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# New route to a face-to-face biscorrole free-base and the corresponding heterobimetallic copper(III)-silver(III) complex<sup>†</sup>

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#### meso-aryl-substituted face-to-face biscorrole Α was synthesised in a two-step reaction and the corresponding homo- and heterobimetallic complexes were obtained and fully characterised.

Metal complexes of face-to-face bismacrocycles containing porphyrins and/or corroles are stimulating continuous endeavor due to their potential applications such as fixation/activation of dioxygen, dinitrogen or dihydrogen.<sup>1,2</sup> The properties of bisporphyrins are altered by changing the bridge and/or the peripheral substituents. Changing the oxidation state of the central metal atom by replacing a porphyrin by a corrole ring gives another freedom degree for tuning the properties of faceto-face systems. Unfortunately, the synthesis of face-to-face biscorroles, especially for the case of asymmetric dimers, is multistep and time consuming.<sup>3</sup>

Here we report a new method for face-to-face biscorrole synthesis, which allows to decrease significantly the number of the reaction steps. Stable monocopper-, biscopper- and bissilverbiscorrole complexes having the metal centers in high oxidation state were obtained and a simplified route to a pure heterobimetallic copper(III)-silver(III) biscorrole was afforded.

The two-step synthesis (starting from easily available and stable compounds) of meso-mesityl substituted biscorrole  $H_{6}-1$  (1 = 4,6-bis[10-(5,15-dimesitylcorrolato)]dibenzothiophene hexaanion) is described in Scheme 1. The synthesis is based on the methods previously reported by Gryko and our group for monocorroles and, in one case, for linear biscorrole.<sup>4</sup> The use of a dibenzothiophene moiety as a rigid spacer is more convenient than for instance the anthracene group which is synthesised according to a multistep reaction.



Scheme 1 Synthesis of biscorrole H<sub>6</sub>-1 and corrole-aldehyde H<sub>3</sub>-2.

The first step of the synthesis is the acid-catalysed condensation of 4,6-diformyldibenzothiophene with four equivalents of 5-mesityldipyrromethane in the presence of TFA. After neutralisation by Et<sub>3</sub>N, the second step—*i.e.* oxidation by DDQ (2,3-dichloro-5,6-dicyano-p-benzoquinone)-is performed. The biscorrole is obtained in 3% yield. The free base is moderately stable and decomposes more rapidly when exposed to light.

Aside from the biscorrole  $H_{6}$ -1, another corrole derivative is detected in the reaction mixture. Indeed, the corrole-aldehyde  $H_3-2$  (7%) results from the condensation of only one aldehyde group with dipyrromethane (Scheme 1) (2 = 4 - [10 - (5, 15 - 15)])dimesitylcorrolato)]-6-formyldibenzothiophene trianion).

The condensation of dipyrromethane with a second aldehyde group seems to be more difficult and probably produces an intermediate which is not very stable in the reaction conditions.

Prolongation of the reaction time or increase of either acid catalyst or substrate concentration consumes the H<sub>3</sub>-2 product, but the formation of  $H_{6}$ -1 is not favoured. Moreover, the more drastic the conditions are the more "scrambling" effect<sup>5</sup> occurs, even for the case of the sterically encumbered mesitylsubstituted dipyrromethane, which is known to minimize this effect. Therefore, milder conditions were used to reduce formation of side products.

Corrole-aldehyde H<sub>3</sub>-2, regarded as a side product, may serve as a starting material for asymmetric bismacrocycle synthesis. This compound is easily available since the synthesis does not require any protection of the aldehyde group and H<sub>3</sub>-2 is easy to separate from  $H_6-1$ . In fact, the corrole-aldehvde may be considered as an intermediate in the synthesis of the symmetric biscorrole  $H_{6}$ -1, but the reaction of this compound with dipyrromethane did not give the expected bismacrocycle. However, when the corresponding copper complex Cu-2 is used (see below), the second corrole moiety formation takes place in 16% yield, leading to the CuH<sub>3</sub>-1 product (Scheme 2). The great advantage of this asymmetric complex synthesis is an easy purification process, as CuH<sub>3</sub>-1 is the only nonpolar reaction product.



Metallation reaction of biscorrole H<sub>6</sub>-1 and the corrolealdehyde  $H_3$ -2 was carried out in mild conditions with copper acetate in the presence of air. The nonpolar orange-brown products Cu<sub>2</sub>-1 and Cu-2 were obtained from H<sub>6</sub>-1 and H<sub>3</sub>-2, respectively, in good yields (about 80%). Unlike the free-base corroles, the complexes are stable and can be also obtained by the condensation reaction of dialdehyde with dipyrromethane in the presence of copper acetate, followed by DDQ oxidation, as already described for free-base corroles. The metallation reaction of H<sub>6</sub>-1 with one equivalent of metal salt was only studied in the copper series. This reaction yielded (for two

<sup>†</sup> Electronic supplementary information (ESI) available: Experimental data. Fig. S1: UV-Vis spectra of Cu<sub>2</sub>-1, Ag<sub>2</sub>-1 and AgCu-1. Table S1: Selected structural data for AgCu-1 and Cu2-1. See http://www.rsc.org/ suppdata/dt/b4/b410249e/

different conditions) an inseparable mixture of  $Cu_2-1$ ,  $CuH_3-1$  and unreacted ligand  $H_6-1$ .

The copper complexes of the studied corroles, which are regarded as very difficult to demetallate even in the presence of strong acids, may be demetallated in the reaction with concentrated HCl and zinc powder. However, this is only achieved in a moderate yield due to the fragile character of the respective free-bases, which lead to non-identified decomposition products.

The free base biscorrole  $H_6-1$  was refluxed under argon in pyridine with 7 equivalents (3.5 per corrole ring) of silver acetate to give  $Ag_2-1$ . These reaction conditions are those followed by Brückner for the preparation of *meso*-(triarylcorrolato)silver.<sup>6</sup> The asymmetric complex AgCu-1 was obtained starting from a monocopper biscorrole CuH<sub>3</sub>-1 in a similar way (Scheme 3). Both silver complexes are bright red-pink, nonpolar and stable.



All the complexes (Cu<sub>2</sub>-1, Ag<sub>2</sub>-1, Cu-2, CuH<sub>3</sub>-1 and AgCu-1) were characterised by MALDI-TOF mass spectrometry, UV-vis spectroscopy and <sup>1</sup>H NMR (see ESI<sup>†</sup>).

The heterobimetallic copper-silver biscorrole AgCu-1 has both cofacially oriented metal centers in rare high oxidation states, namely +3 for each of them. The UV-Vis spectrum of this complex shows features which are close to the superposition of the respective spectra of Ag<sub>2</sub>-1 and Cu<sub>2</sub>-1. This is in accordance with the very poor interaction between both metallocorrole moieties. Similar additivity is shown in the <sup>1</sup>H NMR spectra. For the copper-silver complex AgCu-1, two sets of  $\beta$ -pyrrolic peaks are easily distinguishable for each metallocorrole at room temperature. Those assigned to the silver moiety are narrow and located downfield (9.0-8.4 ppm) compared to Ag<sub>2</sub>-1 (8.9–8.3 ppm). The copper–corrole part of the AgCu-1 complex is marked by broadened and relatively upfield-shifted peaks (7.7-6.8 ppm), as observed for Cu<sub>2</sub>-1 (7.9-6.9 ppm). As a consequence, the diamagnetic character and high oxidation states of both metals are confirmed, as well as the mainly noninteracting character of both cofacial metallocorroles.

Single-crystal X-ray studies of  $Cu_2$ -1 and AgCu-1 revealed the isostructural crystal structures of these complexes.<sup>‡</sup> Their very similar molecular conformations are shown in Fig. 1 (selected structural data are gathered in the ESI<sup>†</sup>).

For Cu<sub>2</sub>-1, the eight Cu–N coordination distances range from 1.883(6) to 1.905(6) Å. They are shorter than those observed for 5,10,15,20-tetraphenylporphyrinatocopper(II), Cu(II)TPP (Cu–N 1.981 Å)<sup>7</sup> and exhibit a similar range of values found in Cu(III) complexes (Cu–N 1.804–1.907 Å).<sup>8</sup> For AgCu-1, the M–N coordination distances range from 1.899(6) to 1.923(6) Å. In both molecular structures it is noteworthy the position of two methyl groups lying inside of the complex cavity. They belong to two different mesityl groups and point to the metal center which is coordinated by the other corrole moiety. The hydrogen-metal distances are 2.72 and 2.85 Å, and 2.58 and 2.66 Å, for AgCu-1 and Cu<sub>2</sub>-1, respectively.

In conclusion, a biscorrole was synthesized according to a very convenient two-step procedure and the corresponding copper and silver complexes stabilizing high oxidation states



Fig. 1 ORTEP drawing of  $Cu_2$ -1 (top) and AgCu-1 (bottom) showing thermal ellipsoids at 50% probability level. Hydrogen atoms have been omitted for clarity.

were obtained. A simple route to asymmetric complexes is also described in this paper.

#### Notes and references

<sup>‡</sup> X-Ray crystallography: single crystals of Cu<sub>2</sub>-1 and AgCu-1 complexes were obtained in the presence of dichloromethane–ethanol. In both cases, all X-ray data were used for direct methods structure determination and full-matrix least-squares refinements on  $F^{2,9}$  Hydrogens were placed at calculated idealized positions and refined with a global isotropic thermal factor as riding atoms.

Crystal data for  $\hat{Cu}_2$ -1·2.5CH<sub>2</sub>Cl<sub>2</sub>·1.5C<sub>2</sub>H<sub>6</sub>O: M = 1652.03, tetragonal, a = 28.0568(6), c = 20.8677(5)Å, V = 16426.7(6)Å<sup>3</sup>, T = 110(2) K, space group  $I\overline{4}$ , Z = 8,  $\mu$ (Mo-K $\alpha$ ) = 0.759 mm<sup>-1</sup>, 15540 reflections measured (all of them unique). Except for CH<sub>2</sub>Cl<sub>2</sub>, the other solvent molecules were found disordered exhibiting partial site occupation factors. The final R(F) was 0.0683 ( $I > 2\sigma(I)$  and 0.1294 (all data). A refinement of racemic twinning was performed, the estimated Flack parameter being 0.47(1). Crystal data for AgCu-1·CH<sub>2</sub>Cl<sub>2</sub>·1.5C<sub>2</sub>H<sub>6</sub>O: M = 1568.97, tetragonal, a = 28.1479(4), c = 20.8620(4) Å, V = 16529.1(5) Å<sup>3</sup>, T = 110(2) K, space group  $I\overline{4}$ , Z = 8,  $\mu$ (Mo-K $\alpha$ ) = 0.635 mm<sup>-1</sup>, 44411 reflections measured, 15026 reflections unique ( $R_{int} = 0.1171$ ). The metals were found disordered between both coordination sites sharing their positions (sofs = 0.578(5)/0.422(5)). The solvent molecules were also found disordered exhibiting partial site occupation factors. The final R(F) was 0.0658 ( $I \ge 2\sigma(I)$ ) and 0.1263 (all data). At convergence, the Flack parameter was -0.02(2). Two accessible voids of 297 Å<sup>3</sup> each and two others of 422 Å3 were respectively found in the unit cells of Cu2-1 and AgCu-1, but residuals did not indicate the presence of further solvent molecules. In both cases the disorder of some CH2Cl2 or C2H6O molecules was unclear. CCDC reference numbers 213082 and 243876. See http://www.rsc.org/suppdata/dt/b4/b410249e/ for crystallographic data in CIF or other electronic format.

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