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Novel hetero-bimetallic metalla-macrocycles based on the bis-1-pyridyl ferrocene $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]$ ligand. Design, synthesis and structural characterization of the complexes $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2](Ag^I)_2{}^{2+}/(Cu^{II})_2{}^{4+}/(Zn^{II})_2{}^{4+}$

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The bidentate sandwich ligand $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]$ has been prepared, structurally characterized and employed in the preparation of the novel supramolecular heterobimetallic metalla-macrocycles $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]Ag_2(NO_3)_2\cdot 1.5H_2O$, $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]Cu_2(CH_3COO)_4\cdot 3H_2O$ and $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]Zn_2Cl_4$.

There is a great current interest in the possibility of using organometallic complexes as ligands in the construction of mixed-metal superstructures.[1] A major issue is that of exploiting the topological, electronic and spin properties of metal centres to construct molecular materials in which metal centres communicate *via* coordination bonds or other non-covalent interactions.[2] Joining metal atoms *via* ligands is at the core of the booming field of coordination network chemistry.[3,4] We are interested in applying supramolecular chemistry approaches to organometallic chemistry, with a focus on crystal engineering strategies.[5]

In this paper we report the synthesis and crystal structure characterization of the bidentate complex $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]$, **1**, and its use as a ligand to prepare the novel hetero-bimetallic metalla-macrocyclic derivatives $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]Ag_2(NO_3)_2\cdot 1.5H_2O$, $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]Cu_2(CH_3COO)_4\cdot 3H_2O$ and $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]Zn_2Cl_4$ [abbreviated in the following as $(\mathbf{1}Ag^I)_2{}^{2+}$, $(\mathbf{1}Cu^{II})_2{}^{4+}$ and $(\mathbf{1}Zn^{II})_2{}^{4+}$], obtained by reacting the ligand with $AgNO_3$, $Cu(CH_3COO)_2$ and $ZnCl_2$, respectively.† All compounds were characterized by single crystal X-ray diffraction.‡

Ferrocene-based pyridyl ligands have been studied for the possibility of exploiting their redox properties in various appplications, such as amperometric sensors for metal ions. The focus, however, has been mainly on mono-substituted ferrocenes,[6] while only few examples of bis-substituted ferrocene pyridyl complexes are known.[7] In particular, aminocobaltocenes and aminoferrocenes have been used to form complexes with Zn^{2+} and Co^{2+} metal ions.[7a] Hosseini and co-workers have reported the synthesis and full characterization of metalla-macrocycles containing flexible bis-*p*-aminopyridine bidentate ligands.[8] Our complex **1** can be seen as the organometallic analogue of the bis-pyridine connector used by Hosseini. The extra feature is that the utilization of a preformed complex as a ligand allows preparation of hetero-metallic metalla-macrocycles with two metal centres.

In view of the conformational freedom of the two Cp–pyridine ligands in **1**, we were also intrigued by the question on whether the ligands would have adopted a cisoid or a transoid conformation upon coordination. Whereas the former conformation leads to the formation a finite coordination geometry, *i.e.* to a molecular complex (*vide infra*), the latter might, in principle, lead to an infinite network.

In the solid state **1** adopts an eclipsed conformation. The two pyridine moieties are parallel and slightly tilted with respect to the Cp planes. The complex $(\mathbf{1}Ag^I)_2{}^{2+}$ has been obtained by reacting **1** with $AgNO_3$. The solid state structure of the hetero-bimetallic system is shown in Fig. 1. The eclipsed conformation observed in crystalline **1** is retained in crystalline $(\mathbf{1}Ag^I)_2{}^{2+}$. The two moieties interact directly with the pyridine ligands, with Ag···N distances of 2.125(8), 2.123(8) and 2.145(8), 2.129(8) Å for the two independent interactions, respectively.

The Ag···Ag distance is 3.500(2) Å. This separation is comparable to that observed in other dimeric Ag complexes.[9] The two nitrate anions play different roles in the crystal structure. While one is directly linked to the other nitrate anion *via* a water bridge, the second anion acts as a bridge between dimeric units as shown in Fig. 1, with O···Ag distances of 2.752(9) and 2.870(1) Å, respectively. A similar ion-pairing link between neighbouring complexes has been observed in the complex with Ag^+ and the diazacyclic bis-pyridine *exo*-ligands.[8] Analogously, neutral ligands (1,4-diazabicyclooctane, tetramethylpyrazine and pyrazine) have been used to link silver carboxylate anions in extended networks.[10]

The complex of **1** with copper, $(\mathbf{1}Cu^{II})_2{}^{4+}$, is shown in Fig. 2. Similarly to $(\mathbf{1}Ag^I)_2{}^{2+}$, the Cp–pyridine ligands are in eclipsed conformation and bridge the two Cu atoms. The Cu···Cu separations are 3.428(5) and 3.473(5) Å. Contrary to what is observed in $(\mathbf{1}Ag^I)_2{}^{2+}$, where the bimetallic unit is unsupported by ligands, the Cu···Cu unit in $(\mathbf{1}Cu^{II})_2{}^{4+}$ is supported by two acetate anions. If one considers the additional acetate ion linked to each Cu atom, the coordination around copper can be described as distorted square pyramidal. The outer O atoms of the dangling acetate units are involved in $OH_{water}\cdots O_{acetate}$ interactions with the water molecules, and/or in short $C\text{–}H\cdots O_{acetate}$ interactions with the CH groups belonging to the six-membered rings of the Cp–pyridine ligands.

The complex with zinc, $(\mathbf{1}Zn^{II})_2{}^{4+}$, is shown in Fig. 3. Contrary to $(\mathbf{1}Cu^{II})_2{}^{4+}$ and $(\mathbf{1}Ag^I)_2{}^{2+}$, the constraint imposed by

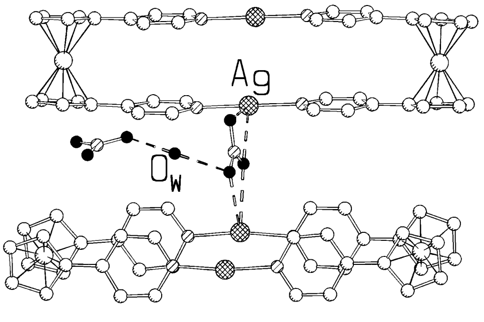

Fig. 1 In complex $(\mathbf{1}Ag^I)_2{}^{2+}$ the two Ag^+ cations interact with the pyridine ligands forming an Fe/Ag^I metalla-macrocycle. O atoms as black spheres; H atoms omitted for clarity.

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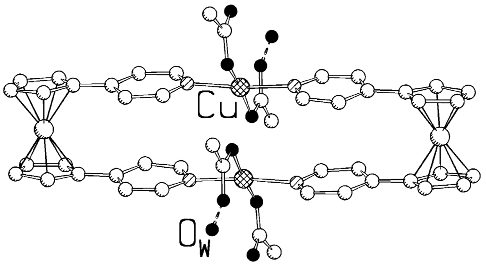

Fig. 2 The Fe/Cu^{II} metalla-macrocycle of **1** with copper, $(\mathbf{1}\text{Cu}^{\text{II}})_2{}^{4+}$. O atoms as black spheres; H atoms omitted for clarity.

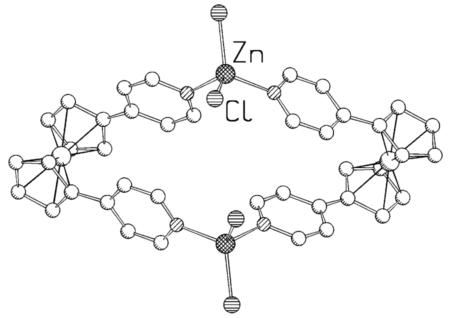

Fig. 3 The Fe/Zn^{II} metalla-macrocycle of **1** with zinc, $(\mathbf{1}\text{Zn}^{\text{II}})_2{}^{4+}$.

the tetrahedral coordination around the zinc centres leads to the formation of a butterfly-type molecule, with the two $ZnCl_2$ units forming the hinge and the ferrocenyl units the wings of the butterfly.

It is interesting to compare the structure of the complex $(\mathbf{1}\text{Ag}^{\text{I}})_2{}^{2+}$ with that obtained by using 1,1′-bis(2-pyridyl)ferrocene.[11a] The location of the N atom does not allow dimerisation but chelation at the Ag atoms. The complex is, however, aggregated in a dimeric unit *via* perchlorate bridges. In a related example, the 1,1′-bis(2-pyridyl)octamethylferrocene is linked to two $PtCl_2(C_2H_4)$ units in a divergent fashion, whereas with Cu^{I} the ligand acts, as in the Ag case, as a chelating ligand.[11b] The utilization of dimetallic units has been demonstrated to be a viable route to obtain a variety of supramolecular and crystal architectures.[12]

In this paper we have shown that preformed organometallic molecules such as **1** with intermolecular bonding capacity can be used to prepare novel mixed-metal macrocyclic complexes. Work is in progress to increase the length of the organometallic spacers and to investigate the role of the counter-ion choice on the complex formation. The presence of network/molecule isomers, whereby the ferrocenyl ligand can take advantage of the conformational freedom around the metal centre to form extended networks rather than finite complexes, is being investigated.

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Notes and references

† All experimental manipulations involving the synthesis of $[Fe(\eta^5\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]$ were carried out under dry argon. Anhydrous solvents (DME, methylcyclohexane, diethyl ether) were purchased from Aldrich in SureSeal® bottles. All other chemicals were obtained from Aldrich and used as received. Synthesis of $[Fe(\eta^5\text{-}C_5H_4C_6H_4N)_2]$: to a solution of 4-bromopyridinium hydrochloride (0.177 g, 0.91 mmol) in dioxane (6.5 mL) was added a 1 M aqueous Na_2CO_3 (4.3 mL) solution to generate 4-bromopyridine, and the suspension was heated to 50 °C. The catalyst $PdCl_2$[1,1′-bis(diphenylphosphino)ferrocene] (0.006 g, 0.007 mmol) was added followed by a mixture of ferrocene–1,1′-diboronic acid (prepared according to literature[13]) (0.100 g, 0.37 mmol) and NaOH(aq) 3 M (0.24 mL) in DME (3 mL). The reaction was refluxed for 2 days. After hydrolysis with ice-water, the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The organic layer was washed with NH_4Cl solution followed by water, dried on Na_2SO_4 and concentrated. The residue was chromatographed on silica gel with CH_2Cl_2/EtOH (95:5) to give 0.065 g of the product as a bright red solid (yield 53%). $(\mathbf{1}\text{Ag}^{\text{I}})_2{}^{2+}$ was obtained by layering a MeOH solution of the $Ag(NO_3)$ (0.006 g, 0.03 mmol, in 5 mL) onto a benzene solution of the ligand 1,1′-bis(4-pyridinyl)ferrocene (0.030 g, 0.09 mmol, in 15 mL). After 2 days the solution was filtered and single crystals were isolated. Similarly, single crystals for complexes $(\mathbf{1}\text{Cu}^{\text{II}})_2{}^{4+}$ and $(\mathbf{1}\text{Zn}^{\text{II}})_2{}^{4+}$ were obtained by layering a MeOH solution of $ZnCl_2$ (0.007 g, 0.05 mmol) or $Cu(CH_3COO)_2\cdot 2H_2O$ (0.007g, 0.03 mmol) over a benzene solution of the ligand **1** (0.037g, 0.1 mmol, in 15 mL). Yields: 63% for $(\mathbf{1}\text{Ag}^{\text{I}})_2{}^{2+}$; 70% for $(\mathbf{1}\text{Zn}^{\text{II}})_2{}^{4+}$; and 68% for $(\mathbf{1}\text{Cu}^{\text{II}})_2{}^{4+}$.

‡ X-Ray diffraction data were collected at 293 K on NONIUS CAD-4 and Bruker Smart CCD diffractometers equipped with a graphite monochromator (Mo-Kα radiation, λ = 0.71073 Å).

Crystal data for **1**: monoclinic, $P2_1/c$, a = 7.746(6), b = 10.462(9), c = 19.738(9) Å, β = 106.60(6)°, V = 1533(2) Å^3, Z = 4, 2694 independent reflections (2778 measured), wR_2 = 0.1786, R_1 = 0.0566. For $(\mathbf{1}\text{Ag}^{\text{I}})_2{}^{2+}$: monoclinic, $P2_1/a$, a = 11.620(3), b = 16.597(8), c = 20.762(6) Å, β = 105.67(2)°, V = 3855(2) Å^3, Z = 4, 6741 independent reflections (6935 measured), wR_2 = 0.1635, R_1 = 0.0504. For $(\mathbf{1}\text{Zn}^{\text{II}})_2{}^{4+}$: orthorhombic, $Pccn$, a = 18.1586(8), b = 14.4554(6), c = 14.4458(1) Å, V = 3791.9(2) Å^3, Z = 4, 2630 independent reflections (26 764 measured), wR_2 = 0.1710, R_1 = 0.0897. For $(\mathbf{1}\text{Cu}^{\text{II}})_2{}^{4+}$: triclinic, $P\bar{1}$, a = 9.9155(7), b = 11.5519(7), c = 23.424(2) Å, α = 85.162(2), β = 90.241(2), γ = 75.431(2)°, V = 2586.7(3) Å^3, Z = 2, 18 329 independent reflections (19 143 measured), wR_2 = 0.2375, R_1 = 0.0996. Metal atoms in $(\mathbf{1}\text{Cu}^{\text{II}})_2{}^{4+}$ (due to heavy decay) and all non-H atoms in the remaining compounds were refined anisotropically. The SHELX97[14a] package was used for structure solution and refinement based on F^2. SCHAKAL99[14b] was used for all graphical representations. CCDC 177935–177938. See http://www.rsc.org/suppdata/cc/b2/b200344a/ for crystallographic data in CIF or other electronic format.

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