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Mechanochemical and solution reactions between $AgCH_3COO$ and $[H_2NC_6H_{10}NH_2]$ yield three isomers of the coordination network $\{Ag[H_2NC_6H_{10}NH_2]^+\}_\infty$†

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Solid-state co-grinding of silver acetate and solid *trans*-1,4-diaminocyclohexane, $[H_2NC_6H_{10}NH_2]$ yields two isomeric coordination networks depending on the crystallization conditions; a third isomeric form is obtained when the same reaction is carried out in solution.

It has long been known that co-grinding and co-milling of solid reactants are viable routes to the synthesis of novel molecular compounds.[1] Recently, mechanochemical methods have begun to be successfully applied also in the field of molecular crystal engineering[2] for the solvent-less preparation of supramolecular aggregates,[3] co-crystals or coordination networks.[4] It has been argued that the preparation of molecular crystals materials *via* solvent-free reactions between or within molecular crystals can be regarded as a *green way* to crystal engineering.[5]

Examples of the utilization of mechanochemical methods in coordination chemistry are not numerous, but interest is increasing because of environmental and sustainability issues. For example, *cis*-platinum complexes *cis*-$(Ph_3P)_2PtCl_2$ and *cis*-$(Ph_3P)_2PtCO_3$ have been prepared mechanochemically from solid reactants,[6] while the supramolecular self-assembly of a number of two- or three-dimensional helicates by mechanochemical methods has been recently reported.[7]

In this communication we report the results of solid-state and solution reactions between silver acetate and *trans*-1,4-diaminocyclohexane $[H_2NC_6H_{10}NH_2]$, this bis-amine having been little exploited as a *divergent* ligand in the construction of coordination networks.[8]

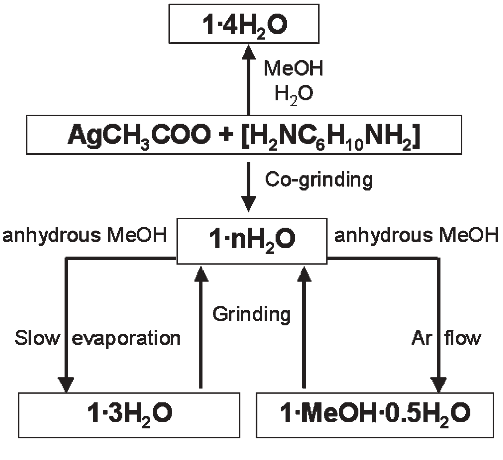
The solid-state co-grinding of $AgCH_3COO$ and $[H_2NC_6H_{10}NH_2]$ in 1 : 1 ratio affords a crystalline powder tentatively formulated as $Ag[H_2NC_6H_{10}NH_2][CH_3COO]\cdot nH_2O$, **1**$\cdot nH_2O$ (see below).‡ Recrystallization of **1**$\cdot nH_2O$ from anhydrous MeOH yields two types of products depending on the solvent evaporation conditions: crystals of $Ag[H_2NC_6H_{10}NH_2][CH_3COO][MeOH]\cdot 0.5H_2O$, **1**$\cdot$MeOH$\cdot 0.5H_2O$, have been obtained by crystallisation under argon flow, while crystals of $Ag[H_2NC_6H_{10}NH_2][CH_3COO]\cdot 3H_2O$, **1**$\cdot 3H_2O$ have been obtained by slow evaporation in the air.‡ Single-crystal X-ray diffraction experiments§ have shown that **1**$\cdot$MeOH$\cdot 0.5H_2O$ and **1**$\cdot 3H_2O$ contain two isomeric forms of the coordination network $\{Ag[H_2NC_6H_{10}NH_2]^+\}_\infty$. If the same reaction between $AgCH_3COO$ and $[H_2NC_6H_{10}NH_2]$ is carried out directly in MeOH/water solution, a third crystalline material is obtained, namely the tetra-hydrate $Ag[H_2NC_6H_{10}NH_2][CH_3COO]\cdot 4H_2O$, **1**$\cdot 4H_2O$. In this latter case, correspondence between bulk powder and single crystals was ascertained by comparing computed and observed powder diffractograms.§

Based on powder diffraction experiments it has been established that both compounds **1**$\cdot 3H_2O$ and **1**$\cdot$MeOH$\cdot 0.5H_2O$ transform into the starting material **1**$\cdot nH_2O$ upon grinding (see supplementary material). Grinding of **1**$\cdot 4H_2O$, on the other hand, leaves the structure unaltered. The whole process is summarized in Scheme 1.

In terms of chemical composition the three compounds differ only in the degree and nature of solvation. The differences in topology are, however, much more dramatic and the three compounds must be regarded as isomers of the same basic coordination network. The relationship between supramolecular isomerism and network topology has been thoroughly discussed.[9]

The crystal structure of **1**$\cdot$MeOH$\cdot 0.5H_2O$ is constituted of a two-dimensional coordination network (see Fig. 1) formed by the divergent bidentate ligand $[H_2NC_6H_{10}NH_2]$ and two silver atoms, which are joined together by an Ag$\cdots$Ag interaction of 3.322(1) Å (see supplementary material) and are asymmetrically bridged by two methanol molecules.

There is a close structural relationship between the coordination networks in **1**$\cdot$MeOH$\cdot 0.5H_2O$ and in **1**$\cdot 3H_2O$. This latter structure is built around a zigzag chain of $Ag^{(+)}\cdots[H_2NC_6H_{10}NH_2]\cdots Ag^{(+)}\cdots[H_2NC_6H_{10}NH_2]\cdots Ag^{(+)}$ units as shown in Fig. 2. The Ag-atom is coordinated in a linear



Scheme 1 Solid-state and solution experiments for the supramolecular reaction of $AgCH_3COO$ and $[H_2NC_6H_{10}NH_2]$.

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† Electronic supplementary information (ESI) available: experimental and calculated X-ray powder diffraction patterns; TGA for **1**$\cdot nH_2O$; detailed packing diagrams with hydrogen bonding interactions. See http://www.rsc.org/suppdata/cc/b5/b503404c/

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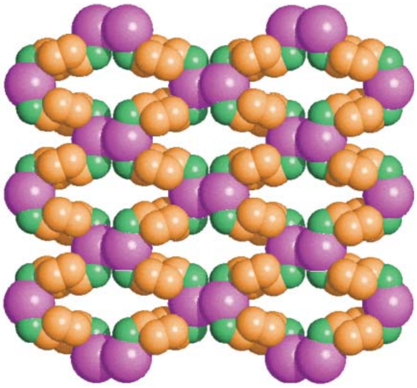

Fig. 1 Crystalline $Ag[H_2NC_6H_{10}NH_2][CH_3COO]\cdot[MeOH]\cdot0.5H_2O$, **1**·MeOH·0.5$H_2O$. The two-dimensional coordination network formed by the divergent bidentate ligand $[H_2NC_6H_{10}NH_2]$, with silver atoms at a distance of 3.322(1) Å. (H atoms not shown for clarity). Relevant distances and angles: Ag–N 2.166(3), 2.168(3) Å, N–Ag–N 166.4(1)°.

fashion. A projection perpendicular to the $[H_2NC_6H_{10}NH_2]$ planes shows how the zigzag chains extend in parallel fashion (Fig. 2). The $Ag^{(+)}\cdots[H_2NC_6H_{10}NH_2]\cdots Ag^{(+)}\cdots[H_2NC_6H_{10}NH_2]\cdots Ag^{(+)}$ chains are bridged together *via* hydrogen bonds involving the N–H donors, the water molecules and the acetate anions.

The tetra-hydrated species $Ag[H_2NC_6H_{10}NH_2][CH_3COO]\cdot4H_2O$, **1**·4$H_2O$ contains an isomeric form of the coordination networks present in **1**·MeOH·0.5H_2O and **1**·3H_2O. Fig. 3 shows how the base and the silver cation form a zigzag network as in **1**·3H_2O, with a notable difference arising from the orientation of the ligands with respect to the silver atoms: while in **1**·3H_2O two ligand bases are in a *cisoid* relative orientation with respect to the silver atom, in **1**·4H_2O the two ligands are *transoid*. This is made possible by the different orientation of the N-atom lone pairs in $[H_2NC_6H_{10}NH_2]$.

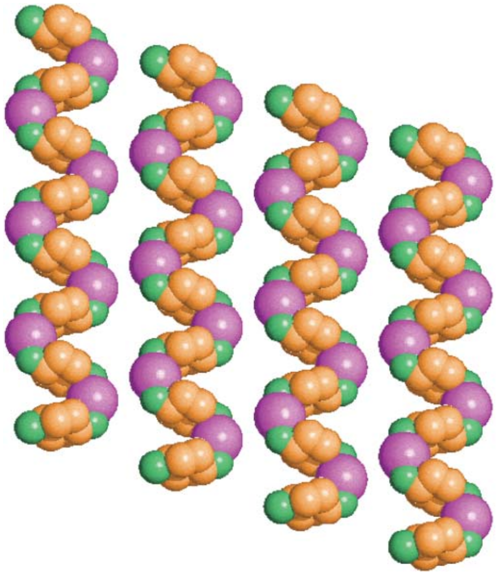

Fig. 2 Crystalline $Ag[H_2NC_6H_{10}NH_2][CH_3COO]\cdot3H_2O$, **1**·3$H_2O$. (a) The fundamental coordination network is build around a zigzag chain of $Ag^{(+)}\cdots[H_2NC_6H_{10}NH_2]\cdots Ag^{(+)}\cdots[H_2NC_6H_{10}NH_2]\cdots Ag^{(+)}$ units. The Ag-atom is coordinated in a linear fashion. (H atoms not shown for clarity). Relevant distances and angles: Ag–N 2.166(3), 2.168(3) Å, N–Ag–N 172.3(1)°.

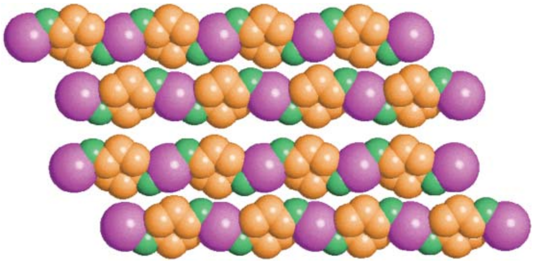

Fig. 3 Crystalline $Ag[H_2NC_6H_{10}NH_2][CH_3COO]\cdot4H_2O$, **1**·4$H_2O$. The ligand bases adopt a *transoid* relative orientation with respect to the silver atom. (H atoms not shown for clarity). Relevant distances and angles: Ag–N 2.137(3), 2.150(3), 2.141(3), 2.134(3) Å, N–Ag–N 179.4(1), 175.3(1)°.

The acetate anions form a hydrated network and interact with the base and the water molecules.

Fig. 4 shows a comparison of the $\{Ag[H_2NC_6H_{10}NH_2]^+\}_\infty$ chains observed in the three compounds. Differences and similarities are due to the flexibility of the N–Ag–N link, and one could think that the coordination polymer is adjusted as a function of the solvent and counter ion interactions.[11d] In the present case, it can be noticed that counterions and solvent molecules form small clusters in **1**·MeOH·0.5H_2O and are grouped into ribbons parallel to the chain in **1**·3H_2O, while in **1**·4H_2O they constitute flat networks, which are sandwiched in between layers of $\{Ag[H_2NC_6H_{10}NH_2]^+\}_\infty$ chains of the type shown in Fig. 3 (see supplementary material).

Primarily, the interest in solvent-free conditions stems from the possibility of obtaining the same product as that from solution *without solvent* because the process is cheaper, less time consuming and often more environmentally friendly. On the other hand one

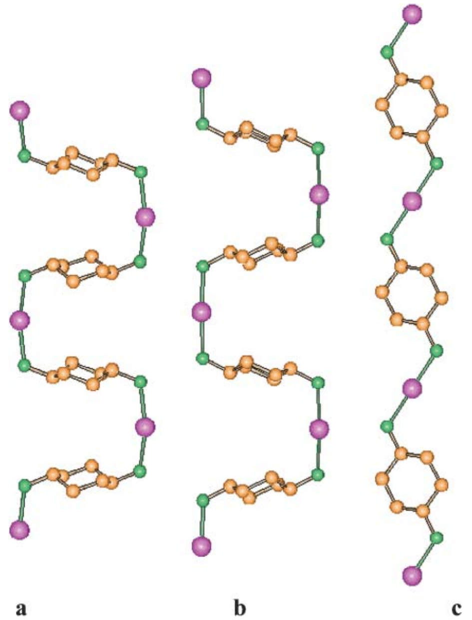

Fig. 4 Comparison between the isomeric $\{Ag[H_2NC_6H_{10}NH_2]^+\}_\infty$ chains in (a) **1**·MeOH·0.5H_2O, (b) **1**·3H_2O, (c) **1**·4H_2O (the same scale has been used for the three chains; H atoms not shown for clarity).

may be interested in solvent-free conditions for the possibility of obtaining products not otherwise accessible from solvents. In this latter case, however, one is often faced with the problem of characterization, because the lack of single-crystals complicates the matter significantly. In the cases discussed in this communication we have shown that isomeric coordination networks are obtained depending on the preparation and crystallisation conditions. The network obtained from solution, **1**·4H_2O, is different from the two networks in **1**·3H_2O and in **1**·MeOH·0.5H_2O. The structures of these latter compounds are related by a "simple" translation of the chains, which in **1**·MeOH·0.5H_2O are at Ag···Ag contact distance and are stabilized by the MeOH bridges. It is also noteworthy that, while grinding of **1**·4H_2O leaves the material unaltered, both **1**·MeOH·0.5H_2O and **1**·3H_2O revert, upon grinding, to the initial solid-state product **1**·$n$$H_2O$, which is thus likely to possess a similar backbone network structure.[10] The unusual reversibility depicted in Scheme 1 suggests that when **1**·$n$$H_2O$ is dissolved in MeOH the coordination polymer obtained by grinding is not completely destroyed, providing the template structure for reassembly and crystal growth of **1**·MeOH·0.5H_2O and **1**·3H_2O. Even though further work is necessary to ascertain the exact structure of compound **1**·$n$$H_2O$, we have provided good evidence that cheap and simple mechanochemical methods can be exploited in the preparation of new coordination networks, a thriving area of crystal engineering.[11]

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Notes and references

‡ All starting materials were purchased from Aldrich. Reagent grade solvents and bi-distilled water were used. Grinding experiment – synthesis of **1**·$n$$H_2O$: 114 mg (1 mmol) of $H_2NC_6H_{10}NH_2$ and 167 mg (1 mmol) of $AgCH_3COO$ were ground together in an agate mortar for 5 min and left to stand for five days before measuring the powder diffractograms. Single crystals of **1**·3H_2O were obtained by recrystallization of **1**·$n$$H_2O$ from anhydrous MeOH in air; single crystals of **1**·MeOH·0.5H_2O were obtained by recrystallization of **1**·$n$$H_2O$ from anhydrous MeOH under argon flow. Synthesis of **1**·4H_2O: 34 mg (0.3 mmol) of $H_2NC_6H_{10}NH_2$ and 50 mg (0.3 mmol) of $AgCH_3COO$ were dissolved in 3 mL of a 1 : 1 methanol/water solution. Thermogravimetric measurements (see supplementary material) indicated the presence of *ca.* 2.5 water molecules per formula unit in **1**·$n$$H_2O$.

§ Crystal data. All data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer, monochromator graphite. **1**·4H_2O: triclinic, *P*-1, a = 8.781(1), b = 12.810(4), c = 13.706(3) Å, α = 95.35(3), β = 90.90(1), γ = 108.90(2)°, V = 1450.5(6) Å^3, Z = 4, 5322 measured reflections, 308 parameters, $wR2$ = 0.0898, $R1$ = 0.0328. **1**·3H_2O: triclinic, *P*-1, a = 6.108(4), b = 10.180(4), c = 11.849(4) Å, α = 105.91(3), β = 97.78(3), γ = 99.37(4)°, V = 686.4(6) Å^3, Z = 2, 2529 measured reflections, 178 parameters, $wR2$ = 0.0753, $R1$ = 0.0273. **1**·MeOH·0.5H_2O: monoclinic, *C*2/*c*, a = 21.574(1), b = 9.844(1), c = 15.773(1) Å, β = 125.34(1)°, V = 2732.5(4) Å^3, Z = 8, 2488 measured reflections, 147 parameters, $wR2$ = 0.0966, $R1$ = 0.0320. All non-H atoms refined anisotropically. SHELXL97[12a] used for structure solution and refinement on F^2, PLATON[12b] and SCHAKAL[12c] for the hydrogen bonding analyses and molecular graphics, respectively. CCDC 266477–266479. See http://www.rsc.org/suppdata/cc/b5/b503404c/ for crystallographic data in CIF or other electronic format. Powder data were collected on a Philips X'Pert automated diffractometer with Cu-Kα radiation, graphite monochromator. The program PowderCell 2.2[12d] was used for calculation of X-ray powder patterns.

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