A Platinum-linked Cyclic Porphyrin Trimer

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A cyclic trimeric porphyrin host is synthesised from monomer *via* alkyne–platinum–alkyne linkages; binding of the octahedral aluminium tris[3-(4-pyridyl)acetylacetonate] guest ligand into the complementary cavity of the host induces an asymmetry, which is readily detected by NMR spectroscopy.

As part a project aimed at catalytically active porphyrins,[1–3] we have been exploring routes to a series of cyclic oligomers that enclose cavities of a range of sizes but similar shapes. The monomeric porphyrin **1** can be converted efficiently into a mixture of butadiyne-linked cyclic oligomers by direct Glaser–Hay coupling of the terminal alkyne groups,[1] and the outcome of such cyclisations can be controlled by suitable ligand templates.[2] We now report the synthesis of an analogous trimer **4**,† which encloses a larger cavity by virtue of a platinum spacer between the alkynes; we also describe a novel Al-centred ligand and the consequences of its binding within the cavity of **4**.

Condensation of terminal alkynes with *trans*-$Pt(PR_3)_2Cl_2$ in amine solvents using Cu^I-catalysis leads to linear alkyne–Pt–alkyne complexes,[4] while bis-alkynes give high-molecular-weight polymers containing this unit.[5,6] Application of the same reaction to **1** in diethylamine yields the cyclic trimer **4** as the major isolated product in 16% yield, together with the expected intermediates, such as **2** and linear dimers. The corresponding cyclic dimer and tetramer are also formed as minor products but have not been thoroughly characterised. The use of diethylamine in this reaction precludes the future use of amine templates[2] to control the cyclisation, so we have sought alternative reaction conditions. Treatment of **1** with Me_3SnNMe_2 gives virtually quantitative conversion[7] to the $SnMe_3$ derivative **3**, which allows coupling to be carried out in toluene with Cu^I-catalysis in the absence of amine,[6] the yield of **4** again being 16%.

We have studied the binding properties of trimer **4** in some detail. Molecular modelling (MM2) suggests that it has a regular triangular geometry with a Zn···Zn distance of 18 Å, which is about 2 Å larger than the corresponding butadiyne-linked trimer.[2a] *s*-Tri-4-pyridyltriazine, **5**, is calculated to fit almost perfectly into the cavity of the smaller trimer, and as expected the binding is in slow exchange on the ^1H NMR timescale;[1] the binding constant exceeds 10^9 dm^3 mol^{-1}. By contrast **5** should be too small to bind simultaneously to the three zinc centres of undistorted **4**. In accordance with this expectation, the NMR signals of the **4·5** complex at room temperature are broad, and the binding constant measured by UV spectroscopic titration is only 3×10^7 dm^3 mol^{-1}.

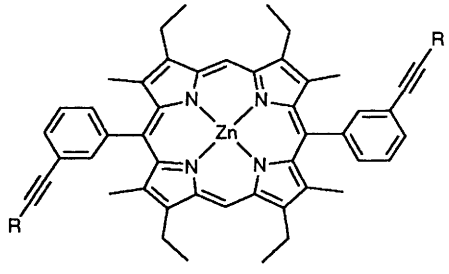
To confirm the optimum binding geometry of **4**, we designed and synthesised the new ligand **6**,‡ which should be complementary, with a N···N distance of 13.3 Å. As expected, the **4·6** complex (Fig. 1) is rather stable, the lower limit for the binding constant being estimated by UV spectroscopy as 1×10^{10} dm^3 mol^{-1}. Despite this high binding affinity, **6** has not yet proved very successful as a template in the preparation of trimer **4** from **3**, the yield only improving to 20% for reasons that are unclear. This is disappointing in the light of our success in templating a wide range of Glaser coupling reactions.[2]

† All new compounds gave satisfactory NMR and mass spectra.

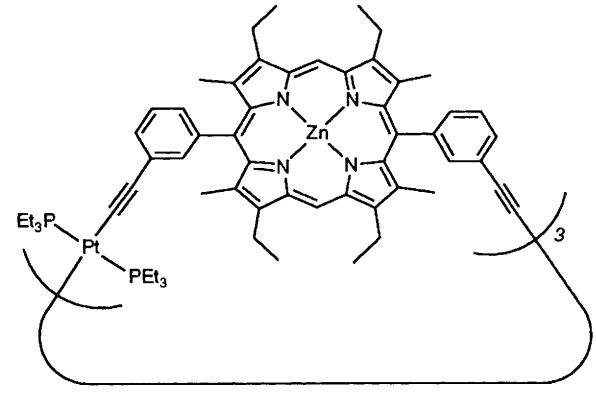
‡ Prepared in good yield by treatment of aluminium trinitrate and 3-(4-pyridyl)pentane-2,4-dione in aqueous methanol with $NaHCO_3$. ^1H NMR: δ H_α, 6H d, 8.63; H_β, 6H d, 7.17; Me_g, 18 H s, 1.90. The dione was prepared by dropwise addition of acetyl chloride to a chloroform solution of 4-methylpyridine at −20 °C.[8]

The **4·6** complex is in slow exchange on the NMR chemical shift timescale, even in the presence of an excess of host or guest. Porphyrin ring currents shift the guest H_α resonances by 6.5 ppm to δ 2.1, while H_β is shifted by 2.3 ppm to δ 4.8 and the guest methyl, Me_g, shifts just 1.5 ppm to δ 0.4. Remarkably, the chirality of the remote octahedral guest ligand is sensed by the host. The porphyrin methyl and ethyl resonances are each split into two signals of equal intensity, while there is only a single *meso* signal. This pattern is to be expected from the molecular symmetry shown in Fig. 1.

An EXSY (NOESY)[9] spectrum of the **4·6** complex acquired in the presence of a 10% excess of ligand confirms the above assignments by showing the rapid free-bound exchange of ligand on the relaxation timescale (Fig. 2). It also shows



1 R = H
2 R = *trans*-$Pt(PEt_3)_2Cl$
3 R = $SnMe_3$



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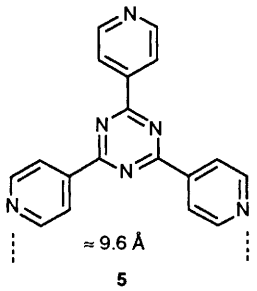

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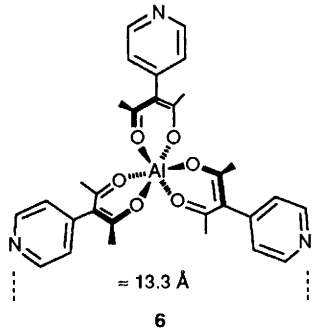

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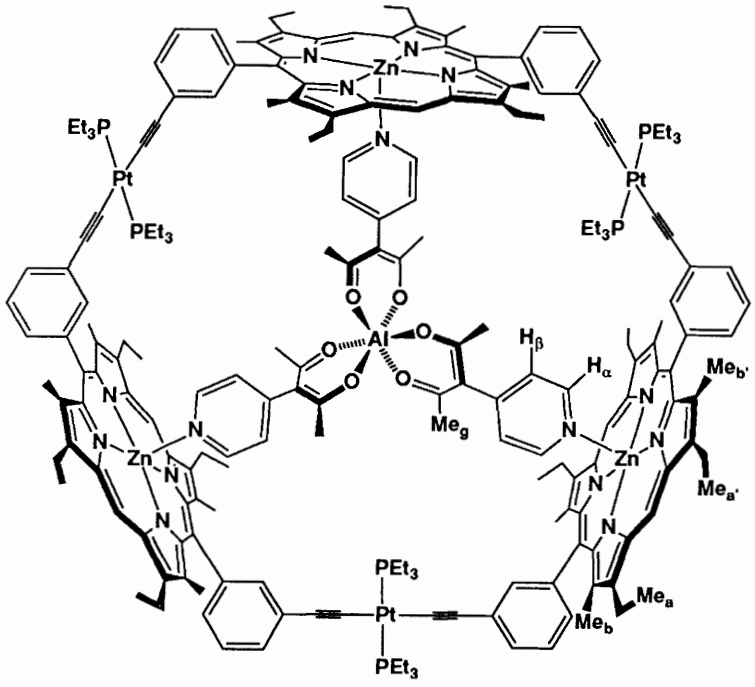

Fig. 1 The **4·6** complex, with diastereotopic methyl groups illustrated on the south-eastern porphyrin

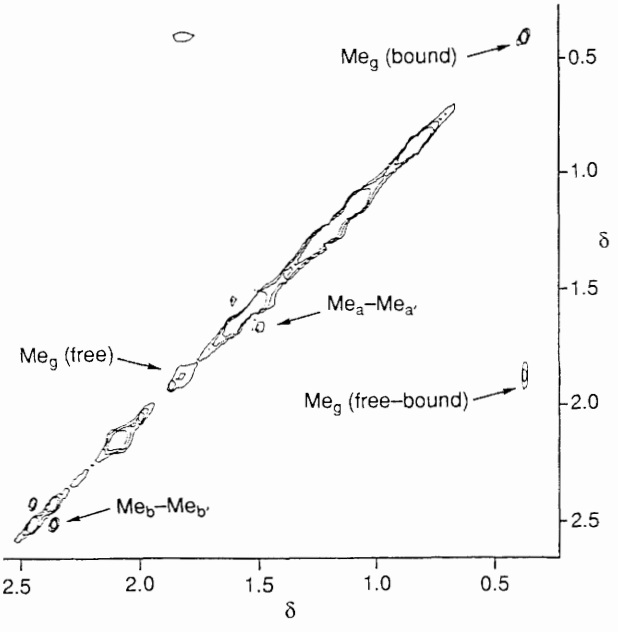

Fig. 2 Part of the 400 MHz ^{1}H NOESY spectrum of the **4·6** complex in the presence of a 10% excess of free ligand **6**; the mixing time was 300 ms, temperature 293 K

exchange of the two diastereotopic triplets (Me_a with $Me_{a'}$) at δ 1.64 and 1.54, and of the singlets (Me_b with $Me_{b'}$) at δ 2.49 and 2.40. This exchange process corresponds to an apparent inversion of configuration at the chiral Al centre but it presumably results from intermolecular exchange of the host with the two enantiomers of the racemic guest.

In summary we have described a new host with the capacity to bind three ligands within an extremely large cavity. Possible catalysis by this and related hosts is being explored.

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