Self-assembly of a supramolecular cube

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In one step, 8 octahedral metal ‘corners’ and 12 ligand ‘edges’ come together to form a supramolecular cube.

Self-assembly[1] templated by metal ions has been used as a strategy to construct compounds with large cavities.[2] Previously, using pyridyl ligands with two coordination sites and square planar metal complexes as corner templates, two-dimensional squares[3] have been synthesised. Three-dimensional architectures result when ligands with a higher number of coordination sites,[4] or metal ions with tetrahedral[5] or octahedral[6] coordination geometries, are used in the self-assembly process. It has been suggested that an appropriate octahedral metal centre could template the self-assembly of a supramolecular cube.[2] Here, we report the one-step self-assembly of 20 components into such a structure.

Reaction of [([9]aneS$_3$)Ru(DMSO)Cl$_2$][7] with a large excess of 4,4-bipyridine, bpy, yielded cationic complex **1** which would appear ideally suited to act as a corner for a supramolecular cube. X-Ray crystallography confirms that the three bpy ligands are oriented at mutual right angles‡ (Fig. 1). As a solid, and in non-coordinating solvents such as dichloromethane and nitromethane, **1** is air and moisture stable. However, solutions of **1** in coordinating solvents are unstable toward solvolysis. Using ^{1}H NMR spectroscopy, the solvolysis of **1** by acetonitrile was monitored. At room temperature, during a process which takes 2 weeks to reach completion, **1** is converted to [([9]aneS$_3$)Ru(bpy)(MeCN)$_2$]$^{2+}$ which has been isolated as its hexafluorophosphate salt and fully characterised by NMR and mass spectrometry, as well as elemental analysis.

Entropic and enthalpic arguments indicate that discrete supramolecular architectures are favoured over polymeric products.[8] Therefore, it was reasoned that the relative lability of **1** could be used to construct supramolecular architectures. If the correct ratio of metal ions and bpy ligands are mixed together in a non-coordinating environment, these components will undergo substitution processes, searching through possible product states to obtain the thermodynamically most stable product. Using nitromethane as the non-coordinating solvent, [([9]aneS$_3$)Ru(DMSO)Cl$_2$] was treated with bpy in an 8 : 12 stoichiometry and the reaction was monitored by ^{1}H NMR spectroscopy.

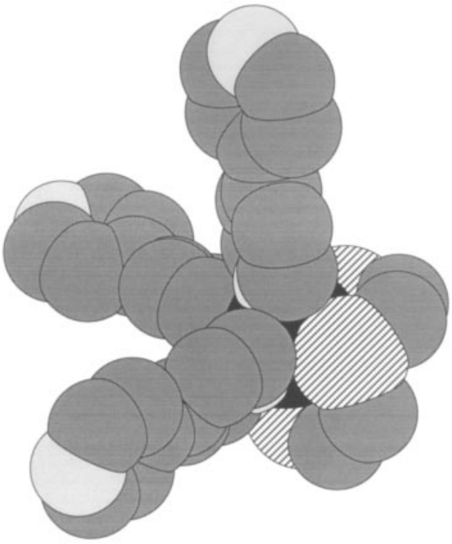

Fig. 1 Space filling model of the crystal structure of cationic complex **1**

Changes in the spectral region due to bpy resonances are highly diagnostic of any self-assembly processes.[3a,4] In contrast to the synthesis of **1**, where the final product is obtained within 3 hours (Fig. 2a), a complex mixture of products is initially formed (Fig. 2b). However, further measurements taken over a period of four weeks (Fig. 2c–e) show a gradual simplification towards a single product, **2.** The slight shift observed in the bpy signals of **2** is due to the hygroscopic nature of the complex, causing the reaction solvent to absorb atmospheric water during the course of the experiment. Addition of diethyl ether to the reaction mixture isolates **2** as a hygroscopic, air and moisture stable, brown–black solid. A variety of data confirm that the structure of **2** is a cube (Fig. 3).

When compared to the ^{1}H NMR spectrum of **1,** it is clear that **2** possesses high symmetry as all the 4-pyridyl rings are now equivalent. Furthermore, the integration confirms that the ratio of bpy ‘edge’ to [9]aneS$_3$ ‘corner’ protons is 1 : 1. This ratio, and the elemental analysis of **2**, is only consistent with closed, highly symmetrical structures such as a cube, or tetrahedron.

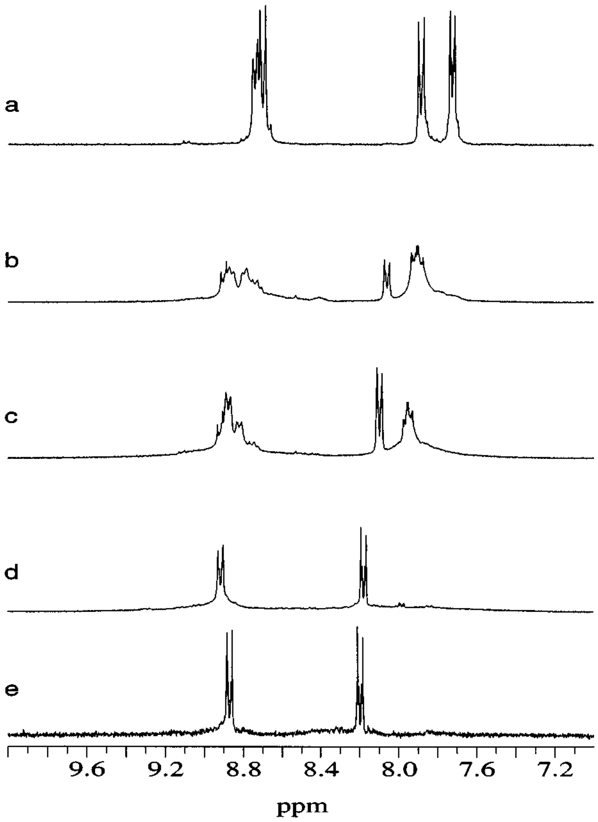

Fig. 2 ^{1}H NMR data for **1** and **2**. a, bpy region (300 Hz in nitromethane) for **1**; b, bpy region (300 Hz in nitromethane) for **2** after 3 days; c, after 1 week; d, after 4 weeks; e, isolated product in MeCN

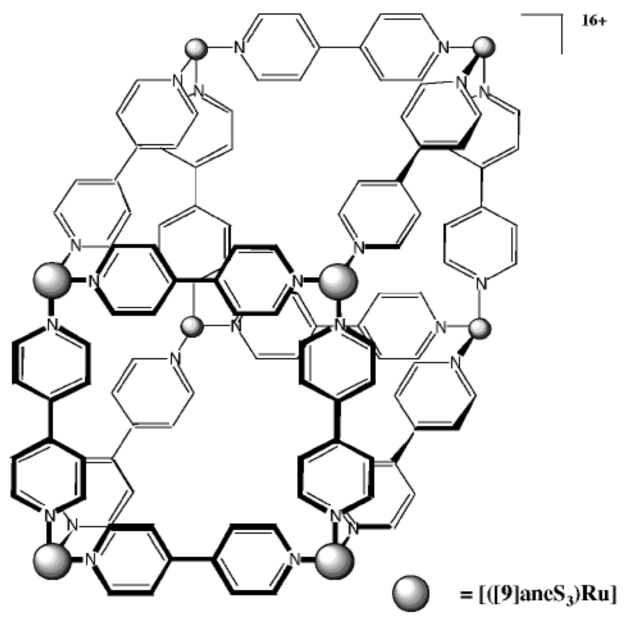

Fig. 3 Structure of **2**

However, structures other than a cube are inconsistent with the crystallographic data for **1** and highly unlikely due to steric reasons**.** For example, a tetrahedral structure would produce strained corners, with three ligands held at mutual 60° angles as they coordinate to each metal ion.

ES-MS studies on **2** show peaks centred on m/z 285 ($[\mathbf{2}\cdot(CF_3SO_3^-)]^{15+}$ requires 285), 351.8 ($[\mathbf{2}\cdot(CF_3SO_3^-)_3]^{13+}$ requires 351.78) 393.5 ($[\mathbf{2}\cdot(CF_3SO_3^-)_4]^{12+}$ requires 393.5), and 502 ($[\mathbf{2}\cdot(CF_3SO_3^-)_6]^{10+}$ requires 502.1). These peaks are not observed by conventional techniques such as FAB-MS and their shapes are consistent with theoretical isotopic patterns.

Unlike **1**, solutions of **2** in coordinating solvents such as acetonitrile are perfectly stable, showing no changes in their ^{1}H NMR spectra over a period of weeks. Again, this anomalous kinetic stability is only consistent with an unstrained cubic structure for **2**, where cooperative interactions within the assembly will 'lock' the ligands into position.

Complexes incorporating Ru^{II} metal centres bridged by oligopyridyl ligands show electrochemical interactions.[9] If the metal centres of **3** are interacting in this manner they will not all oxidise at the same potential. From simple electronic and electrostatic arguments, it is expected that the oxidation of the metal centres in **2** should occur in four steps. During each step a pair of metal ions in diagonally opposed corners of **2** will be oxidised and, for each oxidation, the required anodic potential should be progressively greater.

The electrochemistry of **2** was investigated using cyclic voltammetry. Since all the oxidation processes for **1** and **2** showed varying degrees of irreversibility E_p was obtained using convolution/deconvolution techniques.[10] In contrast to **1**, which displays only one oxidation process, **2** displays three oxidations. The first oxidation wave is at 1.18 V (*vs.* SCE) while the second and third are at 1.38 V and 1.63 V respectively. The first oxidation wave is notably broader than the second and third, consistent with it incorporating two closely overlapping oxidation couples.

The incorporation of electroactive metal centres into the assembly is significant, it opens up the possibility of constructing a variety of novel molecular devices, such as tuneable sensors or multiple state switches. In this context, the host–guest chemistry of **2**, and physical studies on electron/energy transfer within its molecular architecture, are being investigated. The self-assembly of similar structures incorporating other ligands and metal ions will be described elsewhere.

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Notes and References

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‡ *Crystal data* for $C_{40}H_{42}F_{12}N_8P_2RuS_3$: $M = 1122.01$; crystallises from acetonitrile–ethanol as yellow blocks; crystal dimensions $0.43 \times 0.21 \times 0.13$ mm. Triclinic, $a = 10.9913(2)$, $b = 13.2679(2)$, $c = 16.5469(2)$ Å, $\alpha = 88.5080(10)$, $\beta = 80.7680(10)$, $\gamma = 88.1760(10)°$, $U = 2380.06(6)$ Å^3 (based on 10110 reflections, θ range 1.25 to 22.5°), $Z = 2$, $D_c = 1.566$ Mg m^{-3}, space group $P\bar{1}$ (C_i^1, no. 2), Mo-Kα radiation ($\lambda = 0.71073$ Å), μ(Mo-Kα) = 0.615 mm^{-1}, $F(000) = 1136$, $T = 160$ K, 5779 independent reflections [$|F|/\sigma(|F|) > 4.0$]. Refinement converged at a final $R = 0.0697$ ($wR2 = 0.1787$, for all 6156 unique data, 719 parameters) with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density -0.860 and 1.251 e Å^{-3}. A weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0703P)^2 + 16.38P]$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the latter stages of refinement. Data collected were measured on a Siemens Smart CCD area detector with a Siemens LT2 temperature system. Reflections were measured from a hemisphere of data collected of frames each covering 0.3° in ω. Hydrogen atoms were placed geometrically and refined with a riding model (including torsional freedom for methyl groups) and with U_{iso} constrained to be 1.2 (1.5 for methyl groups) $\times$ U_{eq} of the carrier atom. Complex scattering factors were taken from the program SHELXTL.[11] CCDC 182/927.

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