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Syntheses and crystal structures of five two-dimensional networks constructed from staircase-like silver(I) thiocyanate chains and bridging polyamines

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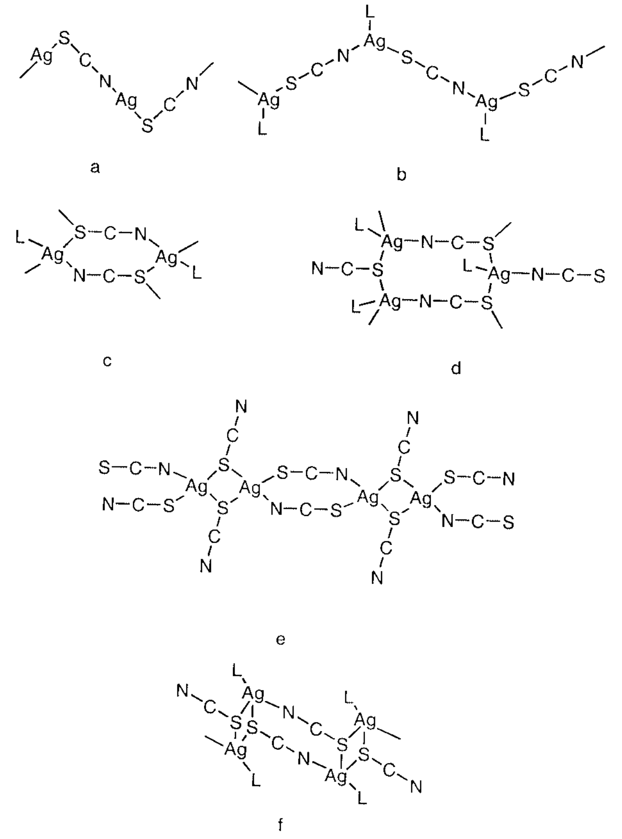
Five co-ordination polymers ${}^{2}_{\infty}[(\mathrm{AgSCN})_2\mathrm{L}]$ (L = 1,2-diaminoethane, 1,3-diaminopropane, 1,4-diaminobutane or 1,5-diaminopentane) and ${}^{2}_{\infty}[(\mathrm{AgSCN})_3\mathrm{L}]$ (L = *N*,*N*′-bis(3-aminopropyl)ethylenediamine) have been synthesized and structurally characterised by single-crystal X-ray diffraction. Each complex contains one-dimensional staircase-like ${}^{1}_{\infty}[(\mathrm{AgSCN})_2]$ chains in which each thiocyanate ligand acts in the μ-*N*,*S*,*S*-bridging mode. Every silver(I) atom in the staircase-like chain is further co-ordinated by a terminal nitrogen atom of the amine ligand to furnish a highly distorted $\mathrm{AgN_2S_2}$ tetrahedral geometry. Both ends of the amine ligands participate in co-ordination, extending the one-dimensional staircase-like ${}^{1}_{\infty}[(\mathrm{AgSCN})_2]$ chains to two-dimensional staircase-like or square-wave like ${}^{2}_{\infty}[(\mathrm{AgSCN})_2\mathrm{L}]$ networks in **1**–**4**, whereas adjacent chelating ethylenediamine entities of the amine ligands in **5** are further interlocked with the $\mathrm{Ag_2}(\mu\text{-}S\text{-SCN})_2$ dinuclear cores, resulting in a different formula ${}^{2}_{\infty}[(\mathrm{AgSCN})_3\mathrm{L}]$.

Introduction

In recent years there has been considerable interest in the development of rational synthetic routes to co-ordination polymers by self-assembly.[1] Self-assembly is heavily influenced by many factors such as the solvent system,[2] template,[3,4] pH value of the solution[4] and counter ion,[5] therefore much work is required to extend knowledge of the relevant structural types and establish proper synthetic strategies leading to the desired species. Silver(I) is good candidate as a soft acid favouring co-ordination to soft bases such as ligands containing sulfur and nitrogen atoms. We and others have exploited the co-ordination flexibility of silver(I) in construction of a large number of co-ordination polymers, exhibiting interesting structural diversity.[5,6] On the other hand, although thiocyanate is a potential bridging ligand, its silver(I) co-ordination polymers are not yet well documented. The simple silver(I) thiocyanate salt was suggested to have a chain structure (Scheme 1a);[7] its adducts with pyridines and other ligands have been shown to be mono- and di-meric complexes,[8] as well as one-dimensional chains and two-dimensional networks containing AgSCN fragments as building blocks (Scheme 1b–e).[9,10] Aliphatic di- or poly-amines usually form metal complexes with chelate co-ordination. In contrast, both 1,2-diaminoethane and 1,3-diaminopropane show bridging co-ordination modes in their silver(I) complexes.[11] Exploiting the bridging ability of both thiocyanate and diamines, we may construct new polymeric co-ordination polymers. We now report herewith five aliphatic di- or tetra-amine adducts of silver(I) thiocyanate, which are two-dimensional co-ordination polymers, namely ${}^{2}_{\infty}[(\mathrm{AgSCN})_2(\mathrm{C_2H_8N_2})]$ **1**, ${}^{2}_{\infty}[(\mathrm{AgSCN})_2(\mathrm{C_3H_{10}N_2})]$ **2**, ${}^{2}_{\infty}[(\mathrm{AgSCN})_2(\mathrm{C_4H_{12}N_2})]$ **3**, ${}^{2}_{\infty}[(\mathrm{AgSCN})_2(\mathrm{C_5H_{14}N_2})]$ **4**, ${}^{2}_{\infty}[(\mathrm{AgSCN})_3(\mathrm{C_8H_{22}N_4})]$ **5**. All are based on staircase-like ${}^{1}_{\infty}[(\mathrm{AgSCN})_2]$ skeletons (Scheme 1f), which have not yet been documented in the AgSCN-containing complexes,[8–10,12–19] and are further bridged by the aliphatic di- or tetra-amine ligands into two-dimensional networks.



Scheme 1

Experimental

All reagents were commercially available and used as received. All samples were thoroughly dried prior to elemental analyses.

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Physical measurements

The C, H, N, S elemental analyses were performed on an Elementar Vario EL elemental analyser. The IR spectra were recorded on a Nicolet 5DX FT-IR spectrophotometer with KBr discs in the 4000–400 cm^{-1} region.

Preparation of metal complexes

${}^{2}_{\infty}[(AgSCN)_2(C_2H_8N_2)]$ 1. To a solution of $AgNO_3$ (0.170 g, 1 mmol) in MeCN–water (1 : 1 v/v) was added an excess of 1,2-diaminoethane (over 3 mmol), followed by an aqueous solution (2 cm^3) of NH_4SCN (0.076 g, 1 mmol). The colourless solution was allowed to stand at room temperature in air avoiding illumination for 24 hours. Large colourless prismatic crystals of complex **1** were obtained, which were collected by filtration, washed with aqueous MeCN and dried in a vacuum desiccator over silica gel (*ca.* 0.294 g, 75% yield based on $AgNO_3$). Calc. for $C_2H_4AgN_2S$: C, 12.26; H, 2.06; N, 14.29; S, 16.36. Found: C, 12.24; H, 2.10; N, 14.34; S, 16.38%. IR data (cm^{-1}): 3472m, 3355m, 3311m, 3253m, 2957m, 2922m, 2866m, 2814m, 2099s, 1591s, 1486w, 1453w, 1382w, 1354w, 1319w, 1065w, 1003s, 904w, 754w, 559w and 448w.

${}^{2}_{\infty}[(AgSCN)_2(C_3H_{10}N_2)]$ 2. This complex was prepared as above using 1,3-diaminopropane instead of 1,2-diaminoethane, as colourless crystals (*ca.* 0.337 g, 83% yield based on $AgNO_3$). Calc. for $C_5H_{10}Ag_2N_4S_2$: C, 14.79; H, 2.48; N, 13.80; S, 15.97. Found: C, 14.82; H, 2.53; N, 13.73; S, 15.85%. IR data (cm^{-1}): 3407m, 3336m, 3275m, 3166m, 2937w, 2869w, 2093s, 1584s, 1488s, 1437m, 1392w, 1328m, 1150w, 1047w, 982w, 904w, 822w, 718w, 530w and 454w.

${}^{2}_{\infty}[(AgSCN)_2(C_4H_{12}N_2)]$ 3. This complex was prepared as above using 1,4-diaminobutane instead of 1,2-diaminoethane, as colourless crystals (*ca.* 0.235 g, 56% yield based on $AgNO_3$). Calc. for $C_3H_6AgN_2S$: C, 17.16; H, 2.88; N, 13.34; S, 15.27. Found: C, 17.20; H, 2.98; N, 13.37; S, 15.25%. IR data (cm^{-1}): 3327s, 3272s, 3149w, 2985w, 2916m, 2866m, 2836m, 2754w, 2106s, 1584s, 1491m, 1438w, 1388w, 1329w, 1294w, 1199w, 1136w, 1084w, 1011s, 904w, 822w, 740w, 580w, 556w, 471w and 444w.

${}^{2}_{\infty}[(AgSCN)_2(C_5H_{14}N_2)]$ 4. This complex was prepared as above using 1,5-diaminopentane instead of 1,2-diaminoethane, as colourless crystals (*ca.* 0.326 g, 76% yield based on $AgNO_3$). Calc. for $C_7H_{14}Ag_2N_4S_2$: C, 19.37; H, 3.25; N, 12.91; S, 14.77. Found: C, 19.40; H, 3.35; N, 12.87; S, 14.79%. IR data (cm^{-1}): 3341m, 3273m, 3155m, 2928s, 2862m, 2092s, 1602s, 1489s, 1397w, 1318w, 1146w, 1113w, 1047w, 995w, 926w, 819w, 729w, 552w, 514w and 450w.

${}^{2}_{\infty}[(AgSCN)_3(C_8H_{22}N_4)]$ 5. This complex was prepared as above using *N*,*N′*-bis(3-aminopropyl)ethylenediamine instead of 1,2-diaminoethane, as colourless crystals (*ca.* 0.453 g, 68% yield based on $AgNO_3$). Calc. for $C_{11}H_{22}Ag_3N_7S_3$: C, 23.63; H, 4.76; N, 16.54; S, 12.26. Found: C, 23.58; H, 4.79; N, 16.49; S, 12.34%. IR data (cm^{-1}): 3436w, 3317m, 3294m, 3260m, 2942m, 2914m, 2844m, 2094s, 1582m, 1458w, 1439w, 1388w, 1353w, 1267w, 1194w, 1168w, 1131w, 1087w, 1042w, 1014w, 945w, 908w, 881w, 851w, 802w, 737w, 583w, 544w, 490w and 449w.

X-Ray crystallography

Diffraction intensities for complexes **1**–**5** were collected at 293 K on a Siemens R3m diffractometer using the ω-scan technique with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The data were corrected for Lorenz-polarisation effects and absorption.[20] The structure solution and full-matrix least-square refinement based on F^2 were performed with the SHELXS 97[21] and SHELXL 97[22] program packages, respectively. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the organic ligands were generated geometrically (C–H 0.96 Å), assigned the same isotropic thermal parameters and included in the structure-factor calculations. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections incorporated.[23] The crystallographic data for the five complexes are summarised in Table 1. Selected bond distances and bond angles are given in Table 2.

CCDC reference number 186/2262.

See http://www.rsc.org/suppdata/dt/b0/b007665l/ for crystallographic files in .cif format.

Results and discussion

Infrared spectra

The infrared spectra of complexes **1**–**5** exhibit characteristic bands for thiocyanate and aliphatic di- or tetra-amine ligands. In general, the bridging M–NCS-M systems exhibit a ν_{CN} absorption well above 2100 cm^{-1}, though it must be noted that ν_{CN} is affected by many factors.[8,24] For **1** a maximum absorption (ν_{CN}) at 2099 cm^{-1} shows that it contains bridging µ-*S*,*S*,*N*-thiocyanate ligands.[17,25] The peaks for ν_{CS} absorptions at 559 and 448 cm^{-1} support this co-ordination mode.[26] In addition, when 1,2-diaminoethane functions as a µ-bridging group between two metal atoms it takes the *trans* form.[27,28] It is also seen that the CH_2 rocking vibration provides the most clear-cut diagnosis of conformation: one peak (A_u) at 754 cm^{-1} for the *trans* form,[29] which is consistent with the crystal structural analysis. The infrared spectra of **2**–**5** are similar to that of **1**; the absorptions in the range 2092–2106 cm^{-1} indicate the existence of bridging µ-*S*,*S*,*N*-thiocyanate.

Crystal structures

The crystal structure of complex **1** consists of a silver(I) thiocyanate–1,2-diaminoethane adduct in 2 : 1 stoichiometry. Each Ag^I is co-ordinated to one nitrogen atom of 1,2-diaminoethane [Ag(1)–N(2) 2.245(4) Å], two different thiocyanate sulfur atoms [Ag(1)–S(1) 2.772(2), Ag(1)–S(1b) 2.853(2) Å] and one nitrogen atom of another thiocyanate ligand [Ag(1)–N(1a) 2.172(4) Å], resulting in a highly distorted tetrahedral co-ordination geometry with bond angles in the range 95.8(1)–150.1(1)° at the metal atom. The Ag–S bond lengths fall in the range 2.36–2.99 Å previously reported in other silver(I) thiocyanate complexes.[8,12,14,15] As shown in Fig. 1, a pair of thiocyanate groups bridge a pair of silver(I) atoms to form an eight-membered $Ag_2(SCN)_2$ parallelogram macrocycle with the bond angle C(1)–S(1)–Ag(1) at 96.9(1)° and C(1a)–N(1a)–Ag(1) at 166.7(3)°, which are comparable to those found in other AgSCN-containing complexes.[9,10,14,17] As the thiocyanate sulfur atom acts in a bridging mode, four Ag–S bonds furnish a four-membered centrosymmetric Ag_2S_2 ring with the bond angles S(1)–Ag(1)–S(1b) at 104.12(3)°, Ag(1)–S(1)–Ag(1b) at 75.88(3)°, and the Ag(1)···Ag(1b) distance at 3.459(2) Å. The four-membered ring has a dihedral angle of 99.7° with the virtually planar eight-membered one, and they share the Ag–S edges to form a one-dimensional staircase-like ${}^{1}_{\infty}[Ag_2(SCN)_2]$ chain, which is unprecedented in the literature (see Scheme 1a–e).[7–10] The staircase-like chains are arranged in an anti-parallel fashion in the cell, and are further interlinked by 1,2-diaminoethane ligands that bridge the metal centres to generate a two-dimensional ${}^{2}_{\infty}[(AgSCN)_2(C_2H_8N_2)]$ network. The bridging 1,2-diaminoethane group takes the *trans* (T) conformation (N-to-N distance 3.816 Å), being similar to that reported previously[27] and different from the chelate 1,2-diaminoethane group in the *gauche* (G) conformation.[30] It is interesting that the bridging connections of the diamine groups with the staircase-like chains result not only in the large

Table 1 Crystal data and structure refinement for complexes **1**–**5**

	1	**2**	**3**	**4**	**5**
Empirical formula	$C_4H_8Ag_2N_4S_2$	$C_5H_{10}Ag_2N_4S_2$	$C_6H_{12}Ag_2N_4S_2$	$C_7H_{14}Ag_2N_4S_2$	$C_{11}H_{22}Ag_3N_7S_3$
Formula weight	392.00	406.03	420.06	434.07	666.10
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P2/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	6.025(4)	5.859(1)	5.994(3)	5.991(3)	8.857(3)
b/Å	6.232(3)	6.440(2)	7.145(5)	6.875(4)	9.860(8)
c/Å	7.292(5)	14.316(5)	7.622(5)	16.187(1)	12.630(1)
α/°	65.91(4)		73.63(5)	85.56(5)	70.21(6)
β/°	77.87(5)	94.520(1)	69.97(4)	82.65(4)	76.11(5)
γ/°	84.49(5)		82.160(5)	80.710(4)	82.010(5)
V/Å^3	244.4(3)	538.5(3)	294.0(3)	651.5(3)	1005.5(6)
Z	1	2	1	2	2
μ(Mo-Kα)/cm^{-1}	4.384	3.984	3.653	3.301	3.213
$R1$ ($I > 2\sigma$)	0.0422	0.0505	0.0600	0.0464	0.0538
$wR2$ (all data)	0.0550	0.0615	0.0799	0.0772	0.0812
Data/parameters	1433/56	1566/61	1423/64	3475/127	4850/218

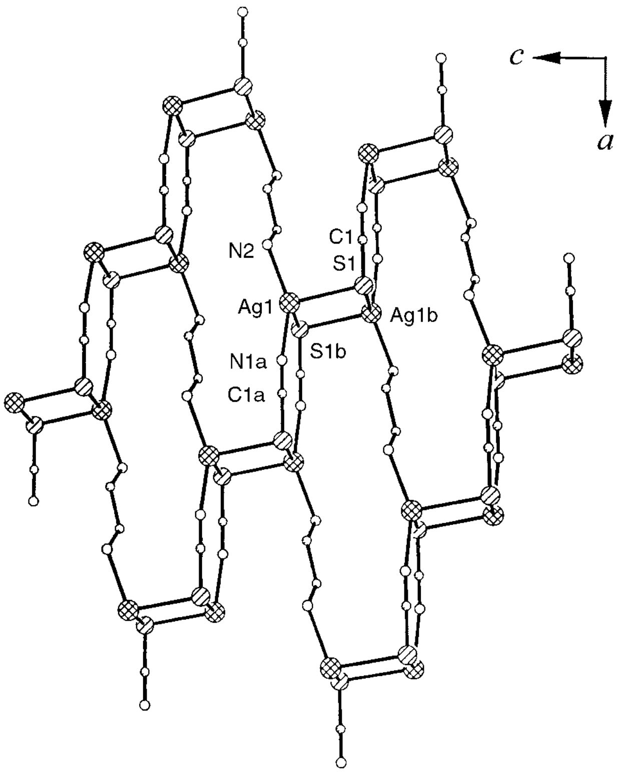

Fig. 1 Top view of the two-dimensional network of complex **1**.

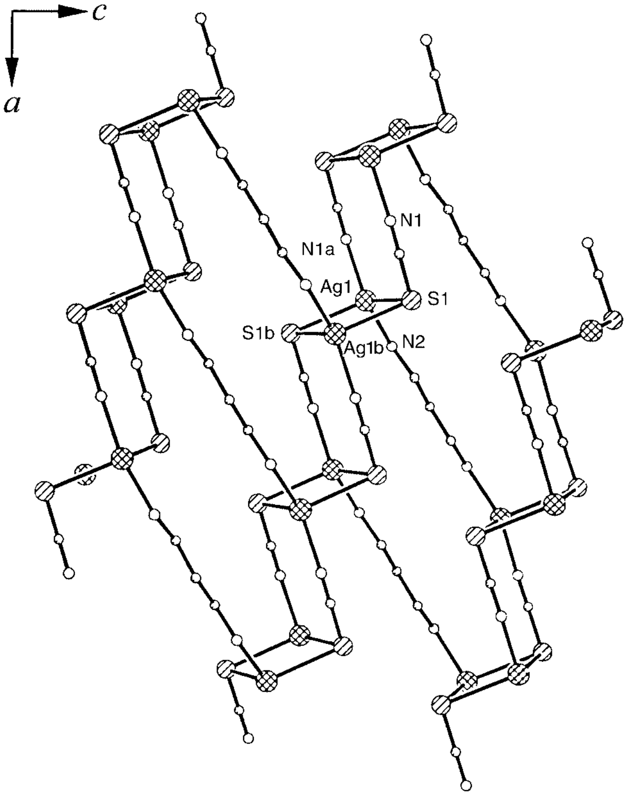

Fig. 2 Top view of the two-dimensional network of complex **2**.

18-membered macrocycles, but also larger, two-dimensional staircase-like layers with the 18-membered macrocycles constituting the steps, as shown in Fig. 1. The two-dimensional networks, related to the translation in the b-axis direction, are stacked in an …AAA… fashion and build up a three-dimensional structure.

The crystal structures of complexes **2**, **3** and **4** are quite similar to that of **1**, and also consist of silver(I) thiocyanate–diamine adducts in a 2:1 molar ratio. As shown in Figs. 2–4, each Ag^I is also in a distorted tetrahedral geometry comprising one diamine nitrogen atom [Ag–N 2.215(4)–2.266(7) Å], two thiocyanate sulfur atoms [Ag–S 2.676(2)–2.868(2) Å] and one nitrogen atom of another thiocyanate ligand [Ag–N 2.178(5)–2.266(7) Å], with the bond angles at the metal atom in the range 94.7(2)–149.1(2)°. In the four-membered Ag_2S_2 rings constructed by four Ag–S bonds the Ag···Ag distances are 3.102(1), 3.278(2) and 3.268(2) Å in **2**, **3**, **4**, respectively, which are shorter than that in **1** and are well below the summed van der Waals radii of two silver atoms (3.44 Å),[31] indicating some weak metal–metal interaction. Similar to **1**, the Ag_2S_2 rings and $Ag_2(SCN)_2$ macrocycles share with the Ag–S edges to furnish staircase-like $^1_\infty[(AgSCN)_2]$ chains in **2**–**4**. These are arranged in an anti-parallel fashion in the cell, and further interlinked by the diamine ligands that bridge the metal centres to generate a two-dimensional $^2_\infty[(AgSCN)_2L]$ (L = 1,3-diaminopropane, 1,4-diaminobutane or 1,5-diaminopentane) network. The bridging diamine ligands display TT (N-to-N 4.931), GTG (N-to-N 5.387) and GTTT (N-to-N 6.792 Å) conformations, respectively. The 1,3-propanediamine ligands are located at crystallographic 2-fold axes, thus the interlinkages of the staircase-like chains in **2** with the diamines, being different from those with 1,2-diaminoethane in **1**, result in the formation of two-dimensional square-wave like sheets in **2**. The two kinds of interlinkages of the staircase-like chains by the diamines in **1** and **2** also occur in **3** (Fig. 3) and **4** (Fig. 4), respectively.

It is also interesting that adjacent layers in complexes **1**–**4** are all related by translation in the b-axis direction in the solid state, being stacked in an …AAA… fashion to build up the three-dimensional structures. The b-axial lengths for each of the four complexes are mainly controlled by the thickness

Table 2 Selected bond lengths (Å) and angles (°) for complexes **1**–**5**

1			
Ag(1)–N(1a)	2.172(4)	Ag(1)–N(2)	2.245(4)
Ag(1)–S(1)	2.772(2)	Ag(1)–S(1b)	2.853(2)
N(1a)–Ag(1)–N(2)	150.1(2)	N(1a)–Ag(1)–S(1)	100.2(1)
N(2)–Ag(1)–S(1)	100.6(1)	N(1a)–Ag(1)–S(1b)	95.8(1)
N(2)–Ag(1)–S(1b)	99.63(9)	S(1)–Ag(1)–S(1b)	104.12(3)
Ag(1)–S(1)–Ag(1b)	75.88(3)	N(1)–C(1)–S(1)	178.9(4)
2			
Ag(1)–N(1a)	2.179(5)	Ag(1)–N(2)	2.215(4)
Ag(1)–S(1)	2.698(2)	Ag(1)–S(1b)	2.784(2)
N(1a)–Ag(1)–N(2)	141.4(2)	N(1a)–Ag(1)–S(1)	101.2(1)
N(2)–Ag(1)–S(1)	104.7(1)	N(1a)–Ag(1)–S(1b)	96.4(1)
N(2)–Ag(1)–S(1b)	100.5(1)	S(1)–Ag(1)–S(1b)	111.10(4)
Ag(1)–S(1)–Ag(1b)	68.90(4)	N(1)–C(1)–S(1)	179.2(5)
3			
Ag(1)–N(1a)	2.262(7)	Ag(1)–N(2)	2.266(7)
Ag(1)–S(1b)	2.701(3)	Ag(1)–S(1)	2.717(2)
N(1a)–Ag(1)–N(2)	124.2(2)	N(1a)–Ag(1)–S(1b)	101.4(2)
N(2)–Ag(1)–S(1b)	115.3(2)	N(1a)–Ag(1)–S(1)	94.7(2)
N(2)–Ag(1)–S(1)	112.5(2)	S(1b)–Ag(1)–S(1)	105.54(5)
Ag(1b)–S(1)–Ag(1)	74.46(5)	N(1)–C(1)–S(1)	178.1(6)
4			
Ag(1)–N(1a)	2.178(5)	Ag(1)–N(3)	2.238(4)
Ag(1)–S(1)	2.760(2)	Ag(1)–S(1b)	2.868(2)
Ag(2)–N(2)	2.244(5)	Ag(2)–N(4)	2.257(5)
Ag(2)–S(2c)	2.676(2)	Ag(2)–S(2d)	2.710(2)
N(1a)–Ag(1)–N(3)	149.1(2)	N(1a)–Ag(1)–S(1)	100.1(1)
N(3)–Ag(1)–S(1)	100.5(1)	N(1a)–Ag(1)–S(1b)	98.6(1)
N(3)–Ag(1)–S(1b)	96.2(1)	S(1)–Ag(1)–S(1b)	109.04(5)
Ag(1)–S(1)–Ag(1b)	71.0(5)	N(2)–Ag(2)–N(4)	125.3(2)
N(2)–Ag(2)–S(2c)	96.4(2)	N(4)–Ag(2)–S(2c)	112.4(1)
N(2)–Ag(2)–S(2d)	101.6(1)	N(4)–Ag(2)–S(2d)	116.0(1)
S(2c)–Ag(2)–S(2d)	101.31(5)	Ag(1)–S(1)–Ag(1b)	70.96(5)
Ag(2e)–S(2)–Ag(2d)	78.69(5)	N(1)–C(1)–S(1)	178.2(5)
N(2)–C(2)–S(2)	179.6(5)		
5			
Ag(1)–N(3)	2.313(5)	Ag(1)–N(2)	2.393(5)
Ag(1)–S(3)	2.439(2)	Ag(1)–S(3a)	2.959(2)
Ag(2)–N(1b)	2.287(6)	Ag(2)–N(5c)	2.307(6)
Ag(2)–S(1)	2.623(2)	Ag(2)–S(2)	2.726(2)
Ag(3)–N(6d)	2.239(6)	Ag(3)–N(4)	2.253(6)
Ag(3)–S(2)	2.735(2)	Ag(3)–S(1)	2.772(2)
N(3)–Ag(1)–N(2)	79.3(2)	N(3)–Ag(1)–S(3)	136.3(1)
N(2)–Ag(1)–S(3)	126.4(1)	N(3)–Ag(1)–S(3a)	100.9(1)
N(2)–Ag(1)–S(3a)	83.7(1)	S(3)–Ag(1)–S(3a)	115.19(5)
Ag(1)–S(3)–Ag(1a)	64.83(5)	N(1b)–Ag(2)–N(5c)	115.0(2)
N(1b)–Ag(2)–S(1)	121.7(2)	N(5c)–Ag(2)–S(1)	101.9(2)
N(1b)–Ag(2)–S(2)	105.9(2)	N(5c)–Ag(2)–S(2)	102.5(2)
S(1)–Ag(2)–S(2)	108.04(6)	N(6d)–Ag(3)–N(4)	132.5(2)
N(6d)–Ag(3)–S(2)	98.7(2)	N(4)–Ag(3)–S(2)	115.7(2)
N(6d)–Ag(3)–S(1)	96.9(2)	N(4)–Ag(3)–S(1)	105.0(2)
S(2)–Ag(3)–S(1)	103.66(6)	Ag(2)–S(1)–Ag(3)	74.64(6)
Ag(2)–S(2)–Ag(3)	73.64(5)	N(5)–C(9)–S(1)	177.7(6)
N(6)–C(10)–S(2)	178.9(6)	N(7)–C(11)–S(3)	177.8(7)

Symmetry transformations: for **1** (a) $x + 1, y, z$; (b) $-x, -y, -z$; for **2** (a) $-x, -y, -z$; (b) $-x + 1, -y, -z$; for **3** as **1**; for **4** (a) $-x, -y, -z + 2$; (b) $-x + 1, -y, -z + 2$; (c) $x - 1, y, z$; (d) $-x + 4, -y + 1, -z + 1$; (e) $x + 1, y, z$; for **5** (a) $-x, -y + 2, -z + 2$; (b) $x, y + 1, z - 1$; (c) $-x + 1, -y + 2, -z + 1$; (d) $-x, -y + 3, -z + 1$.

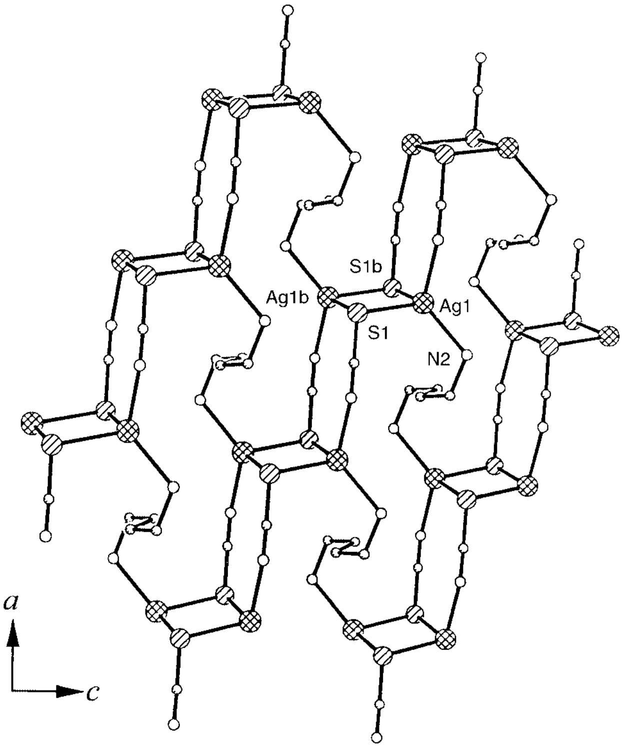

Fig. 3 Top view of the two-dimensional network of complex **3**.

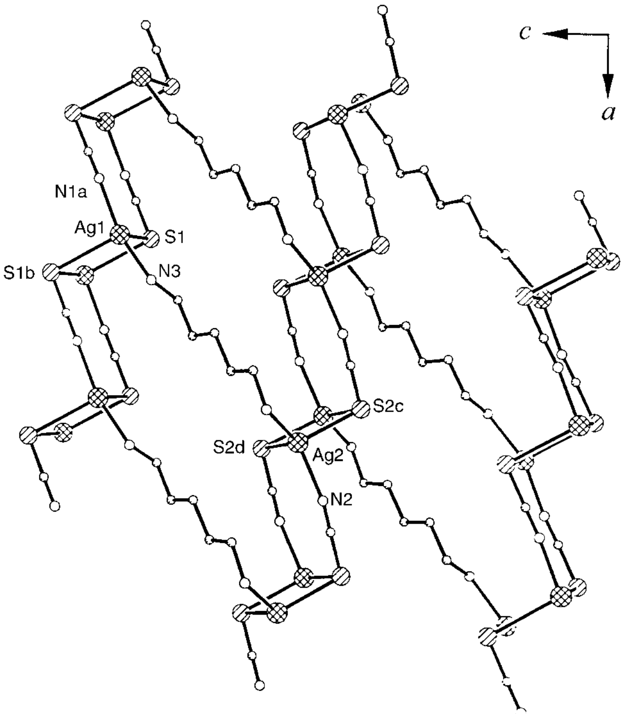

Fig. 4 Top view of the two-dimensional network of complex **4**.

of the layer and the packing interaction. As shown in Table 1, the *b*-axial lengths are similar for **1**–**4**, indicating that these complexes are similar in both the packing fashion and thickness of the layer. Moreover, it is easy to understand the similarity in the *a*-axial lengths, which are mainly governed by the structures of the staircase-like $^{1}_{\infty}[(AgSCN)_2]$ chains in **1**–**4**. On the other hand, the layer's orientations are different in the cells; they are concentrated about the (010) planes in **1**–**3**, about the (011) planes in **4**. Therefore, the *c*-axial lengths are dictated by the conformations and lengths of the diamines, as well as the crystallographic symmetries, showing significant differences in the four complexes.

As illustrated in Fig. 5, there are three crystallographically independent silver(I) atoms in the crystal of complex **5**, and the stoichiometry for the silver(I) thiocyanate–tetraamine is 3 : 1. Each Ag^{I} is located in a highly distorted tetrahedral environment. Among the three metal atoms, Ag(2) and Ag(3) are inteconnected by μ-*N*,*S*,*S*-thiocyanate groups to form

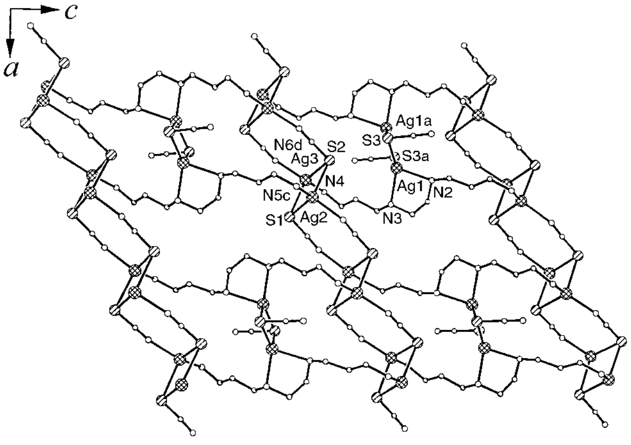

Fig. 5 Top view of the two-dimensional network of complex **5**.

staircase-like ${}^{1}_{\infty}[(\mathrm{AgSCN})_2]$ chains similar to those found in **1**–**4**, featuring similar distorted $\mathrm{AgN_2S_2}$ tetrahedrons with Ag–N and Ag–S bond lengths in the range 2.239(6)–2.307(6) and 2.623(2)–2.772(2) Å, respectively, and the bond angles are in the range 96.9(2)–132.5(2)° at Ag(2) and Ag(3) and 79.3(2)–136.3(1)° at Ag(1). Different from the other two silver(I) atoms, Ag(1) is chelated by an ethylenediamine entity [Ag(1)–N(3) 2.313(5), Ag(1)–N(2) 2.393(5) Å] of a tetraamine, and a pair of inversely related Ag(1) atoms are bridged unsymmetrically by a pair of μ-*S*-thiocyanate groups [Ag(1)–S(3) 2.439(2), Ag(1)–S(3a) 2.959(2) Å] into a dinuclear core. Such μ-*S*-thiocyanate groups, as well as the interlocking of the adjacent ethylenediamine entities of the amine ligands by the dinuclear $[\mathrm{Ag_2}(\mu\text{-}S\text{-SCN})_2]$ cores in the staircase-like sheet, make **5** different from **1**–**4**, constituting a new structural variety. On the other hand, the one-dimensional staircase-like ${}^{1}_{\infty}[(\mathrm{AgSCN})_2]$ chains are further bridged by the tetraamine ligands through the terminal nitrogen atoms to generate two-dimensional staircase-like layers similar to those in **1** and **3**, as shown in Fig. 5. In the two-dimensional layers, the short Ag(1)···Ag(1a) (2.926(1) Å) and Ag(2)···Ag(3) (3.273(1) Å) distances in the four-membered $\mathrm{Ag_2S_2}$ ring also indicate some weak metal–metal interaction.

Conclusions

We describe five new, structurally interesting two-dimensional layered compounds, ${}^{2}_{\infty}[(\mathrm{AgSCN})_2\mathrm{L}]$ and ${}^{2}_{\infty}[(\mathrm{AgSCN})_3\mathrm{L}]$ (L = di- or tetra-amine), constructed from ${}^{1}_{\infty}[\mathrm{Ag_2}(\mu\text{-}N,S,S\text{-SCN})_2]$ chains and the bridging amine ligands. The results show that the different aliphatic diamines did not change the skeletons of the staircase-like ${}^{1}_{\infty}[\mathrm{Ag_2}(\mu\text{-}N,S,S\text{-SCN})_2]$ chains but the conformations and the sizes of the two-dimensional ${}^{2}_{\infty}[\mathrm{Ag_2}(\mu\text{-}N,S,S\text{-SCN})_2(\mu\text{-}N,N'\text{-diamine})]$ layers. The application of the tetraamine containing an ethylenediamine entity furnished a similar ${}^{2}_{\infty}[\mathrm{Ag_2}(\mu\text{-}N,S,S\text{-SCN})_2(\mu\text{-}N,N'\text{-tetraamine})]$ layered complex, in which adjacent tetraamine ligands are further interlocked by the pairs of chelating ethylenediamine entities *via* the $\mathrm{Ag_2}(\mu\text{-}S\text{-SCN})_2$ dinuclear cores.

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References

1 M. Munakata, L. P. Wu and T. Kuroda-Sowa, *Adv. Inorg. Chem.*, 1999, **46**, 173.

2 R. Robson, B. F. Abrahams, S. R. Batten, R. W. Gable, B. F. Hoskins and J. Lieu, in *Supramolecular Architecture*, ed. T. Bein, ACS, Washington, DC, 1992, p. 256.

3 T. L. Honnigar, D. C. MacQuarric, P. D. Rogers and M. J. Zaworotko, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 972; H. Gudbjarlson, K. M. Poirier and M. J. Zaworotko, *J. Am. Chem. Soc.*, 1999, **121**, 2599.

4 M.-L. Tong, X.-M. Chen, B.-H. Ye and S. W. Ng, *Inorg. Chem.*, 1998, **37**, 2645.

5 L. Carlucci, G. Ciani and D. M. Proserpio, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1895; M.-L. Tong, X.-M. Chen, B.-H. Ye and S. W. Ng, *Inorg. Chem.*, 1998, **37**, 5168; A. J. Blake, N. R. Champness, P. Hubberstey, W. S. Li, M. A. Withersby and M. Schröder, *Coord. Chem. Rev.*, 1999, **183**, 117; H.-L. Zhu, Y.-X. Tong and X.-M. Chen, *J. Chem. Soc., Dalton Trans.*, 2000, 4182.

6 M.-L. Tong, X.-M. Chen, B.-H. Ye and L.-N. Ji, *Angew. Chem., Int. Ed.*, 1999, **38**, 2237; M.-L. Tong, S.-L. Zheng and X.-M. Chen, *Chem. Commun.*, 1999, 561; G. Yang, S.-L. Zheng and X.-M. Chen, *Inorg. Chim. Acta*, 2000, **233**, 86; S.-P. Yang, X.-M. Chen and L.-N. Ji, *J. Chem. Soc., Dalton Trans.*, 2000, 2337; M.-L. Tong, X.-M. Chen and S. W. Ng, *Inorg. Chem. Commun.*, 2000, **3**, 436; M.-L. Tong, S.-L. Zheng and X.-M. Chen, *Chem. Eur. J.*, 2000, **6**, 3729.

7 F. A. Cotton and G. Wilkinson, in *Advanced Inorganic Chemistry*, Wiley-Interscience, Singapore, 5th edn., 1988, ch. 18, pp. 940 and 941.

8 G. A. Bowmaker, Effendy, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1998, 2123; G. A. Bowmaker, Effendy, P. J. Harvey, P. C. Healy, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1996, 2449; C. Stockheim, K. Wieghardt, B. Nuber, J. Weiss, U. Flörke and H.-J. Haupt, *J. Chem. Soc., Dalton Trans.*, 1991, 1487.

9 N. K. Mills and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1984, 229.

10 G.-Y. Du, W.-X. Zhang and Y.-P. Fan, *J. Inorg. Chem.* (*Wuji Huaxue Xuebao*), 1987, **3**, 34.

11 E. C. Plappert, D. M. Mingos, S. E. Lawrence and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 1997, 2119; E. Bang, *Acta Chem. Scand., Ser. A*, 1978, **32**, 555; M. Shakibaie-Moghadam, U. Timper and G. Heller, *Z. Naturforsch., Teil B*, 1994, **49**, 627; M. Horner, A. G. Pedroso, J. Beck and J. Strahle, *Z. Naturforsch., Teil B*, 1996, **51**, 686; U. Timper and G. Heller, *Z. Naturforsch., Teil B*, 1994, **49**, 215.

12 E. Bang, *Acta Chem. Scand.*, 1996, **50**, 952.

13 Effendy, J. D. Kidea and A. H. White, *Aust. J. Chem.*, 1997, **50**, 587.

14 L.-N. Rudolph and H. Hartl, *Z. Anorg. Allg. Chem.*, 1997, **623**, 687; L. C. Capacchi, G. F. Gasparri, M. Ferrari and M. Nardelli, *Chem. Commun.*, 1968, 910; A. C. Bonamartini, G. F. Gasparri, M. F. Belicchi and M. Nardelli, *Acta Crystallogr., Sect. C*, 1987, **43**, 407; J. Howatson and B. Morosin, *Cryst. Struct. Commun.*, 1973, **2**, 51; G. A. Bowmaker, Effendy, J. D. Kidea, E. N. de Silva and A. H. White, *Aust. J. Chem.*, 1997, **50**, 627; J.-L. Wang, M. Sun, F.-M. Miao, S.-Y. Wu, F.-S. Gong and X.-H. Duan, *Acta Crystallogr., Sect. C*, 1991, **47**, 2203; A. H. Othman, H.-K. Fun, K. Sivakumar, Y. Farina and I. Baba, *Acta Crystallogr., Sect. C*, 1996, **52**, 1933; J. Pickardt and S. Jing, *Z. Naturforsch., Teil B*, 1994, **49**, 211.

15 Q.-P. Hu, D.-R. Chen, Y.-D. Meng and Y.-P. Fan, *Jiegou Huaxue* (*J. Struct. Chem.*), 1995, **14**, 206.

16 G. A. Bowmaker, Effendy, J. D. Kildea and A. H. White, *Aust. J. Chem.*, 1997, **50**, 577.

17 R. Louis, D. Pelissard and R. Weiss, *Acta Crystallogr., Sect. B*, 1976, **32**, 1480; C. Panattoni and E. Frasson, *Gazz. Chim. Ital.*, 1963, **93**, 601; M. B. Ferrari, G. G. Fava and M. E. V. Tani, *Cryst. Struct. Commun.*, 1981, **10**, 571; R. Louis, Y. Agnus and R. Weiss, *Acta Crystallogr., Sect. B*, 1977, **33**, 1418; R. W. Matthews, M. McPartlin and I. J. Scowen, *Chem. Commun.*, 1996, 309.

18 P. Gans, J. B. Gill and D. P. Fearnley, *J. Chem. Soc., Dalton Trans.*, 1981, 1708.

19 T. Hausler and W. S. Sheldrick, *Chem. Ber.*, 1997, **130**, 371.

20 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.

21 G. M. Sheldrick, SHELXS 97, Program for Crystal Structure Determination, University of Göttingen, 1997.

22 G. M. Sheldrick, SHELXL 97, Program for Crystal Structure Refinement, University of Göttingen, 1997.

23 *International Tables for X-Ray Crystallography*, Kluwer Academic Publisher, Dordrecht, 1992, vol. C, Table 4.2.6.8 and 6.1.1.4.

24 P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 1960, 1912; R. A. Bailey, S. L. Kozak, T. W. Michelsen and W. N. Mills, *Coord. Chem. Rev.*, 1971, **6**, 407.

25 P. Kinell and B. Stranderg, *Acta Chem. Scand.*, 1959, **13**, 1607; J. Lewis, R. S. Nyholm and P. W. Smith, *J. Chem. Soc.*, 1961, 4590.
26 A. Sabatini and I. Bertini, *Inorg. Chem.*, 1965, **4**, 959.
27 D. B. Powell and N. Sheppard, *J. Chem. Soc.*, 1959, 3089.
28 G. Newman and D. B. Powell, *J. Chem. Soc.*, 1961, 447; G. Newman and D. B. Powell, *J. Chem. Soc.*, 1962, 3447; K. Brodersen, *Z. Anorg. Allg. Chem.*, 1959, **298**, 142; K. Brodersen and T. Kahlert, *Z. Anorg. Allg. Chem.*, 1966, **348**, 273; T. Iwamoto and D. F. Shriver, *Inorg. Chem.*, 1971, **10**, 2428.
29 S. Mizushima, I. Ichishma, I. Nakagawa and J. V. Quagliano, *J. Phys. Chem.*, 1955, **59**, 293.
30 A. Nakahara, Y. Saito and H. Kuaroya, *Bull. Chem. Soc. Jpn.*, 1952, **25**, 331.
31 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 411.