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COMMUNICATION

Molecular tectonics: heterometallic coordination networks based on a Pt(II) organometallic metallatecton

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Combinations of a neutral organometallic tecton based on a square planar Pt(II) complex bearing two triphenylphosphine groups and two 4-ethynylpyridyl coordinating moieties in *trans* positions, with various metal halides (MX_2, M = Co(II), Ni(II) Cd(II), X = Cl⁻ or Br⁻) lead to the formation of 2D grid type heterobimetallic coordination networks in the crystalline phase.

Coordination networks,[1] among which metal-organic frameworks (MOFs),[2] are attracting considerable interest owing to their effective or potential applications.[3] The design of these extended architectures may be guided by principles developed in molecular tectonics.[4] Indeed, the formation of periodic networks[5] in the crystalline phase may be achieved by self-assembly processes between programmed complementary organic and metallic tectons. Although many coordination networks and/or MOFs have been reported,[6] the design of heterometallic coordination networks remains of interest.[7] We have reported a series of such architectures using the concept of metallatecton, *i.e.* metal complexes bearing at their periphery at least two divergently oriented coordinating sites, behaving as a connecting building block.[8]

Furthermore, the majority of architectures reported so far are based on combinations of organic tectons and metal cation or metal complexes as connecting nodes.[6] Another possibility, remaining to be explored, would be to combine organometallic tectons, for which the metal is decorated by two divergently oriented coordinating sites using M-C bonds, with metal cations or complexes.

Here we report on combinations of the Pt(II) organometallic tecton **T** (*trans*-[Pt(C≡CPy)₂(PPh₃)₂]) (Fig. 1) with a variety of metal complexes of the MX_2 type with M = Co(II), Ni(II) and Cd(II) and X = Cl⁻ or Br⁻,

leading to the formation of neutral grid type 2D heterometallic (**T**,MX_2) coordination networks.
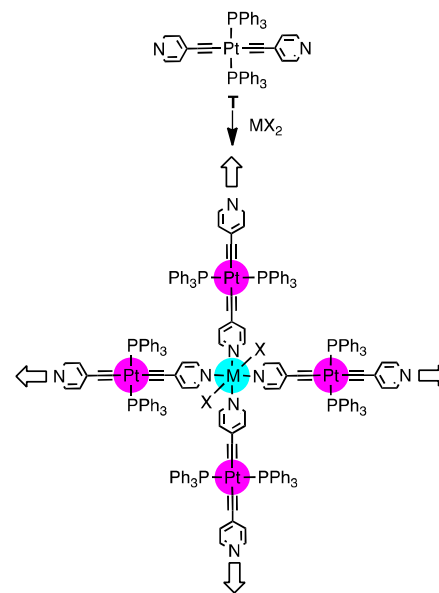

Fig. 1 Strategy for the formation of (**T**,MX_2) heterobimetallic grid type coordination network based on combinations of the organometallic tecton **T** and MX_2 metal complexes.

The design of the bismonodentate linear organometallic tecton **T** is based on a Pt(II) centre adopting a square planar geometry surrounded by two PPh_3 ligands and two 4-ethynylpyridyl coordinating moieties in *trans* configuration. Although, owing to their stability and photonic properties, many neutral Pt(II) organometallic bis-alkyne complexes have been thoroughly studied,[9] the tecton **T**,[10]

surprisingly, has not been used for the generation of coordination networks to date. However, Resnati *et al.* have combined the tecton **T** with 1,4-diiodotetrafluorobenzene for the formation of halogen bonded 1D networks.[11]

For the design of neutral grid type 2D networks, since the organometallic tecton **T** is neutral, MX_2 (M = Co, Ni, Cd and X = Cl⁻, Br⁻) neutral complexes for which the metal cation adopts an octahedral coordination geometry was chosen as 4 connecting nodes. Indeed, for such complex the two anionic ligands occupy the two apical coordination positions leaving thus the square base of the octahedron for the construction of the 2D architecture (Fig. 1). We have previously described this type of strategy.[12]

Metallatecton **T** was synthesized by modifying a reported procedure (see ESI).[10] The condensation of 4-ethynylpyridine, already described[13] with *cis*-$PtCl_2(PPh_3)_2$ in the presence of CuI afforded the tecton **T** in 77% yield. Upon slow diffusion of pentane into a solution of **T** in CH_2Cl_2, crystals suitable for X-ray crystallography (see crystallographic table, ESI) have been obtained (Fig. 2). In the crystal (triclinic, *P-1*), the Pt(II) centre adopts, as expected, a square planar geometry with the two phosphine moieties in *trans* disposition. The P-Pt-C angle is in the 88.2-90.8° range and both the P-Pt-P and C-Pt-C angles are 180.0°. The Pt-P and Pt-C bond lengths are 2.32 Å and 2.00 Å respectively. Pt-C≡C and C≡C-C angles are 178.5 and 177.9° respectively. The structure of **T** has been previously reported however in a different crystal system (monoclinic) and space group (P2(1)/c).[10]
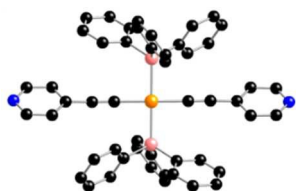

Fig. 2 Crystal structure of the tecton **T**. Hydrogen atoms are omitted for clarity

The formation of grid type 2D networks (Fig. 1) was achieved by slow diffusion of a solution of MX_2 (M(II) = Co, Ni, Cd and X = Cl⁻, Br⁻) in MeOH or EtOH into a solution of **T** in $CHCl_3$, $C_2H_4Cl_2$ or $C_2H_2Cl_4$. Crystals obtained have been analysed by X-ray diffraction on single crystals, powder X-ray diffraction (see crystallographic table, ESI), elemental analysis and TGA (see ESI).

Although the formation of crystals was perfectly reproducible, in all cases, crystals were found to be unstable. Indeed, no proper match between the measured and simulated patterns PXRD using the single crystal data was observed. This could probably result from loss of solvent molecules or phase changes. This is supported by TGA analysis which revealed the decomposition of crystals in the 250-300° range, after loss of solvent molecules in most of cases. However, elemental analyses were found to be in good agreement with the formula determined by X-ray investigations.

Single crystals (triclinic, *P-1*) of (**T**,$CoCl_2$) were obtained upon slow diffusion of a solution of $CoCl_2$ in MeOH into a solution of **T** in $CHCl_3$ (Fig. 3). The crystal, in addition to **T** and $CoCl_2$ contains 1 $CHCl_3$ and 3 H_2O molecules. Due to the positional disorder of the solvent molecules, the structure was refined using data generated by the SQUEEZE algorithmthe.[14] Single crystals (triclinic, *P-1*) of (**T**,$NiCl_2$) have been obtained upon slow diffusion of a $Ni(NO_3)_2$ solution in

MeOH in a solution of **T** in $CHCl_3$ (Fig. 4). The crystal is mainly composed of the tecton T and $NiCl_2$ entities. The exchange between NO_3^- and Cl⁻ anions is most likely due to the presence of residual HCl. In order to verify that, the same procedure was carried out using $NiCl_2$ instead of $Ni(NO_3)_2$. The crystallisation process appeared to be rather fast leading to smaller and twinned crystals.
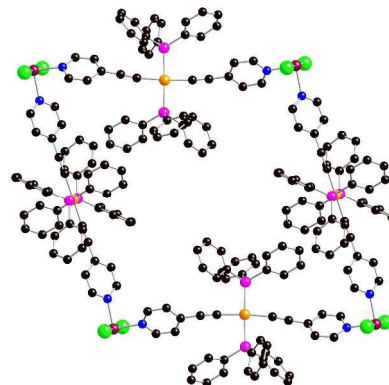

Fig. 3 Portions of the 2D grid type network (**T**,$CoCl_2$). Solvent molecules and hydrogen atoms are omitted for clarity.
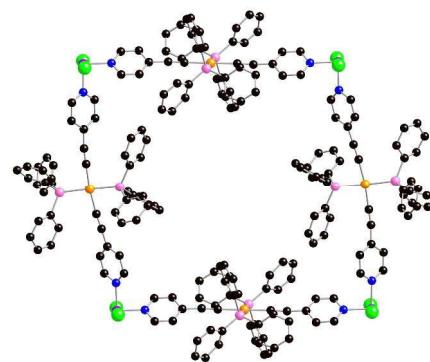

Fig. 4 Portions of the 2D grid type network (**T**,$NiCl_2$). Solvent molecules and hydrogen atoms are omitted for clarity.

For both (**T**,$CoCl_2$) and (**T**,$NiCl_2$), the Pt(II) centre adopts a square planar geometry with Pt-P and Pt-C distances in the 2.30-2.31 Å and 1.99-2.00 Å range respectively. P-Pt-P and C-Pt-C angles are in the 176.5-180.0° and 173.4-175.2° range respectively. For (**T**,$CoCl_2$), Co^{2+} cation adopts a distorted octahedral geometry with Co-N and Co-Cl distances in the 2.14-2.18 Å rand 2.46-2.47 Å range respectively. A similar behaviour is observed for Ni^{2+} in (**T**,$NiCl_2$) with Ni-N and Ni-Cl distances in the 2.08-2.12 and 2.33-2.37 Å range respectively. For (**T**,$CoCl_2$), N-Co-N (cis) angle is in the 86.2-91.5° range, whereas for (**T**,$NiCl_2$), N-Ni-N (cis) angle is in the 87.2-92.3° range.

In both cases, within a single grid unit **G** defined by the four M (M = Co or Ni), two types of tecton **T** differing by their orientation are present. One is oriented along the *y* direction (T_y), whereas the other one is almost oriented along *z* direction (T_z). The grid is formed by two opposite T_y and two opposite T_z. For T_y, the *tilt* angle between the two pyridyl units is 86.2° for (**T**,$CoCl_2$) and 87.5° for (**T**,$NiCl_2$), whereas for T_z the two pyridyl moieties are located in two parallel planes

separated of 0.3 Å for (**T**,CoCl$_2$) and coplanar for (**T**,NiCl$_2$). The P-Pt-**G** angle is 10.8° for (**T**,CoCl$_2$) and 8.3° for (**T**,NiCl$_2$) for **T**$_y$ and 85.8° for (**T**,CoCl$_2$) and 88.9° for (**T**,NiCl$_2$) for **T**$_z$. For (**T**,CoCl$_2$), **T**$_y$ is slightly bent, with a N-Pt-N angle of 167.5°, whereas **T**$_z$ linear with the N-Pt-N angle of 180.0°. For (**T**,CoCl$_2$), the N-Pt-N angle for **T**$_y$ and **T**$_z$ are 168.4° and 180.0° respectively.

For both cases, the 2D grids are eclipsed along the *x* axis leading thus to channels occupied by solvent molecules. The solvent accessible volume for (**T**,CoCl$_2$) and (**T**,NiCl$_2$), as calculated by PLATON software, is 36 % in both cases.[14]

For the combination of the tecton **T** with CdCl$_2$, crystals (triclinic, *P*-1) of (**T**,CdCl$_2$) have been obtained by slow diffusion of a MeOH solution of CdCl$_2$ into a solution of **T** in C$_2$H$_2$Cl$_4$. Crystal, in addition to **T** and CdCl$_2$ contain 2 C$_2$H$_2$Cl$_4$ molecules.

For the combination of the tecton **T** with CdBr$_2$, crystals (triclinic, *P*-1) of (**T**,CdBr$_2$) have been obtained by slow diffusion of a CdBr$_2$ solution in EtOH into a solution of **T** in CHCl$_3$ (Fig. 4 right). Crystals contain 4 CHCl$_3$ and 3 H$_2$O molecules in addition to **T** and CdBr$_2$.

Interestingly, although in both cases a grid type 2D network is formed, whereas for (**T**,CdCl$_2$) a chloride bridged dimer behaving as a connecting node is observed (Fig. 5), for (**T**,CdBr$_2$) the metal center is mononuclear (Fig. 6).
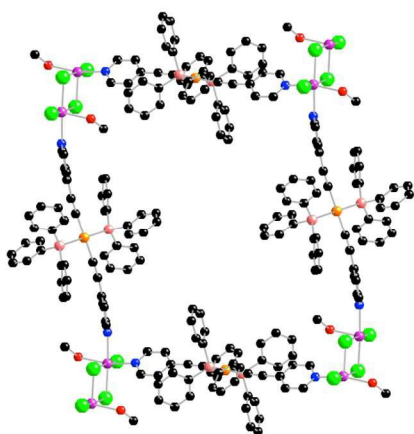

Fig. 5 Portions of the 2D grid type network (**T**,CdCl$_2$). Solvent molecules and hydrogen atoms are omitted for clarity.

For both (**T**,CdCl$_2$) and (**T**,CdBr$_2$), the Pt(II) center adopts, as expected, a square planar geometry, with Pt-P and Pt-C distances in the 2.30-2.32 Å and 1.96-2.00 Å range respectively. For (**T**,CdCl$_2$), P-Pt-P and C-Pt-C angles are 180.0°, whereas for (**T**,CdBr2), P-Pt-P and C-Pt-C angles are in the 176.6-177.8° and 178.9-180.0° ranges, respectively.

For (**T**,CdCl$_2$), the Cd-Cl and Cd-N distances are in the 2.32-2.37 Å and 2.08-2.12 Å range respectively. Cl-Cd-Cl angle is 169.7° for *trans* chlorides and 82.6° for *cis* chlorides within the Cd(II) dimer and 90.6° for *cis* non-bridging chlorides. Finally, the N-Cd-N angle is 86.9°. For (**T**,CdBr$_2$), Cd-Br and Cd-N distances are in the 2.74-2.75 and 2.36-2.39 Å range respectively. Br-Cd-Br angle is 175.37° and N-Cd-N (cis) and N-Cd-N (trans) angles are in the 81.1-99.3 and 175.8-178.4° range respectively.
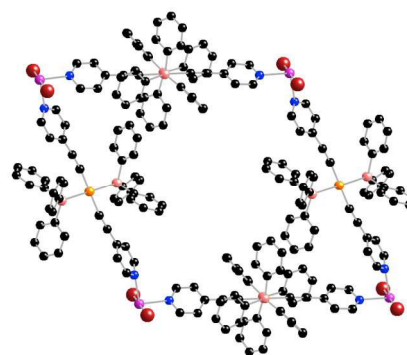

Fig. 6 Portions of the 2D grid type network (**T**,CdBr$_2$). Solvent molecules and hydrogen atoms are omitted for clarity.

For (**T**,CdCl$_2$), the two pyridyl of **T**$_y$ type are located in two parallel planes separated from 1.28 Å and the two pyridyl moieties of **T**$_z$ type are located in two parallel planes separated by 0.44 Å. The P-Pt-**G** angles are respectively 53.6° and 84.1 ° for **T**$_y$ and **T**$_z$. Both **T**$_y$ and **T**$_z$ are linear, with N-Pt-N angles of 180.0°. For (**T**,CdBr$_2$), the two pyridyl of **T**$_y$ type are tilted by 15.3° and the **T**$_z$ type are tilted by 15.0°. The P-Pt-**G** angles are respectively 12.3° and 84.8 ° for **T**$_y$ and **T**$_z$. **T**$_y$ and **T**$_z$ are slightly bent with N-Pt-N angles of 177.5 and 178.0° respectively.

Along the *x* axis, the 2D grids are eclipsed in the case of (**T**,CdCl$_2$), thus creating channels. The solvent accessible volume is 41 %.[14] For (**T**,CdBr$_2$), two consecutive grids are shifted along the x axis and eclipsed along the axis perpendicular to the [1 1 1] plane. The solvent accessible volume is 34 %.[14]

In conclusion, the Pt(II) organometallic complex **T**, bearing two triphenylphosphine groups and two 4-ethynylpyridyl coordinating moieties in *trans* positions, behaves as a linear organometallic tecton. Its combinations with metal halides M(II)X$_2$ (M = Ni, Co, Cd, X = Cl or Br) behaving as 4-connecting nodes lead to the formation of heterobimetallic (Pt,Ni), (Pt,Co) and (Pt,Cd) 2D grid tape architectures (Fig. 7). Combinations of tecton T and its analogues with other metal complexes are currently under investigation.
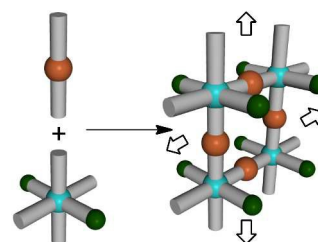

Fig. 7 Schematic representation of the formation of (**T**,MX$_2$) heterobimetallic grid type coordination network based on a combination of the organometallic tecton **T** and MX$_2$ metal complexes. Orange and blue spheres represent Pt(II) and M cation respectively, green sphere represents the X anion.

Notes and references

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† Electronic Supplementary Information (ESI) available: [experimental details, characterisation of new compounds and materials]. Experimental crystallographic data: CCDC 1403450-1403454.

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Graphical abstract

Combinations of a Pt(II) organometallic linear tecton with 4-connecting MX_2 salts lead to the formation of heterobimetallic (Pt,M) 2D grid tape architectures.