B**) are shown (Scheme 1). Ligand **2** was designed as an extended analogue of ligand **1** thus allowing an increase in the size of the metallamacrocycle.

Ligand **1** was first prepared in 8% yield by reacting 1,2,4,5-tetrachlorobenzene with sodium pyrazolate in DMF at 95 ° C for 3 d. The yield could be increased to 68% by using 1,2,4,5-tetrabromobenzene and under reflux for 72 h. Pure compound **1** was obtained as a colourless solid after chromatography (SiO_2, CH_2Cl_2–MeOH) and was characterised by X-ray crystallography† (Fig. 1) which revealed the following relevant bond distances and angles (d_{NN} = 1.37 Å, $d_{C(Ph)N}$ = 1.42 Å; NNCC dihedral angles of −25.8 and −77.2°). Ligand **2** was prepared by a nickel coupling reaction using $NiBr_2(PPh_3)_2$[6] in the presence of Zn and NEt_4I in THF using compound **3** as the starting material. The latter was obtained upon treatment of 1,3,5-benzene by sodium pyrazolate in DMF at 95 °C for 4 d in 22% yield after chromatography [Al_2O_3, CH_2Cl_2–hexane (8/2)].

Cu(II) was selected as the metal ion because of its paramagnetic nature and the fact that it forms pentacoordinated complexes. Both the chloride and triflate Cu(II) complexes have been obtained as single-crystals upon slow diffusion of a MeOH solution of $CuCl_2$ or $Cu(OTf)_2$ (5 mg) into a $CHCl_3$ solution of ligand **1** (2 mg). For both complexes, their structure was investigated in the cystalline state by X-ray crystallography.



Scheme 1

The reaction of **1** and $CuCl_2$ in $CHCl_3$–MeOH afforded a green crystalline material which was structurally characterised by X-ray diffraction (Fig. 2).† The solid contains the complex unit [$\mathbf{1}_2Cu_2(Cl_2(CuCl_4)_2)$] and two MeOH and $CHCl_3$ solvent molecules with no specific interactions with the complex. The cationic part of the complex is indeed a metallamacrocycle composed of two ligands **1**, two Cu(II) cations and two Cl^-

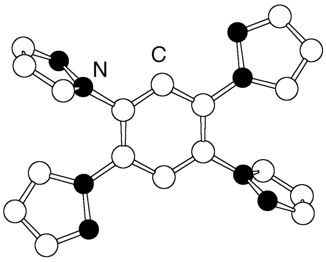


Fig. 1 The X-ray structure of free ligand **1**. H atoms are omitted for clarity, for bond length and distances see text.

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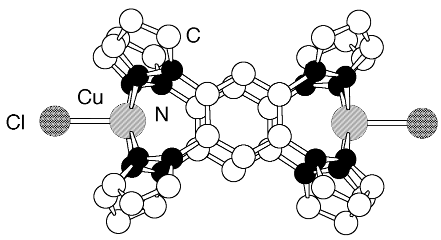

Fig. 2 The X-ray structure of the metalloamacrocycle $[\mathbf{1}_2\mathrm{Cu}_2\mathrm{Cl}_2]^{2+}$ obtained between **1** and CuCl_2. H atoms, anions and solvent molecules are omitted for clarity.

anions. Owing to the parallel orientation of the two phenyl rings, the binuclear metallamacrocycle is of the cyclophane type with an internal cavity of 4.29 × 7.42 Å (Scheme 1). The coordination sphere around the pentacoordinated Cu(II) cations is composed of four nitrogen atoms belonging to two ligands **1** and one chloride anion with a slightly distorted square pyramidal geometry. The two poles of the ligand **1**, composed each of two pyrazolyl moieties (d_{NN} = 1.37 Å, $d_{\mathrm{C(Ph)N}}$ = 1.42 Å; NNCC dihedral angle of 57.8°) and occupying the square base in the coordination sphere around the metal, act as bidentate units and form two seven membered metallarings of type **4A** (Scheme 1) with Cu–N distances of *ca.* 2.01 Å and NCuN angles of 86.9–91.4° (Scheme 1). The axial position is occupied by a Cl anion with Cu–Cl distance of 2.44 Å. The two positive charges on the $[\mathbf{1}_2\mathrm{Cu}_2\mathrm{Cl}_2]^{2+}$ complex are neutralised by a $[\mathrm{CuCl}_4]^{2-}$ anion with d_{CuCl} = 2.283 Å and ClCuCl angle of 90° (Fig. 3).

The $[\mathbf{1}_2\mathrm{Cu}_2(\mathrm{CF}_3\mathrm{SO}_3)_2(\mathrm{CF}_3\mathrm{SO}_3)_2]$ complex was obtained as a blue-violet crystalline solid upon reaction of **1** and $\mathrm{Cu(CF}_3\mathrm{SO}_3)_2$ in CHCl_3–MeOH. The latter complex was also structurally characterised by X-ray diffraction (Fig. 4).† The solid contains the complex unit $[\mathbf{1}_2\mathrm{Cu}_2(\mathrm{CF}_3\mathrm{SO}_3)_2(\mathrm{CF}_3\mathrm{SO}_3)_2]$ and two $\mathrm{CH}_2\mathrm{Cl}_2$ solvent molecules with no specific interactions with the complex. The triflate anions are disordered. The cationic part of the complex of type **4A** (Scheme 1) shows almost identical structural features as the above chloride complex (Scheme 1). Again a metallamacrocycle (internal cavity of 4.16 Å × 7.29 Å) composed of two ligands **1**, two Cu(II) cations and two triflate anions is observed. The coordination sphere around the pentacoordinated Cu(II) cations is, as in the chloride case, comprised of four nitrogen atoms belonging to two ligands **1** and one triflate anion (d_{NN} = 1.38 Å $d_{\mathrm{C(Ph)N}}$ = 1.42 Å; NNCC dihedral angles of −59.6 and 58.9°, Cu–N distances of *ca.* 1.99 Å and NCuN angles of 87.4–92.6°. Interestingly, the axial position is occupied by a triflate anion with Cu–O distance of 2.20 Å. The two positive charges on the $[\mathbf{1}_2\mathrm{Cu}_2(\mathrm{CF}_3\mathrm{SO}_3)_2]^{2+}$ complex are neutralised by two external triflate anions (Fig. 4).

We have previously reported examples of metallatubulanes based on interconnection of metallamacrocyles into infinite 1-D coordination networks with tubular topology.[5,7,8] In relation to this, it may be of interest that, since the two anions occupying the summit of the square pyramid on each Cu centre are oriented in a divergent fashion, by interconnecting the metalloacyclophanes new types of coordination polymers may be obtained using bridging bidentate anionic ligands such as azido or isocyanato anions.

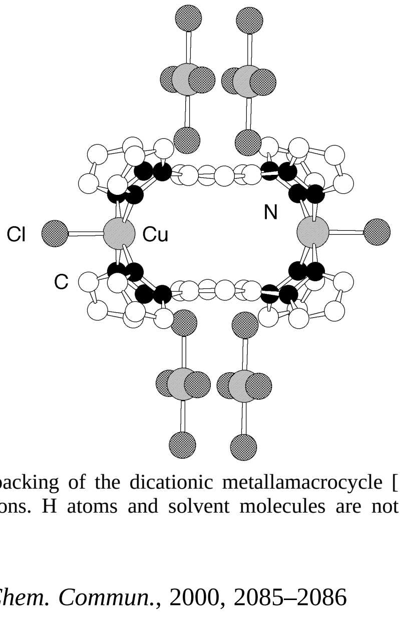

Fig. 3 The packing of the dicationic metallamacrocycle $[\mathbf{1}_2\mathrm{Cu}_2\mathrm{Cl}_2]$ and CuCl_4^{2-} anions. H atoms and solvent molecules are not presented for clarity.

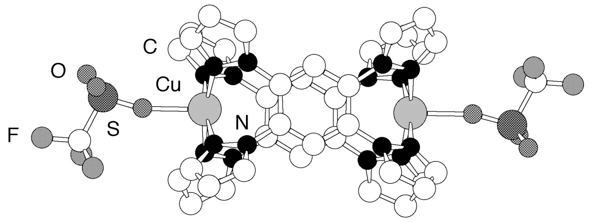

Fig. 4 The X-ray structure of the metallamacrocycle $[\mathbf{1}_2\mathrm{Cu}_2(\mathrm{CF}_3\mathrm{SO}_3)_2]^{2+}$ obtained between **1** and $\mathrm{Cu(CF}_3\mathrm{SO}_3)_2$. Then triflate anions are disordered. H atoms, anions and solvent molecules are omitted for clarity.

In conclusion, the synthesis of paramagnetic binuclear copper metallacyclophanes has been achieved and their solid state structural elucidation revealed that the Cu(II) cation adopts a slightly distorted square pyramidal geometry with the axial position occupied either by chloride or triflate anion. The formation of extended metallacyclophanes using ligand **2** is being currently pursued. Furthermore, the interconnection of the obtained metallamacrocyles leading to paramagnetic coordination networks through the substitution of monodentate coordinated anions by bidentate anions is currently under investigation.

Notes and references

† *Crystal data*: (colourless, 294 K), $\mathrm{C}_{18}\mathrm{H}_{14}\mathrm{N}_8$, M = 342.37, triclinic, a = 6.384(1), b = 7.007(1), c = 9.941(1) Å, $\alpha = \beta$ = 76.00, γ = 80.00, U = 416.5(2) Å^3, Z = 1, space group $P\bar{1}$, D_{c} = 1.36 g cm^{-3}, μ = 0.089 mm^{-1}, 1508 data with $I > 3\sigma(I)$, R = 0.040, R_{w} = 0.0649. $[(\mathbf{1}_2\mathrm{Cu}_2\mathrm{Cl}_2(\mathrm{CuCl}_4))]$, (green, 294 K), $2(\mathrm{CuClC}_{18}\mathrm{H}_{14}\mathrm{N}_8)\cdot\mathrm{CuCl}_4\cdot2\mathrm{CHCl}_3\cdot2\mathrm{MeOH}$, M = 1390.91, orthorhombic, a = 10.0302(5), b = 11.3568(6), c = 23.5388(7) Å, U = 2681.3(4) Å^3, Z = 2, *Immm*, D_{c} = 1.72 g cm^{-3}, μ = 1.830 mm^{-1}, 1486 data with $I > 3\sigma(I)$, R = 0.042, R_{w} = 0.052. $[\mathbf{1}_2\mathrm{Cu}_2(\mathrm{CF}_3\mathrm{SO}_3)_2(\mathrm{CF}_3\mathrm{SO}_3)_2]$, (blue-violet, 173 K), $\mathrm{C}_{38}\mathrm{H}_{28}\mathrm{Cu}_2\mathrm{F}_6\mathrm{N}_{16}\mathrm{O}_6\mathrm{S}_2\cdot2\mathrm{CF}_3\mathrm{SO}_3\cdot2\mathrm{CH}_2\mathrm{Cl}_2$ M = 1577.95, orthorhombic, a = 19.7081(7), b = 17.9293(6), c = 17.1966(6) Å, U = 6076.5(6) Å^3, Z = 4, space group *Cmca* D_{c} = 1.72 g cm^{-3}, μ = 1.121 mm^{-1}, 2127 data with $I > 3\sigma(I)$, R = 0.077, R_{w} = 0.096. Data for all 3 structures have been obtained on a Nonius Kappa CCD (Mo-Kα) diffractometer Structural determinations were performed using the Nonius OpenMolenN package.[9] CCDC 182/1781. See http://www.rsc.org/suppdata/cc/b0/b006665f/ for crystallographic data in .cif format.

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