Supramolecular isomerism in spin crossover networks with aurophilic interactions

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Assembly of FeII, 3-cyanopyridine and [Au(CN)2]− affords, in one-pot reaction, three coordination polymers that represent a genuine example of supramolecular isomerism with strong influence in the spin crossover regime of the FeII ions.

Supramolecular isomerism in coordination polymers has received increasing interest in recent years for fundamental and applied reasons. The occurrence of supramolecular isomerism implies suprastructure diversity for a given building block. This fact represents one of the most important problems in crystal engineering. However, from a fundamental viewpoint suprastructure diversity can also offer means to find out and understand the mechanisms that control the genesis and properties of such crystalline materials. This is particularly meaningful in the realm of the spin crossover (SCO) phenomenon as switchable SCO building blocks are strongly sensitive to subtle structural and electronic modifications. In this respect, SCO building blocks can also be considered as sensitive probes to detect the occurrence of structural or suprastructure diversity.

Self-assembly of [MII(CN)4]2− ([MII = Ni, Pd, Pt] or [MII(CN)4]− ([MII = Cu, Ag, Au]) anions with ligands like pyridine, pyrazine, trans-bispyridylethylenediamine, 4,4′-bipyridine, 3CN-pyridine (3CNpy) or pyrimidine (pmd) and Fe(n) cations has resulted in new 2D and single, double or triple interpenetrated 3D SCO polymers. Some of these compounds combine their cooperative SCO properties (magnetic, chromatic and structural) with different chemical effects as in {Fe(pmd)·[Fe(3-CNpy)2]2}·solvent,3 crystallite-state reactions with allosteric interactions as in {Fe(pmd)·[Fe(3-CNpy)2]2}·H2O,4 or SCO-tuned metallocophilicity as in {Fe(3-CNpy)·[Ag(CN)2]2}·2H2O.4

Continuing this work, we report the crystal structures and physical properties of a new SCO system {Fe(3-CNpy)·[Au(CN)2]2}·nH2O (1), which affords a novel example of supramolecular isomerism. After partial evaporation in argon atmosphere of a solution (MeOH/H2O, 1:1) containing Fe(n), pmd and [Au(CN)2]−, a major product appeared as long yellow needles (1a, n = 2.3) while minor quantities of colourless square (1b, n = 0) and pale-yellow parallelepipeds (1c, n = 0) single crystals were formed in the same reaction.5 It should be stressed that, in similar conditions, the yield may vary in each batch of syntheses.

The structure of 1a has been solved at 293 K (HT) and 120 K (LT) and is isostructural to {Fe(3-CNpy)·[Ag(CN)2]2}·2(3)H2O.4 It adopts the trigonal P3̅ space group irrespective of temperature. The iron atom lies at the inversion centre of an elongated octahedron. The average equatorial bond length defined by the nitrogen atoms of four [Ag(CN)2]− groups [Fe−N = 2.151(14), 2.095(15) Å at HT and LT, respectively] are shorter than those of the axial positions occupied by the 3CNpy groups [Fe−N(3) = 2.193(11) Å (HT), 2.157(12) Å (LT)]. The average change of the equatorial and axial bond distances upon spin change is 0.056 and 0.036 Å, respectively. The HT values of the Fe-N bond distances are consistent with an Fe(n) ion in the high-spin state (HS). However, their values at LT and the corresponding variations indicate a very incomplete SCO process, ca. 30% of Fe(n) are in the low spin state at LT. The quasilinear bimondenate [Ag(CN)2]− groups and iron atoms assemble to form three interpenetrated four-connected 3D networks{Fe[Ag(CN)2]2}·nH2O (1a) with the topology of the NbO (Fig. 1 A, B). The closest approach between nets corresponds to Au···Au contacts, which define cross-sectional trigonal channels running along the a-axis. The Au···Au distance, 3.4212(13) Å (HT) [3.3952(17) Å (LT)], indicates the occurrence of weak aurophilic interactions. Left- and right-handed trigonal channels alternate defining large hexagonal cross-sectional channels partially filled by the 3-CNpy ligands and disordered water molecules.

The crystal structure of 1b has been solved at 293 K (HT) and 105 K (LT) with the monoclinic P21/c space group at both temperatures. There are two crystallographically independent Fe(n) octahedrally distorted sites. The axial positions occupied by the 3-CNpy ligands can be easily differentiated as the relative positions of the CN groups of the 3-CNpy ligands are approximately in a cis configuration for the Fe(1) site and in a trans configuration for the Fe(2) site. It should be noted that in the case of 1a the relative position of these CN groups is the trans configuration. The equatorial positions are occupied by four crystallographically distinct [Au(CN)2]− moieties. The average equatorial and axial Fe−N bond distances are 2.157(9) and 2.244(12) Å for Fe(1) and 2.144(9) and 2.247(11) Å for Fe(2) at HT, respectively. These values correspond to the Fe(1) and Fe(2) sites in the high spin state. Between 130 K and 105 K the crystal changes from white to red and the Fe−N distances of the Fe(1) site decreases by 0.202 Å while

Fig. 1 Top: representation of the NbO network (A) and the triple interpenetration of three NbO networks (B) for 1a. Middle: schematic view of the bilayers of 1b emphasizing the Au···Au interactions (dotted lines) (C) and superposition of a bilayer where the aurophilic interactions take place (D). Bottom: schematic view of 1c showing three consecutive layers (E) and the relative disposition of two layers (F). Atom code: Fe(red), Au (green), N (blue), C (black).
those of site Fe(2) remain practically invariant. These data are consistent with a complete high-spin ↔ low-spin change for site Fe(1). The [Au(CN)2]− groups connect in an alternate way the two iron sites defining a corrugated 2D array of [Fe2Au(CN)3]2−. 10.385 × 10.272 Å (HT) rhombuses. Interestingly, the layers interact by pairs defining bilayers (Fig. 1 C). The cohesive force in the bilayers stems from strong aurophilic interactions. The average Au…”

Compound 1c, crystallizes in the monoclinic C2 space group. Similarly to 1b, the essential structural feature is the occurrence of rectangular [Fe2Au(CN)3]2− (10.582 × 10.422 Å) motives. However, now these motives define an homogeneous and infinite stack of slightly corrugated layers running along the c direction (Fig. 1 E and F). The distance between planes is ca. 5.1540(5) Å, which also corresponds to the shortest Au…”

Yield crystals of the three compounds were formed and separated using binocular lens. Yield ca. 60% (1a), 20% (1b) and 5% (1c) CHN analysis:

<table>
<thead>
<tr>
<th>Compound</th>
<th>C (calc.)</th>
<th>H (calc.)</th>
<th>N (calc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>14.47</td>
<td>14.73</td>
<td>14.47</td>
</tr>
<tr>
<td>1b</td>
<td>14.25</td>
<td>14.55</td>
<td>14.36</td>
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<tr>
<td>1c</td>
<td>14.29</td>
<td>14.46</td>
<td>14.38</td>
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Notes and references

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