80 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 22 °C): $\delta = 3.55$ (16 H, m), 3.70 (8 H, t, $J = 3.2$ Hz), 4.00 (4 H, t, $J = 3.2$ Hz), 4.07 (4 H, t, $J = 3.2$ Hz), 4.21 (3 H, s), 5.77 (2 H, s), 6.44–6.47 (3 H, m), 6.60 (1 H, s), 6.80 (2 H, s), 7.10 (1 H, t, $J = 3.6$ Hz), 8.69 (2 H, d, $J = 6.4$ Hz), 8.72 (2 H, d, $J = 6.4$ Hz), 9.25, (2 H, d, $J = 6.4$ Hz), 9.48(2 H, d, $J = 6.4$ Hz); elemental analysis calcd for $C_{40}H_{52}N_2O_{10}P_2F_{12}$: C 47.63, H 5.00; found: C 47.35, H 5.02.

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[7] The signal corresponding to the methyl group of the heteroditopic molecule in **5** is strongly shifted upfield ($\delta \approx 0.2$) at higher concentration (2.0 M in Figure 1). Similarly, a significant upfield chemical shift is observed for the methyl group of **6** in the ^{1}H NMR spectrum of a 1:1 solution of monotopic components **1b** and **6** ([D$_6$]acetone) at higher concentration (e.g., 2.0 M each). These observations can be explained by the increased concentration of PF_6^- in solution. To demonstrate this experimentally, a solution of **6** in acetone (1.0×10^{-2} M) was mixed with various concentrations of tetrabutylammonium hexafluorophosphate solutions (from 0.1 to 2.0 M) and the ^{1}H NMR spectra were recorded. The higher the concentration of PF_6^-, the greater the upfield chemical shift of the methyl group. On the other hand, the chemical shift of the phenyl group of **6** is independent of the PF_6^- concentration. Therefore, the chemical shifts of H_g (Figure 1) are influenced by complexation, not by the changes of PF_6^- concentration, validating the calculation of p based on the ^{1}H NMR data.

[8] Nearly identical results were obtained by analysis of the NMR signal for H_f.

[9] The expression $n = 1/(1-p)$ assumes that the cyclic species do not contribute to consumption of host and guest sites. In covalent polymer chemistry it is well understood that the percentage of cyclic molecules of any size formed at high concentrations (e.g., 1.0 M) is very small indeed (< 3%) and that linear macromolecules are preferentially formed. For reviews on cyclization versus linear polymerization, see: a) G. Odian, *Principles of Polymerization*, 3rd ed., Wiley, New York, **1991**, p. 73; b) S. C. Hamilton, J. A. Semlyen, *Polymer*, **1997**, *38*, 1685–1691. Therefore, the assumption that the absence of cyclic complexes dramatically increases with concentration is validated.

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[11] Not surprisingly, fibers could be pulled from very concentrated solutions in acetone (> 2.0 M). This observation is indicative of significant linear array extension in the material, consequently giving rise to polymeric properties.

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[13] The solutions were slowly cooled to −95 °C and frozen with an acetone-ethanol/liquid nitrogen bath. The solvent was then removed under high vacuum to obtain red-orange solids. The ^{1}H NMR spectra of 0.1 and 1.0 M solutions in acetone at lower temperatures revealed that the chemical shifts of H_g observed at −20 °C down to slightly above the freezing temperature of the solvent (−94 °C) were unchanged at $\delta = 5.944$ and 5.862, which correspond to n values of 4.3 and 14, respectively.

[14] A 5.0×10^{-1} M solution of **3** in acetone ($n = 5.6$ Table 1) was mixed with the matrix (3-nitrobenzyl alcohol) on the probe. The spectrum was immediately recorded in the positive-ion mode. The relative intensities for the $[M_4 - PF_6]^+$, $[M_3 - PF_6]^+$, and $[M_2 - PF_6]^+$ peaks were 0.29, 1.4, and 22% of the base peak $[M - PF_6]^+$, respectively.

Toposelective and Chiroselective Self-Assembly of [2 × 2] Grid-Type Inorganic Arrays Containing Different Octahedral Metallic Centers

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Katharina Fromm, and Dieter Fenske

The self-assembly of specific supramolecular architectures from a set of organic ligands and metal ions results from the processing of the structural information stored in the ligands by metal ions operating through the algorithm defined by their coordination geometry.[1] It implies the design of ligands presenting suitable features (such as nature, number, and disposition of binding sites) and the choice of appropriate metal ions.

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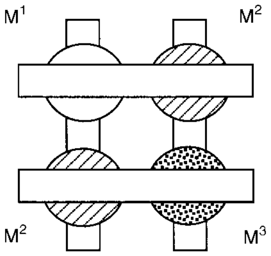
A great variety of complex inorganic architectures have been obtained that may be considered to follow this concept,[1, 2] including, in our own laboratory, double- and triple-helical complexes[1, 2b, 3, 4] as well as rack-[5] and grid-type[6, 7] arrays of metal ions. A higher level of complexity is reached with multicomponent self-assembly of several ligands and metal ions of different types, as in the formation of multicompartmental cylindrical cages.[1, 2a, 8] Ligands made up of different coordination subunits may spontaneously generate species containing different metal ions at specific locations, as has been obtained, for instance, in helicates[9] and in large multicomponent arrays.[10]

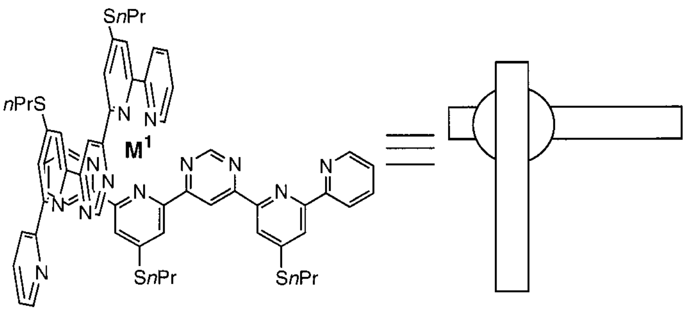
On the other hand, there is a need for strategies providing toposelectivity, that is, strategies allowing the controlled introduction of given metal ions at specific sites and eventually in a given spatial and temporal sequence to form a complex architecture. They may involve sequential assembly procedures and/or protection/deprotection techniques. We now report such a strategy for the synthesis of the inorganic grid-type structures **1a–e**, which contain different metal ions at specific locations. With four metal ions of two types, [2 × 2] grid-type structures may exist as either *anti* or *syn* topoisomers. The controlled generation of the *anti* structures **1a–d** represents an important step towards selecting and addressing individual positions in metallic arrays, and in the design of supramolecular species exhibiting tailored electrochemical, photochemical, and magnetic properties.



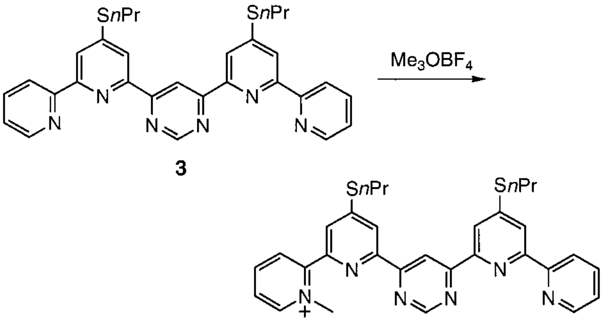
1a $M^1 = M^3 = \mathrm{Ru^{II}}$ $M^2 = \mathrm{Fe^{II}}$
1b $M^1 = M^3 = \mathrm{Ru^{II}}$ $M^2 = \mathrm{Co^{II}}$
1c $M^1 = M^3 = \mathrm{Os^{II}}$ $M^2 = \mathrm{Fe^{II}}$
1d $M^1 = M^3 = \mathrm{Os^{II}}$ $M^2 = \mathrm{Ni^{II}}$
1e $M^1 = \mathrm{Ru^{II}}$ $M^2 = \mathrm{Fe^{II}}$ $M^3 = \mathrm{Os^{II}}$

The self-assembly of [2 × 2] grids from ditopic ligands possessing terpyridine-like binding sites and four identical octahedral metal ions has been described.[5] Complexes **1a–d**, which each contain two different pairs of octahedral metal ions located at opposite corners, were obtained by reaction of the corresponding ruthenium(II) or osmium(II) precursor **2a** or **2b** with a second metal ion ($\mathrm{Fe^{II}}$, $\mathrm{Co^{II}}$, $\mathrm{Ni^{II}}$). To avoid scrambling of the metal centers, it is necessary to introduce the metal ions sequentially in order of increasing lability of the coordination center formed. For this reason, ruthenium(II) and osmium(II) were introduced first.

Different strategies were employed to obtain **2a** and **2b** from ligand **3**.[11] In the case of **2a** it was necessary to proceed by protection of one of the two binding sites by monomethylation of **3** with trimethyloxonium tetrafluoroborate in refluxing 1,2-dichloroethane[12] to give **4** [Eq. (1)]. Methylation of the terminal pyridine heterocycles in **3** was expected to be favored since reaction at the internal pyridine rings is subject to steric hindrance and the pyrimidine nitrogen atoms are less nucleophilic. A small amount of ligand methylated at both terminal pyridine rings was also formed, but could be easily separated by chromatography. The reaction of **4** with $\mathrm{RuCl_3}$ in ethanol/water followed by demethylation with excess diazabicyclo[2.2.2]octane (DABCO)[11] in refluxing acetonitrile affords **2a** as a dark purple solid after purification by chromatography (alumina, acetonitrile/toluene 1/1).



2a $M^1 = \mathrm{Ru^{II}}$
2b $M^1 = \mathrm{Os^{II}}$



3

4

(1)

In contrast, the reaction of ammonium hexachloroosmate with two equivalents of **3** in refluxing ethylene glycol proceeded smoothly to afford directly **2b** (40% yield after chromatography). The higher kinetic inertness of $\mathrm{Os^{II}}$ complexes relative to $\mathrm{Ru^{II}}$ complexes may allow the reaction to be stopped after complexation of one metal ion.

Addition of $\mathrm{Fe(BF_4)_2}$ in acetonitrile to a solution of **2a** or **2b** resulted in a gradual color change from deep purple to dark green over a period of a few minutes. Isolation and purification of the complexes formed yielded **1a** and **1c** as dark green solids in 90 and 70% yield, respectively. The composition of the complexes was verified by fast atom bombardment mass spectrometry (FAB-MS), whereas the diagonal (*anti*) arrangement of the metal ions was confirmed by ^{1}H NMR spectroscopy, which showed different environments for the two binding sites of **3** in the complexes.[13]

During the purification, it was noted that the complexes have an affinity for the chloride anion; the complete exchange of chloride by hexafluorophosphate counteranions required repeated precipitation from solutions of excess $\mathrm{NH_4PF_6}$. In the case of **1a**, FAB-MS analysis of the complex resulting from incomplete anion exchange revealed the presence of at least one chloride ion which was not lost during sample ionization. The presence of chloride ions also affected the ^1H NMR spectrum, particularly the signals for H2 and H5 of the central pyrimidine ring which were considerably broadened and shifted downfield. Similar behavior was observed for **1c**. Strong binding of chloride to a pentanuclear circular helicate has been reported.[4]

Crystals of **1a** suitable for crystallographic analysis were grown by slow diffusion of diethyl ether into a solution in acetonitrile. The resulting crystal structure[14] (Figure 1) confirms the [2 × 2] grid structure of the complex as well as the presence of two chloride anions and one acetonitrile molecule in close proximity. One of the chloride ions is situated 6.815 Å above the plane containing the four metal ions, whereas the other is buried deep within the central cavity of the structure (ca. 1.320 Å below the plane) and it is likely to be the more tightly bound of the two. Both the Ru and Fe ions are in a distorted octahedral environment in which the terminal pyridine rings are pulled in towards the metal center. Whereas [2 × 2] grid structures with four identical metal ions are achiral, **1a** is chiral and both enantiomers are present in the unit cell.

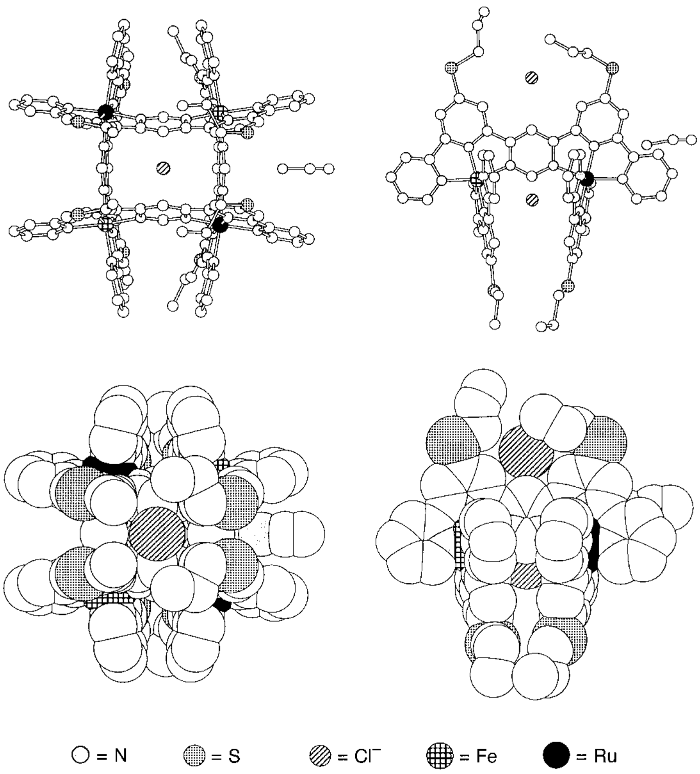


Figure 1. The molecular structure of **1a** as a ball-and-stick (top) and a space-filling representation (bottom) as viewed from the top (left) and from the side (right). Only one of the two enantiomeric forms is shown; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru1–N1 1.991, Ru1–N2 1.958, Ru1–N3 2.036, Fe1–N4 2.008, Fe1–N5 1.923, Fe1–N6 2.020; N1-Ru1-N2 79.3, N2-Ru1-N3 79.2, N4-Fe1-N5 78.7, N5-Fe1-N6 80.2.

The generation of grid structures such as **1a–d** represents an interesting example of chiral selection during the self-assembly process.[15] The precursors **2a** and **2b** are themselves chiral and are obtained as a racemic mixture from achiral components. The formation of a grid structure in the presence of a second metal ion requires combination of two precursors of the same chirality ($R+R$ or $S+S$; Figure 2). The high yields obtained indicate that chiral selection is efficient and that the self-assembly process is diastereoselective. The connection of an *R* and an *S* precursor into the corresponding *meso* diastereomer (*R*,*S*) is precluded for geometric reasons. It is interesting to note the analogy of the disconnection of a [2 × 2] grid structure into two substructures (of type **2**) of the same chirality to the "coupe du roi",[16] in which an achiral object is divided into two identical homochiral components.

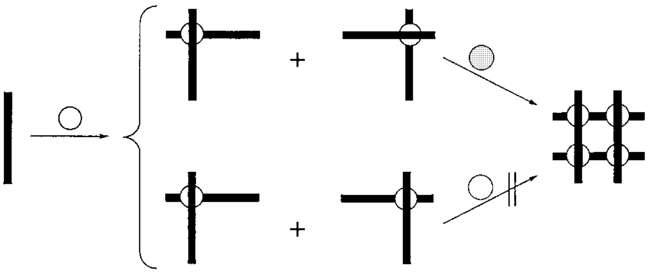


Figure 2. Generation of a [2 × 2] grid-type structure from two chiral precursors; only homochiral (top) but not heterochiral combination (bottom) leads to the grid array.

Metallo-supramolecular structures combining different metal ions may be expected to display interesting optical and electrochemical behavior resulting from the predefined arrangement of the metal centers. This is the case for the grid complexes, where electronic communication between proximal metal centers is ensured by their vicinity and the presence of a bridging pyrimidine unit. Cyclic voltammetry (Table 1) of **2a** and **2b** shows a reversible oxidation wave at +1.12 and +0.92 V versus the standard calomel electrode (SCE), respectively. In the case of **2b**, complexation of Fe^{II} to form **1c** results in a second reversible oxidation wave at +1.52 V, which is assigned to the oxidation of Fe^{II} to Fe^{III}. The

Table 1. Electrochemical data for complexes **2a**, **2b**, **1a**, and **1c**.[a]

Complex [V vs. SCE]	$E^{\ominus\prime}$(ox) [mV]	$\Delta E^{\ominus\prime}$(ox) [V vs. SCE]	$E^{\ominus\prime}$(red) [mV]	$\Delta E^{\ominus\prime}$(red)
2a	+1.12		−0.86	
			−1.03[b]	
2b	+0.92		−0.82	
			−1.04[b]	
1a	+1.32	170	−0.34	
			−0.40	140
			−1.09	
			−1.22	
			−1.46[b]	
1c	+1.01		−0.37	
	+1.52		−0.57	160
			−1.08	
			−1.19	
			−1.35[b]	

[a] Recorded in acetonitrile; scan rate 100 mV s^{-1}; 0.1 M (nBu$_4$N)PF$_6$. [b] Stripping peak.

oxidation of the osmium centers in **1c** is shifted towards higher potentials with respect to that of $[Os^{II}(terpy)_2]$ (+1.01 V; terpy = 2,2′:6′,2″-terpyridine) as a consequence of the presence of the Fe^{II} atoms. In contrast, only one broad oxidation wave at +1.32 V is observed for **1a**; the large separation between the forward and return sweep (170 mV) suggests that this feature consists of two closely spaced oxidation waves. In the negative potential region, ligand-based reductions are observed. A reversible wave (−0.86 and −0.82 V for **2a** and **2b**, respectively) corresponding to reduction of the pyrimidine rings is followed by a second reduction (−1.03 and −1.04 V for **2a** and **2b**, respectively) that leads to adsorption of the formally neutral complex on the electrode. Reduction of the pyrimidine groups in the grid assemblies is facilitated by the increased charge of the complex.

Recently, the [2 × 2] grids of four Co^{II} ions were shown to display molecular-based antiferromagnetic behavior.[17] Mixed-metal grids containing Ru^{II} and Co^{II} (**1b**) and Os^{II} and Ni^{II} (**1d**) were prepared both to examine the versatility of the systems and to explore new materials possessing molecular-based magnetism. Compound **1b** was obtained as a green solid in 90 % yield from a solution of **2a** in nitromethane and $Co(BF_4)_2$. Likewise, the addition of $Ni(ClO_4)_2$ at room temperature to a solution of **2b** in acetonitrile led to the isolation of **1d** as a blue solid in 70 % yield.

The formation of multicomponent metal arrays was extended to systems containing three different metal ions arranged in a predefined order. Indeed, the addition of Fe^{II} ions to an equimolar solution of **2a** and **2b** led to the formation of **1e**, which contains one Ru^{II} and one Os^{II} ion separated by two Fe^{II} ions, as well as **1a** and **1c** in a 2:1:1 ratio. The presence of **1e** and the relative proportion of products was determined by FAB-MS and ^1H NMR spectroscopy.

The ability to introduce different metal ions at chosen positions in a metallosupramolecular array opens the way to the design of new materials possessing specific electrochemical, photochemical, and magnetic properties originating from the interaction of different metal ions held in a particular arrangement. Such systems are of much interest as inorganic supramolecular devices and components for nanotechnology. To this end, the spontaneous but directed assembly of topoisomers of different metal ions (of same or different coordination geometry) represents an important step forward. The additional binding of substrates, such as chloride anions in the central cavity, can be used to further modify their properties. Also of interest in the present self-assembly process is its diastereoselectivity, a form of chiral self-selection, which imposes the exclusive combination of homochiral components in order to form a grid structure. Extensions of the present work towards metallosupramolecular arrangements of higher order and complexity are in progress.

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[14] Crystal data for **1a**: $C_{120}H_{112}Fe_2Ru_2S_8 \cdot 2Cl \cdot 6PF_6 \cdot 3CH_3CN$: data collection one a STOE IPDS diffractometer at 200 K, graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), monoclinic, space group $P2(1)/m$, $a = 17.127(3)$, $b = 29.381(6)$, $c = 18.348(4)$ Å, $\alpha = 90$, $\beta = 105.08(3)$, $\gamma = 90°$, $V = 8915(3)$ Å^3, $Z = 2$, $\mu = 0.59$ mm^{-1}, $F(000) = 3486$, $\rho_{calcd} = 1.294$ Mg m^{-3}, $2\theta_{max} = 52.16°$, $-20 \leq h \leq 9$, $-35 \leq k \leq 30$, $-22 \leq l \leq 22$. Structure solution and refinement: A total of 23755 reflections were collected. Of 12527 independent reflections [R(int) = 0.1231], 12526 were used to fit 368 parameters. The structure was refined against F^2 (full-matrix least squares), GOF on $F^2 = S = 1.073$, $R1 = 0.1675$ [$R1 = 0.2250$ (all data)], $wR2 = 0.4523$ [$wR2 = 0.5358$ (all data)], max./min. residual density: +1.556/−1.877 e Å^{-3}. Owing to the presence of both enantiomers, the metal positions were calculated as a 1:1 mixture of Fe and Ru, which led to a centrosymmetric space group. The whole cationic structure was refined isotropically. All atoms in rings (except for central pyrimidines) are calculated as pertaining to a regular hexagon. The solvent and anionic parts of the structure show severe disorder and were refined isotropically on split positions except for the chlorine anions, which were refined anisotropically. All hydrogen positions are calculated. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-101633. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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