Self-assembly of a bis-tridentate Py_2S_4 ligand and cadmium cation into 1- and 2-D coordination networks†

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Using a Py_2S_4 bis-tridentate ligand and Cd(II), 1- and 2-D coordination networks were obtained and characterised in the solid state; whereas a 1-D network was obtained using the cadmium(II) dichloride salt, a 2-D network was obtained using a mixed chloride and tetrafluoroborate cadmium(II) salt; in the latter case, the inclusion of two $CHCl_3$ molecules within cavities formed by the organic and inorganic fragments was observed.

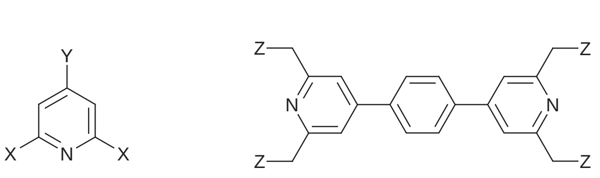
For some time now, intensive research on the design and preparation of coordination networks or polymers has been performed.[1] Although, nearly all cases reported deal with bis- or tris-monodentate systems,[2] examples of coordination polymers using bis-bidentate ligands have also been published.[3,4] On the other hand, only a few examples of characterised systems based on bis-tridentate ligands are known.[5,6]

The formation of coordination networks in the crystalline phase takes place under self-assembly conditions which require, on one hand, the reversible formation of the assembling core by complexation processes and its translation and, on the other hand, the conformity to the packing forces within the crystalline phase. Thus, for simple coordination networks, the choice of the two partners (metal, ligand) is the dominant feature. For porous coordination networks, in addition to the two partners mentioned before, one should also take into account the guest molecules initially occupying the pores. Owing to the fact that tridentate centres form rather stable and non-labile complexes with transition metals, the choice of the metal and the ligand is not obvious and therefore, not many characterised examples are available so far.

Here, we report the synthesis of a new bis-tridentate ligand and its self-assembly into 1- and 2-D coordination polymers using Cd(II) cation.

The design of the linear bis-tridentate ligand **7** (Scheme 1) is based on a combination of two pyridine moieties and four thioether groups. The two tridentate ligands are interconnected by a phenyl ring. Examples of other bis-tridentate ligands have been reported.[7]

Dealing with the metal cation, it has been shown previously that **1** forms a binuclear Cd(II) complex in which the two metal centres are bridged by two Cl^- anions.[8] This type of doubly bridged metal system has been reported for Co(II)[6b] and for Ni(II) complexes.[9]



1 X = CH_2SEt, Y = H
2 X = CO_2H, Y = OH
3 X = CO_2Et, Y = Br
4 X = CH_2OH, Y = Br

5 Z = OH
6 Z = Br
7 Z = SMe

Scheme 1

The synthesis of **7** was achieved starting from chelidamic acid **2**, which was first transformed into **3**.[10] The latter was reduced to **4**.[11] $Pd(PPh_3)_4$ catalysed coupling reaction of **4** with 1,4-phenyldiboronic acid[12] in dry THF gave **5** in 65% yield. Bromination of the latter using 33% HBr–AcOH afforded **6** in 61% yield. Finally, the treatment of **6** with NaSMe in dry THF afforded **7** in 71% yield. The latter, in addition to spectroscopic methods, was characterised by X-ray crystallography.

Upon slow diffusion at room temp. of a MeOH solution containing $CdCl_2{\cdot}xH_2O$ into a $CHCl_3$ solution of **7** (1 : 1 ratio of Cd : **7**), colourless crystals were deposited after 24 h. The X-ray study‡ showed the following features (Fig. 1): the crystal **I** (monoclinic) was composed of **7**, Cd(II), Cl^- anions, $CHCl_3$ and H_2O molecules. **7**, Cd(II) and Cl^- anions formed a neutral, infinite 1-D coordination network (Fig. 2).

Depending on the definition of the assembling core, the 1-D network $(\mathbf{7}Cd_2Cl_4)_n$ thus obtained may be described in two different ways. Considering the metallic core as a binuclear Cd_2Cl_4 unit (Fig. 2), the network may be regarded as resulting from the binding of two such units by the two PyS_2 fragments of **7** leading thus to the exo-tetranuclear Cd(II) complex and the repetition of the binding process leads to the 1-D coordination network. The same system may be also described as resulting from the bridging of consecutive exo-binuclear $\mathbf{7}{\cdot}Cd_2$ units by two Cl^- anions, and the remaining other two Cl^- anions behaving as ancillary ligands. For the ligand part, the pyridine rings were tilted by −37.6 and 38.3° with respect to the phenyl group. The CS and CN distances were roughly the same as those observed for free **7**. The coordination sphere around the Cd cations was composed of one N atom (d_{NCd} = 2.426 Å), two S atoms (d_{SCd} = 2.730, 2.747 Å) and three Cl^- anions. Among the three Cl^- present, two of them were shared between two Cd centres (d_{ClCd} = 2.591, 2.651 Å) whereas the third one was acting as an ancillary ligand (d_{ClCd} = 2.511 Å). The coordination geometry around the metal centre was distorted octahedral with S–Cd–S, Cl–Cd–Cl and N–Cd–Cl angles of 146.5, 172.0 and 175.2°, respectively. Within the $Cd_2{\cdots}Cl_4$ unit, the $Cd{\cdots}Cd$ distance was found to be 3.946 Å. The $CHCl_3$ and H_2O molecules were localised between the 1-D chains.

Interestingly, when instead of using $CdCl_2$, a mixed Cl^- and BF_4^- salt $[CdCl(BF_4)]$ was used, the same diffusion method afforded after two days another type of colourless crystal. The solid state analysis (Fig. 3)‡ showed that the crystal **II** was composed of **7**, Cd(II) cations, Cl^- and BF_4^- anions, $CHCl_3$ and MeOH molecules. **7**, Cd(II) and Cl^- anions formed a cationic infinite 2-D coordination network (Fig. 2). The latter may be described as the result of mutual interconnection of the 1-D coordination polymers described above through Cl^- anions acting now as bridging ligands. In a sense, the poor coordination ability of BF_4^- has created a Cl^- deficiency in the coordination sphere of Cd(II), made up for by an additional Cl^- bridging interaction.

Thus, the 2-D network may be regarded as the translation into two different space directions of an assembling core which may be defined $[\mathbf{7}_4Cd_4Cl_7]^+$ (Fig. 2). The charge neutrality being achieved by BF_4^- anions present in the lattice. Owing to the aromatic nature of the ligand used, the 2-D network was composed of cavities delimited in an alternating fashion by

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† Dedicated to Professor John A. Osborn on the occasion of his 60th birthday.

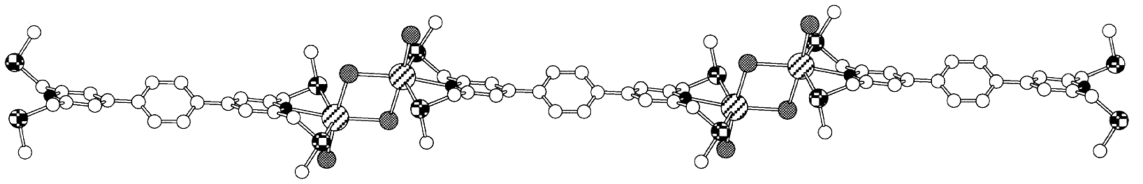

Fig. 1 A section of the X-ray structure of the 1-D coordination network **I** formed between **7** and $CdCl_2$. H atoms, anions and solvent molecules are not presented for clarity.

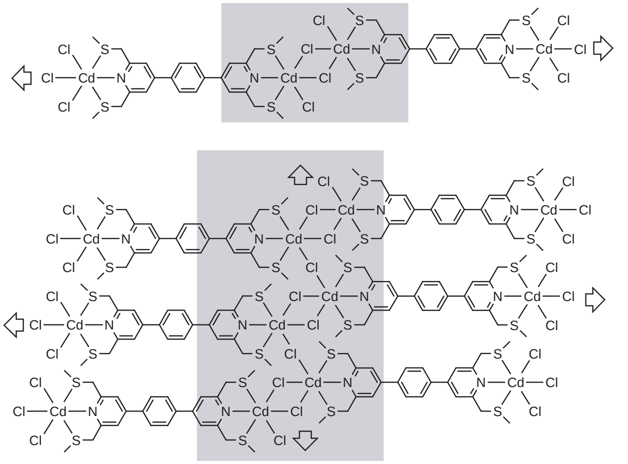

Fig. 2 Partial representation of the 1- and 2-D coordination polymers **I** and **II**.

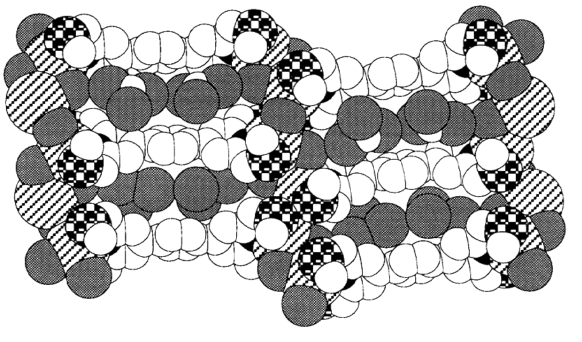

Fig. 3 A section of the X-ray structure of the 2-D coordination network **II** (see text). H atoms, anions and MeOH molecules are not presented for clarity.

organic and inorganic fragments. For **7**, the pyridine rings were tilted by −30.7 and 32.2° with respect to the phenyl group. The C–S and C–N distances were roughly the same as those observed for the free **7** and for the above-mentioned 1-D network. The coordination sphere around the Cd cations was again composed of one N atom (average d_{NCd} = 2.385 Å), two S atoms (average d_{SCd} = 2.697 Å) and three Cl^- anions. Although all three Cl^-, present in the coordination sphere of Cd cation, adopted a bridging role between the metallic centres, two of them were shared between two Cd centres (average d_{ClCd} = 2.608 Å) within the 1-D network, whereas the third one bridged two consecutive linear networks (d_{ClCd} = 2.559 Å) thus leading to a two-dimensional polymer. The coordination geometry around the metal centre was again distorted octahedral with S–Cd–S, Cl–Cd–Cl and N–Cd–Cl angles of 147.6, 169.0 and 163.6°, respectively. With the Cd_4Cl_7 unit, the Cd···Cd distances varied from 3.921 Å for the doubly bridged cations to 4.625 Å for the singly bridged centres. Interestingly, whereas MeOH and BF_4^- anions were localised between the 2-D sheets, the $CHCl_3$ molecules were included within the cyclophane type cavities composing the 2-D network.

In conclusion, using the N_2S_4 bis-tridentate ligand and Cd(II), 1- and 2-D coordination networks were obtained and characterised in the solid state. For the 2-D network the inclusion of two $CHCl_3$ molecules within cavities formed by the organic and inorganic fragments was observed. Based on the same strategy, the formation of magnetic networks using paramagnetic metal cations is currently under investigation.

Notes and references

‡ *Crystal data*: **I** (colorless, 294 K), $C_{12}H_{14}CdCl_2NS_2\cdot CHCl_3\cdot 2H_2O$, M = 575.09, monoclinic, a = 29.037(1), b = 8.4340(2), c = 22.5310(8) Å, β = 126.63(1), U = 4428(2) $Å^3$, Z = 8, space group $C2/c$, D_c = 1.73 g cm^{-3}, Nonius Kappa CCD, Mo-Kα, μ = 1.785 mm^{-1}, 5315 data with $I > 3\sigma(I)$, R = 0.056, R_w = 0.076.

II (colorless, 173 K), $C_{24}H_{28}Cd_2Cl_3N_2S_4\cdot BF_4\cdot 2CHCl_3\cdot CH_3OH$, M = 1161.52, orthorhombic, a = 16.3181(4), b = 14.8660(3), c = 35.9037(8) Å, U = 8709.7(6) $Å^3$, Z = 8, space group $Pbcn$, D_c = 1.77 g cm^{-3}, Nonius Kappa CCD, Mo-Kα, μ = 1.764 mm^{-1}, 4036 data with $I > 3\sigma(I)$, R = 0.051, R_w = 0.061. CCDC 182/1173.

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