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Non-centrosymmetric packing of 1-D coordination networks based on chirality

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Using $CoCl_2$ and a chiral tecton possessing C_2 chirality and based on two coordination poles composed of a pyridine unit connected at the 4-position to a pyridine bearing at the 2 and 6 positions two optically active oxazoline moieties, a polar solid is obtained. The latter results from the acentric packing of directional 1-D coordination networks.

In the crystalline state, the exploitation of tensorial physical properties such as piezo- and pyro-electricity and SHG requires non-centrosymmetric crystals. In the latter case, polarity is an additional desirable property. However, the design of such solids remains a difficult challenge.[1–9] A possible strategy to solve this rather important problem may be based on the design of 1-D directional and *chiral* coordination networks *i.e.* infinite structures formed upon interconnection of chiral organic tectons possessing available sites for metal coordination. The basic concept of this strategy is to avoid, through the use of chirality, the centrosymmetric packing of directional 1-D networks which would generate a non polar crystal. Dealing with 1-D coordination networks, one may distinguish three possibilities based on the nature of tectons used: (1) a combination of centric organic and metallic tectons would lead to non-directional networks, and thus the solid obtained upon packing of such networks will be non-polar by nature (Fig. 1a); (2) a combination of proper acentric tectons will generate directional 1-D networks; however, mainly due to minimisation of dipolar interactions, the centrosymmetric packing of such directional networks would lead again to the formation of non-polar crystals (Fig. 1b); (3) finally, a combination of acentric and chiral tectons would generate chiral and directional 1-D networks which may either pack in parallel or antiparallel fashion depending on the interplay of subtle forces (Fig. 1c). We have been investigating this issue for some time now.[10–12] Whereas many examples corresponding to the first case mentioned above have been published,[13] we have proposed a strategy dealing with the second case.[10,11] In this communication we report our strategy dealing with the third possibility, *i.e.* the use of an acentric and chiral organic tecton and a transition metal complex to generate non-centrosymmetric crystals.

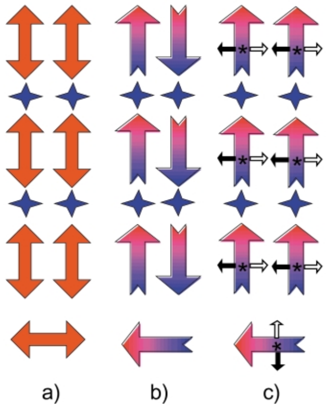


Fig. 1 Schematic representations of parallel packing of 1-D coordination networks formed between a metal and (a) centric achiral tecton, (b) acentric achiral tecton and (c) acentric and chiral tecton.

The strategy leading to the formation of directional 1-D networks based on the use of acentric organic tectons was demonstrated by us both for inclusion[12] and coordination networks.[10,11] In the latter case, we have demonstrated the possibility of using octahedral transition metals such as Co(II). When associated with two coordinating chloride anions occupying the two apical positions on metal cation ($CoCl_2$), a metallatecton offering four free coordination sites in a square planar geometry is obtained. One may use this topological simplification, *i.e.* passage from a hexacoordination in an octahedral mode to a tetracoordination in square geometry, for the design of directional 1-D coordination networks. Indeed, considering the four available coordination sites as a (1,3) set, one may design an organic tecton based on two coordination poles, one of monodentate and the other of tridentate type (Fig. 2).[10,11] Following this strategy, the new organic tecton **6** possessing a C_2 chirality and based on two coordination poles composed of a pyridine unit connected at the 4-position to a pyridine bearing at the 2 and 6 positions two optically active oxazoline moieties was designed and synthesised (Scheme 1).

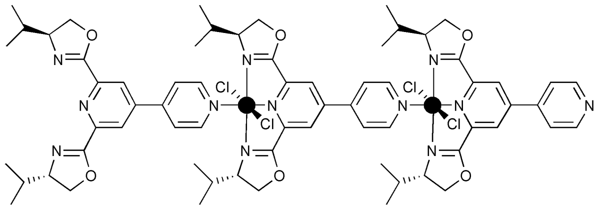
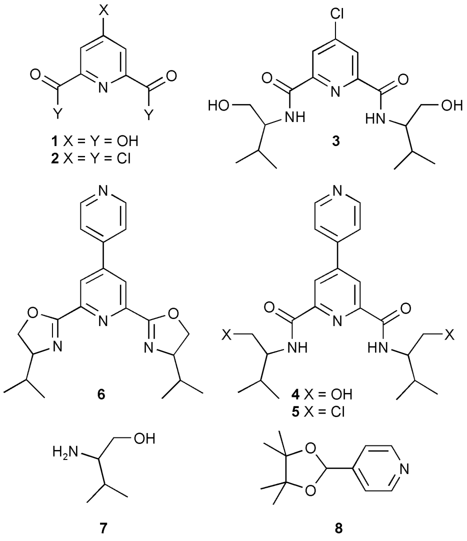


Fig. 2 Representation of a portion of the directional 1-D network formed between the organic chiral tecton **6** and $CoCl_2$.



Scheme 1

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The strategy for the synthesis of **6** was based on the Suzuki coupling between **3**[14] and **8**[15] which were prepared according to published procedures. The starting material for the synthesis of **3** was chelidamic acid **1** which upon treatment with $SOCl_2$ in the presence of a drop of DMF afforded the acylchloride derivative **2**. The chirality of the final ligand **6** was fixed upon treatment of **2** with (*S*)-valinol **7** (0 °C to rt.) in THF in the presence of Et_3N affording the compound **3** in 79% yield. The Suzuki coupling between **3** and **8** in the presence of $Pd(PPh_3)_4$ in DMF and in the presence of Cs_2CO_3 afforded the 4,4′-bipyridine derivative **4** in 89% yield. The latter was further treated with $SOCl_2$ under reflux affording the chloro derivative **5** in 95% yield. The desired compound **6** was obtained in 79% yield upon treatment of **5** by NaH in THF.

Upon slow diffusion at room temperature of an EtOH solution containing $CoCl_2 \cdot 6H_2O$ (5 mg) into a $CHCl_3$ solution of **6** (4 mg), brownish crystals were obtained after *ca*. 48 h. An X-ray diffraction study on a single crystal† revealed, as expected, the presence of directional 1-D networks (Fig. 3). The crystal (monoclinic, non-centrosymmetric space group $C2$) was composed of **6**, Co^{2+} cation, 2 Cl^- and 3 $CHCl_3$ solvent molecules which were found to be disordered. The latter are H-bonded to the Cl atoms coordinated to cobalt centres with C(H)–Cl distance and angle varying between 3.38–3.61 Å and 134–171° respectively. As expected, the two Co cations lying on a 2-fold crystallographic symmetry axes, adopt a distorted octahedral coordination geometry with the two Cl^- anions occupying the two apical positions (d_{Co-Cl} = 2.44 Å) in an almost linear fashion (ClCoCl angle of 178.7°). The remaining four coordination sites on the Co^{2+} centres are occupied by four N atoms belonging to two consecutive tectons **6**, one acting as a tripodal ligand and the other as a monodentate site. Thus, the strongly deformed square base of the octahedron is composed of two pyridine derivatives (d_{Co-N} = 2.09 Å) and two imines belonging to the oxazoline moieties (d_{Co-N} = 2.23 Å). Whereas the two pyridines are disposed in a linear fashion (NCoN angle of 180.0°), for the two imine N atoms, the NCoN angle of 148.8° is far from linearity. Consequently, the N(pyridine)Co-N(imine) angle is 74.4°. Both oxazoline moieties are almost coplanar with the pyridine ring (torsion angle of 2.0°).

Based on a single translation of the assembling core composed of a distorted octahedral Co(II) centre surrounded by two Cl^- anions and four N atoms, a neutral 1-D coordination network is formed. Due to the unsymmetrical and chiral nature of **6**, the 1-D coordination network is chiral and directional. Although, as stated above, for achiral directional 1-D networks, one may expect centric packing,[10,11] owing to the C_2 chirality of **6** and consequently, the chiral nature of the 1-D coordination network formed with $CoCl_2$, a non-centrosymmetric packing is achieved. Significantly, the alignment of the 1-D chains occurs in a parallel, rather than antiparallel fashion.

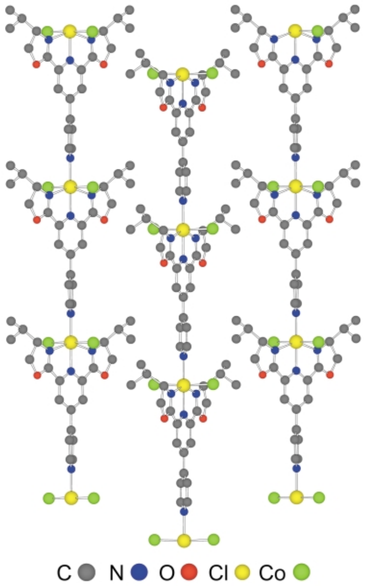

Fig. 3 A portion of the crystal structure of the polar solid obtained upon reacting $CoCl_2$ with the chiral tecton **6** showing the parallel and acentric packing of three consecutive directional 1-D networks.

In conclusion, it has been demonstrated that by using the neutral acentric and chiral tecton **6** and $CoCl_2$, a chiral and directional 1-D coordination network may be obtained in the crystalline phase. The directionality of the network results from the acentric nature of the organic tecton **6**. At this point, it is not possible to ascertain the reasons for the formation of the parallel (polar) *versus* antiparallel (comparatively non polar) packing of the directional 1-D networks. We are currently investigating the generality of this result. Finally, probably owing to the weak dipolar nature of the assembling core, no significant NLO properties could be measured for the polar crystals thus obtained. However, the rational design strategy reported here remains of interest and will be further pursued with more suitable chromophores as assembling nodes of the network.

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Notes and references

† *Crystallographic data* for **1**-$CoCl_2$ (brown crystals, 173 K): $C_{22}H_{26}Cl_2CoN_4O_2 \cdot 3CHCl_3$, M = 866.45, monoclinic, a = 26.1974(8), b = 11.2679(4) c = 16.6366(5) Å, β = 125.960(5), U = 3975.1(2) Å^3, space group C 2, Z = 4, D_c = 1.45 g cm^{-3}, Kappa CCD, Mo-Kα graphite monochromated, 3404 data with $I > 3\sigma(I)$, R = 0.078, Rw = 0.114. Data were collected on a Nonius Kappa CCD and structural determination was achieved using the Nonius OpenMolEn package.[16] CCDC 187538. See http://www.rsc.org/suppdata/cc/b2/b205556m/ for crystallographic data in .cif or other electronic format.

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