

**Coordination Arrays:
Tetranuclear Cobalt(II) Complexes
with [2 × 2]-Grid Structure****

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A major goal in inorganic supramolecular chemistry is the self-assembly of polynuclear coordination arrays through the suitable design of ligands and choice of metal ions in order to generate well-defined architectures in a controlled fashion.^[1] In

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addition to the novel physicochemical properties that such entities may present, they are potentially interesting as components of functional nanostructures.

We have recently investigated three fundamental types of metal ion coordination arrays: racks $[n]R$,^[2, 3] ladders $[2n]L$,^[4] and grids $[m \times n]G$,^[5] where the nuclearity of different species is given by $[n]$, $[2n]$, and $[m \times n]$ (n represents the rank) and where the ligand components are oriented more or less orthogonal to each other. Two-dimensional gridlike structures are of particular interest as their architectures may serve as a basis for the construction of information storage devices.^[6] Such arrays of metal ions could represent ion dots that might be addressable photo- or electrochemically; they would be of still smaller size than quantum dots^[7] and would form spontaneously by self-assembly—microfabrication would therefore not be required.^[11]

To form “orthogonal” coordination arrays one may either combine tetrahedrally coordinated metal ions and bidentate ligands (such as 2,2'-bipyridine derivatives)^[4, 5] or octahedrally coordinated metal ions and tridentate ligands (such as 2,2':6',2''-terpyridine units).^[2, 3] For both of these combinations the ligands are arranged in a more or less perpendicular fashion as required for the construction of grid-type complexes. However, by using metal ions presenting octahedral coordination rather than those which prefer a tetrahedral^[5, 8] environment, one may expect a wider variety of interesting physical and chemical properties.^[9] We describe here the synthesis, characterization, and electrochemical properties of the $[2 \times 2]G$ Co^{II} complexes **1a–c** based on the bis-tridentate ligands **2a–c**.

Ligands **2a–c** were synthesized by Stille cross-coupling reactions between stannyl bipyridines and dichloropyrimidines.^[10] The ligands vary in the substitution at the 2-position of the central pyrimidine ring ($R = \text{H}, \text{Me}$) and at the 5-position of the

terminal pyridine ring ($R = \text{H}, \text{Me}$). The steric effect of the substituent in the pyrimidine 2-position was previously shown to influence the relative disposition of ancillary ligands in $[2]R$ -diruthenium(II) complexes.^[2] The 5-methyl groups on the terminal pyridine ring in **2c** were introduced to allow functionalization of the grid-type structure for incorporation into more complex systems.

Mixing equimolar amounts of cobalt acetate tetrahydrate and ligands **2a**, **2b**, or **2c** in methanol at reflux led to the assembly of the $[2 \times 2]G$ tetracobalt(II) complexes **1a–c** in high yields (typically ranging from 80 to 85% after precipitation as their PF_6^- , AsF_6^- , or SbF_6^- salts). The elemental analyses of **1a–c** indicate a 1:1 ligand-to-metal ratio.

The electrospray mass spectrum of **1b** shows only the peaks from multiply charged cationic species, due to loss of the hexafluorophosphate counteranions. It unequivocally confirms the grid structures in solution, in agreement with data from analytical ultracentrifugation studies.^[11]

Slow diffusion of methanol into saturated acetonitrile solutions of the complexes gave crystalline materials. Single crystals of the complex $[\text{Co}_4(\mathbf{2b})_4](\text{SbF}_6)_8$ of sufficient quality were obtained, and its structure was determined by X-ray crystallography.^[12, 13]

The asymmetric unit contains a single cation and eight SbF_6^- counteranions of which two are highly disordered (Figure 1). The complex cation is composed of four ligands **2b** and four cobalt cations arranged in a $[2 \times 2]$ -grid-type structure of distorted D_{2d} symmetry. The metal ions lie almost perfectly in a plane (mean deviation of 0.13 Å) and form a slightly distorted square (angles of 88.8–91.4°) with Co,Co distances of 6.41–

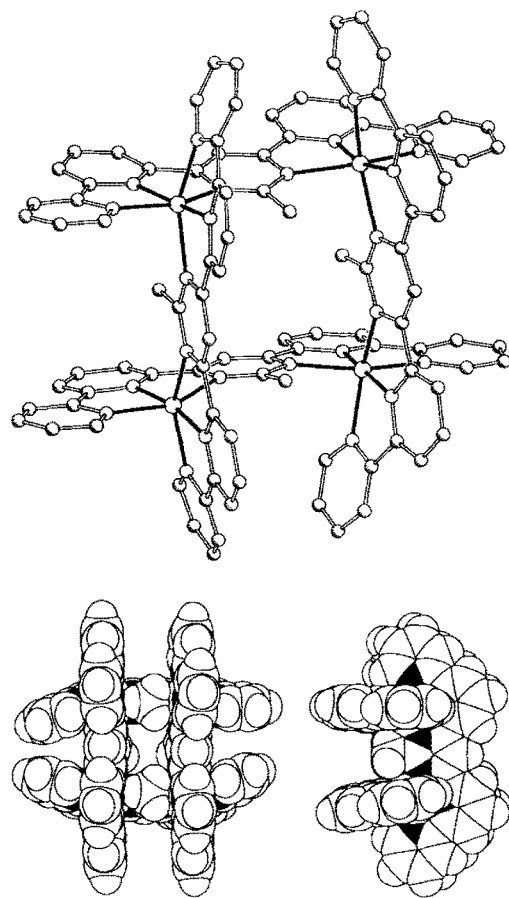
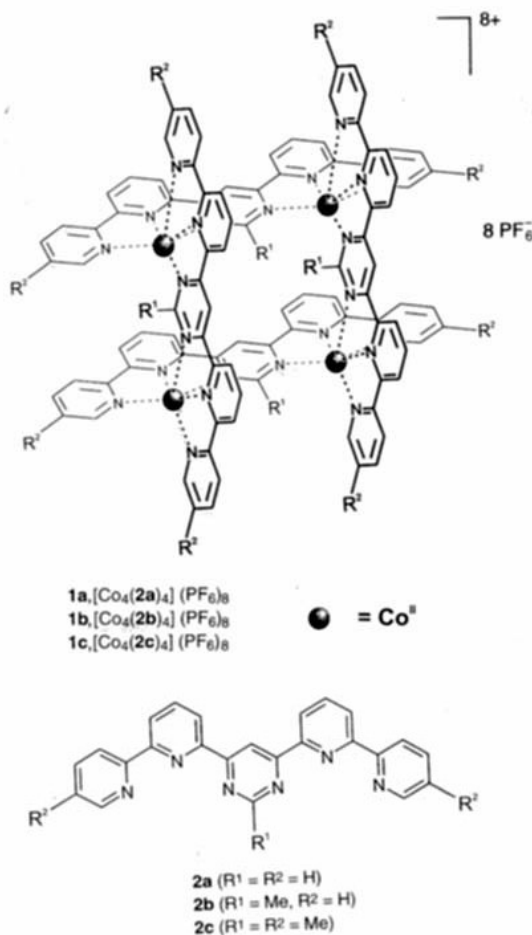


Figure 1. Crystal structure of the tetracobalt $[2 \times 2]$ -grid-type complex cation $[\text{Co}_4(\mathbf{2b})_4]^{8+}$ of **1b**. Top: ball-and-stick representation (hydrogen atoms omitted for clarity); bottom: two views in space-filling representation.

6.52 Å. They display a distorted octahedral coordination to two perpendicularly oriented ligand fragments. The average Co,N distances are 2.10 (pyridine-N) and 2.23 Å (pyrimidine-N); the average Co,Co distance is 6.35 Å. The complex cation is roughly a parallelepiped with almost parallel walls and dimensions $20 \times 20 \times 14$ Å (total volume 5600 Å³).

The self-assembly of the $[2 \times 2]$ -grids complies with the principle of "maximum coordination site occupation"^[1, 14] and may further be rationalized in terms of the appropriate design of the ligand and choice of its dimensional properties, which exclusively lead to the generation of the closed grid structure instead of a coordination polymer. Indeed, the formation of the latter is hindered by the steric repulsion that would arise between the partially overlapping terminal pyridines in the polymeric structure.

The degree of metal–metal interaction in polynuclear complexes is highly dependent on the nature of the bridging ligand.^[15] Ligands **2a** and **2b** were previously shown to mediate electronic interactions between the metal ions within $[2]R-Ru^{II}$ rack-type complexes.^[2, 3] In the present grid complexes, each Co^{II} ion is connected at a distance of 6.5 Å to its two nearest neighbors through the pyrimidine moieties, whilst the Co^{II} ion at the opposite corner is farther away (Co^{II}...Co^{II}: 9.2 Å).

Interaction between the metal ions may be indicated by the redox properties of the complexes. Complex **1a** undergoes reversible oxidations of the cobalt centers at +0.46, +0.66, and +0.91 V (vs. SCE in DMF).^[16] These values are more positive than those found in [Co^{II}(terpy)₂](PF₆)₂.^[17a] The first four reductions at -0.14, -0.24, -0.44, and -0.83 V are ascribed to the Co^{II}→Co^I reduction process and occur at a less negative potential than those of [Co^{II}(terpy)₂](PF₆)₂.^[17a] and of a related dinuclear Co^{II} complex of seixipyrindine.^[17b] The next four reversible one-electron reductions are ascribed to ligand-localized reductions at -0.83, -1.09, -1.33, and -1.77 V. Complexes **1b** and **1c** also undergo multiple redox processes.^[13]

As a first approximation the observed trends in electrochemical behavior may be explained by the high charge of the tetranuclear Co^{II} grids, which—just for electrostatic reasons—makes these complexes easier to reduce than their mononuclear counterparts. In addition, the electronic interactions between the metal ions may make a significant contribution to the altered redox potentials of the Co^{II} ions. Magnetization studies on compound **1b** indicate an antiferromagnetic exchange interaction between the Co^{II} ions.^[18]

The UV spectra of the complexes **1a–c** in acetonitrile show broad and highly intense absorption bands at 275 and 345 nm, which may be assigned to nonresolved, ligand-centered (LC) $\pi-\pi^*$ transitions. In the visible region, the broad bands centered between 440–450 nm are assigned to Co^{II}–bipyridine MLCT transitions, and the broad shoulder at about 550 nm could be due to a Co^{II}–pyrimidine MLCT transition.

The present results demonstrate the directed synthesis of $[2 \times 2]$ -grid-type coordination arrays of octahedrally coordinated metal ions by a simple, yet efficient self-assembly approach. This approach is general and has been applied to other metal ions to generate grids of Ni^{II}, Zn^{II}, Cd^{II}, and Cu^{II}.^[13] The appropriate shape of the ligands ensures a rigid and discrete spacing between the metal ions. The physicochemical properties of complexes **1a–c** indicate that electronic interactions exist between the Co^{II} ions and that coordination arrays of grid type may be suitable building blocks for the construction of molecular information storage devices. For instance, single grids embedded into a highly ordered monolayer might be individually addressable by altering their redox state with the tip of a scanning–tunneling microscope. Another strategy could be the construction of

devices in which the metal ions within the coordination arrays form magnetic domains. Investigations of higher ranking racks, ladders, and grids containing different bridging groups as well as other transition metal ions are being pursued.^[19]

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