

Paper

# Silver co-ordination compounds with aliphatic nitriles containing amino nitrogen as H bond donor or additional metal binding site: formation of a ring, a chain, a polymeric sheet and a 3D polymeric channeled structure

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Received 3rd July 2002, Accepted 15th July 2002

Published on the Web 30th July 2002

Three co-ordination polymers and a discrete 20-membered macrometallacycle were prepared by crystallization of silver salts with the conformationally flexible, polyfunctional ligands *N*-(2-cyanoethyl)glycine (ceg), 3,3'-iminodipropionitrile (idpn) and tris(2-cyanoethyl)amine (tca). Single-crystal X-ray analyses of [Ag<sub>2</sub>(tca)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (**1**), [Ag(idpn)]ClO<sub>4</sub> (**2**), [Ag(ceg)]CF<sub>3</sub>SO<sub>3</sub> (**3**) and [Ag(ceg)]ClO<sub>4</sub>·0.5H<sub>2</sub>O (**4**) revealed a bimetallic macrocycle (**1**), a 2D sheet structure with 4.8<sup>2</sup> topology (**2**), a 3D network structure with rhomboid channels (**3**) and a 1D chain structure (**4**). The rhomboid channels in **3** are generated by 36-membered macrometallacyclic subunits consisting of four Ag atoms and four ceg ligands with ceg binding through the carboxylate group and the nitrile nitrogen. The amino nitrogen of ceg is protonated and serves as a hydrogen bond donor for the triflate anions that are incorporated into the macrocycles, thus stabilizing the channeled structure.

## Introduction

The construction of co-ordination polymers by self-assembly of polydentate organic ligands and transition metal ions is a rapidly growing area of research that has received considerable interest in recent years. A wide variety of infinite networks has been reported having intriguing topologies and in some cases exhibiting interesting properties like microporosity, host-guest chemistry, molecular magnetism or non-linear optical behavior.<sup>1-4</sup> While rigid ligands with fixed bridging angles, like bipyridine, pyrimidine, pyrazine, pyridazine, are preferred candidates for a rational design of network structures,<sup>1-4</sup> bidentate ligands with conformationally flexible, aliphatic spacers<sup>5</sup> preclude prediction and control of the topologies, but are nevertheless attractive for the construction of co-ordination polymers, since their flexibility provides a high degree of adaptability to *e.g.* the inclusion of counterions or other guest molecules in the resultant networks. Ag(I) that easily adopts various coordination geometries is particularly suited to accommodate different architectures. Some examples of Ag and other d<sup>10</sup> metal co-ordination polymers with flexible symmetric bis- or poly-nitrile ligands have been reported.<sup>6-10</sup> Bis-nitrile ligands having long aliphatic spacers, like *e.g.* sebaconitrile [NC(CH<sub>2</sub>)<sub>8</sub>CN],<sup>10</sup> preferably form interpenetrated networks so that large void volumes in the overall structure are prevented.

In the present work we studied the network-forming abilities of aliphatic nitrile ligands containing a central amino nitrogen, namely *N*-(2-cyanoethyl)glycine (ceg), 3,3'-iminodipropionitrile (idpn) and tris(2-cyanoethyl)amine (tca) (Chart 1). The amino nitrogen can employ different functions: first, it can serve as an additional metal binding site. Since N(amine)/N(nitrile) chelation is precluded for geometric reasons, the formation of networks is anticipated. Alternatively, upon becoming protonated and consequently non-co-ordinating under the reaction conditions, the ammonium nitrogen is a potential H donor for counterions and/or solvent molecules. The latter case is particularly interesting, because H bonding interactions can play a significant role in the assembly of

networks and ligands that possess co-ordination sites as well as hydrogen bond donating sites are becoming increasingly important in the field of co-ordination polymers.<sup>11</sup>

Here we report the X-ray structures of [Ag<sub>2</sub>(tca)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (**1**), [Ag(idpn)]ClO<sub>4</sub> (**2**), [Ag(ceg)]CF<sub>3</sub>SO<sub>3</sub> (**3**) and [Ag(ceg)]ClO<sub>4</sub>·0.5H<sub>2</sub>O (**4**) having a dinuclear structure (**1**), a 2D sheet structure (**2**), a 1D chain structure (**4**) and a 3D network structure with rhomboid channels stabilized by H bonded triflate anions (**3**).

## Experimental

### Syntheses

Idpn and ceg were purchased from Aldrich. Tca was prepared according to ref. 12. All chemicals and solvents were reagent grade and used without further purification.

**CAUTION:** Perchlorate salts of metal complexes are potentially explosive and should be handled carefully in small quantities only.

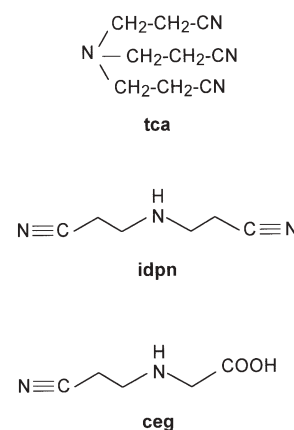


Chart 1

**[Ag<sub>2</sub>(tca)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> 1.** AgClO<sub>4</sub>·H<sub>2</sub>O (225 mg, 1.00 mmol) was dissolved in water (6 cm<sup>3</sup>) and added to a solution of tca (88 mg, 0.50 mmol) in methanol (12 cm<sup>3</sup>). The pH was brought to 2.8 by 1 N HClO<sub>4</sub>. After keeping the solution at 4 °C overnight a white precipitate was filtered off (145 mg, 76%). Recrystallization from water/ethanol (1 : 2) yielded colorless needles of **1** suitable for X-ray analysis. Found: C, 28.2; H, 3.1; N, 14.7. C<sub>18</sub>H<sub>24</sub>Ag<sub>2</sub>Cl<sub>2</sub>N<sub>8</sub>O<sub>8</sub> requires C, 28.2; H, 3.2; N, 14.6%. IR (cm<sup>-1</sup>): 2965 m, 2940 m, 2857 s, 2277 m (C≡N), 2248 m (C≡N), 1469 m, 1416 m, 1330 w, 1281 m, 1240 w, 1092 vs (ClO<sub>4</sub><sup>-</sup>), 729 w, 624 m (ClO<sub>4</sub><sup>-</sup>), 416 w, 397 w.

**[Ag(idpn)]ClO<sub>4</sub> 2.** AgClO<sub>4</sub>·H<sub>2</sub>O (225 mg, 1.00 mmol) and idpn (62 mg, 0.50 mmol) were dissolved in ethanol/water (2 : 1, 12 cm<sup>3</sup>) and brought to pH 3.9 by 1 M HClO<sub>4</sub>. Slow evaporation of the solution at 4 °C afforded colorless crystals of **2** in 59% yield. Found: C, 21.5; H, 2.8; N, 13.1. C<sub>6</sub>H<sub>9</sub>AgClN<sub>3</sub>O<sub>4</sub> requires C, 21.8; H, 2.8; N, 12.7%. IR (cm<sup>-1</sup>): 2954 m, 2859 m, 2253 m (C≡N), 1464 m, 1418 m, 1152 vs (ClO<sub>4</sub><sup>-</sup>), 1115 vs (ClO<sub>4</sub><sup>-</sup>), 1086 vs (ClO<sub>4</sub><sup>-</sup>), 941 w, 768 m, 627 m (ClO<sub>4</sub><sup>-</sup>).

**[Ag(ceg)]CF<sub>3</sub>SO<sub>3</sub> 3.** X-Ray suitable crystals of complex **3** were obtained by mixing AgCF<sub>3</sub>SO<sub>3</sub> (257 mg, 1.00 mmol) and ceg (128 mg, 1.00 mmol) in methanol/water (1 : 1, 12 cm<sup>3</sup>, pH 4) followed by slow evaporation of the solution at 4 °C. Yield: 20%. Found: C, 18.9; H, 2.1; N 7.4. C<sub>6</sub>H<sub>8</sub>AgF<sub>3</sub>N<sub>2</sub>O<sub>5</sub>S requires C, 18.7; H, 2.1; N, 7.3%. IR (cm<sup>-1</sup>): 3168 m, 2253 w (C≡N), 1621 s, 1589 s, 1411 m, 1264 s (CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>), 1229 s, 1172 s, 1037 s, 763 w, 642 s, 576 w, 520 m.

**[Ag(ceg)]ClO<sub>4</sub>·0.5H<sub>2</sub>O 4.** Complex **4** crystallized at 4 °C from a solution of AgClO<sub>4</sub>·H<sub>2</sub>O (225 mg, 1.00 mmol) and ceg (64 mg, 0.50 mmol) in ethanol/water (2 : 1, 7.5 cm<sup>3</sup>). yield: 56%. Found: C, 18.1; H, 2.6; N 8.4. C<sub>5</sub>H<sub>8</sub>AgClN<sub>2</sub>O<sub>6.5</sub> requires C, 17.9; H, 2.4; N, 8.4%. IR (cm<sup>-1</sup>): 3087 m, br, 3003 m, 2968 m, 2931 m, 2253 m (C≡N), 1614 s, 1573 s, 1491 m, 1389 m, 1329 m, 1310 m, 1145 vs (ClO<sub>4</sub><sup>-</sup>), 1115 vs (ClO<sub>4</sub><sup>-</sup>), 1086 vs (ClO<sub>4</sub><sup>-</sup>), 965 w, 874 m, 809 w, 627 m (ClO<sub>4</sub><sup>-</sup>), 534 m.

### Instrumentation

<sup>1</sup>H NMR spectra were recorded on a Varian Mercury spectrometer at 200.13 MHz. using sodium 3-trimethylsilylpropylsulfonate as internal reference. The pK<sub>a</sub> values for tca, idpn and ceg were obtained from graphs of chemical shifts *versus*

uncorrected pH (pH\*) values. Infrared spectra of KBr pellets were taken on a Bruker IFS 28 FT-spectrometer.

### Crystal structure analyses

Crystal data for compounds **1–4** were collected at room temperature on an Enraf-Nonius-KappaCCD diffractometer<sup>13</sup> using graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å). For data reduction and cell refinement the programs DENZO and SCALEPACK were used.<sup>14</sup> The structures were solved by conventional direct (**1**) or Patterson methods (**2–4**) and subsequent Fourier syntheses and refined by full-matrix least squares on F<sup>2</sup> using the SHELXTL PLUS, SHELXL-93 and SHELXL-97 programs.<sup>15</sup> Except for O(1w) in **4** all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in the final Fourier-difference maps and refined isotropically (ammonium and methylene hydrogen atoms in **3** and the amino hydrogen atom in **2**) or generated geometrically and given isotropic thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Crystallographic data and details of refinement are reported in Table 1.

### Results and discussion

The strong electron-withdrawing character of cyano groups has a significant influence on the acid–base properties and consequently on the co-ordination behavior of mixed amine(ammonium)/nitrile ligands. The different numbers of cyano groups in ceg, idpn and tca result in pK<sub>a</sub> values for the central ammonium nitrogens ranging from 7.5 for ceg over 5.5 for Hidpn<sup>+</sup> to ≈ 1 for Htca<sup>+</sup> as determined by pD-dependent <sup>1</sup>H NMR spectra. Therefore the central amino nitrogen of idpn can be expected to participate as a co-ordination site in the self-assembly of silver ions with the ligand even in acidic solution. Replacement of one cyanoethyl group by a carboxylate group offers a ligand with hydrogen bond donating functionality under acidic conditions. In the third case the involvement of the amino nitrogen as a donor site is counteracted by the presence of *three* strongly electron-withdrawing cyanoethyl groups. The three situations (co-ordination site, H bond donor, non-co-ordinating part of the aliphatic spacer) are realized in the structures of [Ag<sub>2</sub>(tca)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (**1**), [Ag(idpn)]ClO<sub>4</sub> (**2**), [Ag(ceg)]CF<sub>3</sub>SO<sub>3</sub> (**3**) and [Ag(ceg)]ClO<sub>4</sub>·0.5H<sub>2</sub>O (**4**) that have been obtained by co-crystallisation of tca, idpn and ceg with silver salts from acidic ethanol/water or methanol/water solutions.

**Table 1** Crystal data for **1–4**<sup>a</sup>

	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
Empirical formula	C <sub>9</sub> H <sub>12</sub> AgClN <sub>4</sub> O <sub>4</sub>	C <sub>6</sub> H <sub>9</sub> AgClN <sub>3</sub> O <sub>4</sub>	C <sub>6</sub> H <sub>8</sub> AgF <sub>3</sub> N <sub>2</sub> O <sub>5</sub> S	C <sub>5</sub> H <sub>9</sub> AgClN <sub>2</sub> O <sub>6.5</sub>
Formula weight	383.55	330.48	385.07	344.46
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	P1̄	P2 <sub>1</sub> /n	P2 <sub>1</sub> /c	P1̄
<i>a</i> /Å	7.490(1)	8.592(1)	5.459(1)	5.639(1)
<i>b</i> /Å	8.149(1)	12.656(1)	18.467(1)	5.936(1)
<i>c</i> /Å	11.406(1)	9.938(1)	11.634(1)	16.698(1)
<i>α</i> /°	104.79(1)			82.29(1)
<i>β</i> /°	102.02(1)	100.93(1)	94.86(1)	89.57(1)
<i>γ</i> /°	93.13(1)			86.33(1)
<i>V</i> /Å <sup>3</sup>	654.1(1)	1061.1(2)	1168.6(2)	552.7(1)
<i>Z</i>	2	4	4	2
μ(Mo-Kα)/mm <sup>-1</sup>	1.760	2.149	1.959	2.081
<i>T</i> /K	293	293	293	293
No. measured reflections	5265	5839	8571	3815
No. independent reflections	2736	2239	2634	2276
No. observed reflections [ <i>I</i> > 2σ( <i>I</i> )]	1733	1207	1767	1508
Final <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> indices [ <i>I</i> > 2σ( <i>I</i> )] <sup>b</sup>	0.032, 0.079	0.042, 0.105	0.028, 0.067	0.044, 0.127
(all data)	0.059, 0.105	0.085, 0.162	0.068, 0.162	0.078, 0.209

<sup>a</sup>Click here for full crystallographic data (CCDC 182728–182731). <sup>b</sup>*R*<sub>1</sub> = Σ||*F*<sub>o</sub>| - |*F*<sub>c</sub>||/Σ|*F*<sub>o</sub>|; *wR*<sub>2</sub> = [Σ*w*(*F*<sub>o</sub><sup>2</sup> - *F*<sub>c</sub><sup>2</sup>)<sup>2</sup>/Σ*w*(*F*<sub>o</sub><sup>2</sup>)<sup>2</sup>]<sup>1/2</sup>; *w*<sup>-1</sup> = σ<sup>2</sup>(*F*<sub>o</sub><sup>2</sup>) + (*aP*)<sup>2</sup>; *P* = (*F*<sub>o</sub><sup>2</sup> + 2*F*<sub>c</sub><sup>2</sup>)/3; *a* = 0.0391 for **1**, 0.0623 for **2**, 0.0630 for **3**, and 0.0771 for **4**.

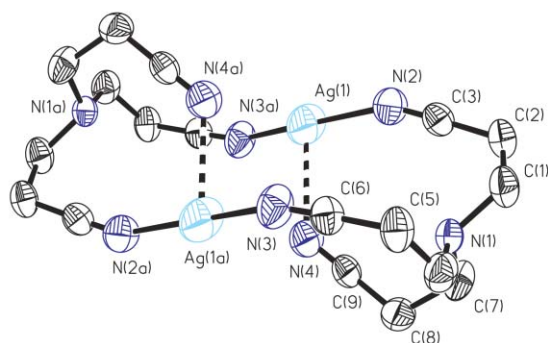


Fig. 1 View of the cation of **1** with the atom numbering scheme.

Table 2 Bond lengths [Å] and angles [°] in **1**

Ag(1)–N(2)	2.172(2)	Ag(1)–N(3) <sup>a</sup>	2.167(2)
Ag(1)···N(4)	2.667(2)	Ag(1)···N(4) <sup>a</sup>	2.802(2)
N(2)–Ag(1)–N(3) <sup>a</sup>	169.06(9)	N(2)–Ag(1)–N(4)	87.48(9)
N(3) <sup>a</sup> –Ag(1)–N(4)	96.53(9)		

Symmetry operation:  $a -x, -y, -z$ .

### Crystal structure of [Ag<sub>2</sub>(tca)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (**1**)

As shown in Fig. 1 two tca molecules and two silver ions assemble in a 20-membered macrocycle. Each silver ion is co-ordinated by two ligands through nitrile nitrogens in a roughly linear geometry. The Ag–N and C≡N bond lengths [2.167(2), 2.172(2), 1.113(4) and 1.119(3) Å, see Table 2] fall in the normal range (2.18–2.33 and 1.07–1.15 Å),<sup>16</sup> while the Ag–N≡C bond angles of 153.5(3) [C(3)–N(2)–Ag(1)] and 155.2(2)° [C(6)–N(3)–Ag(1)] are more acute than usually found in silver nitrile complexes (166–176°).<sup>16</sup> The transannular Ag(1)···Ag(1a) distance is 3.98 Å. The third side-arm of each ligand is directed towards one silver and a short contact of 2.667(2) Å is observed between its nitrile nitrogen and the metal indicating a weak binding interaction so that the silver ions have T-shaped N<sub>3</sub> co-ordination spheres. Probably due to its extremely weak basicity the amino nitrogen does not participate in the co-ordination. In the crystal packing discrete macrocycles stack along the *x*-axis. The perchlorate ions are located between neighbouring stacks. The shortest contact between Ag and perchlorate oxygen is 2.801(3) Å [Ag(1)···O(2),  $-1 - x, -y, -z$ ] so that the counter anions are not co-ordinated.

### Crystal structure of [Ag(idpn)]ClO<sub>4</sub> (**2**)

As anticipated due to geometry and p*K*<sub>a</sub> value idpn uses its three co-ordination sites to generate a network structure with silver ions. Fig. 2 gives a view of the 2D sheet structure of [Ag(idpn)]<sub>n</sub><sup>+</sup> (**2**). Each Ag is co-ordinated by three idpn ligands in a trigonal planar geometry, with one ligand binding through the amine nitrogen and two ligands binding through a nitrile nitrogen. In addition, one perchlorate oxygen participates in a weak interaction with Ag [Ag···O(2) 2.635(5) Å]. Ag–N and C≡N bond lengths fall in the normal range (see Table 3), the Ag–N≡C group is completely linear. The 3-connecting Ag atoms and the 3-connecting idpn ligands form an infinite wavy sheet containing 32- and 12-membered rings and representing a 4.8<sup>2</sup> net.<sup>17</sup> The 12-membered rings are built up by two Ag atoms and two halves of two different ligands, while the larger macrocycles are formed by four Ag atoms, two ligands and two halves of two ligands. Thus, within the larger rings the Ag atoms are alternately bridged by 5- and 9-membered linkers. In the crystal packing parallel sheets stack in the *a*-direction. The perchlorate counterions are situated between neighbouring layers that are 8.592 Å apart. Weak hydrogen bonding interactions occur between the perchlorate

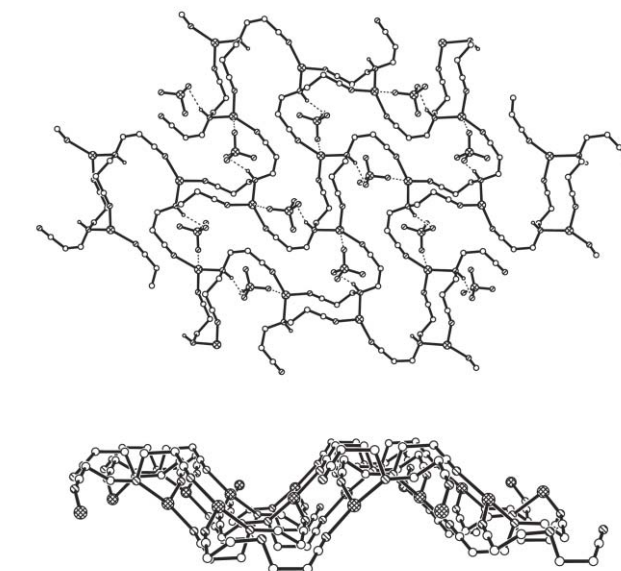
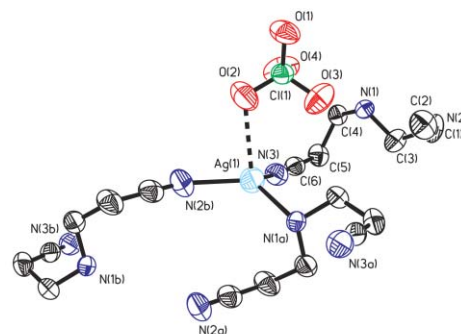


Fig. 2 Co-ordination environment of Ag in **2** with the atom numbering scheme (top), sheet structure of **2** viewed down the *x*-axis, click image or here to access a 3D representation (middle) and side view of the wavy sheet (bottom). Ag, Cl: cross-hatched circles; N: hatched circles and C: empty circles.

Table 3 Bond lengths [Å] and angles [°] in **2**

Ag(1)–N(1) <sup>a</sup>	2.304(4)	Ag(1)–N(2) <sup>b</sup>	2.235(5)
Ag(1)–N(3)	2.270(5)	Ag(1)···O(2) <sup>c</sup>	2.635(5)
N(1) <sup>a</sup> –Ag(1)–N(2) <sup>b</sup>	112.2(2)	N(1) <sup>a</sup> –Ag(1)–N(3)	114.3(1)
N(2) <sup>b</sup> –Ag(1)–N(3)	125.4(2)	N(3)–Ag(1)–O(2) <sup>c</sup>	91.5(2)

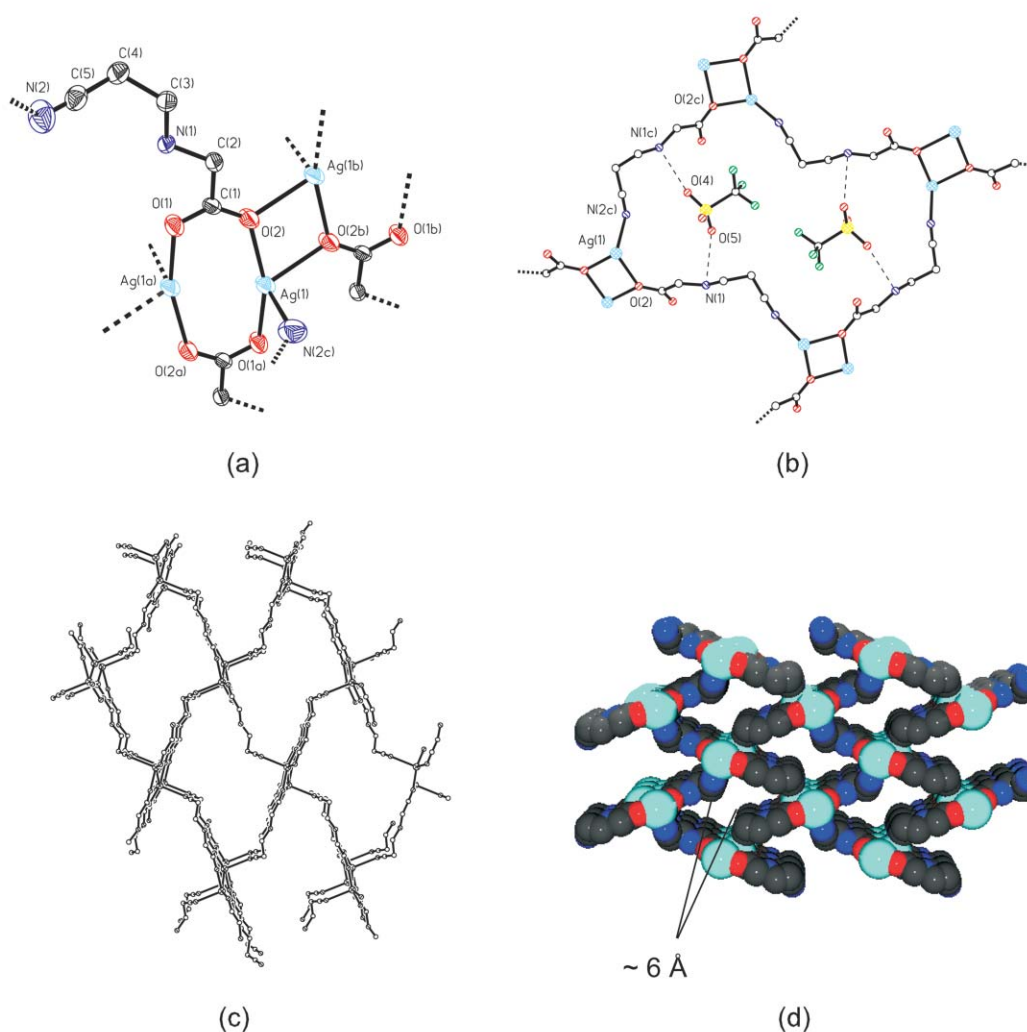
Symmetry operations:  $a -\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$ ;  $b \frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$ ;  $c \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$ .

oxygen O(3) and the amino nitrogen [O(3)···N(1) 3.267(7) Å, N(1)–H(10) 0.92(5) Å, H(10)···O(3) 2.41(5) Å, N(1)–H(10)···O(3) 155(4)°,  $-1/2 + x, 1/2 - y, -1/2 + z$ ].

### Crystal structure of [Ag(ceg)]CF<sub>3</sub>SO<sub>3</sub> (**3**)

The asymmetric unit of **3** comprises one silver atom, one neutral ligand in its zwitterionic form and one (unco-ordinated) CF<sub>3</sub>SO<sub>3</sub><sup>−</sup> counterion (Fig. 3a). Each ligand binds to one silver atom through the cyano nitrogen and to three silver atoms through the carboxylate group so that the Ag(ceg) units are interconnected into a cationic three-dimensional network. The basic structural motif of the network is a 36-membered macrocycle consisting of 4 silver atoms and 4 ligand molecules (Fig. 3b). Within the ring the ligands bridge adjacent Ag atoms through the nitrile nitrogen and the carboxylate oxygen O(2). The four silver atoms form a parallelogram with dimensions of 10.7 × 11.0 Å. The C≡N bond length of 1.133(5) Å falls in the normal range (1.07–1.15 Å),<sup>16</sup> the Ag–N bond length of 2.508(3) Å (see Table 4) is significantly longer than the values





**Fig. 3** (a) Co-ordination environment of Ag in **3** with the atom numbering scheme. (b) 36-membered ring formed by Ag and ceg with H bonding interactions between N(1)–H and CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> indicated. (c) and (d) 3D network structure with rhomboid-shaped channels running along the *x*-axis.<sup>23</sup> Counterions are omitted for clarity. Click image (c) or here to access a 3D representation.

usually found for Ag–nitrile complexes (2.18–2.33 Å).<sup>16</sup> The Ag–N≡C bond angle of 122.6(3)° is extremely acute. Although Ag–N≡C bond angles are normally close to linear (166–176°),<sup>16</sup> some examples of similarly severely bent M–N≡C arrangements have been reported in the literature.<sup>18</sup> As indicated in Fig. 3b the carboxylate oxygen O(2) forms a single-atom bridge to a silver of an adjacent ring (Ag⋯Ag = 3.6 Å) thus generating an infinite 2D structure of fused macrocycles. μ<sub>3</sub>-bridging of the carboxylate group to a third Ag results in a 3D structure of parallel rings that are slightly off-set stacked along the crystallographic *a* axis with the shortest metal–metal distance between the layers being 2.863(1) Å. The short Ag⋯Ag distance that is clearly below the sum of the van der Waals radii (3.44 Å)<sup>19</sup> is a consequence of the bite angle of the carboxylate group and does not imply metallophilic (d<sup>10</sup>⋯d<sup>10</sup>) interactions. Overall, each Ag has an O<sub>3</sub>N co-ordination sphere and adopts a severely distorted four-co-ordinate geometry with the valence angles ranging from 78.5 to 159.9°.

The 3D network structure of **3** containing cationic, rhomboid-shaped channels running parallel to the *x*-axis is displayed in Fig. 3c and 3d. The channels that make up 43% of the cell volume<sup>20</sup> are filled by the CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> counterions. Strong hydrogen bonds are formed between the ammonium nitrogen of the ligands and the triflate oxygens (Table 4, Fig. 3b). The effective cavity size as measured by the shortest distance between the van der Waals surfaces of opposing sides is approximately 6.1 Å × 13.0 Å.

#### Crystal structure of [Ag(ceg)]ClO<sub>4</sub>·0.5H<sub>2</sub>O (**4**)

The 1D co-ordination polymer depicted in Fig. 4a was obtained, when ClO<sub>4</sub><sup>-</sup> was used as the counterion for Ag/ceg. In [Ag(ceg)]ClO<sub>4</sub>·0.5H<sub>2</sub>O (**4**) two Ag atoms are bridged by two carboxylate groups at a distance of 2.855(1) Å which is a typical value for carboxylate-bridged silver complexes (2.78–3.05 Å).<sup>21</sup> The dimeric entities are connected through two monatomic carboxylate bridges [Ag⋯Ag 3.610(1) Å] to form an infinite straight chain extending along the *a*-direction. In contrast to compound **3**, Ag adopts a distorted T-shaped O<sub>3</sub> co-ordination sphere (Table 5), the nitrile group of ceg remains unco-ordinated. The Ag–O bond lengths (Table 5) compare well with those observed in related Ag–carboxylate compounds, where Ag–O(axial) and Ag–O(equatorial) bond

**Table 4** Bond lengths [Å], angles [°] and hydrogen-bonding interactions [Å] in **3**

Ag(1)–N(2) <sup>a</sup>	2.508(3)	Ag(1)–O(1) <sup>b</sup>	2.225(2)
Ag(1)–O(2)	2.241(2)	Ag(1)–O(2) <sup>c</sup>	2.412(3)
N(2) <sup>a</sup> –Ag(1)–O(1) <sup>b</sup>	93.7(1)	N(2) <sup>a</sup> –Ag(1)–O(2) <sup>c</sup>	102.6(1)
N(2)–Ag(1)–O(2)	100.2(1)	O(1)–Ag(1)–O(2) <sup>b</sup>	159.80(9)
O(1) <sup>b</sup> –Ag(1)–O(2) <sup>c</sup>	112.51(8)	O(2)–Ag(1)–O(2) <sup>c</sup>	78.57(9)
N(1)⋯O(3) <sup>d</sup>	2.948(4)	N(1)⋯O(4) <sup>e</sup>	2.777(4)
N(1)⋯O(5)	2.799(4)		

Symmetry operations: *a* –*x*, ½ + *y*, ½ – *z*; *b* –*x*, –*y*, 1 – *z*; *c* 1 – *x*, –*y*, 1 – *z*; *d* –1 + *x*, –½ – *y*, –½ + *z*; *e* *x*, –½ – *y*, –½ + *z*.

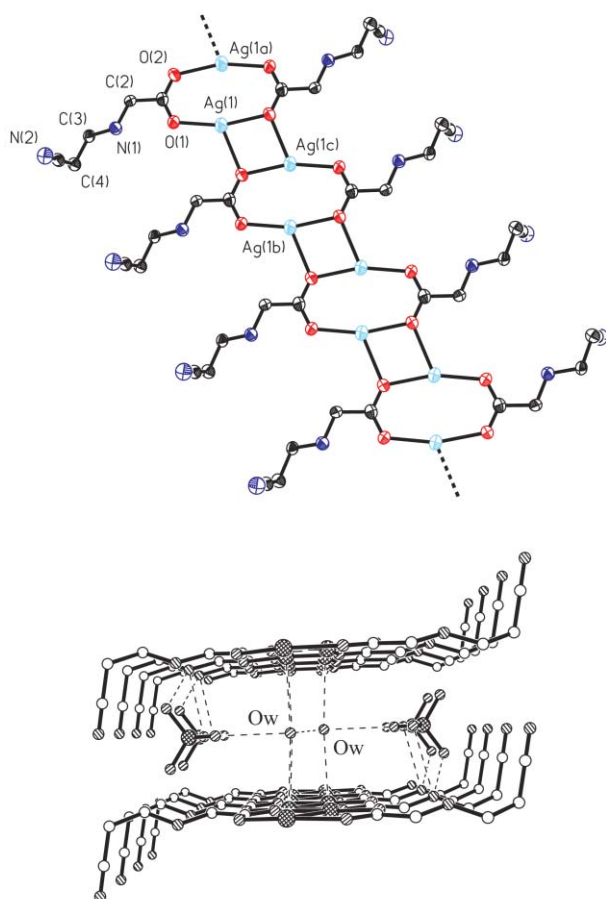


Fig. 4 Chain motif in **4** and crystal packing viewed down the *x*-axis. Click bottom image or here to access a 3D representation.

Table 5 Bond lengths [Å], angles [°] and hydrogen-bonding interactions [Å] in **4**

Ag(1)–O(1)	2.190(3)	Ag(1)–O(2) <sup>a</sup>	2.229(4)
Ag(1)–O(2) <sup>b</sup>	2.438(4)		
O(1)–Ag(1)–O(2) <sup>a</sup>	163.5(1)	O(1)–Ag(1)–O(2) <sup>b</sup>	117.6(1)
O(2) <sup>a</sup> –Ag(1)–O(2) <sup>b</sup>	78.7(2)		
O(1w)⋯O(5)	2.92(1)	N(1)⋯O(3) <sup>b</sup>	3.009(5)
N(1)⋯O(4) <sup>b</sup>	3.146(6)	N(1)⋯O(6) <sup>c</sup>	3.018(5)

Symmetry operations: *a*  $-x, -y, 1 - z$ ; *b*  $1 + x, y, z$ ; *c*  $1 + x, -1 + y, z$ .

distances typically range from 2.2–2.3 and 2.4–2.5 Å, respectively.<sup>21</sup> With the shortest Ag–O(perchlorate) distance being 4.013(4) Å the counterions are non-co-ordinating. In the crystal packing (Fig. 4b) adjacent chains are linked through weak interactions between Ag and water of crystallization [O(1w)⋯Ag(1) 2.949(8) Å,  $-1 + x, 1 + y, z$  and O(1w)⋯Ag(1) 2.995(8) Å,  $-1 + x, y, z$ ]. As found for **3**, the counter anions hydrogen bond with the ammonium nitrogen of the ceg ligand, however, the longer O⋯N separations (Table 5) indicate much weaker interactions.

**3** and **4** are examples of co-ordination polymers whose structures vary with the counterions present. There are several co-ordination polymers described in the literature that adopt different topologies and dimensionalities when the counterion is changed.<sup>22</sup> The hydrogen bonding pattern in **3**, where the macrocycles accommodate two triflate anions each of which forms strong H bonds to two adjacent sides of the rhomboid ring, suggests that formation of the macrometallacyclic network is supported by a template effect of the anions of appropriate size. The anions stabilizing the rhomboid channels may also prevent formation of an interpenetrated network

structure as observed in other 3D polymers — *e.g.* in [Cu<sup>I</sup>(NC(CH<sub>2</sub>)<sub>4</sub>CN)<sub>2</sub>]NO<sub>3</sub><sup>8a</sup> — where void volume is avoided by interpenetration of networks. Unfortunately, attempts to prepare Ag complexes of ceg with other anions (NO<sub>3</sub><sup>−</sup>, PF<sub>6</sub><sup>−</sup>, BF<sub>4</sub><sup>−</sup>) gave only non-crystalline, glassy materials whose structures could not be elucidated.

### Spectroscopic properties of 1–4

<sup>1</sup>H NMR spectra in D<sub>2</sub>O indicate complete dissociation of the Ag complexes into Ag<sup>+</sup> and the respective “free” ligand in solution. Owing to the presence of metal bound and unco-ordinating (or weakly binding) cyano groups in **1**, the infrared spectrum displays two ν(C≡N) stretching vibration bands at 2248 and 2277 cm<sup>−1</sup>. The band at lower wavenumbers coincides with that of the “free” ligand, the second band is shifted by 29 cm<sup>−1</sup> to higher frequencies as expected upon metal co-ordination. By contrast, the ν(C≡N) band in the infrared spectra of **2** and **3** appears to be insensitive to Ag co-ordination. The ν(C≡N) stretching vibration frequency in the spectrum of **3** shows no significant change in comparison with that of the “free” ligand (2252 cm<sup>−1</sup>), while it is shifted by 5 cm<sup>−1</sup> to lower wavenumbers upon Ag co-ordination to the cyano nitrogens of idpn. In the case of **3** this is in accordance with the relatively long Ag–N bond distance of 2.508(3) Å indicating a weak Ag–N bond. Furthermore, the negatively charged carboxylate ligand reduces the electron-withdrawing effect of silver. The Ag–N bond length in **2** [2.235(5) and 2.270(5) Å] corresponds to an intermediate bond strength and therefore does not explain the essentially unchanged ν(C≡N) stretching vibration frequency. σ-donation shifts ν(C≡N) bands to higher wavenumbers, while π-back-bonding has the reverse effect. However, the situation should be similar in **2** and **1**. The splitting of the ν(ClO<sub>4</sub><sup>−</sup>) band in **2** (1152, 1115, 1086 cm<sup>−1</sup>) and **4** (1145, 1115, 1086 cm<sup>−1</sup>) is consistent with hydrogen bonding interactions between the amine/ammonium nitrogen and the counterions.

### Conclusion

In summary 1D, 2D and 3D silver(i) co-ordination polymers and a macrocyclic, dinuclear complex with amine/nitrile ligands where the amino (ammonium) nitrogen represents a metal binding site (**2**), a H bond donor for counterions (**3** and **4**) or a non-co-ordinating member of the aliphatic spacer (**1**) have been described. **2** and **3** are built up by 32- and 36-membered macrometallacyclic subunits, respectively. However, the shapes of the rings differ significantly leading to distinct features in the overall structure. While in **3** rhomboid macrocycles generate a channeled structure, long, narrow macrocycles are formed in **2** with distances of approximately 3.2 and 15.9 Å between the van der Waals surfaces of opposing sides (6.1 and 13.0 Å in **3**) so that the structure of **2** contains no effective void space. It is noted that the connectivity patterns in the macrometallacycles are different and the structures are not completely comparable, but the distinct shapes of the rings in **2** and **3** underline the role of the H bond donating ability of ceg for the formation of the larger cavities found in **3**.<sup>†</sup> In addition the formation of the channeled, non-interpenetrated structure of **3** is supported by the presence of triflate as a counterion of suitable nature and dimensions to be hosted in the 36-membered macrocycles and to fill the resulting void space. The effect of the counterion is reflected by the structure of **4**.

<sup>†</sup>When idpn was reacted with AgClO<sub>4</sub> in more acidic solution (pH 2.6) so that the amino nitrogen becomes protonated and non-co-ordinating (as in the case of ceg), only the perchlorate salt of idpnH<sup>+</sup> crystallized from the reaction mixture. Crystal data for idpnH<sup>+</sup>ClO<sub>4</sub><sup>−</sup>: C<sub>6</sub>H<sub>10</sub>CIN<sub>3</sub>O<sub>4</sub>, monoclinic, space group *C2/c*, *a* = 7.882(1) Å, *b* = 8.684(1) Å, *c* = 13.872(1) Å, β = 92.27(1)°, *Z* = 4.

## Acknowledgements

This work was supported by the Ministerium für Wissenschaft und Forschung, NRW (Lise-Meitner-Habilitationsstipendium) and the Fonds der Chemischen Industrie (FCI). We thank Professor Bernhard Lippert for the continuous support of our work.

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