Amine-rich Silver Complexes of *rac-trans*-1,2-Diaminocyclohexane

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The use of the diamine *rac-trans*-1,2-diaminocyclohexane (*LL*) as a major component of the solvent system allows the isolation of crystalline silver complexes with higher ratios of *LL* to silver (up to 4 : 1, compared to the previously obtained 1 : 1 in ethanolic solution). The complexes obtained and crystallographically characterized were $(LL)_2AgNO_3$ (**1**), $(LL)_3Ag(OAc)(H_2O)_2$ (**2**) and $(LL)_4AgBr(H_2O)_3$ (**3**). Additionally, the silver-free compounds $(LL)\cdot(H_2O)$ (**4**) and $(LL)_3\cdot HCl$ (**5**) were obtained as by-products. Complex **1** is a chain polymer with one bridging and one terminal *LL* ligand; the chains are homochiral. Complex **2** contains isolated $[(LL)_3Ag]^+$ cations with one chelating and two monodentate ligands. Complex **3** contains dimeric $[(LL)_2AgBr]_2$ units; the additional *LL* molecules are not coordinated to the metal. Compound **5** consists of one diamine with imposed twofold symmetry, one half-protonated diamine in which the acidic hydrogen site is half-occupied (it is involved in a disordered hydrogen bond N–H···N across a twofold axis) and a chloride anion on a twofold axis. In all five structures, the components pack so as to form clearly defined hydrophilic and hydrophobic areas. In the former, classical hydrogen bonds are formed. Except for a few borderline cases of three-center bonds, these are all two-center systems. The appreciable number of these (*e. g.* 20 for compound **3**) renders the layer structures quite complex, but in most cases they can be analyzed in terms of smaller units.

Key words: Silver, Hydrogen Bonds, Chiral Ligands, Amines

Introduction

The coordination properties of silver(I) are extremely varied and flexible with respect to coordination number and geometry. It follows that, depending on one's point of view, the ion is either a challenging or an almost impossible candidate for "crystal engineering". Nevertheless, it is possible to derive some primitive rules of thumb. In recent studies of amine complexes of silver(I) with halogenido [1] or disulfonylamido [2, 3] ligands we were able to show that the use of the liquid amine itself as part of the solvent system can lead to unusual stoichiometries, often with a higher amine content than in "normal" complexes. In a fascinating study of silver complexes of the rigid ligand *trans*-1,2-diaminocyclohexane [4] Englert and co-workers have shown that complexes of the stoichiometry Ag(*LL*)*X* are formed (*LL* = diamine, *X* = anion, which may be weakly coordinated), which contain polymeric chains …Ag-*LL*-Ag-*LL*…; Ag···Ag contacts may be observed between or within chains. The racemic diamine formed heterochiral chains, whereas the enantiomerically pure (*SS*) diamine necessarily formed homochiral chains. The anions chosen were nitrate, acetate and tetrafluoroborate, and some complexes crystallized as hydrates. However, all syntheses were performed in ethanolic solution. We therefore wished to investigate if compounds of differing stoichiometry could be obtained by using a much higher ligand concentration (with the diamine as part of the solvent system). We used racemic *trans*-1,2-diaminocyclohexane (*LL*) [5] and the same silver salts as Englert, plus the silver halides. Not all attempts provided crystals, but we were able to determine the structures of silver complexes with the following stoichiometries: $(LL)_2AgNO_3$ (**1**), $(LL)_3Ag(OAc)(H_2O)_2$ (**2**) and $(LL)_4AgBr(H_2O)_3$ (**3**). As by-products we also obtained $(LL)\cdot(H_2O)$ (**4**) and $(LL)_3\cdot HCl$ (**5**).

Results and Discussion

The nitrate complex **1** has a diamine to silver ratio of 2 : 1; it is the only compound in this paper that did not crystallize with adventitious water. The asymmetric unit is shown in Fig. 1. The silver displays a trigonal coordination by three amine nitrogens (Ag–N

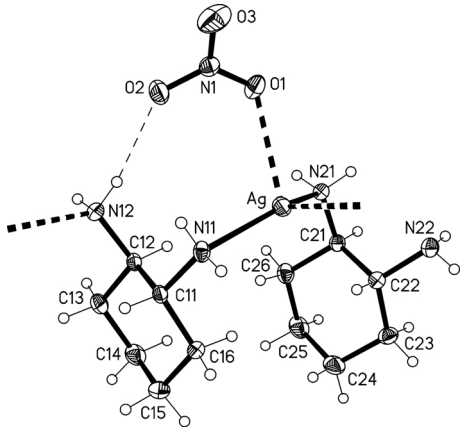

Fig. 1. The asymmetric unit of compound **1**. Ellipsoids correspond to 50 % probability levels. Weak interactions and the connections to the next units in the polymeric chain (see text) are shown as dashed bonds. Selected bond lengths (Å) and angles (deg): Ag–N11 2.2593(16), Ag–N21 2.2633(18), Ag–N12$^{\#1}$ 2.4425(17), Ag–O1 2.7435(15); N11–Ag–N21 145.71(6), N11–Ag–N12$^{\#1}$ 96.83(6), N21–Ag–N12$^{\#1}$ 114.06(6), N11–Ag–O1 107.33(5), N21–Ag–O1 81.39(5), N12$^{\#1}$–Ag–O1 102.07(5). Symmetry operator $^{\#1}$: $-x+3/2$, $y+1/2$, $-z+1/2$.

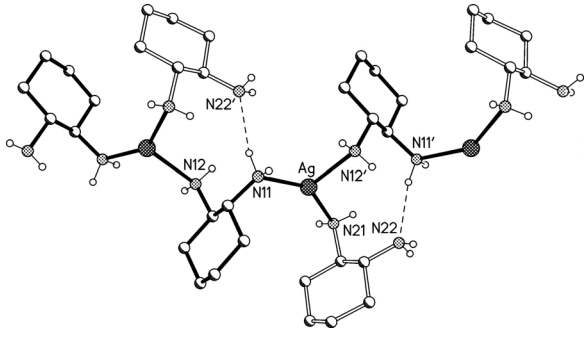

Fig. 2. Part of the chain polymer of **1**. Dashed lines indicate hydrogen bonds. Primes indicate symmetry-equivalent atoms.

2.259(2)–2.443(2) Å), plus a weak contact to nitrate oxygen O1 of 2.744(2) Å, which causes the silver atom to lie 0.273(1) Å out of the plane of the three nitrogen atoms. One diamine ligand bridges silver atoms *via* atoms N11 and N12, leading to a chain of the known type ...Ag-*LL*-Ag-*LL*...; the second diamine is terminal *via* N21. The trigonal angles at silver are very irregular, with the widest angle N11–Ag–N21 145.71(6)° opposite the longest bond Ag–N12′. Within the chain, which is built up *via* the 2_1 screw axis (Fig. 2), the Ag···Ag′ separation is 5.9822(5) Å and the torsion angle Ag–N11···N12–Ag′ is −158.65(6)°. Perhaps the most interesting feature of the structure is the *homochiral* nature of the chain (despite the use of the *racemic* diamine); not only are the ligands within the asymmetric unit both *RR*, but the 2_1 operator causes the entire chain to consist of *RR* ligands.

Table 1. Hydrogen bonds (Å and deg) for compound **1**[a].

D–H···*A*	*d*(D–H)	*d*(H···*A*)	*d*(D···*A*)	∠(D*H*A)
N11–H01···N22$^{\#2}$	0.90(2)	2.25(2)	3.131(2)	168(2)
N11–H02···N1$^{\#3}$	0.86(2)	2.54(2)	3.267(2)	142.3(18)
N11–H02···O1$^{\#3}$	0.86(2)	2.23(2)	3.076(2)	166(2)
N12–H03···O2	0.86(2)	2.20(3)	3.043(2)	166(2)
N12–H04···O1$^{\#4}$	0.86(3)	2.25(3)	3.081(2)	162(2)
N21–H05···O2$^{\#5}$	0.84(3)	2.23(3)	3.016(2)	155(2)
N22–H07···O3$^{\#5}$	0.89(2)	2.41(3)	3.177(3)	144(2)
N22–H08···N1$^{\#1}$	0.83(3)	2.67(3)	3.445(3)	155(2)
N22–H08···O2$^{\#1}$	0.83(3)	2.52(3)	3.117(3)	130(2)
C24–H24A···O3$^{\#6}$	0.99	2.47	3.338(3)	146

[a] Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x+3/2$, $y+1/2$, $-z+1/2$; $^{\#2}$ $-x+3/2$, $y-1/2$, $-z+1/2$; $^{\#3}$ $x+1$, y, z; $^{\#4}$ $-x+1/2$, $y-1/2$, $-z+1/2$; $^{\#5}$ $-x+1/2$, $y+1/2$, $-z+1/2$; $^{\#6}$ $x+1/2$, $-y+3/2$, $z-1/2$.

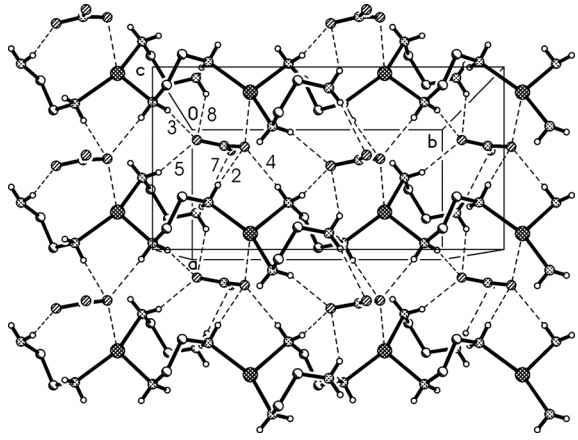

Fig. 3. Classical hydrogen bonds H···O and Ag···O1 contacts (all shown as thin dashed bonds) between the polymeric chains (horizontal) and the interstitial nitrate ions in compound **1**. For clarity, the diamine ligands have been pruned to $\{C(NH_2)\}_2$ units. For one nitrate, a set of hydrogen bonds is numbered according to the number of the donor hydrogen. Hydrogen bond no. 1 (within the chain) is not shown here, but can be seen explicitly in Fig. 2.

As would be expected, the packing involves several classical hydrogen bonds (Table 1). All the NH donors form such hydrogen bonds except H06, but several are quite long [6], and some are borderline three-center systems. The hydrogen bonds from H03 and H01 are shown in Figs. 1 and 2, respectively. Most of the hydrogen bonds involve the nitrate oxygen atoms as acceptors; these lie between the ...Ag-*LL*-Ag-*LL*... chains (Fig. 3). In some cases the nitrate nitrogen atom appears to be a weak acceptor, but these contacts are

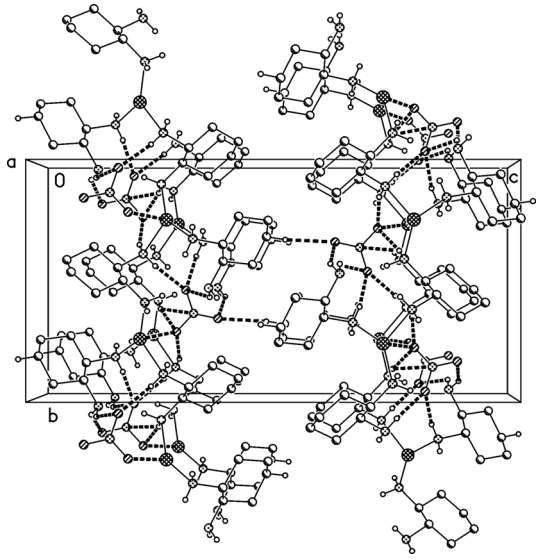

Fig. 4. General view of the packing of compound **1** showing hydrophilic (at $z \approx 1/4, 3/4$) and hydrophobic regions, connected in the center by C–H···O contacts.

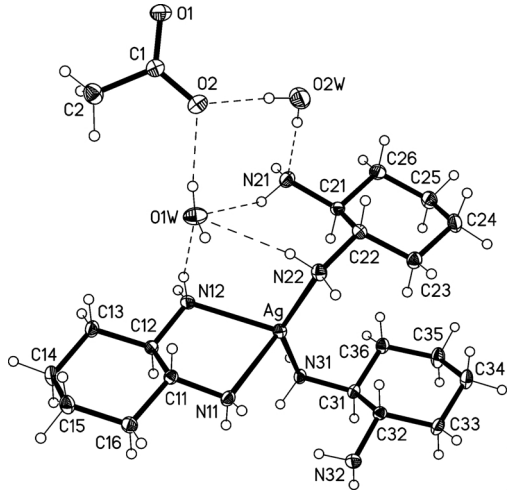

Fig. 5. The asymmetric unit of compound **2** with ellipsoids at the 50 % level. Hydrogen bonds are shown as thin dashed lines. Selected bond lengths (Å) and angles (deg): Ag–N31 2.2809(9), Ag–N22 2.3031(9), Ag–N12 2.4052(9), Ag–N11 2.4362(9); N31–Ag–N22 141.28(3), N31–Ag–N12 111.40(3), N22–Ag–N12 102.53(3), N31–Ag–N11 103.05(3), N22–Ag–N11 103.88(3), N12–Ag–N11 73.81(3).

not included in Fig. 3. Similarly to the structure of the 1 : 1 complexes [4], the structure of **1** is separated into hydrophilic (at $z \approx 1/4, 3/4$) and hydrophobic regions (Fig. 4), but the separation is less strict; one C–H···O contact acts as a bridge between the regions.

The acetate derivative **2** contains three diamines per silver, and these are all coordinated; one (N11; N12; *SS*) acts as a chelating ligand, whereas the other two (coordinating to silver *via* N22 and N31) are *RR* and monodentate. The isolated cations thus formed display non-crystallographic twofold symmetry to a good approximation (r. m. s. d. 0.07 Å) and involve Ag–N distances varying from 2.2809(9) to 2.4362(9) Å, with the longest bonds being formed to the chelating ligand. The bite angle is 73.81(3)°, whereas the angle subtended by the monodentate ligands is very wide at 141.28(3)°. The acetate ion is not coordinated to silver, nor are the two water molecules, and there are no significant Ag···O contacts. The asymmetric unit is shown in Fig. 5.

The various residues of **2** pack in such a way as to form clearly defined hydrophilic and hydrophobic regions; it is easiest to appreciate this overview first (Fig. 6). All potential hydrogen bond donors are involved in contacts (Table 2) that could be regarded as classical hydrogen bonds, although some H···*A* distances are long; we have arbitrarily included H05···O1W (2.63 Å) while omitting H011···O1 (2.75 Å) from the Figures. Water molecule 1 is a donor in two and an acceptor in four hydrogen bonds,

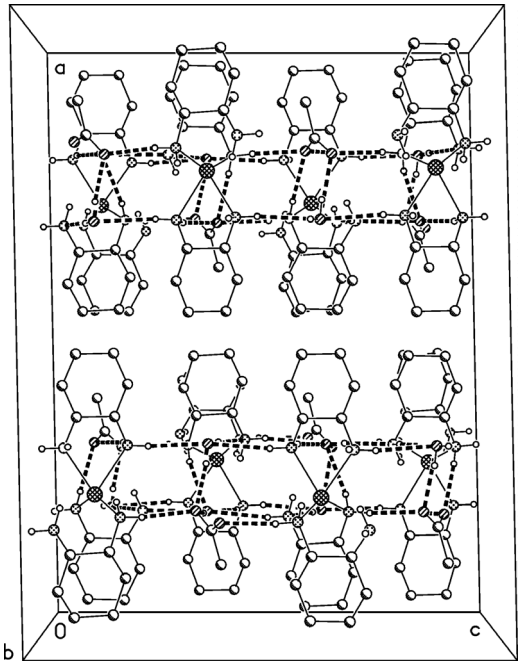

Fig. 6. Overview of the packing of compound **2**, showing classical hydrogen bonding (thick dashed lines) in the hydrophilic regions at $x \approx 1/4, 3/4$.

Table 2. Hydrogen bonds (Å and deg) for compound **2**[a].

D–H···*A*	*d*(D–H)	*d*(H···*A*)	*d*(D···*A*)	∠(D*H*A)
N11–H001···O2W$^{\#1}$	0.852(15)	2.551(16)	3.3851(14)	166.5(14)
N11–H002···O1$^{\#2}$	0.859(14)	2.268(14)	3.0813(12)	158.0(12)
N12–H003···O2W$^{\#3}$	0.868(17)	2.560(17)	3.4053(14)	165.0(15)
N12–H004···O1W	0.851(15)	2.334(15)	3.1574(13)	162.9(13)
N21–H005···O1W	0.897(17)	2.628(16)	3.3660(13)	140.0(13)
N21–H006···O1W$^{\#3}$	0.850(16)	2.539(16)	3.3804(13)	170.8(14)
N22–H007···O2$^{\#1}$	0.885(16)	2.333(16)	3.2091(13)	170.2(14)
N22–H008···O1W	0.903(16)	2.426(16)	3.2998(13)	162.8(13)
N31–H009···O1$^{\#3}$	0.880(15)	2.278(15)	3.1499(12)	170.5(14)
N31–H010···O1$^{\#2}$	0.890(15)	2.249(15)	3.1128(12)	163.6(13)
N32–H011···O1$^{\#2}$	0.880(18)	2.753(17)	3.5255(13)	147.2(14)
N32–H012···O2W$^{\#2}$	0.836(17)	2.334(17)	3.1315(14)	159.6(14)
O1W–H013···O2	0.792(19)	2.028(19)	2.8139(12)	171.4(18)
O1W–H014···N32$^{\#4}$	0.805(17)	2.062(18)	2.8649(13)	175.4(17)
O2W–H015···O2	0.82(2)	1.94(2)	2.7497(13)	172.4(19)
O2W–H016···N21	0.812(19)	2.074(19)	2.8855(14)	177.2(18)

[a] Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x+1/2, y+1/2, -z+3/2$; $^{\#2}$ $x, y+1, z$; $^{\#3}$ $-x+1/2, -y+1/2, -z+1$; $^{\#4}$ $-x+1/2, y-1/2, -z+3/2$.

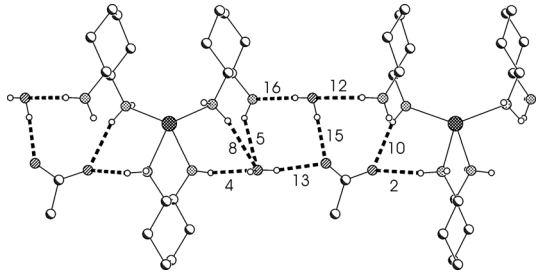

Fig. 7. Packing of compound **2**; part of a polymeric ribbon formed by cations, acetates and water molecules. The ribbon direction is parallel to the *b* axis, and the view direction is parallel to the *c* axis. Hydrogen bonds are indicated by thick dashed lines and are numbered according to the number of the hydrogen acting as donor.

whereas water 2 is a donor in two and an acceptor in three hydrogen bonds. The total coordination number of 6 for water 1 is high; this may be associated with, or accommodated by, some relatively long H···O contacts. The complete packing within one hydrophilic region is clearly complicated. The clearest substructure is recognisable as a ribbon formed by translation parallel to the *b* axis (Fig. 7); cations are bridged by acetates and waters. However, if the "double" hydrophilic layer of Fig. 6 is reduced to just one layer by removing some of the connecting "struts" (hydrogen bonds 8, 10, 15), then a clearer view (Fig. 8) results in which each hydrogen bond except 8 and 15 can be seen at least once. The ribbons from Fig. 7 are seen vertically and edge-on in the regions $z \approx 1/8, 3/8, 5/8, 7/8$.

Compound **3** has the highest ratio of diamine to silver (4 : 1), but only two of the diamines are coordinated to the metal; these are of opposite chirality. Fig. 9a shows the asymmetric unit and the hydrogen bonds therein. The silver moiety is extended to a dimer $Ag_2Br_2(LL)_4$ *via* an inversion center, with angles of 115.57(1)° at silver and of 64.43(1)° in the central four-membered ring (Fig. 9b).

Table 3. Hydrogen bonds (Å and deg) for compound **3**[a].

D–H···*A*	*d*(D–H)	*d*(H···*A*)	*d*(D···*A*)	∠(D*H*A)
N11–H001···O1W	0.866(18)	2.473(18)	3.2729(17)	154.0(14)
N11–H002···O2W	0.858(18)	2.336(18)	3.1920(16)	175.9(16)
N12–H003···O3W$^{\#2}$	0.836(18)	2.630(18)	3.4271(17)	159.9(15)
N12–H004···O1W	0.872(19)	2.282(19)	3.1382(17)	167.2(16)
N21–H006···O1W	0.862(17)	2.213(18)	3.0413(16)	161.1(15)
N22–H007···Br$^{\#3}$	0.869(19)	2.95(2)	3.8188(12)	175.0(16)
N22–H008···Br	0.870(18)	2.839(18)	3.6592(13)	157.7(14)
N31–H009···O2W$^{\#2}$	0.887(19)	2.549(19)	3.3964(17)	160.2(16)
N31–H010···O3W$^{\#2}$	0.871(19)	2.622(19)	3.4704(18)	165.0(15)
N32–H011···O3W$^{\#2}$	0.822(18)	2.324(19)	3.1166(18)	162.2(17)
N32–H012···O3W$^{\#4}$	0.853(18)	2.296(18)	3.1483(16)	176.3(16)
N41–H013···O2W	0.821(19)	2.456(19)	3.2677(18)	170.2(17)
N41–H014···O1W$^{\#5}$	0.855(18)	2.320(18)	3.1590(16)	167.2(16)
N42–H016···Br$^{\#1}$	0.857(18)	2.817(18)	3.6693(14)	173.0(15)
O1W–H017···N32	0.787(13)	2.005(14)	2.7896(16)	175(2)
O1W–H018···N42	0.776(13)	2.070(14)	2.8373(16)	170(2)
O2W–H019···N12$^{\#5}$	0.784(13)	2.118(13)	2.8949(16)	171.0(19)
O2W–H020···N22$^{\#1}$	0.784(13)	2.131(13)	2.9140(16)	176.2(19)
O3W–H021···N31	0.787(13)	2.127(13)	2.9082(16)	172(2)
O3W–H022···N41	0.778(13)	2.105(14)	2.8627(17)	165(2)

[a] Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x+1, -y+1, -z+1$; $^{\#2}$ $-x+1, -y+1, -z$; $^{\#3}$ $-x, -y+1, -z+1$; $^{\#4}$ $x-1, y, z$; $^{\#5}$ $x+1, y, z$.

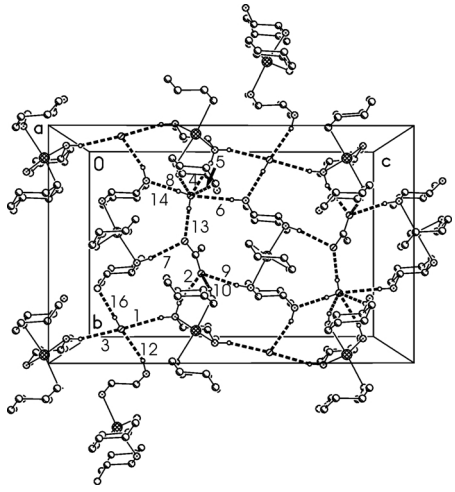

Fig. 8. Packing of compound **2**; general view parallel to *a* in the region $x \approx 1/8$. For clarity, the "double" hydrophilic layer of Fig. 6 has been reduced to one component. Hydrogen bonds are indicated by thin dashed lines and are numbered according to the number of the hydrogen acting as donor.

Since compound **3** contains no fewer than 22 potential classical hydrogen bond donors, a complex pack-

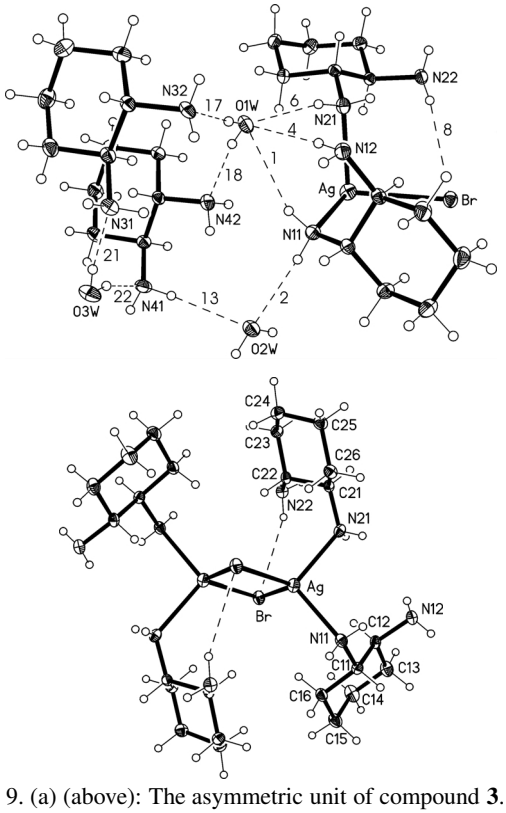

Fig. 9. (a) (above): The asymmetric unit of compound **3**. Ellipsoids represent 50 % probability levels. Hydrogen bonds are numbered according to the number of the hydrogen donor. (b) (below): The inversion-symmetric dimer of the silver moiety in **3**. Selected bond lengths (Å) and angles (deg): Ag–N11 2.3584(12), Ag–N21 2.3713(12), Ag–Br$^{\#1}$ 2.7238(3), Ag–Br 2.7742(2), Ag$\cdots$Ag$^{\#1}$ 2.9311(3); N11–Ag–N21 102.77(4), N11–Ag–Br$^{\#1}$ 109.74(3), N21–Ag–Br$^{\#1}$ 115.28(3), N11–Ag–Br 114.24(3), N21–Ag–Br 98.21(3), Br$^{\#1}$–Ag–Br 115.572(7), Ag$^{\#1}$–Br–Ag 64.425(7). Symmetry operator $^{\#1}$: $-x+1$, $-y+1$, $-z+1$.

ing system is to be expected. In fact 20 of these actually form hydrogen bonds, although some are very long (Table 3); H005 and H015 form only H$\cdots A$ contacts > 2.8 Å (A = N, O), and we do not consider these as structurally significant. Water molecules 1 and 3 act as donors in two and acceptors in four hydrogen bonds, and water molecule 2 as a donor in two and as an acceptor in three hydrogen bonds. Ten of the hydrogen bonds can be recognized within the asymmetric unit (Fig. 9a). The general overview is as expected complex, but shows the formation of hydrophilic areas at $y \approx 1/2$ (Fig. 10). A convenient subdivision of the structure consists of the non-coordinated diamines and the waters. These combine to form ribbons, which also involve ten independent hydrogen bonds, parallel to the

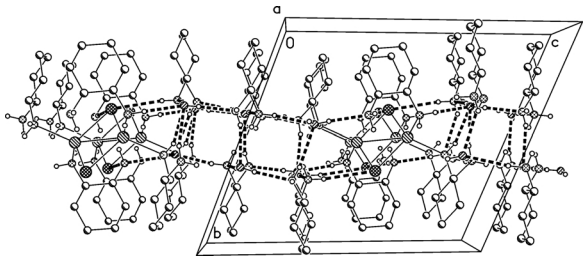

Fig. 10. General packing diagram of compound **3**. Hydrogen bonds are indicated by thick dashed lines.

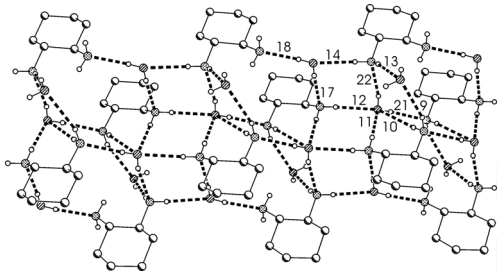

Fig. 11. The "silver-free" substructure of compound **3**. Hydrogen bonds are indicated by thick dashed lines and are numbered according to the number of the donor hydrogen. View direction approximately parallel to the b axis.

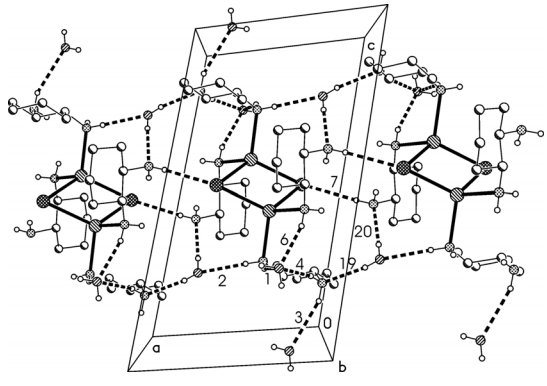

Fig. 12. Packing diagram of the silver-containing moiety of compound **3** and the various residues connected to it by hydrogen bonding. Hydrogen bonds are indicated by thick dashed lines and are numbered according to the number of the donor hydrogen.

a axis and to (001) in the region $z \approx 0$ (Fig. 11). Within the ribbons, several sets of annelated eight-membered rings can be recognized. Right of center in Fig. 10, a set of three approximate rectangles can be seen. The topmost ring, homodromic and of graph set $R_4^4(8)$, is comprised of hydrogen bonds 12, 14, 17 and 22; below this, 11 and 12 form an inversion-symmetric ring $R_4^2(8)$. A similar set of three rings can be seen further to the right and oriented obliquely; above, $R_4^3(8)$ with

Table 4. Hydrogen bonds (Å and deg) for compound **4**[a].

D–H···*A*	*d*(D–H)	*d*(H···*A*)	*d*(D···*A*)	∠(D*H*A)
N1–H01···O1W	0.909(12)	2.273(12)	3.1515(9)	162.3(10)
N1–H02···O1W$^{\#1}$	0.875(12)	2.455(12)	3.3034(9)	163.3(11)
N2–H03···O1W$^{\#2}$	0.889(12)	2.527(12)	3.4117(9)	173.8(10)
N2–H04···O1W$^{\#3}$	0.903(12)	2.581(12)	3.4031(9)	151.7(10)
O1W–H05···N1$^{\#3}$	0.907(12)	1.970(12)	2.8738(8)	174.2(12)
O1W–H06···N2$^{\#4}$	0.870(12)	2.033(12)	2.9017(9)	176.5(12)

[a] Symmetry transformations used to generate equivalent atoms: $^{\#1}$ *x*, –*y*, *z*–1/2; $^{\#2}$ *x*, –*y*, *z*+1/2; $^{\#3}$ –*x*, –*y*, –*z*+1; $^{\#4}$ *x*, *y*–1, *z*.

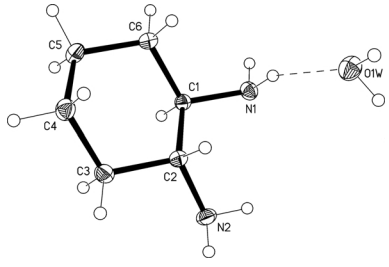

Fig. 13. Structure of the diamine monohydrate **4** in the crystal. Ellipsoids correspond to 50 % probability levels.

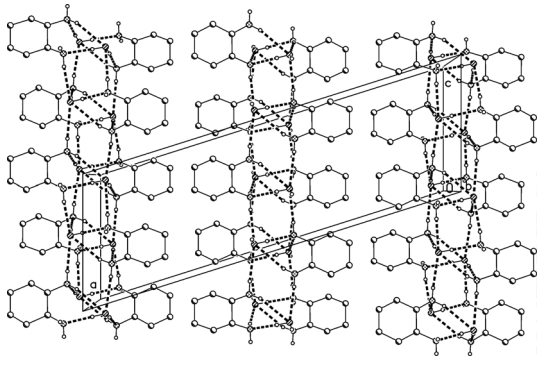

Fig. 14. General packing diagram of compound **4**, showing the hydrophilic double layers at $x \approx 0, 1/2, 1$. Hydrogen bonds are indicated by thick dashed lines. Hydrogen bonds 4 and 5 are formed across the center of the double layers (see Fig. 15).

hydrogen bonds 9, 13, 22, and 10, and below this a homodromic and inversion-symmetric $R_4^4(8)$ system with hydrogen bonds 10 and 21.

An alternative view omits the free diamines and shows the silver complexes linked to form ribbons parallel to the *a* axis (Fig. 12), involving eight independent hydrogen bonds. In this way, the subset figures accommodate all contacts except for H016···Br (connecting the silver and non-silver substructures).

The diamine monohydrate **4** (Fig. 13) arose as an unexpected by-product identified as a different type of crystal in the tubes that also produced **3**. Perhaps surprisingly, it is a solid, whereas the free diamine is

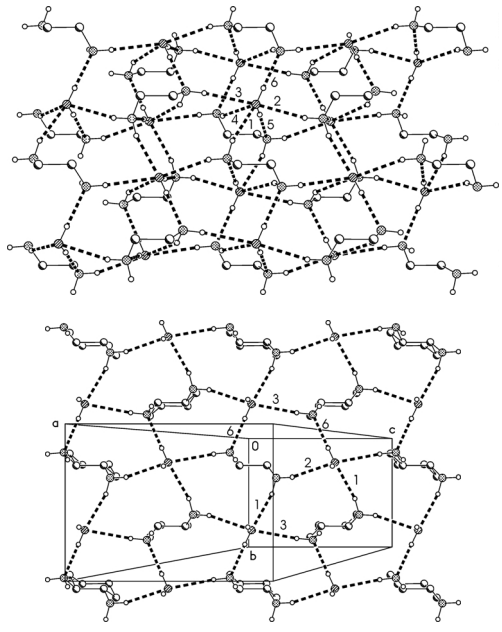

Fig. 15. (a) (top) Packing diagram of compound **4** showing the double layer structure parallel to (100). For clarity, the diamines have been pruned to $\{C(NH_2)\}_2$ units. (b) (below) View of a single layer in the region $x \approx 0.4$, involving only four independent hydrogen bonds (see text). Hydrogen bonds are indicated by thick dashed lines and are numbered (in (a) around an arbitrary water molecule) according to the number of the donor hydrogen.

a liquid [7]. The overall packing diagram (Fig. 14) shows the formation of hydrophilic layers at $x \approx 0, 1/2$. The six hydrogen bonds (Table 4) combine to form a (double) layer structure parallel to (100), and all six involve the water molecule either as donor or acceptor. The hydrogen bond system within the double layer is quite complex (Fig. 15a), but can be more easily interpreted when reduced to a single layer, which (Fig. 15b) involves only the hydrogen bonds 1, 2, 3, and 6. Again, the use of graph sets is helpful; in the single layers, hydrogen bonds 1 (×2), 2, 3 combine to form rings $R_4^2(11)$, and hydrogen bonds 2, 3, 6 (×2) to form homodromic rings $R_4^4(11)$. The linkages that couple the single to double layers involve the same diamine molecule and hydrogen bonds 4 and 5, with graph set $R_2^2(7)$.

Compound **5**, which arose presumably as a consequence of decomposition/hydrolysis of dichloromethane, has the unusual stoichiometry (*LL*)$_3$·HCl. The asymmetric unit consists of one diamine (N21, N22, *etc.*) with imposed twofold symmetry, one half-protonated diamine (N11, N12, *etc.*) in which the hy-

Table 5. Hydrogen bonds (Å and deg) for compound **5**[a].

D–H···*A*	*d*(D–H)	*d*(H···*A*)	*d*(D···*A*)	∠(D*H*A)
N11–H01···Cl$^{\#4}$	0.935(19)	2.525(19)	3.4508(14)	170.3(15)
N11–H02···Cl$^{\#5}$	0.89(2)	2.75(2)	3.6359(13)	177.4(16)
N12–H03···N12$^{\#2}$	0.90(3)	1.93(3)	2.822(3)	170(3)
N12–H04···N21	0.880(17)	2.269(17)	3.115(2)	161.2(14)
N12–H05···N11$^{\#3}$	0.97(2)	2.02(2)	2.9587(19)	161.2(14)
N21–H07···Cl	0.92(2)	2.55(2)	3.3689(17)	149.8(18)

[a] Symmetry transformations used to generate equivalent atoms: $^{\#2}$ $-x+1, y, -z+1/2$; $^{\#3}$ $x, -y+3/2, -z+1/2$; $^{\#4}$ $-x+3/2, -y+3/2, -z+1$; $^{\#5}$ $x, y, z-1$.

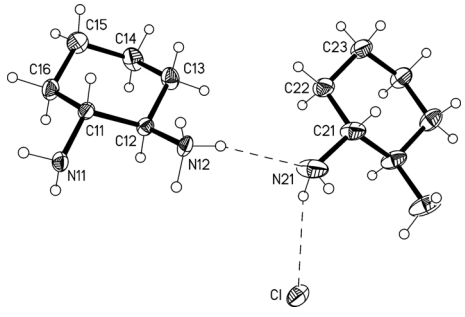

Fig. 16. Ellipsoid diagram (50 % probabilities) of compound **5** in the crystal. Only the asymmetric unit is numbered. Hydrogen bonds are indicated by thin dashed lines.

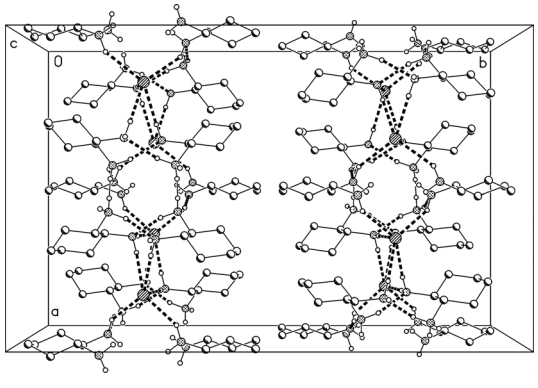

Fig. 17. General packing diagram of compound **5**. Hydrogen bonds are indicated by thick dashed lines.

drogen H03 is half-occupied (it is the donor hydrogen in a disordered hydrogen bond N12–H03···N12′ across a twofold axis) and a chloride anion on a twofold axis (Fig. 16). The overall packing (Fig. 17) again displays clearly defined hydrophilic (at $y \approx 1/4$, $3/4$) and hydrophobic areas. Six of the seven potential classical hydrogen bond donors indeed function as such (Table 5); H06 has no acceptor within reasonable distance (H06···Cl 3.04 Å is too long). The hydrogen bonds combine to form a layer structure parallel to (010) (Fig. 18). The chloride ion

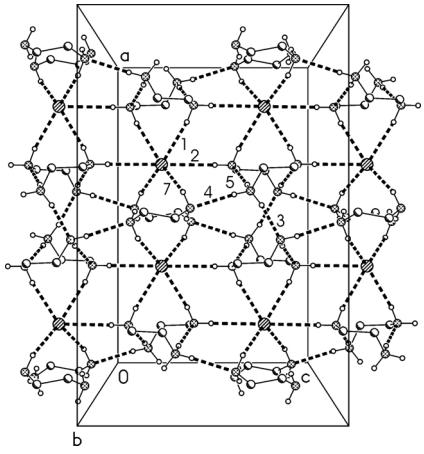

Fig. 18. Packing diagram of compound **5** showing the layer structure parallel to (010) in the region $y \approx 1/4$. For clarity, the diamines have been pruned to $\{C(NH_2)\}_2$ units. Hydrogen bonds are indicated by thick dashed lines and are numbered according to the number of the donor hydrogen. Only one position of the disordered hydrogen bond involving H03 is shown.

accepts three independent hydrogen bonds and six in all.

In view of the success of the "amine solvent" methods in providing complexes of unusual stoichiometry (this paper and refs. [1 – 3]), it is planned to extend the studies to other silver salts.

Conclusions

The use of the diamine *rac-trans*-1,2-diaminocyclohexane (*LL*) as a major component of the solvent system allows the isolation of crystalline silver complexes with higher ratios of *LL* to silver (up to 4 : 1, compared to the previously obtained 1 : 1 in ethanolic solution, although not all the diamines were coordinated for the highest ratio). This would in general terms be expected from Le Chatelier's principle! The "amine solvent" method is however restricted to amines that are liquids at r. t. In two out of three silver complexes thus obtained, the polymeric chain structure obtained for all 1 : 1 complexes [4] is no longer observed. All packing diagrams show a clear separation of hydrophilic and hydrophobic areas. In the former, extensive systems of classical hydrogen bonds are observed. The structures provide few new guidelines for crystal engineering of silver salts; there are simply too many degrees of freedom (*e. g.* ligand/metal ratio, coordination number, monomeric/polymeric nature, degree of hydration).

Table 6. Crystal data for compounds **1** – **5**.

	1	**2**	**3**	**4**	**5**
Formula	$C_{12}H_{28}AgN_5O_3$	$C_{20}H_{49}AgN_6O_4$	$C_{24}H_{62}AgBrN_8O_3$	$C_6H_{16}N_2O$	$C_{18}H_{43}ClN_6$
M_r	398.26	545.52	698.60	132.21	379.03
Crystal size, mm^3	$0.3 \times 0.13 \times 0.09$	$0.24 \times 0.18 \times 0.11$	$0.19 \times 0.12 \times 0.05$	$0.25 \times 0.15 \times 0.15$	$0.45 \times 0.28 \times 0.23$
T, K	133(2)	100(2)	100(2)	100(2)	133(2)
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	orthorhombic
Space group	$P2_1/c$	$C2/c$	$P\bar{1}$	$C2/c$	$Ccca$
a, Å	5.9673(6)	24.1181(9)	8.6746(6)	26.2440(8)	16.1001(9)
b, Å	11.4967(10)	11.7884(4)	13.6442(8)	6.8442(2)	25.9749(14)
c, Å	23.414(2)	18.1469(7)	15.4676(14)	9.0631(3)	10.3471(6)
α, deg	90	90	107.143(4)	90	90
β, deg	92.072(4)	91.150(2)	98.895(4)	107.551(2)	90
γ, deg	90	90	106.832(4)	90	90
V, Å^3	1605.2	5158.4	1615.8	1552.1	4327.1
Z	4	8	2	8	8
D_{calc}, g cm^{-3}	1.65	1.41	1.44	1.13	1.16
μ(MoK_α), mm^{-1}	1.3	0.8	1.9	0.08	0.2
Transmissions	0.741 – 0.894	0.825 – 0.916	0.780 – 0.911	no correction	no correction
F(000), e	824	2320	824	592	1680
$2\theta_{max}$, deg	61.0	67.8	63.5	66.3	56.6
Measured reflections	25767	135445	77605	48116	38363
Independent reflections	4913	10381	10945	2964	2698
R_{int}	0.036	0.050	0.042	0.038	0.072
Refined parameters	222	345	422	106	142
Restraints	0	0	15	1	0
$R(F)$ [$F \geq 4\sigma(F)$]	0.025	0.022	0.025	0.036	0.040
$wR(F^2)$ (all data)	0.055	0.053	0.054	0.104	0.110
GoF (F^2)	1.05	1.03	1.02	1.04	1.00
$\Delta\rho$ (max / min) e Å^{-3}	0.51 / −0.56	0.54 / −0.32	0.73 / −0.51	0.45 / −0.15	0.33 / −0.18

Experimental Section

Synthesis of the crystals

The relevant silver salt (*ca.* 100 – 200 mg) was dissolved in the diamine (5 mL) and the solution distributed over several small test-tubes and then overlayered with a precipitant (diethyl ether or petroleum ether). For each system, varying concentrations and liquid ratios were employed. All tubes were stored in a refrigerator at *ca.* 5 °C for several weeks and were additionally protected from light using aluminum foil. The silver complexes were of limited stability in air, with a tendency to lose the excess amine; the use of protective oil for crystal preparation and mounting was essential, and it proved impossible to obtain elemental analyses. Compound **4** was identified as a small number of crystals from the same system that provided **3**. The fluoroborate system provided no crystals; the microcrystalline deposit was therefore dissolved in dichloromethane and again overlayered with precipitant. A few crystals of **5** formed slowly, presumably accompanied by decomposition of the dichloromethane (the only possible source of chlorine in the system).

X-Ray structure analyses

Crystals were mounted on glass fibers in inert oil. Intensity measurements were performed on Bruker area detectors (SMART or APEX-2) using monochromated MoK_α radiation. Absorption corrections for compounds **1** – **3** were performed on the basis of multi-scans; no correction was applied to **4** and **5**. Structures were refined anisotropically against F^2 using the program SHELXL-97 [8]. NH and OH hydrogens were refined freely (in some cases with distance restraints), other hydrogens using a riding model or rigid methyl groups. Crystal data are presented in Table 6. *Special features*: For compound **5**, the acidic hydrogen H03 is disordered over a twofold axis between N12 and a symmetry-equivalent atom thereof.

CCDC 777655 (**1**), 777656 (**2**), 777657 (**3**), 777658 (**4**), 777659 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgement

S. D. I. was supported by the Erasmus Programme.

[1] C. Wölper, M. D. Polo Bastardés, I. Dix, D. Kratzert, P. G. Jones, *Z. Naturforsch*. **2010**, *65b*, 647 – 673.

[2] C. Wölper, V. Lozano, E.-M. Zerbe, P. G. Jones, *Z. Naturforsch*. **2010**, *65b*, in preparation.

[3] E.-M. Zerbe, Dissertation, Technische Universität Braunschweig, Papierflieger Verlag, Clausthal-Zellerfeld, **2006**.

[4] I. Kalf, M. Braun, Y. Wang, U. Englert, *CrystEng Comm* **2006**, *8*, 916 – 922; one structure was taken for comparison purposes from H.-L. Zhu, X.-M. Zhang, G.-F. Liu, D.-Q. Wang, *Z. Anorg. Allg. Chem.* **2003**, *629*, 1059 – 1062.

[5] In contrast to the liquid racemate (m. p. 14 – 15 °C) the enantiomerically pure diamine is a solid at room temperature (various m. p. *ca.* 40 °C are quoted by suppliers) and therefore unsuitable for use as a solvent without special precautions.

[6] Of the various types of hydrogen bond observed in this study, 32 N–H···O interactions displayed H···O distances of 2.20 – 2.63 (av. 2.39) Å, whereas for ten O–H···N interactions the H···N distances lay in the range 1.97 – 2.13 (av. 2.07) Å. It should however be pointed out that the former type had no clear upper distance limit, and the decision as to which contacts correspond to "genuine" hydrogen bonds was arbitrary in some cases. Other types were too infrequent to form a meaningful average value.

[7] A total of nine amine and (especially) diamine hydrates were structurally investigated: S. Janeda, D. Mootz, *Z. Naturforsch*. **1998**, *53b*, 1197 – 1202; *ibid.* **1999**, *54b*, 103 – 108. In several cases a hydrogen-bonded water substructure was observed, but this is not the case for **4**.

[8] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, Universität Göttingen, Göttingen (Germany) **1997**, See also: G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112 – 122.