

Controlling the formation of discrete complexes or a 1-D directional coordination network by the binding ability of anions†

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Based on the coordination ability of ClO_4^- , BF_4^- and Cl^- anions, a switch from discrete octahedral $\text{Co}(\text{II})$ complexes to a directional 1-D network was demonstrated using organic tectons based on a pyridine unit as a monodentate coordination site and a terpyridine moiety as a tridentate coordination pole; whereas with non-coordinating anions discrete mononuclear complexes were obtained, for Cl^- anion a 1-D coordination network was obtained in the presence of CoCl_2 under self-assembly conditions; the X-ray study on a single crystal revealed the centrosymmetric packing of the 1-D networks.

The self-assembly process based on the use of metals and organic ligands is a powerful strategy allowing generation of polynuclear assemblies displaying a variety of finite architectures.¹ The same strategy is also currently used to prepare coordination networks which are infinite assemblies possessing translational symmetry.²

Let us focus on 1-D coordination networks obtained by a single translation of an assembling core defined by the coordination of the metal to the organic tecton. Although many examples of 1-D networks using metals with linear coordination geometries and bis-monodentate tectons have been prepared, for metals adopting other coordination geometries such as square planar, tetrahedral or octahedral only a rather small number of investigations have been reported. The majority of coordination networks reported so far are based on 4,4'-bipyridine,³ however, few examples based on bis-bidentate^{4,5} or tetrakis-monodentate^{6,7} ligands have been also reported. Finally, only a few structurally characterised networks based on bis-tridentate tectons have been published.^{8–10}

For coordination networks based on metal cations and anionic organic tectons bearing the same but opposite charges, the charge compensation criteria is fulfilled. In this case, the design of the network may be based on the match between the coordination features of the metal and the organic tecton. However, when charge neutrality is not achieved by the two partners, the presence of a third component is required thus leading to a three-component system. For a combination of neutral tectons and metal cations, based on the binding ability of the anion, two possibilities may be considered. Non-coordinating anions would mainly play a charge compensating role without interfering directly with the metal centres, whereas coordinating anions form direct bonds with the metal cation. In the latter case, one may take advantage of this requirement to control the coordination sphere around the metal cation. For example, for metal centres adopting O_h geometry, the use of bulky and coordinating anions such as Cl^- would lead to the occupation of the two axial positions thus leaving the square planar base for construction of coordination networks.¹¹

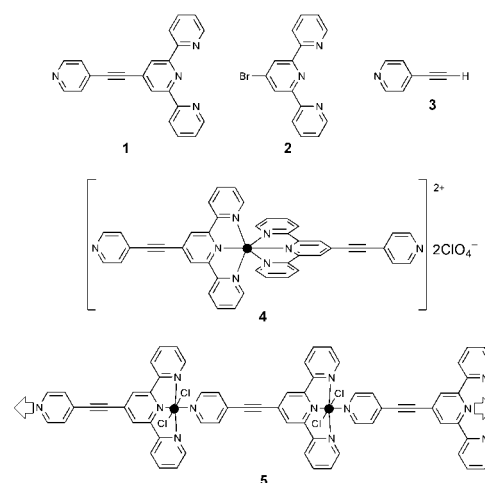
Here we report the design and synthesis of a tecton **1** and, depending on the coordinative nature of the anion (Cl^- , ClO_4^-), the formation of either a discrete complex **4** or a 1-D directional network **5** using $\text{Co}(\text{II})$ complexes.

Ligand **1** (Scheme 1) is based on a combination of a pyridine (py) and terpyridine (terpy) units. The junction between the mono- and tri-dentate units was achieved using an ethynyl spacer. The latter was chosen because it should minimise possible steric effects affecting the packing of 1-D networks in the solid state and should allow electronic communication between the py and terpy sites.¹² An example of a py directly connected to a terpy has been reported by Constable *et al.*¹³

For $\text{Co}(\text{II})$ cations adopting O_h geometry, in the case of non-coordinating anions such as ClO_4^- , all six available coordination positions may be occupied by two terpy moieties belonging to two molecules of **1** acting as ligands thus leading to a discrete complex **4** (Scheme 1). However, in the presence of coordinating anions such as Cl^- , the two anions would occupy the two axial positions leaving four coordination sites located at the square planar plane of the octahedron. Then **1** may act as a tecton by connecting the metal centres into a 1-D network such as **5**. Indeed, the four available coordination positions may be occupied by a terpy moiety belonging to one tecton **1** and by the py unit belonging to another tecton **1**, leading by a single translation of an assembling core defined as $[\text{py-CoCl}_2\text{-terpy}]$, to a 1-D network. Moreover, owing to the unsymmetrical nature of **1**, a directional 1-D network should be obtained. The latter point is of interest for directional physical properties if one could avoid centrosymmetric packing of directional 1-D networks.

The starting material for the synthesis of **1** was **2**¹⁴ which was prepared according to published procedures.¹⁴ The synthesis of **1** was achieved by coupling **2** with **3**¹⁵ in the presence of $\text{Pd}(\text{OAc})_2$ and Ph_3P in Et_3N under reflux for 48 h. Pure ligand **1** was obtained as a white powder in 98% yield after chromatography (Al_2O_3 , hexane–diethyl ether 6:4).

Upon slow diffusion at room temp. of a MeOH solution containing $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (4 mg) into a CHCl_3 solution of **1** (5 mg), orange crystals were obtained after *ca.* 4 h. An X-ray study† on a single-crystal showed the presence of **4** with the following relevant features: the crystal (monoclinic) was



Scheme 1

† Dedicated to François Mathey on the occasion of his 60th birthday.

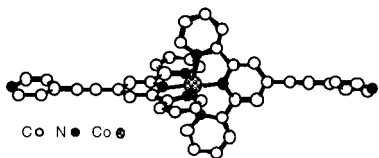


Fig. 1 X-Ray crystal structure of the mononuclear Co complex **4**. ClO_4^- anions, H atoms and solvent molecules are omitted for clarity. For distances and angles see text.

composed of **1**, Co^{2+} , 2ClO_4^- and 2CHCl_3 . For the cationic complex **4** comprised of one cation and two ligands **1**, the metal adopts a distorted O_h geometry with all six coordination positions occupied by 6 N atoms belonging to two terpy units. Whereas the two N–Co distance are 1.88 and 1.92 Å in the case of both central py units, the other N–Co distances are between 2.00 and 2.14 Å. For nitrogen atoms in *cis* disposition the N–Co–N angle varies from 78.5 to 103.0°, whereas for those in *trans* configuration, the N–Co–N angle varies from 156.9 to 178.4° (Fig. 1). No specific interactions between **4** and ClO_4^- anions are observed. Interestingly, the same observations were made for an analogous ligand (in which the terpy unit was connected by the same ethynyl spacer to the py moiety at the position 3) upon treatment with $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (synthesis and X-ray data not reported here).

Upon slow diffusion at room temp. of a MeOH solution containing $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (6 mg) in to a CH_2Cl_2 solution of **1** (6 mg.), purple crystals were obtained after *ca.* 24 h. An X-ray study[‡] revealed the presence of the 1-D network **5**. The crystal (monoclinic) was composed of **1**, Co^{2+} , 2Cl^- and 1 CH_2Cl_2 . As expected for the coordinating Cl^- anion, a directional 1-D neutral network based on the interconnection of CoCl_2 units by **1** is observed. The assembling core is a distorted octahedral $\text{Co}(\text{II})$ complex for which the coordination sphere is composed of two Cl^- and four N atoms. The two Cl^- anions occupy the two axial positions with a Co–Cl distance of *ca.* 2.463 Å and Cl–Co–Cl angle of 179.5°. The square base of the octahedron is composed of one py belonging to **1** and one terpy unit belonging to next tecton **1** with Co–N distances of 2.131 Å for the py unit and 2.048 Å for the central py of the terpy moiety. The other two Co–N distances are *ca.* 2.162 Å. Whereas the Cl–Co–N angle varies from 88.6 to 91.3°, the N–Co–N angle varies between *ca.* 76.7 and 103.3°. The N–Co–N angle between the py and the central py unit of the terpy moiety is 180.0°. The py and the terpy units are not coplanar but are tilted by *ca.* 112° (Fig. 2).

Owing to the unsymmetrical nature of **1**, the 1-D network is directional by nature. In principle, a directional 1-D network may either be packed in centrosymmetric or non-centrosymmetric modes in the crystalline phase. In the example reported here, the directional networks are positioned in a parallel fashion but oriented in opposite directions, thus leading to an

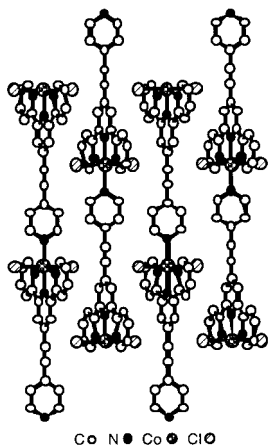


Fig. 2 A portion of the X-Ray crystal structure of the directional 1-D network **5** showing the packing of consecutive networks in 'head-to-tail' fashion. H atoms and solvent molecules are omitted for clarity. For distances and angles see text.

overall non-directional system (Fig. 2). This centrosymmetric packing may be due to cancellation of dipolar moments.

In conclusion, using a neutral tecton such as **1** and $\text{Co}(\text{II})$, depending on the its coordination ability, the role of the auxiliary anions in directing either the formation of discrete complexes or a 1-D network was demonstrated. Indeed, unsymmetrical ligand **1** based on two different coordination poles and non-coordinating anions such as ClO_4^- lead to the formation of a discrete $\text{Co}(\text{II})$ octahedral complex **4**, whereas, for a coordinating anion such as Cl^- , the self-assembly of CoCl_2 and **1** leads to the formation of a neutral and directional 1-D network **5** in the solid state. The directional 1-D networks are packed parallel to each other with opposite orientation. Since the discrete complex **4** possesses two non-coordinating pyridine units, it may act as an exo-ligand and thus may be used as a metallatecton¹⁶ for generating heteronuclear coordination networks. This aspect is under current investigation.

Notes and references

[‡] Crystal data: **4**: (orange, 173 K), $\text{C}_{44}\text{H}_{28}\text{CoN}_8 \cdot 2\text{CHCl}_3 \cdot 2\text{ClO}_4$, $M = 1165.36$, monoclinic, space group $P2_1/c$, $a = 8.8059(2)$, $b = 34.3527(7)$, $c = 16.8241(4)$ Å, $\beta = 104.779(5)$, $U = 4921.0(2)$ Å³, $Z = 4$, $D_c = 1.57$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 0.845$ mm⁻¹, 3744 data with $I > 3\sigma(I)$, $R = 0.077$, $R_w = 0.087$. **5**: (purple, 173 K), $\text{C}_{22}\text{H}_{14}\text{Cl}_2\text{CoN}_4 \cdot \text{CH}_2\text{Cl}_2$, $M = 549.16$, monoclinic, space group $P2_1/n$, $a = 8.7151(7)$, $b = 13.792(1)$, $c = 10.2996(5)$ Å, $\beta = 112.095(5)$, $U = 1147.1(1)$ Å³, $Z = 2$, $D_c = 1.59$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 1.234$ mm⁻¹, 1295 data with $I > 3\sigma(I)$, $R = 0.063$, $R_w = 0.074$. Data were collected on a Nonius Kappa CCD and structural determination was achieved using the Nonius OpenMolenN package.¹⁸ CCDC 163354 and 163355. See <http://www.rsc.org/suppdata/cc/b1/b102042k/> for crystallographic data in CIF or other electronic format.

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