Molecular tectonics: design and generation of charge assisted H bonded hybrid molecular networks based on amidinium cations and thio- or isothio-cyanatometallates

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Received (in XXX, XXX) 1st January 2007, Accepted 1st January 2007

First published on the web 1st January 2007

DOI: 10.1039/b000000x

Upon combining the bis amidinium dication **1**-2H⁺ with thiocyanatometallates M(SCN)₄²⁻ (M = Pd,
10 Hg) or isothiocyanatometallates Cu(NCS)₄²⁻ anions behaving as H-bond donor and acceptors
respectively, three new hybrid molecular networks have been obtained in the crystalline phase and
structurally characterized by X-ray diffraction on single crystals. Whereas for the combination of
tecton **1**-2H⁺ and both Pd(SCN)₄²⁻ and Hg(SCN)₄²⁻ anions analogous 1-D H-bonded networks were
observed, for Cu(NCS)₄²⁻ anion a 2-D network was obtained. Based on structural features of both
15 components, the formation of the two types of networks is discussed.

Introduction

The design and generation of hybrid molecular networks¹
combining organic and metal complexes are attracting
considerable interest over the last years. Among various
20 possible design principles, the most used one is based on the
use of the first coordination sphere through direct
interconnection between organic building blocks or tectons^{2,3}
and metal centres. This strategy affords coordination networks
or MOFs.⁴ An alternative approach consists in exploiting
25 specific interactions at the second coordination sphere around
metal centres.^{3,5} In particular, using simultaneously
directional H-bonding and charge-charge electrostatic
interactions, one may generate robust networks. The viability
of this approach has been demonstrated.⁶⁻⁸ We have previously
30 illustrated this strategy by combining bis amidinium based
tectons such as **1**-2H⁺ (Scheme) and its analogues with a
variety of cyanometallate M(CN)_n^{m-} anions (M = Au or Ag (n
= 2, m = 1); M = Ni, Pd, Pt (n = 4, m = 2); M = Fe, Co, Cr (n
= 6, m = 3) and M = Fe, Ru (n = 6, m = 4) offering linear
35 square planar and octahedral geometries respectively.⁶
Furthermore, we have also reported the formation H-bonded
networks between cationic tectons and oxalatometallates
anions.⁹

Scheme

Pursuing our effort along these lines, we have extended our
investigation to thiocyanatometallates M(SCN)₄²⁻ and
isothiocyanatometallates Cu(NCS)₄²⁻ anions, which present
45 interesting geometrical and structural features. Other
examples of molecular networks based on the formation of D-
H...S or D-H...N hydrogen bonds along with S...S
interactions have been reported in the literature.¹⁰

Here we report our studies on the formation of three new 1-

50 D and 2-D charge assisted H-bonded networks generated upon
combination of the dicationic tecton **1**-2H⁺ and M(SCN)₄²⁻ (M
= Pd, Hg) and Cu(NCS)₄²⁻ anions.

Results and discussion

55 Molecular networks are periodic architectures generated by
self-assembly processes between molecular tectons.¹ Their
design requires the fine tuning of the recognition events
taking place between tectons. For charge assisted H-bond
based networks, one needs to combine anionic (H-bond
60 acceptor) and cationic (H-bond donor) components.⁵
Thiocyanometallate and isothiocyanometallate anions have
been targeted as H-bond acceptor partners because, when
associated with metal centres, they display interesting
coordination modes leading to a variety of possible H-bond
65 patterns. Indeed, as shown in figure 1, depending on the
nature of the metal, SCN⁻ anion may bind to the metal through
either thiocyanato (M-SCN) or isothiocyanato (M-NCS)
coordination's mode.¹¹ Although, owing to the non linear
disposition of M, S and C atoms, thiocyanometallate anions
70 differ from their cyanometallate analogues by size and by
geometry, in terms of H-bonding, they behave in a similar
fashion (Fig. 1). For isothiocyanometallate complexes, often
unstable in solution and generated *in situ*, due to the presence
of three free lone pairs on sulphur, although in terms of
75 coordination geometry they are similar to cyanometallate
anions, as H-bond acceptors, they offer different possibilities.

Figure 1

80 In order to investigate these features, we have chosen to study
the following stable complexes : Pd(SCN)₄²⁻ (square planar
geometry around Pd centre), Hg(SCN)₄²⁻ (Td geometry for Hg

cation) anions as thiocyanometallate species and $\text{Cu}(\text{NCS})_4^{2-}$ (square planar geometry around Cu) anion as isothiocyanometallate complex.

Taking into account both the charged and geometrical characteristics of the above mentioned anions, the tecton $\mathbf{1-2H}^+$ appeared as the most appropriate candidate to obtain hybrid inorganic/organic networks. Indeed, the bisamidine $\mathbf{1}$ behaves as a dibase and thus may undergo double protonation leading to the dicationic tecton $\mathbf{1-2H}^+$ (see scheme). The latter offers two equivalent sets of two acidic hydrogen atoms on each face of the molecule and thus must behave as a tetra H-bond donor. It is important to note that due to the difference in the pK_a values between $[\text{MX}_4]^{2-}$ ($\text{X} = \text{NCS}$ or SCN) anions and unprotonated $\mathbf{1}$, protons should be localised on the nitrogen atoms of $\mathbf{1}$, offering the possibility of combining strong hydrogen bonds with electrostatic charge-charge interactions. Furthermore, the association of the dianionic complexes with the dicationic tecton $\mathbf{1-2H}^+$, by ensuring charge compensation, would lead to the formation of neutral networks. Finally, the use of rigid phenylene spacer connecting the two amidinium cycles at positions 1 and 4 imposes a distance of *ca* 7 Å between two acidic N atoms localized on the same face of the tecton.¹² This structural features is important since it should control the mode of H-bonding with $[\text{MX}_4]^{2-}$ anions. In principle, for the combination of $\mathbf{1-2H}^+$ dication with tetrathiocyanide anions such as $\text{M}(\text{SCN})_4^{2-}$ ($\text{M} = \text{Pd}$ or Hg), one would expect a dihapto mode of H-bonding *i.e.* formation of two H-bonds with same anion on the same face of the tecton leading to the generation of a neutral 1-D network (Fig. 2a). This type of interactions and network's dimensionality have been previously demonstrated for $[\text{MCN}_4]^{2-}$ ($\text{M} = \text{Ni}$, Pd and Pt) anions.⁶ However, for isothiocyanometallate such as $\text{Cu}(\text{NCS})_4^{2-}$, owing to linear nature of the NCS- ligand and the presence of three lone pairs on the sulphur atom capable of acting as H-bond acceptor (Fig. 1), one can not rule out a monohapto mode of H-bonding and thus the formation of a 2-D network (Fig. 2b).

Figure 2

The combination of $\mathbf{1-2H}^+$ with $[\text{MX}_4]^{2-}$ ($\text{M} = \text{Pd}$, Hg ; $\text{X} = \text{SCN}$, or $\text{M} = \text{Cu}$; $\text{X} = \text{NCS}$) leads to the formation of crystalline materials, which were structurally characterised by X-ray diffraction on single crystals (see experimental section). In the case of Hg and Pd species, single crystals were obtained from an aqueous solution using a 1/1 ratio of $\mathbf{1-2H}^+ / [\text{MX}_4]^{2-}$, whereas in the case of Cu complex, a 1/1/2 ratio of $\mathbf{1-2H}^+ / \text{Cu}^{2+} / \text{NCS}^-$ was used.

For all three combinations, crystals are exclusively composed of $\mathbf{1-2H}^+$ dication and $[\text{MX}_4]^{2-}$ dianion, no water molecules are present in the lattice implying that the cohesion of the crystal is ensured by the two components.

For the dication $\mathbf{1-2H}^+$, in all three cases (Fig. 3-5), the average C-N distance of *ca* 1.31 Å and average N-C-N angle of *ca* 121.5° respectively are close to the average values

observed for ($\mathbf{1-2H}^+$, 2Cl^-) salt (1.31 Å and 122.3°).¹² The two 6-member amidinium cycles adopts, as previously observed, a half chair conformation and are almost parallel and coplanar but tilted with respect to the phenylene ring with the NCCC dihedral angle varying between -48° and 47°. The average distance of *ca* 7 Å between nitrogen atoms belonging to two amidinium units and localised on the same side of the molecule is almost the same as the one observed for ($\mathbf{1-2H}^+$, 2Cl^-) salt.¹²

For both $\text{Pd}(\text{SCN})_4^{2-}$ (Fig. 3a) and $\text{Hg}(\text{SCN})_4^{2-}$ (Fig. 4a), neutral 1-D H-bonded networks are formed by mutual interconnection of the dicationic and dianionic units through a dihapto mode of H-bonding taking place between acidic N-H groups and N atom of the thiocyanide ligand (Fig. 2a). The formed H-bonds are strong with the N...N distance in the range of 2.89 Å and 2.96 Å for the Pd complex and 2.85 Å and 2.97 Å for the Hg complex. The 1-D networks are arranged along the *c* axis for Hg and along the *b* axis for Pd. In the crystal, the 1-D networks are packed in a parallel and antiparallel fashions along the *b* axis for Hg (Fig. 4b) and along the *c* axis for Pd (Fig. 3b). The distance between two consecutive metal centres within the 1-D networks is 12.32 Å (Pd) and 14.3 (Hg) Å, whereas, a distance of 7.16 Å (Pd) and 7.18 Å (Hg) is observed for two metal centres belonging to two consecutive chains.

For the Pd(II) complex, the latter adopts a distorted square geometry with a Pd-S distances of 2.33(8) Å. The S-C and C≡N distance are in the range of 1.67(8) and 1.68(6) Å and 1.15(3) Å and 1.16(3) Å respectively. These distances are close to those generally observed for $\text{Pd}(\text{SCN})_4^{2-}$ anion. The SPdS angle varies between 89.3(2) and 106.0(8)°. As expected (Fig. 1b), the Pd-S bond is bend with PdSC angle varying between 105.5(8)° and 106.1(8)°. The thiocyanide ligand is almost linear with the NCS angle of 176.5(2)°.

Figure 3

For the Hg(II) complex, the coordination geometry around the metal is a distorted tetrahedron with Hg-S, S-C and C≡N distances varying between 2.49(2) Å - 2.57(17) Å, 1.65(6) - 1.68(8) Å and 1.14(8) Å - 1.16(8) Å respectively (Fig. 4). The SHgS angle varies between 97.9(5)° and 116.2(7)°. The Hg-SC bond is bend, as expected, with the HgSC angle of varying between 101.4(6)° and 104.8(2)°. The thiocyanide ligand is almost linear with the NCS angle of varying between 174.3(6) and 177.7(6)°.

Figure 4

Unexpectedly, the isothiocyanocuprate anion $\text{Cu}(\text{NCS})_4^{2-}$ behaves differently (Fig. 5). Indeed, in that case, the dicationic and dianionic tectons are interconnected by H-bonds through a tetra-monohapto mode of interaction between NH groups of $\mathbf{1-2H}^+$ and S atoms (S...N distances in the range of 3.32 Å - 3.40 Å). In average, this distance is compatible with the one reported for other examples of NH...S H bond.¹³ As expected from the *ca* 109° S-lone pairs-S-C angle for the

isothiocyanide ligand (Fig. 1c), the CS $\cdots$ N fragment is bend with an angle varying between 83.6(17) $^\circ$ and 91.3(18) $^\circ$. Each dicationic tecton 1-2H $^+$ is H-bonded to four Cu(NCS) $_4^{2-}$ anions (Fig. 5a) and each dianion is surrounded by four 1-2H $^+$ dications (Fig. 5b). Consequently, the mutual interconnection between anionic and cationic units leads to the formation of a neutral 2-D network (Fig. 5c). Consecutive sheets are packed along the *a* axis.

Figure 5

The coordination geometry around the Cu(II) centre is a distorted tetrahedron with Cu-N distance varying between 1.96(16) Å and 1.97(16) Å. The C $\equiv$ N and C-S distances are 1.16(2) Å, and 1.64(18) Å respectively. The N-Cu-N angles varies between 89.6(7) $^\circ$ and 90.4(7) $^\circ$. The isothiocyanide ligand is nearly linear with the N-C-S angles of 177.7(16) $^\circ$. The rather short S $\cdots$ S distance of 4.18 Å implies some S $\cdots$ S interactions. Within the 2-D network, the Cu(II) centres form a square with a Cu $\cdots$ Cu distance of 11.98 Å (Fig. 5c). The distance between two metal centres belonging to two consecutive sheets is 6.23 Å.

Conclusions

The combination of the dicationic tecton 1-2H $^+$ with thiocyanometallate (Pd(SCN) $_4^{2-}$ and Hg(SCN) $_4^{2-}$) or isothiocyanometallate (Cu(NCS) $_4^{2-}$) leads to the formation of three new neutral 1-D and 2-D periodic H-bonded infinite architectures. Based on structural features of the dicationic and dianionic partners, the formation of 1-D networks through the establishment of H-bonds of the dihapto type was predicted (Fig. 2a) and indeed observed both for Pd(SCN) $_4^{2-}$ and Hg(SCN) $_4^{2-}$. However, the formation of the 2-D network resulting from the interconnection of 1-2H $^+$ dications and Cu(NCS) $_4^{2-}$ dianions through a tetra monohapto mode on H-bonding was not predicted but observed. This shift in the mode of H-bonding remains unclear and necessitate further studies.

The generation of H-bonded networks based on the combination of tecton 1-2H $^+$ and analogues with a variety of hexathiocyanometallate and hexaisothiocyanometallate are currently under investigation.

Experimental part

Materials

The chemicals purchased from commercial sources (Strem, Lancaster Chemicals) were used without further purification. The organic bisamidinium tecton **1** was prepared as previously reported and was used as its hydrochloride salt.¹² Both compounds K $_2$ [Pd(SCN) $_4$]¹⁴ and K $_2$ [Hg(SCN) $_4$]¹⁵ were prepared following published procedures.

Crystallisation

(1-2H $^+$, [Pd(SCN) $_4$] $^{2-}$): In a 8 mm diameter crystallization tube, upon slow diffusion through a ethanol layer (1 mL) of an aqueous solution (1 mL) of 1-2H $^+$, 2Cl $^-$ (7.6 mg, 0.024 mmol) into an aqueous solution (1 mL) of K $_2$ [Pd(SCN) $_4$] (10 mg, 0.024 mmol), red-orange single crystals ([Pd(SCN) $_4$][C $_{14}$ H $_{20}$ N $_4$]) were obtained in quantitative yield at room temperature after several days. Anal.: Calcd. for C $_{18}$ H $_{20}$ N $_8$ PdS $_4$: C, 37.04; H, 3.43; N, 19.20%. Found: C, 35.11; H, 3.43; N, 19.23%. IR data (KBr/pellet, cm $^{-1}$): 3167, 3015, 2098, 1648, 1607, 1540, 1506, 1455, 1370, 1311, 1308, 1275, 1199, 803, 670 and 505.

(1-2H $^+$, [Hg(SCN) $_4$] $^{2-}$): In a 8 mm diameter crystallization tube, upon slow diffusion through a ethanol layer (1 mL) of an aqueous solution (1 mL) of 1-2H $^+$, 2Cl $^-$ (6.2 mg, 0.0195 mmol) into an aqueous solution (1 mL) of K $_2$ [Hg(SCN) $_4$] (10 mg, 0.0195 mmol), colourless single-crystals ([Hg(SCN) $_4$][C $_{14}$ H $_{20}$ N $_4$]) were obtained at room temperature after several days in quantitative yield. Anal. Calcd. for C $_{18}$ H $_{20}$ HgN $_8$ S $_4$: C, 31.89; H, 2.95; N, 16.53%. Found: C, 29.77; H, 2.93; N, 16.67%. IR data (KBr/pellet, cm $^{-1}$): 3190, 3027, 2096, 1651, 1617, 1557, 1470, 1371, 1311, 1186, 801, 684 and 510.

(1-2H $^+$, [Cu(NCS) $_4$] $^{2-}$): An aqueous solution (2 mL) of Cu(NO $_3$) $_2$ ·3H $_2$ O (10 mg, 0.041 mmol), was added to an aqueous solution (2 mL) of NH $_4$ NCS (6.3 mg, 0.082 mmol) and the mixture was stirred at 50 $^\circ$ C. A EtOH (3 mL) solution of 1-2H $^+$, 2Cl $^-$ (13.1 mg, 0.041 mmol) was stirred at 50 $^\circ$ C before it was allowed to cool to room temperature. The latter was gently layered on top of the solution containing Cu(NO $_3$) $_2$ ·3H $_2$ O and NH $_4$ NCS. Upon slow evaporation at room temperature, green single crystals of following formula [Cu(NCS) $_4$][C $_{14}$ H $_{20}$ N $_4$] were obtained after several days in quantitative yield. Anal.: Calcd. for C $_{18}$ H $_{20}$ CuN $_8$ S $_4$: C, 39.98; H, 3.70; N, 20.73%. Found: C, 37.46; H, 3.77; N, 20.83%. IR data (KBr/pellet, cm $^{-1}$): 3440, 3185, 3144, 3036, 2105, 1652, 1613, 1555, 1457, 1362, 1304, 1196, 854, 756 and 501.

X-Ray Crystallography

Data were collected at 173(2) K on a Bruker APEX8 CCD Diffractometer equipped with an Oxford Cryosystem liquid N $_2$ device, using graphite-monochromated Mo-K α (λ = 0.71073) radiation. For all structures, diffraction data were corrected for absorption. The structures were solved using SHELXS-97 and refined by full matrix least-squares on F^2 using SHELXL-97. The hydrogen atoms were introduced at calculated positions and not refined (riding model).¹⁶ CCDC 663025-663027 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge

at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (Internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk.

Crystallographic data for (1-2H⁺, [Pd(SCN)₄]²⁻):
C₁₈H₂₀N₈PdS₄, M = 583.06, *Triclinic*, *a* = 7.1632(4) Å, *b* = 12.3179(7) Å, *c* = 13.0249(6) Å, α = 94.640(2)°, β = 96.935(2)°, γ = 91.823(2)°, *U* = 1136.11(10) Å³, Space group *P*-1, *Z* = 2, μ = 1.208 mm⁻¹, Refls measured : 29893, Independent Refls : 6697, *R*_{int}: 0.0287, Final *R* indices [*I*>2σ(*I*)] : *R*1 = 0.0282, *wR*2 = 0.0754, *GOF* = 1.082.

Crystallographic data for (1-2H⁺, [Hg(SCN)₄]²⁻):
C₁₈H₂₀HgN₈S₄, M = 677.25, *Monoclinic*, *a* = 7.18500(10) Å, *b* = 12.6540(2) Å, *c* = 26.1910(6) Å, β = 95.7000(8)°, *U* = 2369.49(7) Å³, Space group *P*2₁/*c*, *Z* = 4, μ = 6.871 mm⁻¹, Refls measured : 12059, Independent Refls : 6889, *R*_{int}: 0.0706, Final *R* indices [*I*>2σ(*I*)] : *R*1 = 0.0492, *wR*2 = 0.0706, *GOF* = 1.030.

Crystallographic data for (1-2H⁺, [Cu(NCS)₄]²⁻):
C₁₈H₂₀CuN₈S₄, M = 540.20, *Monoclinic*, *a* = 6.2310(2) Å, *b* = 15.8090(4) Å, *c* = 11.6190(4) Å, β = 96.7880(13)°, *U* = 1136.52(6) Å³, Space group *P*2₁/*c*, *Z* = 2, μ = 1.352 mm⁻¹, Refls measured : 6064, Independent Refls : 3325, *R*_{int}: 0.0205, Final *R* indices [*I*>2σ(*I*)] : *R*1 = 0.0322, *wR*2 = 0.0802, *GOF* = 1.014.

Acknowledgements

This research was partly supported by a grant from the Ministry of Research and Technology to G. M. Thanks to Université Louis Pasteur, Institut Universitaire de France and CNRS for financial support.

Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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Graphical abstract

Upon combining the bisamidinium dication **1**-2H⁺ with thiocyanatometallates M(SCN)₄²⁻ (M = Pd, Hg) or isothiocyanatometallates Cu(NCS)₄²⁻ anions three new hybrid 1- and 2-D H bonded molecular networks respectively have been generated and structurally characterized by X-ray diffraction on single crystals.