Self-assembly of Rigid-rack Multimetallic Complexes of Rotaxane-type

Hanadi Sleiman,[a] Paul Baxter,[a] Jean-Marie Lehn*[a] and Kari Rissanen[b]

[a] *Laboratoire de Chimie Supramoléculaire, Institut Le Bel, Université Louis Pasteur, 4 rue Blaise Pascal, 67000 Strasbourg, France†*
[b] *Department of Chemistry, University of Joensuu, PL 111, FIN-80100 Joensuu, Finland*

Reaction of copper(I) ions with the oligobipyridine ligands **1** and the macrocycle **2** leads to the self-assembly of the di- and tri-nuclear rigid-rack complexes **3** of rotaxane type, whose nature has been confirmed by determination of the crystal structure of **3b**.

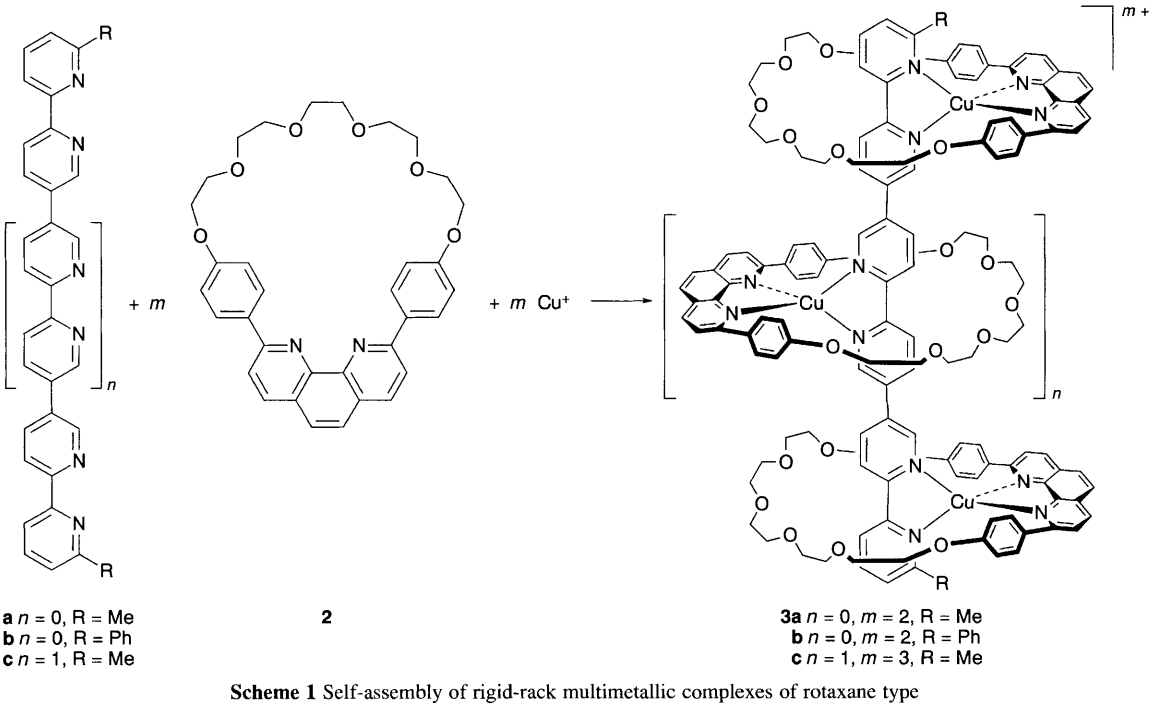
Self-assembly is a process by which organized supramolecular species are spontaneously generated from their predesigned components in high yield and with high specificity.[1] It gives access in a single operation to functional supramolecular architectures that may be of interest for the design of molecular devices performing directional electron and energy transfer. Thus, the self-assembly of inorganic structures of increasing sophistication has been achieved. Our own work has notably been concerned with the self-assembly of double and triple helical metal complexes,[2] of multicomponent, cylindrical complexes[3] and of multimetallic inorganic grids.[4]

We have been interested in the generation of ordered arrays of metal ions displaying geometries of rack,[5] ladder[3b] or grid[4] type. In particular, extended multinuclear complexes based on rigid linear ligands, present well-defined spatial orientation that renders them suitable components of potential molecular devices. The design of a suitable system made use of the rigid linear ligands built on 2,2′-bipyridine (bpy) subunits **1**, available from earlier work,[3] and of a macrocyclic 1,10-phenanthroline (phen) component **2**.[6] Assembly of **1** and **2** by means of metal ions of tetrahedral coordination geometry, notably copper(I) ions, may be expected to yield rigid multimetallic complexes of type **3** (Scheme 1).† A macrocyclic structure **2** was used in order to prevent two such ligands from coordinating to the same copper centre and thus competing with the multicomponent self-assembly process.

The synthetic procedure is described for **3a**. To a solution of **1a** (5.9 mg, 0.0175 mmol) and **2** (20 mg, 0.035 mmol)‡ in 2 ml dichloromethane is added [Cu(MeCN)$_4$][PF$_6$] (13.2 mg, 0.035 mmol) in 2 ml acetonitrile under an argon atmosphere. The dark red–brown solution is stirred at room temperature for 12 h to give **3a** in high yield.§ For the trimetallic species **3c** the complexation was carried out in refluxing acetonitrile for 48 h. Compounds **3a–c** were characterized by ^{1}H NMR including ^{1}H–^{1}H COSY experiments, ^{13}C NMR, FAB-MS and gave the correct elemental analyses.

The construction of complexes **3** was confirmed by the X-ray crystal structure determination of **3b**¶ (Fig. 1), which showed that two macrocycles **2** are indeed threaded onto the linear quaterpyridine (qp) ligand to form a dimetallic rotaxane. The qp ligand in **3b** presents a planar arrangement between the central rings, demonstrating the high degree of spatial organization of such molecules. Complex **3b** possesses a C_2 axis passing through the middle of the central C–C bond of the qp unit and perpendicular to the plane of this ligand. The structure is centrosymmetric and is in the transoid conformation: the pentaoxyethylene fragment of one ligand **2** faces the phen fragment of the other ligand **2** on the qp backbone. The copper(I) centres are encapsulated by the phenyl groups on the 6-position of qp and on the 2- and 9-positions of the phen unit. This would explain the high stability of this complex towards dilution, chromatography§ and reversible electrochemical oxidation.|| The phen moieties and the phenyl groups on the 6-position of the qp are oriented face-to-face and the distance between them is *ca.* 3.4 Å, suggestive of a π-stacking interaction.

Compounds **3** represent rigid-rack complexes of rotaxane type and are formed in high yields by self-assembly. Rotaxanes and polyrotaxanes have recently been the subject of increasing interest owing to the development of efficient methods for their construction,[8–10] in particular using metal-ion templates and ligand **2**.[11]



1a *n* = 0, R = Me
b *n* = 0, R = Ph
c *n* = 1, R = Me

2

3a *n* = 0, *m* = 2, R = Me
b *n* = 0, *m* = 2, R = Ph
c *n* = 1, *m* = 3, R = Me

Scheme 1 Self-assembly of rigid-rack multimetallic complexes of rotaxane type

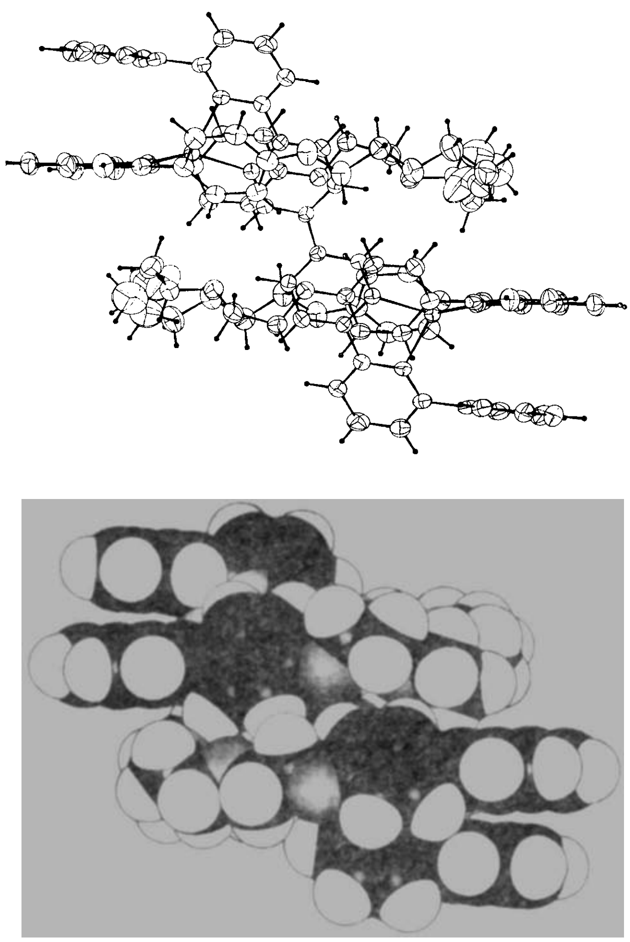


Fig. 1 ORTEP plot (*a*) and space filling representation (*b*) of the crystal structure of **3b**

The generation of the rigid trimetallic rotaxane complex **3c** establishes the generality of this self-assembly process. The structure of **3c** was inferred from the close similarity of its ^{1}H NMR spectrum to the spectra of the dimetallic complexes **3a**,**b**. Each of the phen peaks present in the spectrum of **3a** is doubled into two sets of peaks, of intensities 2 : 1 in the spectrum of **3c**. These correspond respectively to the outer and inner phen units threaded onto the sexipyridine ligand.

The present results represent a general method for the self-assembly of rigid-rack multimetallic complexes of rotaxane type displaying a high degree of spatial organization. The construction of these extended structures illustrates the potential of self-assembly as a highly specific and economical synthetic tool for the generation of large functional architectures. It also provides systems for the exploration of the kinetic and mechanistic features of supramolecular threading processes. Finally, complexes such as **3** may serve as rigid components of potential molecular devices.

We thank Patrick Maltèse for carrying out the ^{1}H–^{1}H COSY studies on complexes **3a**–**c**. H. Sleiman thanks the C.N.R.S for a 1993–94 postdoctoral fellowship.

Received, 29th December 1994; Com. 4/07851I

Footnotes

† URA 422 of the C.N.R.S.

‡ The quaterpyridine and sexipyridine ligands **1** were prepared as described before.[3] The macrocyclic phenanthroline ligand **2** was synthesized by a modification of the literature method.[6]

§ **3a** was formed quantitatively from **1a**, **2** and $[Cu(MeCN)_4][PF_6]$ and is isolated by precipitation from acetone–ether as a dark red solid; **3b** was isolated as a dark red solid in 85% yield by chromatography (silica gel, 1 : 1 acetone–dichloromethane); **3c** was isolated in 90% yield as a dark red precipitate by vapour diffusion of diethyl ether into a filtered acetone solution of the reaction mixture.

¶ Crystals of **3b** were grown by slow evaporation of diethyl ether into a nitromethane solution of **3b**. *Crystal data* for $C_{100}H_{90}Cu_2N_8O_{12}{}^{2+}\cdot 2PF_6{}^-\cdot MeNO_2$ (disordered over two sites)$\cdot H_2O$ (disordered over two sites), dark red crystals, $M_r = 2091.94$; triclinic, space group $P\bar{1}$ (no. 2); $a = 1267.8(6)$, $b = 1404.6(8)$, $c = 1493.7(8)$ pm, $\alpha = 75.77(5)$, $\beta = 81.17(4)$, $\gamma = 79.55(4)°$; $V = 2518(2) \times 10^6$ pm^3, $Z = 1$; $D_c = 1.369$ g cm^{-3}; Mo-Kα ($\lambda = 0.7107$ Å); $\mu = 0.54$ mm^{-1}; $F(000) = 1080$; $T = 296 \pm 1$ K; crystal dimensions: $0.30 \times 0.30 \times 0.55$ mm; NICOLET R3 diffractometer; corrections: Lorentz and polarization, empirical absorption correction (DIFABS[7a]) with minimum and maximum correction coefficients 0.715 and 1.185; $2\theta = 3–50°$; *hkl* range: $h = -14 \rightarrow 15$, $k = -15 \rightarrow 16$, $l = 0 \rightarrow 17$; 9374 measured (1429 I or $\sigma I < 0$), 7596 unique reflections ($R_{int} = 0.055$), 4209 with $I > 3\sigma I$. The structure was solved using SHELXS.[7b] Refinement: full-matrix least squares, 655 parameters, $R = 0.067$, $R_w = 0.079$ $\{w = w'. [1.0–(\Delta F/6\sigma F)^2]^2$, where w' = Chebychev polynomial for F_c with three coefficients (1.22, 1.23 and 0.705)$\}$, all non-hydrogen atoms refined anisotropically, H atoms calculated to their idealized positions (C–H = 1.00 Å) and included in the final structure factor calculations with fixed isotropic temperature factors ($U = 0.08$ Å^2) but not refined (CRYSTALS[7c]). Some geometrical restraints were used for the disordered (occupancy 0.5) nitromethane molecule: C–N 1.450(1), N–O 1.150(1) Å and C–N–O and O–N–O 120.0(1)°. Rather high residual electron density was treated as a disordered H_2O molecule with occupancy factor 0.5 (H-atoms could not be located nor calculated). $S = 1.06$. Convergence, max. shift/error < 0.10. A final difference map displayed no electron density higher than 0.74 e Å^{-3}.

Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at The Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

|| Preliminary electrochemical studies on **3b** (cyclic voltammetry) show a reversible oxidation peak at +0.21 V and a reduction peak at −1.94 V (*vs.* ferrocene); C. Arana, unpublished results

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