

## Molecular tectonics: design of 2-D networks by simultaneous use of charge-assisted hydrogen and coordination bonds

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### Supplementary information

#### Contents

#### Experimental part

##### *General:*

All reagents were purchased from commercial sources and used without further purification.

<sup>1</sup>H-NMR spectra were recorded at room temperature on a Bruker ACI (300 MHz) NMR spectrometer.

FT-IR spectra were recorded on a Perkin Elmer spectrometer.

Powder diffraction studies (PXRD) diagrams were collected on a Bruker D8 diffractometer using monochromatic Cu-K $\alpha$  radiation with a scanning range between 3.8 and 40° using a scan step size of 2°/mn.

X-Ray diffraction Data were collected on a Bruker SMART CCD diffractometer with Mo-K $\alpha$  radiation. The structures were solved using SHELXS-97 and refined by full matrix least-squares on F2 using SHELXL-97 with anisotropic thermal parameters for all non hydrogen atoms. The hydrogen atoms were introduced at calculated positions and not refined (riding model).<sup>1</sup> CCDC 729992–729997 contain the supplementary crystallographic data. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

##### *Synthesis:*

Compound **1** was prepared using a new procedure leading to a higher yield *via* condensation of succinonitrile (13.8 g; 0.17 mmol) and 1,3-Diaminopropane (24.8 g; 0.33 mmol) in the presence of P<sub>2</sub>S<sub>5</sub> in catalytic amount. The yellow solution was heated at 90°C until complete formation of a solid. The solid was crushed, filtrated and dissolved in warm toluene to remove impurities. After evaporation, the crude product was recrystallized from CHCl<sub>3</sub>/toluene.

Compound **2** was prepared according to a published procedure.<sup>2</sup>

##### *Crystallization conditions:*

##### *Compound 2:*

A stock solution (8 ml) of **2** was prepared by dissolving a mixture of 40 mg of **2**, 1 ml of a diluted aqueous solution of Et<sub>3</sub>N (1 ml Et<sub>3</sub>N in 24 ml H<sub>2</sub>O) and 7 ml of water. In a test tube (1 cm diameter), to a layer of DMSO (1 ml) a layer of THF (0.3 ml) was added and then 1 ml of

<sup>1</sup> G. M. Sheldrick, *Programs for the Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany, 1996.

<sup>2</sup> H. Sugihara, H. Arakawa et al.; *J. Chem. Soc., Dalton Trans.*, 2000, 2817.

the stock solution of **2** was gently introduced. Crystals were obtained after few days by slow liquid diffusion.

**Complex ( $I^{2+}$ ,  $2^{2-}$ ):**

In a crystallization tube (3 mm diameter), a  $\text{CHCl}_3$  solution (0.5 ml) of **1** (1 mg) was carefully layered with a DMSO solution (0.5 ml) of **2** (2.2 mg). Colourless crystals were obtained by slow diffusion after few days.

**Complex [ $(\text{Ag}^+-(2,2^-))$ ]:**

In a crystallization tube (3 mm diameter), a DMSO solution (0.5 ml) of **2** (1.3 mg) was first layered with a buffer solution (0.5 ml) composed of DMSO and EtOH in 1/1 ratio and then an EtOH solution (0.5 ml) of  $\text{AgPF}_6$  (3.5 mg) was added. Yellow crystals were obtained by slow diffusion after few days.

**( $I^{2+}$ ,  $2^{2-}$ ,  $\text{Ag}^+$ ,  $\text{SbF}_6^-$ )**

In a crystallising tube (1 cm diameter), the mixing of **1** (6.4 mg) and **2** (8.8 mg) in water (3 ml) afforded a clear solution (pH of *ca* 7) to which 5 drops of butanol was added. The mixture was first gently layered with an EtOH solution (0.5 ml) containing 0.03% MeOH followed by a solution of  $\text{AgSbF}_6$  (3.5 mg) in EtOH (0.5 ml) containing 0.03% MeOH. Slightly yellowish crystals suitable for X-ray diffraction on single crystals were obtained after few days.

**( $I^{2+}$ ,  $2^{2-}$ ,  $\text{Ag}^+$ ,  $\text{PF}_6^-$ )**

The same procedure as above was applied using 3.5 mg of  $\text{AgPF}_6$ .

**( $I^{2+}$ ,  $2^{2-}$ ,  $\text{Ag}^+$ ,  $\text{AsF}_6^-$ )**

Again, the same procedure was applied using 3.2 mg of  $\text{AgSbF}_6$ .

**Crystallographic data:**

**2:**  $\text{C}_{14}\text{H}_8\text{N}_2\text{O}_4$ ,  $M = 268.22$ , *Monoclinic*,  $a = 9.7547(10) \text{ \AA}$ ,  $b = 7.5702(6) \text{ \AA}$ ,  $c = 15.2163(16) \text{ \AA}$ ,  $\beta = 104.189(3)^\circ$ ,  $U = 1089.37(18) \text{ \AA}^3$ , Space group  $P2(1)/c$ ,  $Z = 4$ ,  $\mu = 0.123 \text{ mm}^{-1}$ , Refls measured: 5993, Independent Refls : 2394 [ $R(\text{int}) = 0.0343$ ], Final  $R$  indices [ $I > 2\sigma(I)$ ]:  $R_1 = 0.0465$ ,  $wR_2 = 0.1143$ ,  $R$  indices (all data):  $R_1 = 0.0666$ ,  $wR_2 = 0.1302$ ,  $\text{GOF} = 1.015$ .

**( $I^{2+}$ ,  $2^{2-}$ ):**  $\text{C}_{26}\text{H}_{28}\text{Cl}_{16}\text{N}_6\text{O}_4$ ,  $M = 701.24$ , *Orthorhombic*,  $a = 10.0015(12) \text{ \AA}$ ,  $b = 14.7201(17) \text{ \AA}$ ,  $c = 21.396(2) \text{ \AA}$ ,  $U = 3150.0(6) \text{ \AA}^3$ , Space group  $P2(1)2(1)2(1)$ ,  $Z = 4$ ,  $\mu = 0.588 \text{ mm}^{-1}$ , Refls measured: 19376, Independent Refls : 6424 [ $R(\text{int}) = 0.0893$ ], Final  $R$  indices [ $I > 2\sigma(I)$ ]:  $R_1 = 0.0672$ ,  $wR_2 = 0.1549$ ,  $R$  indices (all data):  $R_1 = 0.0870$ ,  $wR_2 = 0.1709$ ,  $\text{GOF} = 1.241$ .

**[ $(\text{Ag}^+-(2,2^-))$ ]:**  $\text{C}_{32}\text{H}_{27}\text{AgN}_4\text{O}_{10}\text{S}$ ,  $M = 767.51$ , *Monoclinic*,  $a = 13.5409(10) \text{ \AA}$ ,  $b = 7.4008(6) \text{ \AA}$ ,  $c = 15.2713(9) \text{ \AA}$ ,  $\beta = 101.533(3)^\circ$ ,  $U = 1499.49(19) \text{ \AA}^3$ , Space group  $P2/c$ ,  $Z = 2$ ,  $\mu = 0.811 \text{ mm}^{-1}$ , Refls measured: 12347, Independent Refls : 3438 [ $R(\text{int}) = 0.0448$ ], Final  $R$  indices [ $I > 2\sigma(I)$ ]:  $R_1 = 0.0716$ ,  $wR_2 = 0.1812$ ,  $R$  indices (all data):  $R_1 = 0.1093$ ,  $wR_2 = 0.2058$ ,  $\text{GOF} = 1.030$ .

**( $I^{2+}$ ,  $2^{2-}$ ,  $\text{AgPF}_6$ ):**  $\text{C}_{50}\text{H}_{60}\text{AgF}_6\text{N}_{12}\text{O}_{10}\text{P}$ ,  $M = 1241.94$ , *Monoclinic*,  $a = 21.4159(17)$ ,  $b = 23.109(3) \text{ \AA}$ ,  $c = 5.4593(6) \text{ \AA}$ ,  $\beta = 99.117(6)^\circ$ ,  $U = 2667.7(5) \text{ \AA}^3$ , Space group  $C2/m$ ,  $Z = 2$ ,  $\mu = 0.499 \text{ mm}^{-1}$ , Refls measured : 10864, Independent Refls : 3089 [ $R(\text{int}) = 0.1427$ ], Final  $R$  indices [ $I > 2\sigma(I)$ ]:  $R_1 = 0.1026$ ,  $wR_2 = 0.2352$ ,  $R$  indices (all data):  $R_1 = 0.1840$ ,  $wR_2 = 0.3095$ ,  $\text{GOF} = 1.065$ .

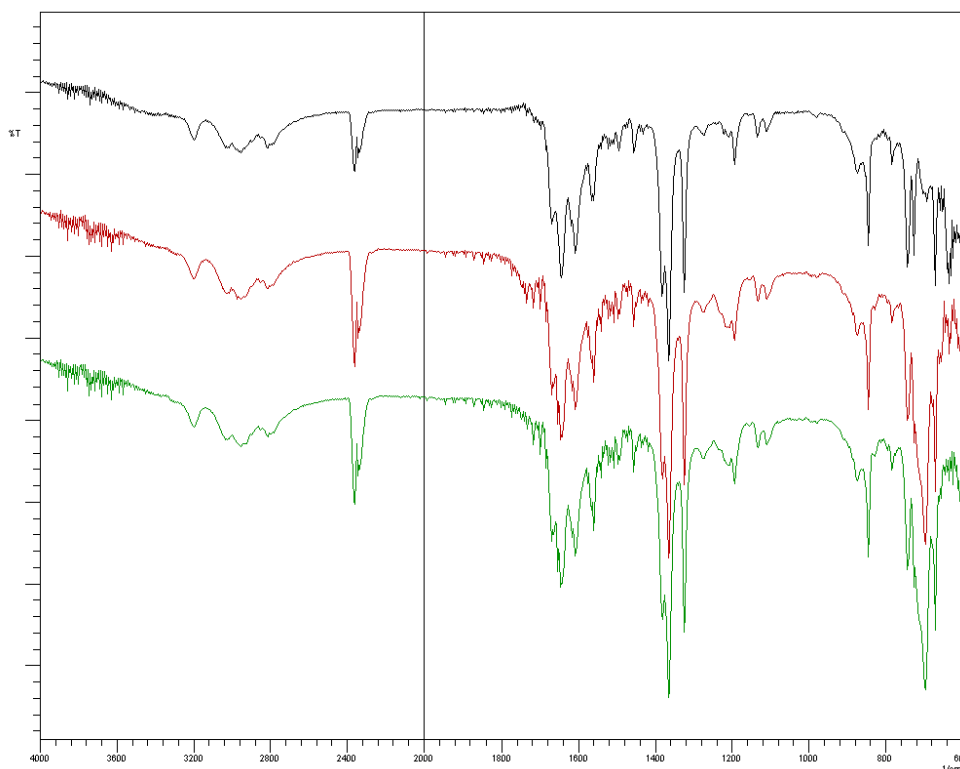
( $1^{2+}$ ,  $2^{2-}$ , AgAsF<sub>6</sub>): C<sub>50</sub>H<sub>60</sub>AgAsF<sub>6</sub>N<sub>12</sub>O<sub>10</sub>, M = 1285.89, *Monoclinic*, a = 21.538(2), b = 23.019(2) Å, c = 5.3934(5) Å, β = 98.638(5)° U = 2643.7(4) Å<sup>3</sup>, Space group C2/m, Z = 2, μ = 1.094 mm<sup>-1</sup>, Refls measured : 10656, Independent Refls : 3089 [R(int) = 0.0767], Final R indices [I > 2σ(I)]: R1 = 0.0854, wR2 = 0.1778, R indices (all data): R1 = 0.1335, wR2 = 0.2019, GOF = 1.042.

( $1^{2+}$ ,  $2^{2-}$ , AgSbF<sub>6</sub>): C<sub>50</sub>H<sub>60</sub>AgF<sub>6</sub>N<sub>12</sub>O<sub>10</sub>Sb, M = 1332.72, *Monoclinic*, a = 21.8809(18), b = 23.0194(18) Å, c = 5.3675(5) Å, β = 98.574(4)° U = 2673.3(4) Å<sup>3</sup>, Space group C2/m, Z = 2, μ = 0.962 mm<sup>-1</sup>, Refls measured : 12061, Independent Refls : 3122 [R(int) = 0.0670], Final R indices [I > 2σ(I)]: R1 = 0.0824, wR2 = 0.2115, R indices (all data): R1 = 0.1222, wR2 = 0.2547, GOF = 1.053.

### Characterization:

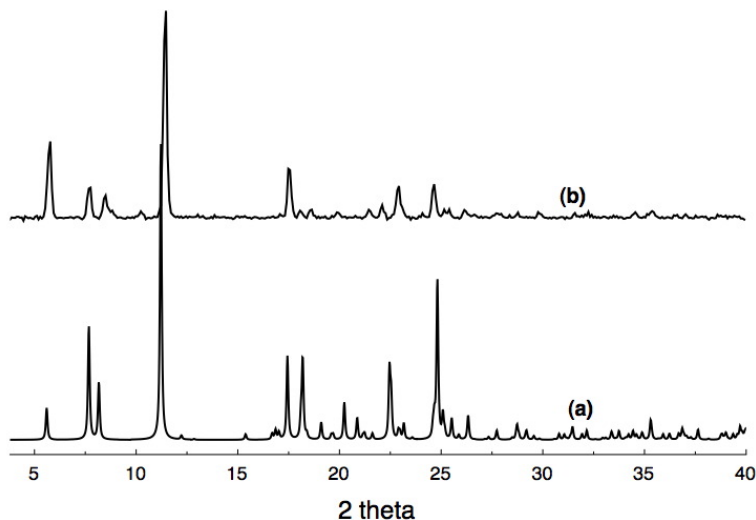
( $1^{2+}$ ,  $2^{2-}$ , Ag<sup>+</sup>, XF<sub>6</sub><sup>-</sup>) (X = P, As and Sb):

### IR spectra

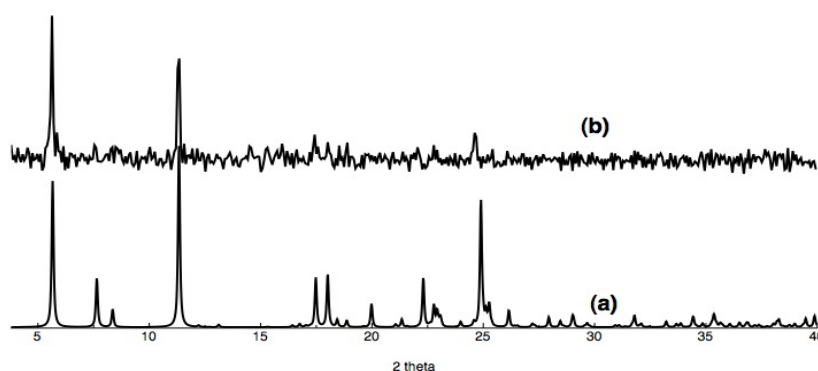


**Figure S1** : IR spectra (600 - 4000 cm<sup>-1</sup>) for ( $1^{2+}$ ,  $2^{2-}$ , Ag<sup>+</sup>, PF<sub>6</sub><sup>-</sup>) (green), ( $1^{2+}$ ,  $2^{2-}$ , Ag<sup>+</sup>, AsF<sub>6</sub><sup>-</sup>) (red) and ( $1^{2+}$ ,  $2^{2-}$ , Ag<sup>+</sup>, SbF<sub>6</sub><sup>-</sup>) (black).

## PXRD Pattern



**Figure S2:** Comparison of the simulated (a) and recorded (b) PXRD patterns for ( $1^{2+}$ ,  $2^{2-}$ ,  $Ag^+$ ,  $AsF_6^-$ ).



**Figure S3:** Comparison of the simulated (a) and recorded (b) PXRD patterns for ( $1^{2+}$ ,  $2^{2-}$ ,  $Ag^+$ ,  $PF_6^-$ ).

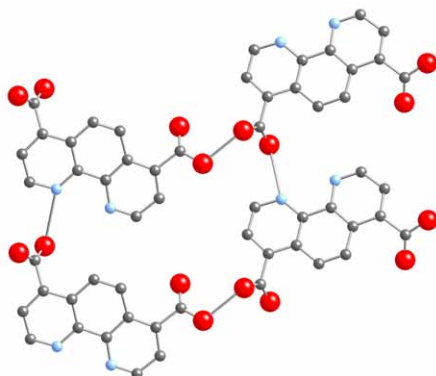
## Structural description

**2**

The solid-state structure of **2** was investigated by X-ray diffraction on single crystal. Compound **2** crystallizes in the absence of solvent molecules (*Monoclinic*, Space group *P2(1)/c*).

Owing to the simultaneous presence of both H-bond donor (carboxylic moieties) and acceptor (N atoms of the phenanthroline unit) sites, a H-bonded 2-D network is formed (Fig. S4). Compound **2**, is in the zwitterionic form and thus behaves as a non-symmetric unit. Indeed, among the two N atoms ( $d_{C-N}$  in the range of 1.319(2) - 1.362(2) Å), only the protonated one is engaged in a H-bond with one of the O atoms of the carboxylate moiety belonging to the neighbouring **2** ( $d_{N...O} = 2.782(3)$  Å). Among the two carboxylic groups, which are not coplanar with the plane of phenanthroline (CCCO dihedral angles of  $-58^\circ$  and  $24^\circ$ ), one behaves as a carboxylate ( $d_{C-O}$  of 1.243(2) and 1.256(2) Å) and the other as carboxylic acid ( $d_{C-O}$  of 1.213(2) and 1.311(2) Å). As expected, the carboxylate unit forms two H-bonds with

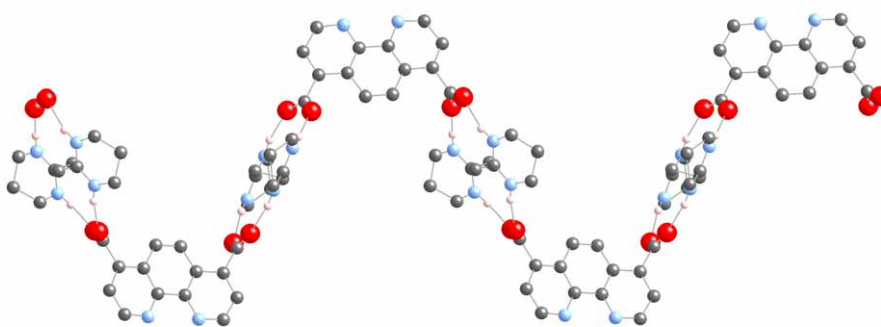
a carboxylic unit belonging to the neighbouring moiety ( $d_{O...O} = 2.516 \text{ \AA}$ ) and with the protonated N atom of the phenanthroline of another neighbouring molecule **2** ( $d_{N...O} = 2.782(3) \text{ \AA}$ ).



**Figure S4:** A portion of the solid-state structure of **2** showing the formation of a 2-D network and the H-bonding pattern. H atoms are not presented for sake of clarity. For bond distances and angles see text.

#### Structural description of ( $1^{2+}$ , $2^{2-}$ )

Complex ( $1^{2+} + 2^{2-}$ ) with a 1/1 ratio, crystallizes (*Orthorhombic*, Space group  $P2(1)2(1)2(1)$ ) with two chloroform molecules (figure S5). Owing to the simultaneous presence of both H-bond acceptor (carboxylic moieties of **2**) and donor (N atoms of the bisamidinium **1**) sites, a zig-zag type H-bonded 1-D network is formed. The latter results from an almost perfect recognition pattern between  $1^{2+}$  and  $2^{2-}$  (figure S5, see also figure 2 in the manuscript). Both carboxylic groups of  $2^{2-}$ , which are not coplanar with the plane of the phenanthroline moiety (CCCO dihedral angles of  $58^\circ$  and  $90^\circ$ ), behave as carboxylate ( $d_{C-O}$  varying between  $1.221(7)$  and  $1.244(7) \text{ \AA}$ ). As expected, the carboxylate moieties are recognized by the cyclic amidium groups, through a dihapto mode of hydrogen bonding ( $d_{N...O} =$  varying between  $2.663(7)$  and  $2.762(7) \text{ \AA}$ ).

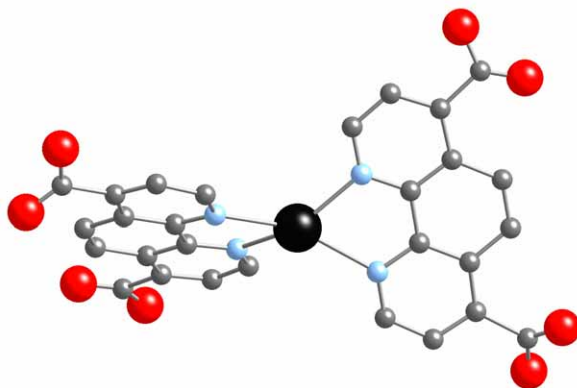


**Figure S5 :** A portion of the solid-state structure of ( $1^{2+}$ ,  $2^{2-}$ ) showing the formation of a neutral zigzag 1-D network and the H-bonding pattern. H atoms, except those involved in H-bonding, are not presented for sake of clarity. For bond distances and angles see text.

#### Structural description of $[(Ag^+-(2,2^-))]$ complex

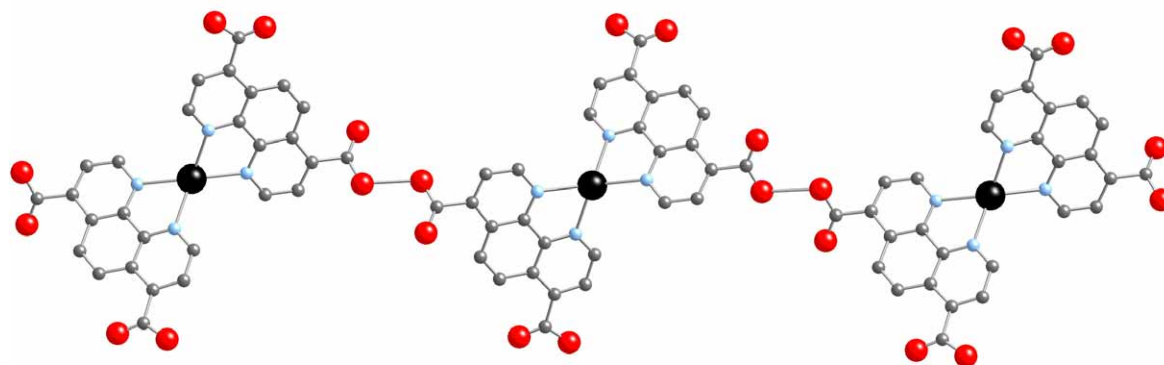
The  $[(Ag^+-(2,2^-))]$  complex crystallizes (*Monoclinic*, Space group  $P2/c$ ) in the presence of DMSO and EtOH solvent molecules (figure S6).

The silver cation is surrounded by two phenanthroline ligands. Around the metallic centre, the ligands are twisted with a dihedral angle of  $51^\circ$ , consequently, that the geometry around the silver atom is a severely deformed tetrahedron with  $\text{NAgN}$  angles varying between  $70.72^\circ(16)$  and  $152.6^\circ(2)$  and  $d_{\text{Ag-N}}$  distances of  $2.279(5)$  and  $2.381(4)$ .



**Figure S6:** A portion of the solid-state structure of  $[(\text{Ag}^+-(2,2^-))]$  complex. H atoms are not presented for sake of clarity. For bond distances and angles see text.

The complex is neutral and chemically, among the four carboxylic groups, only one is deprotonated. However, crystallographically, owing to the disorder present for two out of the four carboxylic groups, only two types of carboxylic moieties are observed consisting of two carboxylic groups with  $d_{\text{C-O}}$  of  $1.178(7)$  and  $1.309(7)$  Å and two disordered carboxylic units as a 1/1 mixture of carboxylic and carboxylate groups with average  $d_{\text{C-O}}$  of  $1.223(10)$  and  $1.274(10)$  Å. The individual complexes are interconnected through the disordered carboxylic units by a monohapto mode of H bonding with  $\text{OH}\cdots\text{O}$  distance of  $2.510(8)$  Å affording a 1-D H-bonded network (figure S7).



**Figure S7:** A portion of the solid-state structure of  $[(\text{Ag}^+-(2,2^-))]$  complex showing the formation of a 1-D H bonded network. H atoms are not presented for sake of clarity. For bond distances and angles see text.

## Energetical analysis : methodology

### 1. ( $\mathbf{1}^{2+}$ , $\mathbf{2}^{2-}$ , $\text{Ag}^+$ , $\text{PF}_6^-$ ) network

Computations have been done after scaling all C-H, N-H and O-H bond lengths to their standards values (1.08 Å, 0.98 Å and 0.97 Å respectively). In order to minimize computation time a primitive unit-cell ( $a = b = 15.753$  Å,  $c = 5.460$ ,  $\alpha = \beta = 96.183^\circ$ ,  $\gamma = 94.355^\circ$ ) was selected. The new symmetry operators acting on this transformed unit-cell were: #1 = (x,y,z); #2 = (-y,-x,-z); #3 = (-x,-y,-z) and #4 = (y,x,z). As methanol molecules were found disordered between two equivalent positions, the (#1,#3) symmetry mask was applied to atoms C16 and O3. Three H-atoms have also been added to atom C16 (tetrahedral arrangement) after minimization of unit-cell steric energy using non-empirical short-range repulsive potentials derived from the Gordon-Kim electron gas model that are known to correlate extremely well with experimental van der Waals or non-bonded radii.<sup>3</sup> One H-atom has also been added to atom O3 in such a way to make a perfectly linear H-bond with atom O2 located at 280 pm. Table 1 gives the corresponding atomic coordinates referred to the primitive unit-cell. Being bonded to disordered atoms, the same occupancy factor (0.5) and symmetry mask was applied to these four H-atoms.

H-atom	x/a	y/a	z/a
H1 (O3)	0.71025	1.18998	0.11686
H2 (C16)	0.64271	1.32860	0.30003
H3 (C16)	0.72489	1.30675	0.52428
H4 (C16)	0.64147	1.22693	0.40754

**Table 1:** Optimized H-atoms positions computed by the PACHA software for the ( $\mathbf{1}^{2+}$ ,  $\mathbf{2}^{2-}$ ,  $\text{Ag}^+$ ,  $\text{PF}_6^-$ ) framework.

Using the coordinates given in table 1 a unit-cell displaying the ( $\mathbf{1}^{2+}$ ,  $\mathbf{2}^{2-}$ ,  $\text{Ag}^+$ ,  $\text{PF}_6^-$ ) stoichiometry was generated. The structure may be described as corrugated 2D sheets made of  $[\text{Ag}(\mathbf{2}^{2-})_2]$  tectons H-bonded to two ( $\mathbf{2}^{2-}$ ) units (generation with a search radius of 2.39 Å) and stacked together by  $[\text{PF}_6]^-$  anions and methanol molecules to form a 3D-structure (generation with a search radius of 2.40 Å). This very compact packing of the sheets corresponding to twice the van der Waals radius of an H-atom ( $r_w = 1.20$  Å<sup>4</sup>) is worth noticing and justifies a 3D treatment despite its intrinsic 2D-topology. The partial charges on each atoms in this network was evaluated from the 3D unit-cell using a Madelung-summation technique (convergence parameter  $G = 0.188$  Å<sup>-1</sup> for  $-2 \leq h,k,l \leq +2$ ) and an electronegativity equalization principle<sup>5</sup> using Allen's absolute electronegativity scale<sup>6</sup> and atomic radii corresponding to the most diffuse principal maxima in the radial distribution function  $r^2\psi^2(r)$  estimated from relativistic atomic wave-functions  $\psi(r)$  solutions of the Dirac equations.<sup>7</sup> The corresponding atomic parameterization is given in table 2. Equalization of all electronegativities was observed at  $\langle \text{EN} \rangle = 15.05$  eV, leading to the following global charge distribution obtained by summing partial charges according to the stoichiometry of each moiety (only two significant digits are given in order to take into account the various uncertainties coming from the estimated standard deviations on each atomic coordinate):

<sup>3</sup> M.A. Spackman, *J. Chem. Phys.*, **85** (1986) 6579.

<sup>4</sup> A. Bondi, *J. Phys. Chem.*, **68** (1964) 441.

<sup>5</sup> (a) M. Henry, *CHEMPHYSICHEM*, **3** (2002) 561; (b) M. Henry, in "Advances in Quantum Chemical Bonding Structures", M.V. Putz Ed., Transworld Research Network, Kerala (2008) p. 153.

<sup>6</sup> (a) L. C. Allen, *J. Am. Chem. Soc.*, **111** (1989) 9003; (b) J. B. Mann, T. L. Meek, L. C. Allen, *J. Am. Chem. Soc.*, **122** (2000) 2780; (c) J. B. Mann, T. L. Meek, E. T. Knight, J. F. Capitani, L. C. Allen, *J. Am. Chem. Soc.*, **122** (2000) 5132.

<sup>7</sup> J. T. Waber, D. T. Cromer, *J. Chem. Phys.*, **42** (1965) 4116.

$$Q(\mathbf{1}^{2+}) = +1.01; Q(\text{Ag}) = +0.76; Q(\text{MeOH}) = +0.08; Q(\mathbf{2}^{2-}) = -0.96; Q(\text{PF}_6) = -1.02$$

Relative to their formal charges, the methanol molecule is found to play the role of a solvent acting as a weak electron donor while a 100% ionic interaction is observed for the hexafluorophosphate anion. Tectons that displays the lowest ionicities are  $\mathbf{1}^{2+}$  (51% ionicity) and  $\mathbf{2}^{2-}$  (48% ionicity). In contrast with the hexafluorophosphate anion, some covalency (24%) is observed for the silver cation. Relative to individual oxidation states on each atom, the overall ionic character of this framework was found to be 12.9%, a good indication of the molecular nature of interactions between the different tectons. Table 3 gives the self-energies that may be derived from this structure by considering either the whole network or some sub-nets obtained by removing one or several tectons. From this table, it is possible to derive an unambiguous energetic partition among the various interactions responsible for the self-assembly of this framework.

Atom	Electronegativity $\chi$ / eV	Atomic radius r/pm
H	13.61	53.0
C	15.05	62.0
N	18.13	52.1
O	21.36	45.0
F	24.80	39.6
P	13.33	91.8
As	13.08	99.2
Sb	11.74	116.6
Ag	11.05	128.6

**Table 2:** Allen's atomic electronegativities [4] and atomic radii [5] used for estimating the chemical hardness  $\eta = (e^2/4\pi\epsilon_0) \cdot (1/r)$  needed for computing partial charges distributions according to the electronegativity equalization principle [3].

The energetic analysis will be made using four tectons  $\{\text{AgPF}_6\}$ ,  $\{\text{MeOH}\}$ ,  $\{\mathbf{1}^{2+}\}$  and  $\{\mathbf{2}^{2-}\}$ . Table 4 shows the energetic effect  $\Delta$  induced on each tecton on going from a neutral molecular entity in the vacuum ( $SE_{\text{vac}}$ ) to a sub-net displaying no interactions with other tectons (see table 3). The positive value observed for  $\{\text{AgPF}_6\}$  points to an anti-cooperation between these tectons in the solid-state owing to F...F repulsions between polyatomic anions dominating over Ag...F attractions. However, this anti-cooperative effect is quite negligible in view of the very large negative value characterizing either the isolated  $\{\text{AgPF}_6\}$  entity or the  $\{\text{AgPF}_6\}$  sub-net. On the other hand a weak cooperation is evidenced for the  $\{\mathbf{2}^{2-}\}$  tecton obviously due to the pairing through the missing Ag-atom. The two other tectons are virtually not affected by their encapsulation in the network. Having characterized the non-interacting isolated entities, the total interaction energy was now evaluated as:

$$\Delta E_{\text{tot}} = SE(\text{net}) - SE(\text{MeOH}) - SE(\mathbf{1}^{2+}) - SE(\mathbf{2}^{2-}) - SE(\text{AgPF}_6) = -762 \text{ kJ}\cdot\text{mol}^{-1}$$

Considering individual interactions between the tectons, this interaction energy includes 2 H-bonds between the methanol molecule and one carboxylate group of a  $\mathbf{2}^{2-}$  ligand, 8 H-bonds between the carboxylate groups of the  $\mathbf{2}^{2-}$  ligands and the amidinium groups of the  $\mathbf{1}^{2+}$  ligand, 4 Ag-N coordination bonds and a packing energy of the 2D-sheets through hexafluorophosphate anions.



Net or sub-net	Stoichiometry	SE /kJ.mol <sup>-1</sup>	Symbol
( <b>1</b> <sup>2+</sup> , <b>2</b> <sup>2-</sup> , Ag <sup>+</sup> , PF <sub>6</sub> <sup>-</sup> )	H <sub>60</sub> C <sub>50</sub> N <sub>12</sub> O <sub>10</sub> AgPF <sub>6</sub>	-3435	SE(net)
2MeOH	[H <sub>4</sub> CO] <sub>2</sub>	-203	SE(MeOH)
2( <b>1</b> <sup>2+</sup> )	[H <sub>10</sub> C <sub>5</sub> N <sub>2</sub> ] <sub>4</sub>	-477	SE( <b>1</b> <sup>2+</sup> )
2( <b>2</b> <sup>2-</sup> )	[H <sub>3</sub> C <sub>7</sub> NO <sub>2</sub> ] <sub>4</sub>	-477	SE( <b>2</b> <sup>2-</sup> )
Ag(PF <sub>6</sub> )	AgPF <sub>6</sub>	-1516	SE(AgPF <sub>6</sub> )
[Ag( <b>2</b> <sup>2-</sup> ) <sub>2</sub> ( <b>1</b> <sup>2+</sup> ) <sub>2</sub> ](PF <sub>6</sub> )	H <sub>52</sub> C <sub>48</sub> N <sub>12</sub> O <sub>8</sub> AgPF <sub>6</sub>	-3182	SE*(MeOH)
[Ag( <b>2</b> <sup>2-</sup> ) <sub>2</sub> ](PF <sub>6</sub> ).2MeOH	H <sub>20</sub> C <sub>30</sub> N <sub>4</sub> O <sub>10</sub> AgPF <sub>6</sub>	-2529	SE*( <b>1</b> <sup>2+</sup> )
[Ag( <b>1</b> <sup>2+</sup> ) <sub>2</sub> ](PF <sub>6</sub> ).2MeOH	H <sub>48</sub> C <sub>22</sub> N <sub>8</sub> O <sub>2</sub> AgPF <sub>6</sub>	-2297	SE*( <b>2</b> <sup>2-</sup> )
[( <b>2</b> <sup>2-</sup> ) <sub>2</sub> ( <b>1</b> <sup>2+</sup> ) <sub>2</sub> ].2MeOH	[H <sub>30</sub> C <sub>25</sub> N <sub>6</sub> O <sub>5</sub> ] <sub>2</sub>	-1527	SE*(AgPF <sub>6</sub> )
[( <b>2</b> <sup>2-</sup> ) <sub>2</sub> ( <b>1</b> <sup>2+</sup> ) <sub>2</sub> ]	[H <sub>13</sub> C <sub>12</sub> N <sub>3</sub> O <sub>2</sub> ] <sub>4</sub>	-1285	SE(HB)
Ag(PF <sub>6</sub> ).2MeOH	H <sub>8</sub> C <sub>2</sub> O <sub>2</sub> AgPF <sub>6</sub>	-1753	SE*(HB)
[Ag( <b>2</b> <sup>2-</sup> ) <sub>2</sub> ](PF <sub>6</sub> )	H <sub>12</sub> C <sub>28</sub> N <sub>4</sub> O <sub>8</sub> AgPF <sub>6</sub>	-2192	SE(Ag <b>2</b> <sup>2-</sup> )
( <b>1</b> <sup>2+</sup> ) <sub>2</sub> .2MeOH	[H <sub>24</sub> C <sub>11</sub> N <sub>4</sub> O] <sub>2</sub>	-681	SE*(Ag <b>2</b> <sup>2-</sup> )
[Ag( <b>1</b> <sup>2+</sup> ) <sub>2</sub> ](PF <sub>6</sub> )	H <sub>40</sub> C <sub>20</sub> N <sub>8</sub> AgPF <sub>6</sub>	-2080	SE(Ag <b>1</b> <sup>2+</sup> )
( <b>2</b> <sup>2-</sup> ) <sub>2</sub> .2MeOH	[H <sub>10</sub> C <sub>15</sub> N <sub>2</sub> O <sub>5</sub> ] <sub>2</sub>	-750	SE*(Ag <b>1</b> <sup>2+</sup> )

**Table 3:** Self-energies (SE) for the whole net and some derived sub-nets in the crystal structure of (**1**<sup>2+</sup>, **2**<sup>2-</sup>, Ag<sup>+</sup>, PF<sub>6</sub><sup>-</sup>). All values have been rounded to the nearest integer in order to take into account the various uncertainties coming from the estimated standard deviations on each atomic coordinate. The interaction energy of any sub-net A characterized by its self-energy SE(A) extracted from the whole network characterized by its self-energy SE(net) is given by the difference  $E_{\text{int}}(\text{A}) = \text{SE}(\text{net}) - [\text{SE}(\text{A}) + \text{SE}^*(\text{A})]$ , where SE\*(A) is the self-energy of the sub-net remaining after removal of sub-net A.

Tecton	SE <sub>vac</sub> /kJ.mol <sup>-1</sup>	Δ /kJ.mol <sup>-1</sup>
MeOH	-101	-1
<b>1</b> <sup>2+</sup>	-237	0
<b>2</b> <sup>2-</sup>	-231	-15
Ag(PF <sub>6</sub> )	-1538	+22

**Table 4:** Self-energies of isolated molecular tectons ignoring space-group symmetry (SE<sub>vac</sub>) and differences with solid-state values SE<sub>ss</sub> (see table 3):  $\Delta = \text{SE}_{\text{ss}} - 2 \times \text{SE}_{\text{vac}}$  for {MeOH}, {**1**<sup>2+</sup>} and {**2**<sup>2-</sup>} tectons. The SE<sub>vac</sub> value for the {AgPF<sub>6</sub>} tecton corresponds to an Ag...P distance of 1062 pm (shortest distance observed in the crystal structure) with  $\Delta = \text{SE}_{\text{ss}} - \text{SE}_{\text{vac}}$ .

The binding energy of the methanol molecule will first be considered and evaluated in different ways considering either the whole net  $\Delta E_0$  or sub-nets ( $\Delta E_n$  with  $1 \leq n \leq 6$ ) in order to probe interaction energies with each tecton alone or with pairs of tectons. From table 3, the following energetic partition is readily retrieved:

$$\begin{aligned} \Delta E_0(\text{MeOH} \dots \text{OOC}) &= [\text{SE}(\text{net}) - \text{SE}(\text{MeOH}) - \text{SE}^*(\text{MeOH})]/2 = -25 \text{ kJ.mol}^{-1} \\ \Delta E_1(\text{MeOH} \dots \mathbf{2}^{2-} \dots \text{AgPF}_6) &= [\text{SE}^*(\mathbf{1}^{2+}) - \text{SE}(\text{MeOH}) - \text{SE}(\text{Ag}\mathbf{2}^{2-})]/2 = -67 \text{ kJ.mol}^{-1} \\ \Delta E_2(\text{MeOH} \dots \mathbf{2}^{2-}) &= [\text{SE}^*(\text{Ag}\mathbf{1}^{2+}) - \text{SE}(\text{MeOH}) - \text{SE}(\mathbf{2}^{2-})]/2 = -35 \text{ kJ.mol}^{-1} \\ \Delta E_3(\text{MeOH} \dots \mathbf{2}^{2-} \dots \mathbf{1}^{2+}) &= [\text{SE}^*(\text{AgPF}_6) - \text{SE}(\text{MeOH}) - \text{SE}(\text{HB})]/2 = -20 \text{ kJ.mol}^{-1} \\ \Delta E_4(\text{MeOH} \dots \text{AgPF}_6) &= [\text{SE}^*(\text{HB}) - \text{SE}(\text{MeOH}) - \text{SE}(\text{AgPF}_6)]/2 = -17 \text{ kJ.mol}^{-1} \\ \Delta E_5(\text{MeOH} \dots \text{AgPF}_6 \dots \mathbf{1}^{2+}) &= [\text{SE}^*(\mathbf{2}^{2-}) - \text{SE}(\text{MeOH}) - \text{SE}(\text{Ag}\mathbf{1}^{2+})]/2 = -7 \text{ kJ.mol}^{-1} \\ \Delta E_6(\text{MeOH} \dots \mathbf{1}^{2+}) &= [\text{SE}^*(\text{Ag}\mathbf{2}^{2-}) - \text{SE}(\text{MeOH}) - \text{SE}(\mathbf{1}^{2+})]/2 = -0.5 \text{ kJ.mol}^{-1} \end{aligned}$$

The  $\Delta E_0$  value referring to the interaction with all three tectons cooperating together is well in line with a standard hydrogen bond between two O-atoms. The stabilizing effect of binding the  $\{\text{AgPF}_6\}$  tecton to the  $2^{2-}$  ligand ( $\Delta E_2$  vs  $\Delta E_1$ ) and the destabilizing effect of binding the  $\{1^{2+}\}$  tecton to the  $2^{2-}$  ligand ( $\Delta E_3$  vs  $\Delta E_2$ ) is worth noticing while binding of both tectons has a neat destabilizing effect ( $\Delta E_2$  vs  $\Delta E_0$ ). This also shows that methanol interacts first with the  $\{2^{2-}\}$  tecton through H-bonding ( $\Delta E_1$ ,  $\Delta E_2$ ,  $\Delta E_3$ ), then with the  $\{\text{AgPF}_6\}$  tecton through electrostatic polarization ( $\Delta E_4$ ,  $\Delta E_5$ ) and finally ignores almost completely the  $\{1^{2+}\}$  tecton ( $\Delta E_6$ ).

The binding energy of the  $\{\text{AgPF}_6\}$  tecton was considered next and referring again to table 3, the following energetic partition was retrieved:

$$\begin{aligned}\Delta E_0(\text{PF}_6\text{Ag}\dots\text{N}_4) &= [\text{SE}(\text{net}) - \text{SE}(\text{AgPF}_6) - \text{SE}^*(\text{AgPF}_6)]/4 = -98 \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta E_1(\text{PF}_6\text{Ag}\dots 2^{2-}\dots 1^{2+}) &= [\text{SE}^*(\text{MeOH}) - \text{SE}(\text{AgPF}_6) - \text{SE}(\text{HB})]/4 = -95 \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta E_2(\text{PF}_6\text{Ag}\dots 2^{2-}\dots \text{MeOH}) &= [\text{SE}^*(2^{2-}) - \text{SE}(\text{AgPF}_6) - \text{SE}^*(\text{Ag}1^{2+})]/4 = -66 \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta E_3(\text{PF}_6\text{Ag}\dots 2^{2-}) &= [\text{SE}(\text{Ag}2^{2-}) - \text{SE}(\text{AgPF}_6) - \text{SE}(2^{2-})]/4 = -50 \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta E_4(\text{PF}_6\text{Ag}\dots 1^{2+}\dots \text{MeOH}) &= [\text{SE}^*(2^{2-}) - \text{SE}(\text{AgPF}_6) - \text{SE}^*(\text{Ag}2^{2-})]/2 = -50 \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta E_5(\text{PF}_6\text{Ag}\dots 1^{2+}) &= [\text{SE}(\text{Ag}1^{2+}) - \text{SE}(\text{AgPF}_6) - \text{SE}(1^{2+})]/2 = -7 \text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$

The energy associated to the Ag-N coordination bond with free carboxylate ends is thus  $-50 \text{ kJ}\cdot\text{mol}^{-1}$  ( $\Delta E_3$ ) and becomes strongly stabilized after H-bonding with the  $\{1^{2+}\}$  and  $\{\text{MeOH}\}$  tectons ( $\Delta E_0$ ). As expected the largest stabilization is observed after H-bonding with the  $\{1^{2+}\}$  tecton ( $\Delta E_3$  vs  $\Delta E_1$ ) rather than with the methanol molecule ( $\Delta E_3$  vs  $\Delta E_2$ ). As before a rather strong electrostatic polarization mediated by the  $\{1^{2+}\}$  tecton ( $\Delta E_4$ ) is observed between the  $\{\text{MeOH}\}$  tecton and the  $\{\text{AgPF}_6\}$  tecton.

Finally, the H-bonding interaction between the two  $\{2^{2-}\}$  and  $\{1^{2+}\}$  tectons leads to the following energetic partition:

$$\begin{aligned}\Delta E_0(\text{COO}\dots\text{HN}) &= [\text{SE}(\text{net}) - \text{SE}(1^{2+}) - \text{SE}^*(1^{2+})]/8 = -54 \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta E_1(1^{2+}\dots 2^{2-}\dots \text{AgPF}_6) &= [\text{SE}^*(\text{MeOH}) - \text{SE}(1^{2+}) - \text{SE}(\text{Ag}2^{2-})]/8 = -64 \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta E_2(1^{2+}\dots 2^{2-}) &= [\text{SE}(\text{HB}) - \text{SE}(1^{2+}) - \text{SE}(2^{2-})]/8 = -41 \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta E_3(1^{2+}\dots 2^{2-}\dots \text{MeOH}) &= [\text{SE}(\text{AgPF}_6) - \text{SE}(1^{2+}) - \text{SE}^*(\text{Ag}1^{2+})]/8 = -38 \text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$

Adding the methanol molecule has thus a clear destabilizing effect ( $\Delta E_1$  vs  $\Delta E_0$  or  $\Delta E_2$  vs  $\Delta E_3$ ). On the other hand, going from the 1D ( $1^{2+}\dots 2^{2-}$ ) chain to the 2D ( $1^{2+}\dots 2^{2-}\dots \text{AgPF}_6$ ) has a neat stabilizing effect ( $\Delta E_2$  vs  $\Delta E_1$ ). Consequently, a pretty well equilibrated energetic balance within the  $\{1^{2+}\}\{2^{2-}\}\{\text{AgPF}_6\}$  sheet exists between the (COO...HN) H-bonding interaction on one hand:  $8\times\Delta E_0(\text{COO}\dots\text{HN}) = -432 \text{ kJ}\cdot\text{mol}^{-1}$  and the (Ag-N) coordination interaction on the other hand:  $4\times\Delta E_0(\text{PF}_6\text{Ag}\dots\text{N}_4) = -392 \text{ kJ}\cdot\text{mol}^{-1}$  with a slight preference for the H-bonding connection mode.

## 2. ( $1^{2+}$ , $2^{2-}$ , $\text{Ag}^+$ , $\text{SbF}_6^-$ )

Computations have been done after scaling all C-H, N-H and O-H bond lengths to their standards values (1.08 Å, 0.98 Å and 0.97 Å respectively). In order to minimize computation time a primitive unit-cell ( $a = b = 15.880 \text{ Å}$ ,  $c = 5.368$ ,  $\alpha = \beta = 95.895^\circ$ ,  $\gamma = 92.905^\circ$ ) was selected with the same symmetry operators as before and the same (#1,#3)

symmetry mask applied to atoms C16 and O3. Table 5 gives the atomic coordinates of H-atoms that have been added to the hydroxyl group (perfectly linear H-bond with atom O2 located at 281 pm) and to the methyl group after steric energy minimization: referred to the primitive unit-cell.

H-atom	x/a	y/a	z/a
H1 (O3)	0.71542	1.18903	0.10546
H2 (C16)	0.65247	1.22725	0.43687
H3 (C16)	0.63966	1.32284	0.30037
H4 (C16)	0.72710	1.31401	0.52475

**Table 5:** Optimized H-atoms positions computed by the PACHA software for the ( $1^{2+}$ ,  $2^{2-}$ ,  $Ag^+$ ,  $SbF_6^-$ ) framework.

Using the coordinates given in table 5 a unit-cell displaying the ( $1^{2+}$ ,  $2^{2-}$ ,  $Ag^+$ ,  $SbF_6^-$ ) stoichiometry was generated. Generation of the corrugated sheet was possible with a search radius of 2.37 Å and transition towards a 3D-structure was observed with a search radius of 2.42 Å justifying again a 3D treatment owing to the very small van der Waals gap. After Madelung-summation (convergence parameter  $G = 0.189 \text{ \AA}^{-1}$  for  $-2 \leq h,k,l \leq +2$ ) and application of the atomic parameterization given in table 2, equalization of all electronegativities was observed at  $\langle EN \rangle = 14.95 \text{ eV}$ , leading to the new global charge distribution given with two significant digits:

$$Q(1^{2+}) = +0.95; Q(Ag) = +0.77; Q(MeOH) = +0.07; Q(2^{2-}) = -0.96; Q(SbF_6) = -0.90$$

Relative to their formal charges, the methanol molecule is found to play the role of a solvent acting as a weak electron donor and a 10% covalent character is evidenced for the hexaantimoniate anion. Tectons that displays the lowest ionicities are  $1^{2+}$  (47% ionicity) and  $2^{2-}$  (48% ionicity) with almost the same partial covalency (23%) for the silver cation. Relative to individual oxidation states on each atom, the overall ionic character of this framework has increased up to 13.5%, pointing again to the existence of a molecular network. Table 6 gives the self-energies that may be derived from this structure by considering as before either the whole network or some sub-nets obtained by removing one or several tectons. Energetic analysis was performed using the same four tectons  $\{AgSbF_6\}$ ,  $\{MeOH\}$ ,  $\{1^{2+}\}$  and  $\{2^{2-}\}$ . Table 7 shows the energetic effect  $\Delta$  induced on each tecton on going from a neutral molecular entity in the vacuum ( $SE_{vac}$ ) to a sub-net displaying no interactions with other tectons (see table 6). There is significantly less anti-cooperation between  $\{AgSbF_6\}$  tectons in the solid-state owing to less F...F repulsions between polyatomic anions. Other charged tectons show weak cooperation while methanol molecules are virtually not affected by their encapsulation in a network. The total interaction energy is found to be lower relative to the  $\{PF_6\}$ -net:

$$\Delta E_{tot} = SE(net) - SE(MeOH) - SE(1^{2+}) - SE(2^{2-}) - SE(AgPF) = -667 \text{ kJ.mol}^{-1}$$

Net or sub-net	Stoichiometry	SE /kJ.mol <sup>-1</sup>	Symbol
( $1^{2+}$ , $2^{2-}$ , $Ag^+$ , $SbF_6^-$ )	$H_{60}C_{50}N_{12}O_{10}AgSbF_6$	-3705	SE(net)
2MeOH	$[H_4CO]_2$	-206	SE(MeOH)
2( $1^{2+}$ )	$[H_{10}C_5N_2]_4$	-481	SE( $1^{2+}$ )
2( $2^{2-}$ )	$[H_3C_7NO_2]_4$	-483	SE( $2^{2-}$ )
Ag( $SbF_6$ )	$AgSbF_6$	-1868	SE( $AgSbF_6$ )
$[Ag(2^{2-})_2(1^{2+})_2](SbF_6)$	$H_{52}C_{48}N_{12}O_8AgSbF_6$	-3450	SE*(MeOH)
$[Ag(2^{2-})_2](SbF_6).2MeOH$	$H_{20}C_{30}N_4O_{10}AgSbF_6$	-2899	SE*( $1^{2+}$ )
$[Ag(1^{2+})_2](SbF_6).2MeOH$	$H_{48}C_{22}N_8O_2AgSbF_6$	-2552	SE*( $2^{2-}$ )

$[(2^{2-})_2(1^{2+})_2].2\text{MeOH}$	$[\text{H}_{30}\text{C}_{25}\text{N}_6\text{O}_5]_2$	-1549	$\text{SE}^*(\text{AgSbF}_6)$
$[(2^{2-})_2(1^{2+})_2]$	$[\text{H}_{13}\text{C}_{12}\text{N}_3\text{O}_2]_4$	-1301	$\text{SE}(\text{HB})$
$\text{Ag}(\text{SbF}_6).2\text{MeOH}$	$\text{H}_8\text{C}_2\text{O}_2 \text{AgSbF}_6$	-2079	$\text{SE}^*(\text{HB})$
$[\text{Ag}(2^{2-})_2](\text{SbF}_6)$	$\text{H}_{12}\text{C}_{28}\text{N}_4\text{O}_8\text{AgSbF}_6$	-2604	$\text{SE}(\text{Ag}2^{2-})$
$(1^{2+})_2.2\text{MeOH}$	$[\text{H}_{24}\text{C}_{11}\text{N}_4\text{O}]_2$	-690	$\text{SE}^*(\text{Ag}2^{2-})$
$[\text{Ag}(1^{2+})_2](\text{SbF}_6)$	$\text{H}_{40}\text{C}_{20}\text{N}_8\text{AgSbF}_6$	-2328	$\text{SE}(\text{Ag}1^{2+})$
$(2^{2-})_2.2\text{MeOH}$	$[\text{H}_{10}\text{C}_{15}\text{N}_2\text{O}_5]_2$	-756	$\text{SE}^*(\text{Ag}1^{2+})$

**Table 6:** Self-energies (SE) for the whole net and some derived sub-nets in the crystal structure of  $(1^{2+}, 2^{2-}, \text{Ag}^+, \text{SbF}_6^-)$ . All values have been rounded to the nearest integer in order to take into account the various uncertainties coming from the estimated standard deviations on each atomic coordinate. The interaction energy of any sub-net A characterized by its self-energy  $\text{SE}(\text{A})$  extracted from the whole network characterized by its self-energy  $\text{SE}(\text{net})$  is given by the difference  $E_{\text{int}}(\text{A}) = \text{SE}(\text{net}) - [\text{SE}(\text{A}) + \text{SE}^*(\text{A})]$ , where  $\text{SE}^*(\text{A})$  is the self-energy of the sub-net remaining after removal of sub-net A.

Tecton	$\text{SE}_{\text{vac}} / \text{kJ.mol}^{-1}$	$\Delta / \text{kJ.mol}^{-1}$
MeOH	-103	0
$1^{2+}$	-239	-3
$2^{2-}$	-239	-5
$\text{Ag}(\text{SbF}_6)$	-1871	+3

**Table 7:** Self-energies of isolated molecular tectons ignoring space-group symmetry ( $\text{SE}_{\text{vac}}$ ) and differences with solid-state values  $\text{SE}_{\text{ss}}$  (see table 6):  $\Delta = \text{SE}_{\text{ss}} - 2 \times \text{SE}_{\text{vac}}$  for  $\{\text{MeOH}\}$ ,  $\{1^{2+}\}$  and  $\{2^{2-}\}$  tectons. The  $\text{SE}_{\text{vac}}$  value for the  $\{\text{AgSbF}_6\}$  tecton corresponds to an  $\text{Ag} \dots \text{Sb}$  distance of 1087 pm (shortest distance observed in the crystal structure) with  $\Delta = \text{SE}_{\text{ss}} - \text{SE}_{\text{vac}}$ .

The binding energy of the methanol molecule was evaluated as before by considering either the whole net  $\Delta E_0$  or sub-nets ( $\Delta E_n$  with  $1 \leq n \leq 6$ ) leading to the following energetic partition:

$$\begin{aligned} \Delta E_0(\text{MeOH} \dots \text{OOC}) &= [\text{SE}(\text{net}) - \text{SE}(\text{MeOH}) - \text{SE}^*(\text{MeOH})]/2 = -25 \text{ kJ.mol}^{-1} \\ \Delta E_1(\text{MeOH} \dots 2^{2-} \dots \text{AgSbF}_6) &= [\text{SE}^*(1^{2+}) - \text{SE}(\text{MeOH}) - \text{SE}(\text{Ag}2^{2-})]/2 = -45 \text{ kJ.mol}^{-1} \\ \Delta E_2(\text{MeOH} \dots 2^{2-}) &= [\text{SE}^*(\text{Ag}1^{2+}) - \text{SE}(\text{MeOH}) - \text{SE}(2^{2-})]/2 = -34 \text{ kJ.mol}^{-1} \\ \Delta E_3(\text{MeOH} \dots 2^{2-} \dots 1^{2+}) &= [\text{SE}^*(\text{AgSbF}_6) - \text{SE}(\text{MeOH}) - \text{SE}(\text{HB})]/2 = -21 \text{ kJ.mol}^{-1} \\ \Delta E_4(\text{MeOH} \dots \text{AgSbF}_6) &= [\text{SE}^*(\text{HB}) - \text{SE}(\text{MeOH}) - \text{SE}(\text{AgSbF}_6)]/2 = -3 \text{ kJ.mol}^{-1} \\ \Delta E_5(\text{MeOH} \dots \text{AgSbF}_6 \dots 1^{2+}) &= [\text{SE}^*(2^{2-}) - \text{SE}(\text{MeOH}) - \text{SE}(\text{Ag}1^{2+})]/2 = -9 \text{ kJ.mol}^{-1} \\ \Delta E_6(\text{MeOH} \dots 1^{2+}) &= [\text{SE}^*(\text{Ag}2^{2-}) - \text{SE}(\text{MeOH}) - \text{SE}(1^{2+})]/2 = -1.5 \text{ kJ.mol}^{-1} \end{aligned}$$

The  $\Delta E_0$ ,  $\Delta E_2$  and  $\Delta E_3$  values are found to be virtually unaffected by the  $\{\text{AgPF}_6\} \leftrightarrow \{\text{AgSbF}_6\}$  substitution. The stabilizing effect of binding the  $\{\text{AgSbF}_6\}$  tecton to the  $2^{2-}$  ligand ( $\Delta E_2$  vs  $\Delta E_1$ ) appears to be however neatly reduced. As before, methanol interacts first with the  $\{2^{2-}\}$  tecton through H-bonding ( $\Delta E_1$ ,  $\Delta E_2$ ,  $\Delta E_3$ ), then with the  $\{\text{AgPF}_6\}$  tecton through a neatly reduced electrostatic polarization ( $\Delta E_4$ ,  $\Delta E_5$ ) and again ignores almost completely the  $\{1^{2+}\}$  tecton ( $\Delta E_6$ ).

Concerning the binding energy of the  $\{\text{AgSbF}_6\}$  tecton, the following energetic partition was retrieved from table 6:

$$\begin{aligned} \Delta E_0(\text{SbF}_6\text{Ag} \dots \text{N}_4) &= [\text{SE}(\text{net}) - \text{SE}(\text{AgSbF}_6) - \text{SE}^*(\text{AgSbF}_6)]/4 = -72 \text{ kJ.mol}^{-1} \\ \Delta E_1(\text{SbF}_6\text{Ag} \dots 2^{2-} \dots 1^{2+}) &= [\text{SE}^*(\text{MeOH}) - \text{SE}(\text{AgSbF}_6) - \text{SE}(\text{HB})]/4 = -70 \text{ kJ.mol}^{-1} \end{aligned}$$

$$\begin{aligned}\Delta E_2(\text{SbF}_6\text{Ag}\dots\mathbf{2}^{2-}\dots\text{MeOH}) &= [\text{SE}^*(\mathbf{1}^{2+}) - \text{SE}(\text{AgSbF}_6) - \text{SE}^*(\text{Ag}\mathbf{1}^{2+})]/4 = -69 \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta E_3(\text{SbF}_6\text{Ag}\dots\mathbf{2}^{2-}) &= [\text{SE}(\text{Agpdc}) - \text{SE}(\text{AgSbF}_6) - \text{SE}(\mathbf{2}^{2-})]/4 = -63 \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta E_4(\text{SbF}_6\text{Ag}\dots\mathbf{1}^{2+}\dots\text{MeOH}) &= [\text{SE}^*(\mathbf{2}^{2-}) - \text{SE}(\text{AgSbF}_6) - \text{SE}^*(\text{Ag}\mathbf{2}^{2-})]/2 = +3 \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta E_5(\text{SbF}_6\text{Ag}\dots\mathbf{1}^{2+}) &= [\text{SE}(\text{Ag}\mathbf{1}^{2+}) - \text{SE}(\text{AgSbF}_6) - \text{SE}(\mathbf{1}^{2+})]/2 = +11 \text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$

The energy associated to the Ag-N coordination bond with free carboxylate groups was found to be more stable at  $-63 \text{ kJ}\cdot\text{mol}^{-1}$  ( $\Delta E_3$ ) becoming only slightly stabilized after H-bonding with the  $\{\mathbf{1}^{2+}\}$  and  $\{\text{MeOH}\}$  tectons ( $\Delta E_0$ ). In contrast with the  $\{\text{PF}_6\}$ -net the stabilization energy is almost the same after H-bonding with the  $\{\mathbf{1}^{2+}\}$  tecton ( $\Delta E_3$  vs  $\Delta E_1$ ) or with the methanol molecule ( $\Delta E_3$  vs  $\Delta E_2$ ). Another difference is now the occurrence of a small destabilizing electrostatic polarization mediated by the  $\{\mathbf{1}^{2+}\}$  tecton ( $\Delta E_4$  and  $\Delta E_5$ ).

The H-bonding interaction between the two  $\{\mathbf{2}^{2-}\}$  and  $\{\mathbf{1}^{2+}\}$  tectons leads to the following energetic partition:

$$\begin{aligned}\Delta E_0(\text{COO}\dots\text{HN}) &= [\text{SE}(\text{net}) - \text{SE}(\mathbf{1}^{2+}) - \text{SE}^*(\mathbf{1}^{2+})]/8 = -41 \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta E_1(\mathbf{1}^{2+}\dots\mathbf{2}^{2-}\dots\text{AgPF}_6) &= [\text{SE}^*(\text{MeOH}) - \text{SE}(\mathbf{1}^{2+}) - \text{SE}(\text{Ag}\mathbf{2}^{2-})]/8 = -46 \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta E_2(\mathbf{1}^{2+}\dots\mathbf{2}^{2-}) &= [\text{SE}(\text{HB}) - \text{SE}(\mathbf{1}^{2+}) - \text{SE}(\mathbf{2}^{2-})]/8 = -42 \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta E_3(\mathbf{1}^{2+}\dots\mathbf{2}^{2-}\dots\text{MeOH}) &= [\text{SE}^*(\text{AgSbF}_6) - \text{SE}(\mathbf{1}^{2+}) - \text{SE}^*(\text{Ag}\mathbf{1}^{2+})]/8 = -39 \text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$

Adding the methanol molecule has thus a slight destabilizing effect ( $\Delta E_1$  vs  $\Delta E_0$  or  $\Delta E_2$  vs  $\Delta E_3$ ) while going from the 1D ( $\mathbf{1}^{2+}\dots\mathbf{2}^{2-}$ ) chain to the 2D ( $\mathbf{1}^{2+}\dots\mathbf{2}^{2-}\dots\text{AgSbF}_6$ ) shows also a neatly reduced stabilizing effect ( $\Delta E_2$  vs  $\Delta E_1$ ). As before it exists a pretty well equilibrated energetic balance within the  $\{\mathbf{1}^{2+}\}\{\mathbf{2}^{2-}\}\{\text{AgSbF}_6\}$  sheet between the (COO...HN) H-bonding interaction on one hand:  $8\times\Delta E_0(\text{COO}\dots\text{HN}) = -328 \text{ kJ}\cdot\text{mol}^{-1}$  and the (Ag-N) coordination interaction on the other hand:  $4\times\Delta E_0(\text{SbF}_6\text{Ag}\dots\text{N}_4) = -288 \text{ kJ}\cdot\text{mol}^{-1}$ .

### 3. ( $\mathbf{1}^{2+}$ , $\mathbf{2}^{2-}$ , $\text{Ag}^+$ , $\text{AsF}_6^-$ )

Computations have been done after scaling all C-H, N-H and O-H bond lengths to their standards values (1.08 Å, 0.98 Å and 0.97 Å respectively). In order to minimize computation time a primitive unit-cell ( $a = b = 15.762 \text{ Å}$ ,  $c = 5.3934$ ,  $\alpha = \beta = 95.89^\circ$ ,  $\gamma = 93.81^\circ$ ) was selected with the same symmetry operators as before and the same (#1,#3) symmetry mask applied to atoms C16 and O3. Table 8 gives the atomic coordinates of H-atoms that have been added to the hydroxyl group (perfectly linear H-bond with atom O2 located at 281 pm) and to the methyl group after steric energy minimization: referred to the primitive unit-cell.

H-atom	x/a	y/a	z/a
H1 (O3)	0.72818	1.19299	0.07411
H2 (C16)	0.66311	1.33257	0.34142
H3 (C16)	0.71768	1.26329	0.52735
H4 (C16)	0.62855	1.22293	0.31314

**Table 8:** Optimized H-atoms positions computed by the PACHA software for the ( $\mathbf{1}^{2+}$ ,  $\mathbf{2}^{2-}$ ,  $\text{Ag}^+$ ,  $\text{AsF}_6^-$ ) framework.

Using the coordinates given in table 8 a unit-cell displaying the ( $\mathbf{1}^{2+}$ ,  $\mathbf{2}^{2-}$ ,  $\text{Ag}^+$ ,  $\text{AsF}_6^-$ ) stoichiometry was generated. Generation of the corrugated sheet was possible with a search radius of 2.37 Å and transition towards a 3D-structure was observed with a search radius of 2.42 Å justifying again a 3D treatment owing to the very small van der Waals gap. After

Madelung-summation (convergence parameter  $G = 0.189 \text{ \AA}^{-1}$  for  $-2 \leq h,k,l \leq +2$ ) and application of the atomic parameterization given in table 2, equalization of all electronegativities was observed at  $\langle EN \rangle = 14.04 \text{ eV}$ , leading to the new global charge distribution given with two significant digits:

$$Q(\mathbf{1}^{2+}) = +1.01; Q(\text{Ag}) = +0.77; Q(\text{MeOH}) = +0.08; Q(\mathbf{2}^{2-}) = -0.97; Q(\text{AsF}_6) = -1.01$$

Relative to their formal charges, the methanol molecule is found to play the role of a solvent acting as a weak electron donor while a 100% ionic interaction is observed for the hexafluoroarsenate anion. Tectons that displays the lowest ionicities are  $\mathbf{1}^{2+}$  (51% ionicity) and  $\mathbf{2}^{2-}$  (49% ionicity). In contrast with the hexafluorophosphate anion, some covalency (23%) is observed for the silver cation. Relative to individual oxidation states on each atom, the overall ionic character of this framework was found to be 12.6%, a good indication of the molecular nature of interactions between the different tectons. Table 9 gives the self-energies that may be derived from this structure by considering as before either the whole network or some sub-nets obtained by removing one or several tectons. Energetic analysis was performed using the following four tectons  $\{\text{AgAsF}_6\}$ ,  $\{\text{MeOH}\}$ ,  $\{\mathbf{1}^{2+}\}$  and  $\{\mathbf{2}^{2-}\}$ . Table 10 shows the energetic effect  $\Delta$  induced on each tecton on going from a neutral molecular entity in the vacuum ( $SE_{\text{vac}}$ ) to a sub-net displaying no interactions with other tectons (see table 9). The positive value observed for  $\{\text{AgAsF}_6\}$  points to an anti-cooperation between these tectons in the solid-state owing to F...F repulsions between polyatomic anions dominating over Ag...F attractions. This anti-cooperative effect is again quite negligible in view of the very large negative value characterizing either the isolated  $\{\text{AgAsF}_6\}$  entity or the  $\{\text{AgAsF}_6\}$  sub-net. A weak cooperation is evidenced for the  $\{\mathbf{2}^{2-}\}$  tecton obviously due to the pairing through the missing Ag-atom. The two other tectons are virtually not affected by their encapsulation in the network. Having characterized the non-interacting isolated entities, the total interaction energy was now evaluated as:

$$\Delta E_{\text{tot}} = SE(\text{net}) - SE(\text{MeOH}) - SE(\mathbf{1}^{2+}) - SE(\mathbf{2}^{2-}) - SE(\text{AgAsF}_6) = -730 \text{ kJ.mol}^{-1}$$

Net or sub-net	Stoichiometry	SE /kJ.mol <sup>-1</sup>	Symbol
$(\mathbf{1}^{2+}, \mathbf{2}^{2-}, \text{Ag}^+, \text{AsF}_6^-)$	$\text{H}_{60}\text{C}_{50}\text{N}_{12}\text{O}_{10}\text{AgAsF}_6$	-3217	SE(net)
2MeOH	$[\text{H}_4\text{CO}]_2$	-203	SE(MeOH)
$2(\mathbf{1}^{2+})$	$[\text{H}_{10}\text{C}_5\text{N}_2]_4$	-478	SE( $\mathbf{1}^{2+}$ )
$2(\mathbf{2}^{2-})$	$[\text{H}_3\text{C}_7\text{NO}_2]_4$	-476	SE( $\mathbf{2}^{2-}$ )
Ag(AsF <sub>6</sub> )	AgAsF <sub>6</sub>	-1330	SE(AgAsF <sub>6</sub> )
$[\text{Ag}(\mathbf{2}^{2-})_2(\mathbf{1}^{2+})_2](\text{AsF}_6)$	$\text{H}_{52}\text{C}_{48}\text{N}_{12}\text{O}_8\text{AgAsF}_6$	-2974	SE*(MeOH)
$[\text{Ag}(\mathbf{2}^{2-})_2](\text{AsF}_6).2\text{MeOH}$	$\text{H}_{20}\text{C}_{30}\text{N}_4\text{O}_{10}\text{AgAsF}_6$	-2329	SE*( $\mathbf{1}^{2+}$ )
$[\text{Ag}(\mathbf{1}^{2+})_2](\text{AsF}_6).2\text{MeOH}$	$\text{H}_{48}\text{C}_{22}\text{N}_8\text{O}_2\text{AgAsF}_6$	-2071	SE*( $\mathbf{2}^{2-}$ )
$[(\mathbf{2}^{2-})_2(\mathbf{1}^{2+})_2].2\text{MeOH}$	$[\text{H}_{30}\text{C}_{25}\text{N}_6\text{O}_5]_2$	-1526	SE*(AgAsF <sub>6</sub> )
$[(\mathbf{2}^{2-})_2(\mathbf{1}^{2+})_2]$	$[\text{H}_{13}\text{C}_{12}\text{N}_3\text{O}_2]_4$	-1293	SE(HB)
Ag(AsF <sub>6</sub> ).2MeOH	$\text{H}_8\text{C}_2\text{O}_2 \text{ AgAsF}_6$	-1547	SE*(HB)
$[\text{Ag}(\mathbf{2}^{2-})_2](\text{AsF}_6)$	$\text{H}_{12}\text{C}_{28}\text{N}_4\text{O}_8\text{AgAsF}_6$	-2025	SE(Ag $\mathbf{2}^{2-}$ )
$(\mathbf{1}^{2+})_2.2\text{MeOH}$	$[\text{H}_{24}\text{C}_{11}\text{N}_4\text{O}]_2$	-681	SE*(Ag $\mathbf{2}^{2-}$ )
$[\text{Ag}(\mathbf{1}^{2+})_2](\text{AsF}_6)$	$\text{H}_{40}\text{C}_{20}\text{N}_8\text{AgAsF}_6$	-1857	SE(Ag $\mathbf{1}^{2+}$ )
$(\mathbf{2}^{2-})_2.2\text{MeOH}$	$[\text{H}_{10}\text{C}_{15}\text{N}_2\text{O}_5]_2$	-735	SE*(Ag $\mathbf{1}^{2+}$ )

**Table 9:** Self-energies (SE) for the whole net and some derived sub-nets in the crystal structure of ( $1^{2+}$ ,  $2^{2-}$ ,  $Ag^+$ ,  $AsF_6^-$ ). All values have been rounded to the nearest integer in order to take into account the various uncertainties coming from the estimated standard deviations on each atomic coordinate. The interaction energy of any sub-net A characterized by its self-energy SE(A) extracted from the whole network characterized by its self-energy SE(net) is given by the difference  $E_{int}(A) = SE(net) - [SE(A) + SE^*(A)]$ , where  $SE^*(A)$  is the self-energy of the sub-net remaining after removal of sub-net A.

Tecton	$SE_{vac} / kJ.mol^{-1}$	$\Delta / kJ.mol^{-1}$
MeOH	-102	+1
$1^{2+}$	-237	-3
$2^{2-}$	-235	-6
Ag( $AsF_6$ )	-1350	+20

**Table 10:** Self-energies of isolated molecular tectons ignoring space-group symmetry ( $SE_{vac}$ ) and differences with solid-state values  $SE_{ss}$  (see table 6):  $\Delta = SE_{ss} - 2 \times SE_{vac}$  for  $\{MeOH\}$ ,  $\{1^{2+}\}$  and  $\{2^{2-}\}$  tectons. The  $SE_{vac}$  value for the  $\{AgAsF_6\}$  tecton corresponds to an Ag...As distance of 1070 pm (shortest distance observed in the crystal structure) with  $\Delta = SE_{ss} - SE_{vac}$ .

The binding energy of the methanol molecule was evaluated as before by considering either the whole net  $\Delta E_0$  or sub-nets ( $\Delta E_n$  with  $1 \leq n \leq 6$ ) leading to the following energetic partition:

$$\begin{aligned} \Delta E_0(\text{MeOH} \dots \text{OOC}) &= [SE(\text{net}) - SE(\text{MeOH}) - SE^*(\text{MeOH})]/2 = -20 \text{ kJ.mol}^{-1} \\ \Delta E_1(\text{MeOH} \dots 2^{2-} \dots \text{AgAsF}_6) &= [SE^*(1^{2+}) - SE(\text{MeOH}) - SE(\text{Ag}2^{2-})]/2 = -51 \text{ kJ.mol}^{-1} \\ \Delta E_2(\text{MeOH} \dots 2^{2-}) &= [SE^*(\text{Ag}1^{2+}) - SE(\text{MeOH}) - SE(2^{2-})]/2 = -28 \text{ kJ.mol}^{-1} \\ \Delta E_3(\text{MeOH} \dots 2^{2-} \dots 1^{2+}) &= [SE^*(\text{AgAsF}_6) - SE(\text{MeOH}) - SE(\text{HB})]/2 = -15 \text{ kJ.mol}^{-1} \\ \Delta E_4(\text{MeOH} \dots \text{AgAsF}_6) &= [SE^*(\text{HB}) - SE(\text{MeOH}) - SE(\text{AgAsF}_6)]/2 = -7 \text{ kJ.mol}^{-1} \\ \Delta E_5(\text{MeOH} \dots \text{AgAsF}_6 \dots 1^{2+}) &= [SE^*(2^{2-}) - SE(\text{MeOH}) - SE(\text{Ag}1^{2+})]/2 = -6 \text{ kJ.mol}^{-1} \\ \Delta E_6(\text{MeOH} \dots 1^{2+}) &= [SE^*(\text{Ag}2^{2-}) - SE(\text{MeOH}) - SE(1^{2+})]/2 = 0 \text{ kJ.mol}^{-1} \end{aligned}$$

The methanol molecule has here a less stabilizing effect ( $\Delta E_0$  value) relative to the  $\{AgPF_6\}$  or  $\{AgSbF_6\}$  cases. The stabilizing effect of binding the  $\{AgAsF_6\}$  tecton to the  $2^{2-}$  ligand ( $\Delta E_2$  vs  $\Delta E_1$ ) is larger relative the  $\{AgSbF_6\}$  case and smaller relative the  $\{AgPF_6\}$  case. As before, methanol interacts first with the  $\{2^{2-}\}$  tecton through H-bonding ( $\Delta E_1$ ,  $\Delta E_2$ ,  $\Delta E_3$ ), then with the  $\{AgAsF_6\}$  tecton through a weak electrostatic polarization ( $\Delta E_4$ ,  $\Delta E_5$ ) ignoring completely the  $\{1^{2+}\}$  tecton ( $\Delta E_6$ ).

Concerning the binding energy of the  $\{AgAsF_6\}$  tecton, the following energetic partition was retrieved from table 6:

$$\begin{aligned} \Delta E_0(\text{AsF}_6\text{Ag} \dots \text{N}_4) &= [SE(\text{net}) - SE(\text{AgAsF}_6) - SE^*(\text{AgAsF}_6)]/4 = -90 \text{ kJ.mol}^{-1} \\ \Delta E_1(\text{AsF}_6\text{Ag} \dots 2^{2-} \dots 1^{2+}) &= [SE^*(\text{MeOH}) - SE(\text{AgAsF}_6) - SE(\text{HB})]/4 = -88 \text{ kJ.mol}^{-1} \\ \Delta E_2(\text{AsF}_6\text{Ag} \dots 2^{2-} \dots \text{MeOH}) &= [SE^*(1^{2+}) - SE(\text{AgAsF}_6) - SE^*(\text{Ag}1^{2+})]/4 = -66 \text{ kJ.mol}^{-1} \\ \Delta E_3(\text{AsF}_6\text{Ag} \dots 2^{2-}) &= [SE(\text{Ag}2^{2-}) - SE(\text{AgAsF}_6) - SE(2^{2-})]/4 = -55 \text{ kJ.mol}^{-1} \\ \Delta E_4(\text{AsF}_6\text{Ag} \dots 1^{2+} \dots \text{MeOH}) &= [SE^*(2^{2-}) - SE(\text{AgAsF}_6) - SE^*(\text{Ag}2^{2-})]/2 = -30 \text{ kJ.mol}^{-1} \\ \Delta E_5(\text{AsF}_6\text{Ag} \dots 1^{2+}) &= [SE(\text{Ag}1^{2+}) - SE(\text{AgAsF}_6) - SE(1^{2+})]/2 = -25 \text{ kJ.mol}^{-1} \end{aligned}$$

The energy associated to the Ag-N coordination bond with free carboxylate ends ( $\Delta E_3$  value) is the same as that observed in the  $\{AgPF_6\}$  case and becomes also strongly stabilized after

H-bonding with the  $\{1^{2+}\}$  and  $\{\text{MeOH}\}$  tectons ( $\Delta E_0$ ). As expected the largest stabilization is observed after H-bonding with the  $\{1^{2+}\}$  tecton ( $\Delta E_3$  vs  $\Delta E_1$ ) rather than with the methanol molecule ( $\Delta E_3$  vs  $\Delta E_2$ ). In contrast with the  $\{\text{AgSbF}_6\}$  case, a rather strong electrostatic polarization mediated by the  $\{1^{2+}\}$  tecton ( $\Delta E_4$ ) is observed between the  $\{\text{MeOH}\}$  tecton and the  $\{\text{AgAsF}_6\}$  tecton.

The H-bonding interaction between the two  $\{2^{2-}\}$  and  $\{1^{2+}\}$  tectons leads to the following energetic partition:

$$\Delta E_0(\text{COO}\dots\text{HN}) = [\text{SE}(\text{net}) - \text{SE}(1^{2+}) - \text{SE}^*(1^{2+})]/8 = -51 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta E_1(1^{2+}\dots 2^{2-}\dots\text{AgPF}_6) = [\text{SE}^*(\text{MeOH}) - \text{SE}(1^{2+}) - \text{SE}(\text{Ag}2^{2-})]/8 = -59 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta E_2(1^{2+}\dots 2^{2-}) = [\text{SE}(\text{HB}) - \text{SE}(1^{2+}) - \text{SE}(2^{2-})]/8 = -42 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta E_3(1^{2+}\dots 2^{2-}\dots\text{MeOH}) = [\text{SE}^*(\text{AgSbF}_6) - \text{SE}(1^{2+}) - \text{SE}^*(\text{Ag}1^{2+})]/8 = -39 \text{ kJ}\cdot\text{mol}^{-1}$$

Adding the methanol molecule has thus a slight destabilizing effect ( $\Delta E_1$  vs  $\Delta E_0$  or  $\Delta E_2$  vs  $\Delta E_3$ ) while going from the 1D ( $1^{2+}\dots 2^{2-}$ ) chain to the 2D ( $1^{2+}\dots 2^{2-}\dots\text{AgPF}_6$ ) shows also a neat stabilizing effect ( $\Delta E_2$  vs  $\Delta E_1$ ). As before it exists a pretty well equilibrated energetic balance within the  $\{1^{2+}\}\{2^{2-}\}\{\text{AgPF}_6\}$  sheet between the (COO...HN) H-bonding interaction on one hand:  $8\times\Delta E_0(\text{COO}\dots\text{HN}) = -408 \text{ kJ}\cdot\text{mol}^{-1}$  and the (Ag-N) coordination interaction on the other hand:  $4\times\Delta E_0(\text{PF}_6\text{Ag}\dots\text{N}_4) = -360 \text{ kJ}\cdot\text{mol}^{-1}$ .