Heteropolymetallic copper(II)–gold(III) dithiocarbamate [2]catenanes *via* magic ring synthesis†‡

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A rare class of mixed-metal [2]catenane has been assembled *via* magic ring synthesis of dinuclear copper(II) and gold(III) dithiocarbamate macrocycles.

Inspired by their topological beauty and potential uses in the fabrication of prototype molecular switches, machines, motors and sensory devices, the interest being shown in the design and synthesis of interlocked macrocyclic molecules, the catenanes,[1] is ever increasing. In particular, the labile metal–ligand coordination bond has been exploited in the high yield preparations of catenanes isolated under thermodynamic control.[2]

We recently reported on the utility of the dithiocarbamate (dtc) ligand as a coordinating group in the transition metal directed construction of polymetallic nanosized assemblies,[3] macrocycles[4] and cryptands.[5]

In this communication, we report a rare class of mixed-metal catenane[6] with the facile synthesis of a series of novel heteropolymetallic copper(II)–gold(III) dtc [2]catenanes, where the unique combination of copper(II) dtc coordinate bond lability and favourable mixed-metal copper(II)–gold(III) dtc ligand charge transfer effects are responsible for catenane formation.

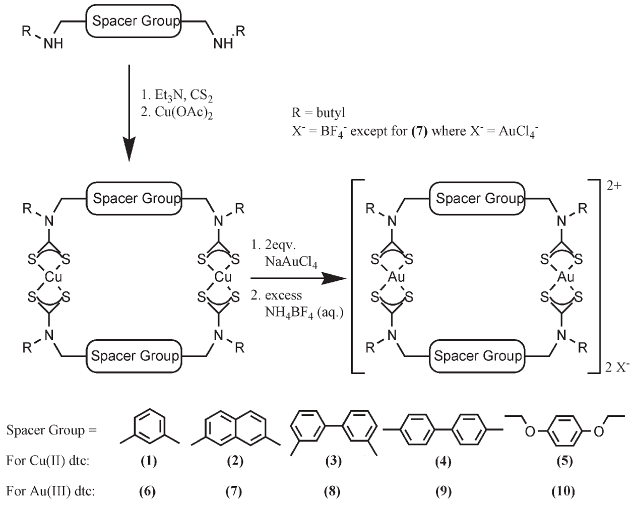
The stimulus for investigating the potential utility of transition metal dtc macrocycles in catenane formation came from the discovery that partial oxidation of a dinuclear copper(II) naphthyl dtc macrocycle **(2)** resulted in the assembly of a mixed-valence tetranuclear copper(II)–copper(III) dtc [2]catenane.[7] The combination of the unique affinity between the electron-rich copper(II) dtc and positively charged electron-deficient copper(III) dtc moieties, coupled with dtc coordinate bond lability are the crucial factors thought to be responsible for catenane formation. In order to further test this hypothesis, it was reasoned that the synthesis of novel heteropolymetallic copper(II)–gold(III) dtc catenanes may result from a magic ring synthesis of appropriately designed dinuclear copper(II) dtc macrocycles and positively charged gold(III) dtc macrocyclic analogues.

The general strategy used for the synthesis of the dinuclear copper(II) dtc macrocyclic compounds involved the metal-directed assembly of the appropriate dtc ligand with copper(II) salts (Scheme 1). The secondary amine precursors were prepared by simple alkylation reactions of the appropriate dibromo or ditosyl spacer compound and primary amine. *In situ* formation of the dtc ligands on addition of CS_2 and base, followed by copper(II) acetate produced the dinuclear copper(II) dtc macrocycles in yields ranging from 25–50%.

Transmetallation reactions of the dinuclear copper(II) dtc macrocycles with sodium tetrachloroaurate afforded the corresponding dinuclear gold(III) dtc macrocycles in yields of 60–80% (Scheme 1). Anion exchange using aqueous ammonium tetrafluoroborate gave the BF_4^- salts of the gold(III) dtc macrocycles except for macrocycle **(7)** where elemental analysis indicated the tetrachloroaurate counter anion could not be exchanged.

Electrospray mass spectrometry (ESMS) was initially used to investigate catenane formation. Equimolar solutions of copper(II) dtc macrocycle **(2)** in CH_2Cl_2 and gold(III) dtc macrocycle **(7)** in MeCN were mixed and analysed by ESMS which revealed the formation of a novel heteropolymetallic Cu(II)–Au(III) catenane **(11)** (Scheme 2 and Fig. 1). The whole range of copper(II) and gold(III) dtc macrocycles were subsequently mixed and their mass spectra recorded (Table 1).

It is noteworthy that the ESMS results in Table 1 provide evidence for the formation of heteropolymetallic Cu(II)–Au(III) dtc [2]catenanes for all 1:1 mixtures of copper(II) macrocycles with the dinuclear gold(III) dtc macrocycle **(7)** containing the naphthalene spacer group except for the *m*-xylyl spaced **(1)** where the macrocyclic cavity is presumably too small for catenation. Since catenane formation was not observed in any of the other 1:1



Scheme 1 General synthesis of dinuclear copper(II) and gold(III) dtc macrocycles.

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† Dedicated to Professor Jean-Pierre Sauvage on the occasion of his 60th birthday.

‡ Electronic supplementary information (ESI) available: experimental procedures and conditions for cyclic voltammetric studies. See http://www.rsc.org/suppdata/cc/b4/b418453j/

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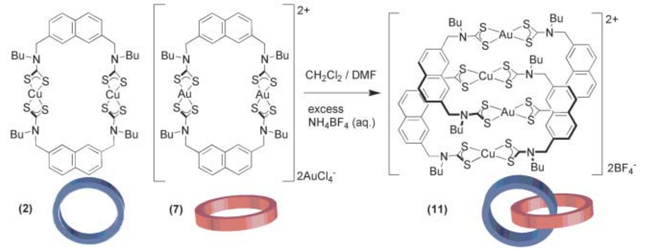


Scheme 2 Synthesis of Cu(II)–Au(III) dtc [2]catenane **(11)**.

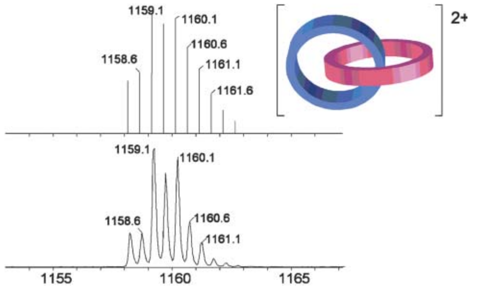


Fig. 1 ESMS spectrum of the Cu(II)–Au(III) catenane **(11)** (bottom); the isotope model (top).

mixtures (Table 1), this suggests it is the unique intramolecular gold(III) dtc–naphthalene–gold(III) dtc separation distance of macrocycle **(7)** in combination with favourable acceptor–donor–acceptor gold(III)–copper(II)–gold(III) dithiocarbamate electrostatic sandwich interactions between the three metal centres that contributes to the production and stability of the respective heteropolymetallic [2]catenanes (Fig. 2a). The two gold(III) dtc centres of macrocycle **(7)** in effect create an ideal complementary electron deficient cavity for the interpenetration of an electron rich copper(II) dtc moiety.

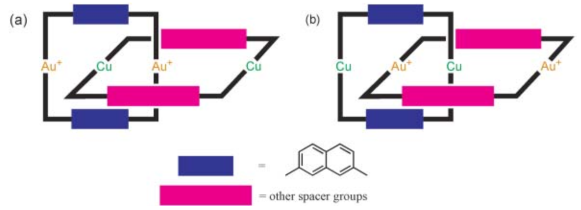
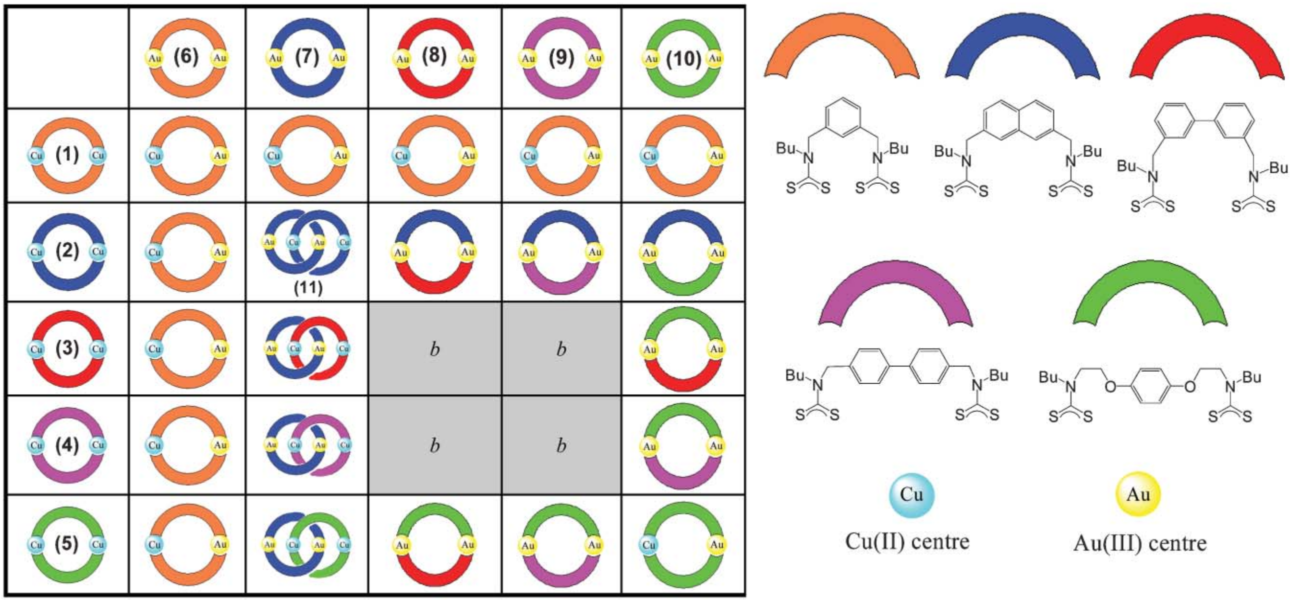


Fig. 2 Diagram illustrating (a) the acceptor–donor–acceptor interaction between the two gold(III) centres of **(7)** and copper(II) macrocycles of appropriate size and (b) the donor–acceptor–donor interaction between two copper(II) centres of **(2)** and gold(III) macrocycles **(8)**, **(9)** and **(10)**.

In contrast, no catenane species were detected by ESMS in 1:1 mixtures of the naphthalene spaced copper(II) dtc macrocycle **(2)** and gold(III) macrocycles **(8)**, **(9)** and **(10)** (Table 1). This indicates that the donor–acceptor–donor copper(II)–gold(III)–copper(II) dithiocarbamate electrostatic interactions are not of sufficient strength to favour and stabilise catenane formation (Fig. 2b).

Interestingly, mixed dtc ligand systems were observed for a number of 1:1 mixtures of copper(II) and gold(III) macrocycles where the respective aryl spacer groups were of similar size (Table 1). For example, the 1:1 mixture of *p*-biphenyl spaced **(4)** and hydroquinone spaced **(10)** gave a mixed *p*-biphenyl–hydroquinone dinuclear gold(III) species. In addition, transmetallation was observed for the *m*-xylyl spaced species where the dtc ligand spacer size is too small for mixed ligand species to form (Table 1). These competing ligand exchange and transmetallation reaction pathways highlight the lability of the transition metal dtc coordinate bond, even in the case of gold(III).

Table 1 ESMS results on catenane formation[a]



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[a] Note that all results shown in this table were obtained from freshly prepared 1:1 mixtures of Cu(II) and Au(III) dtc macrocycles in CH$_2$Cl$_2$–MeCN 1:1 at 290 K. Prominent ESMS signals were observed for all species shown. [b] No new species observed in ESMS.

Attempts were made to isolate Cu(II)–Au(III) catenane species that were detected in the ESMS experiments. Equimolar samples of copper(II) and gold(III) dtc macrocycles were dissolved in dichloromethane and DMF respectively, and the solutions were stirred for two hours at room temperature. The resulting products were anion exchanged with excess aqueous ammonium tetrafluoroborate. Interestingly, only catenane **(11)** was successfully isolated in 84% yield (Scheme 2) and characterised by ESMS, electrochemical investigations, electron paramagnetic resonance studies (*vide infra*) and elemental analysis.[8]

All other mixtures afforded mixed ligand or mixed metal dinuclear macrocyclic species which suggests that the respective [2]catenanes detected by ESMS are kinetic products. This was confirmed by ESMS experiments performed on 1:1 mixtures of dinuclear copper(II) and gold(III) dtc macrocycles over a longer time scale. After initial mixing of the copper(II) macrocycles with the gold(III) macrocycle **(7)**, molecular ions assigned to [2]catenane species were observed. However, allowing the mixtures to stand at room temperature for two hours, the re-recorded mass spectra of the equilibrated solutions no longer contained catenane species. The mass spectra were dominated by thermodynamically favoured transmetallation and ligand exchanged products.

The electrochemical properties of the isolated copper(II)–gold(III) dtc [2]catenane **(11)** were investigated using cyclic voltammetry.‡ The Cu(II)/(III) dtc redox couple of **(11)** consists of a broad quasi-reversible wave ($E_{1/2} = 0.21$ V, $\Delta E = 0.13$ V) suggesting two overlapping waves. In comparison to the CV of dinuclear copper(II) dtc macrocycle **(2)**, the Cu(II)/(III) dtc redox couple of the isolated catenane **(11)** is anodically shifted by 60 mV. An anodic shift of the Cu(II)/(III) dtc redox couple suggests that the presence of the intercalated electron-deficient positively charged gold(III) dtc moiety disfavours copper(II) dtc oxidation.

Solution X-band EPR spectra of the dinuclear Cu(II) dtc macrocycle **(2)** and the Cu(II)–Au(III) dtc catenane **(11)** were recorded at 296 K in dichloromethane–toluene (10:1 v/v) (Fig. 3). Mononuclear Cu(dtc)$_2$ complexes give sharp four-line spectra in fluid solution due to hyperfine coupling (A) of the unpaired electron and the Cu nucleus ($I = 3/2$).[9] The EPR spectrum of dinuclear Cu(II) dtc macrocycle **(2)** is considerably more complex than this (Fig. 3), indicating significant magnetic exchange coupling (J) between the two Cu(II) ions. If $|J| \gg |A|$ then we would expect a 1:2:3:4:3:2:1 septet due to hyperfine coupling to both Cu ions with the splitting half that of the monomer; if $|J| \ll |A|$ we would see a monomer spectrum. In the regime where $|J| \approx |A|$ complicated spectra result; the form of the spectrum in Fig. 3 is consistent with $|J/A| \approx 2$,[10] and detailed simulations are in progress on the fluid and frozen solution spectra to confirm this. Of note is the observation that the EPR spectrum of catenane **(11)** is less complicated than that of **(2)** (Fig. 3), appearing monomeric with $A = 77$ G and $g = 2.044$. Thus, the formation of the Cu(II)–Au(III) dtc catenane insulates the Cu(II) centres and rigidifies the structure leading to the observation of a simple EPR spectrum. In fact, the solution EPR spectrum of **(11)** is comparable to that of a typical mononuclear Cu(II) dtc complex.[9]

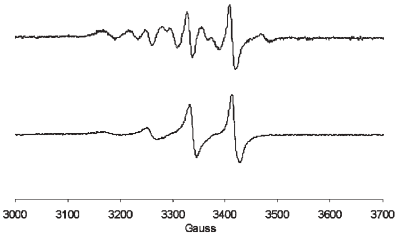

Fig. 3 EPR spectra of dinuclear copper(II) dtc macrocycle **(2)** (top) and copper(II)–gold(III) dtc catenane **(11)** (bottom) in CH_2Cl_2–toluene 9:1 at 290 K.

In summary, a novel class of mixed-metal [2]catenanes has been assembled *via* magic ring synthesis of dinuclear copper(II) and gold(III) dtc macrocycles. In particular, a heteropolymetallic copper(II)–gold(III) dtc [2]catenane containing naphthalene spacer groups was prepared in high yield. A variety of related heteropolymetallic tetranuclear copper(II)–gold(III) [2]catenanes were also identified by electrospray mass spectrometry. Attempts to isolate these interlocked species resulted in the formation of mixed ligand or mixed metal dinuclear macrocycles which suggests these catenanes are kinetic products.

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