Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1538). Services for accessing these data are described at the back of the journal.

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Molecular aggregation in selected crystalline 1:1 complexes of hydrophobic D- and L-amino acids. III.† The L-leucine and L-valine series

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Abstract

The amino acids L-leucine (L-Leu) and L-valine (L-Val) have been cocrystallized with D-aminobutanoic acid (D-Abu), D-2-aminopentanoic acid (D-Nva) and D-methionine (D-Met) to form six complexes, L-Leu:D-Abu, $C_6H_{13}NO_2{\cdot}C_4H_9NO_2$, L-Leu:D-Nva, $C_6H_{13}NO_2{\cdot}C_5H_{11}NO_2$, L-Leu:D-Met, $C_6H_{13}NO_2{\cdot}C_5H_{11}NO_2S$, L-Val:D-Abu, $C_5H_{11}NO_2{\cdot}C_4H_9NO_2$, L-Val:D-Nva, $C_5H_{11}NO_2{\cdot}C_5H_{11}NO_2$ and L-Val:D-Met, $C_5H_{11}NO_2{\cdot}C_5H_{11}NO_2S$. A fourth L-Leu complex, with D-Val, $C_6H_{13}NO_2{\cdot}C_5H_{11}NO_2$ has also been studied. The crystals of these amino acid complexes are all divided into distinct hydrophilic and hydrophobic layers. The D- and L-amino acids are all related by pseudo-inversion in the L-Leu complexes and by pseudo-glide planes in the L-Val series. Similarities and differences in the crystal packing and molecular conformations of L-Leu/L-Val, as well as of the partner molecules, are discussed.

Comment

In general, the crystal structures of hydrophobic amino acids fall within the following three categories: (*a*) pure enantiomers, (*b*) racemates and (*c*) 1:1 complexes of two different hydrophobic amino acids with opposite chirality at C^{α} (there are no known crystal structures incorporating two different hydrophobic amino acids with the same chirality at C^{α}). Previously we have presented the crystal structures of seven complexes involving L-isoleucine (L-Ile; Dalhus & Görbitz, 1999*a*) as well as five complexes involving D-norleucine (D-Nle; Dalhus & Görbitz, 1999*b*), all belonging to category (*c*). In the present paper we focus on L-Leu and L-Val complexes.

Since both L-Leu and L-Val have branched side chains, the complexes L-Leu:D-Abu, **1**, L-Leu:D-Nva, **2**, L-Leu:D-Met, **3**, L-Val:D-Abu, **5**, L-Val:D-Nva, **6**, and L-Val:D-Met, **7**, include one branched and one unbranched amino acid, while in L-Leu:D-Val, **4**, both amino acids are branched. All seven crystal structures are divided into distinct hydrophilic and hydrophobic layers (Figs. 1–7). This is a consequence of the dual character of hydrophobic amino acids: the charged α-amino and α-carboxylate groups engage in hydrogen bonding with each other, while the side chains are involved in van der Waals interactions only.

L-amino acid
L-Val : $R_1 = -CH(CH_3)_2$
L-Leu : $R_1 = -CH_2CH(CH_3)_2$

D-amino acid
D-Abu : $R_2 = -CH_2CH_3$
D-Nva : $R_2 = -CH_2CH_2CH_3$
D-Met : $R_2 = -CH_2CH_2SCH_3$
D-Val : $R_2 = -CH(CH_3)_2$

1 = L-Leu:D-Abu
2 = L-Leu:D-Nva
3 = L-Leu:D-Met
4 = L-Leu:D-Val
5 = L-Val:D-Abu
6 = L-Val:D-Nva
7 = L-Val:D-Met

In the four L-Leu complexes **1**–**4**, the polar parts of the amino acids are related by pseudo inversion in space groups $P2_1$ (**1**, **3** and **4**) and $P\overline{1}$ (**2**) (Figs. 1–4). The molecular conformation of L-Leu is identical in all four

† Part II: Dalhus & Gorbitz (1999*b*).

complexes, with χ^1 *trans*, $\chi^{2,1}$ *gauche*$^+$ and $\chi^{2,2}$ *trans* (Tables 1–4). Furthermore, the molecular arrangements in **1** (Fig. 1) and **4** (Fig. 4) are almost identical, with the pseudo-inversion centres located at (x = 0.92, z = 0.25) and (x = 0.87, z = 0.19), respectively.

In all three L-Val complexes, on the other hand, (Figs. 5–7), the D- and L-molecules are related by pseudo-glide planes normal to the unique b axis. The additional $-CH_2-$ group in the L-Leu side chain compared with L-Val thus has a decisive effect on the molecular packing arrangement in the complexes. As in the L-Leu series, the conformation of L-Val remains unchanged as the D-amino acids are varied in the present series: $\chi^{1,1}$ *trans* and $\chi^{1,2}$ *gauche*$^-$ (Tables 5, 6 and 7). It should

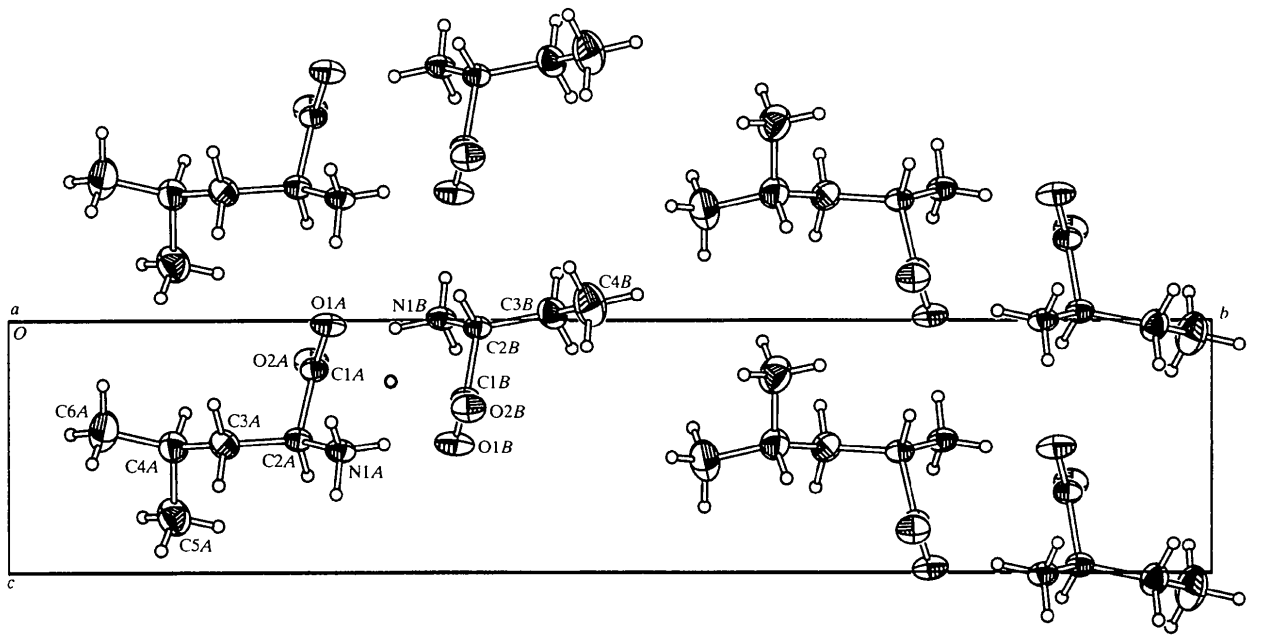

Fig. 1. The molecular packing diagram for L-Leu:D-Abu, (**1**). Displacement ellipsoids are drawn at the 75% probability level and H atoms are shown as spheres of an arbitrary radius. The pseudo inversion centre is indicated with an open circle.

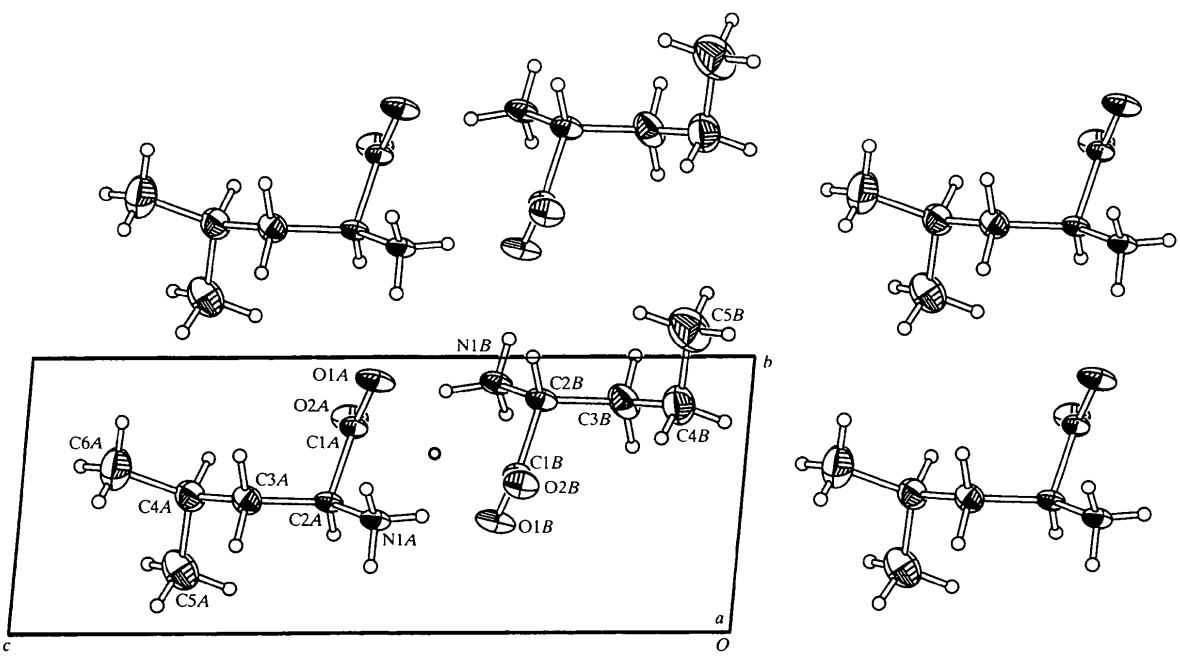

Fig. 2. The molecular packing diagram for L-Leu:D-Nva, (**2**). Displacement ellipsoids are drawn at the 75% probability level and H atoms are shown as spheres of an arbitrary radius. The pseudo inversion centre is indicated with an open circle.

be noted that the two complexes L-Leu:D-Val, **4**, and L-Val:D-Leu are mirror images.

The amino acids Nva (norvaline, 2-aminopentanoic acid) and Abu (2-aminobutanoic acid) differ from Leu and Val, respectively, by a single $-CH_3$ group only (see scheme). The racemate DL-Leu (Di Blasio *et al.*, 1975) and the closely related complex L-Leu:-D-Nva, (**2**), both have a (pseudo) centre of symmetry. In contrast, both the triclinic polymorph of DL-Val (Dalhus & Görbitz, 1996*a*) and the monoclinic form (Mallikarjunan & Thyagaraja Rao, 1969) with inversion-related enantiomers are structurally quite different from

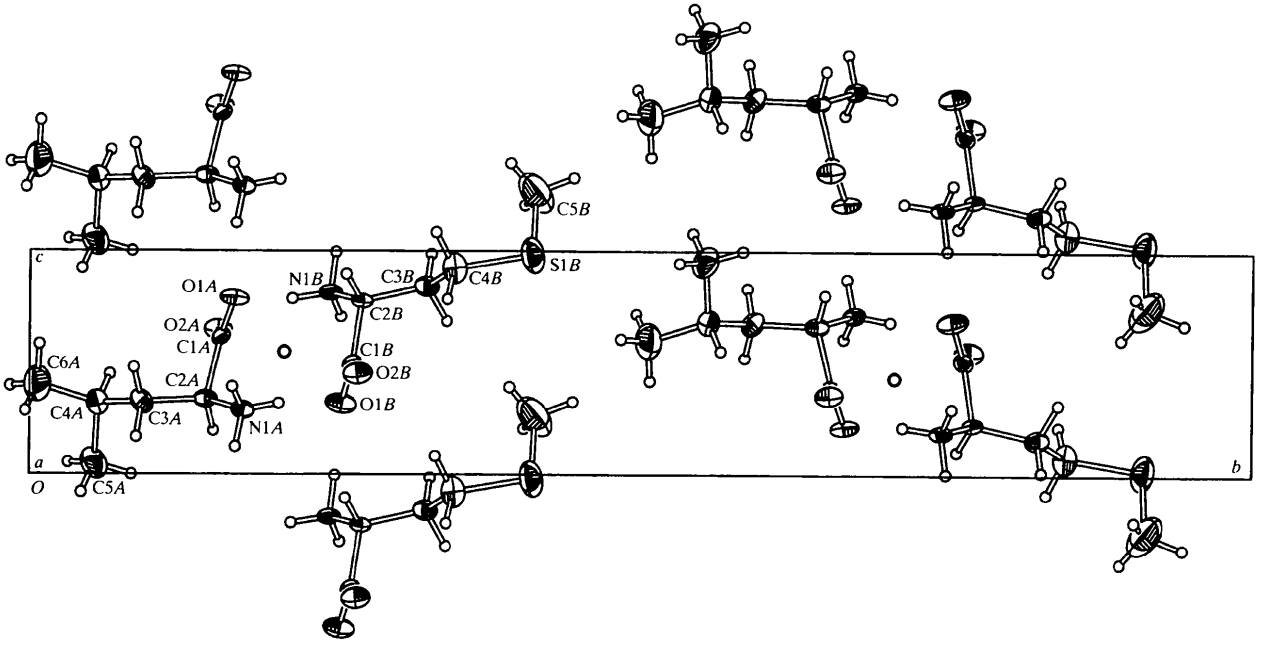

Fig. 3. The molecular packing diagram for L-Leu:D-Met, (**3**). Displacement ellipsoids are drawn at the 75% probability level and H atoms are shown as spheres of an arbitrary radius. The pseudo inversion centre is indicated with an open circle.

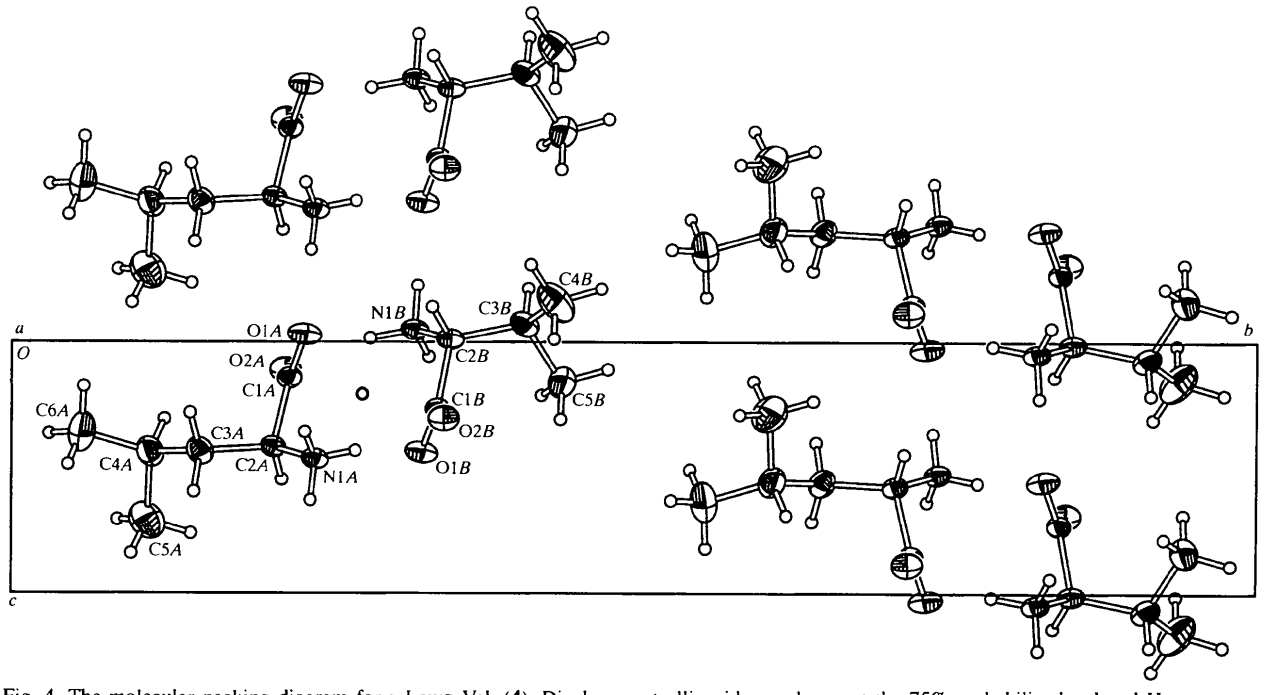

Fig. 4. The molecular packing diagram for L-Leu:D-Val, (**4**). Displacement ellipsoids are drawn at the 75% probability level and H atoms are shown as spheres of an arbitrary radius. The pseudo inversion centre is indicated with an open circle.

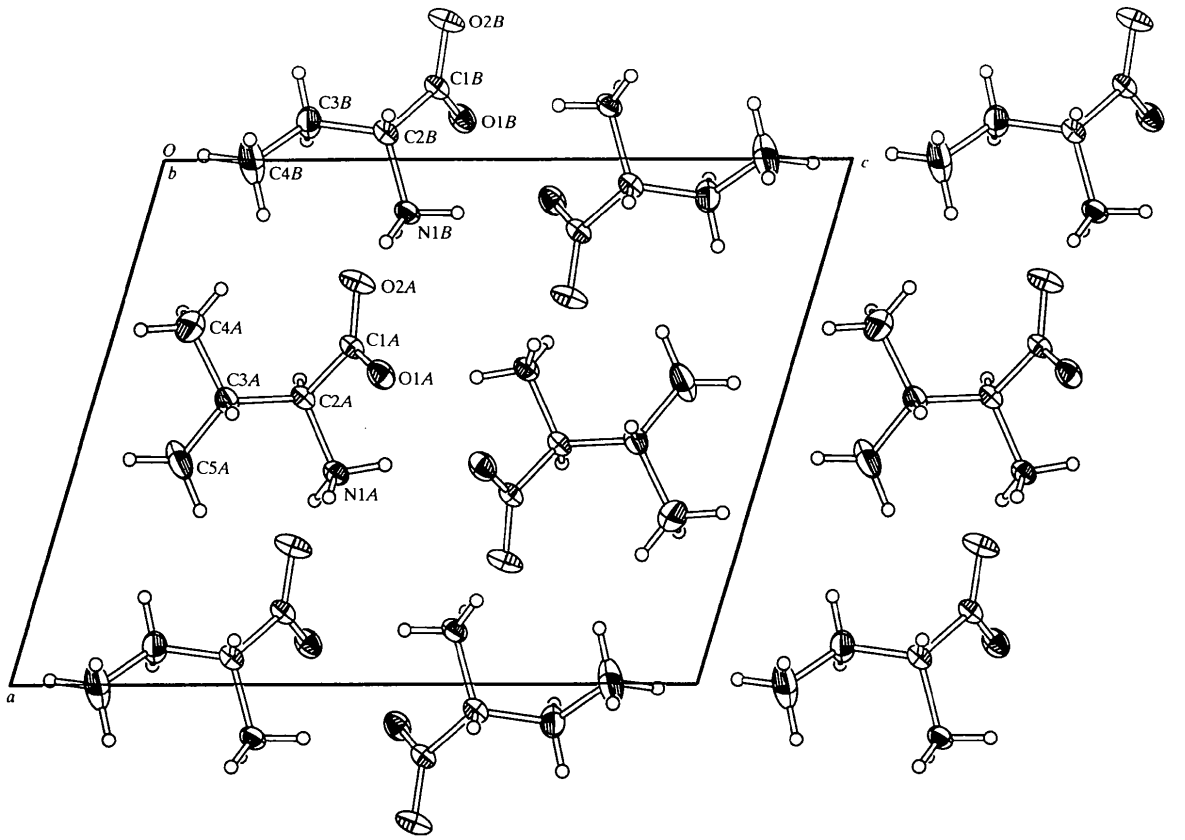

Fig. 5. The molecular packing diagram for L-Val:D-Abu, (**5**). Displacement ellipsoids are drawn at the 75% probability level and H atoms are shown as spheres of an arbitrary radius.

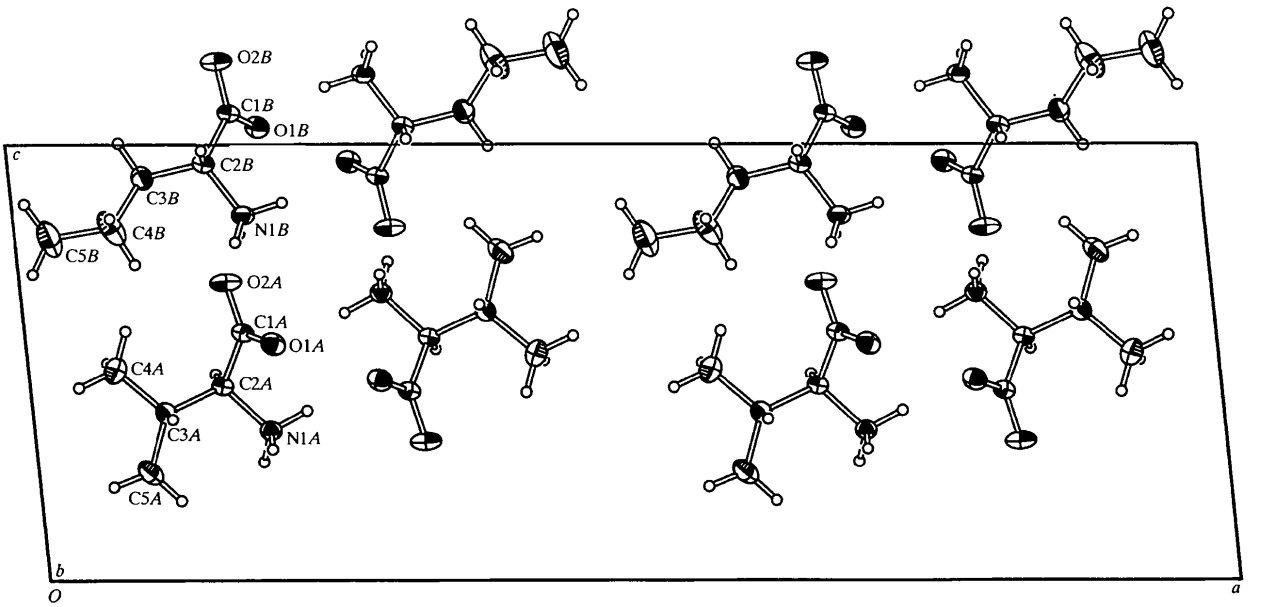

Fig. 6. The molecular packing diagram for L-Val:D-Nva, (**6**). Displacement ellipsoids are drawn at the 75% probability level and H atoms are shown as spheres of an arbitrary radius.

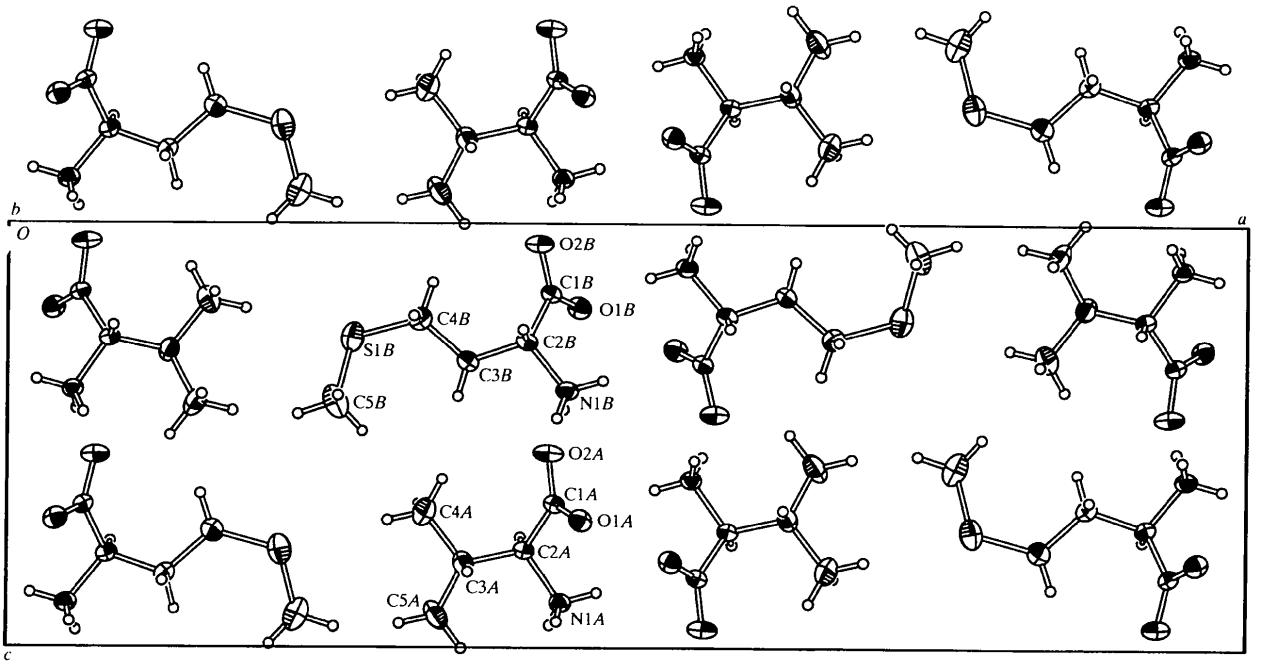

Fig. 7. The molecular packing diagram for L-Val:D-Met, (7). Displacement ellipsoids are drawn at the 75% probability level and H atoms are shown as spheres of an arbitrary radius.

the related L-Val:D-Abu complex, **5**, in which the molecules form pseudo-glide planes (Fig. 5).

Methionine (Met) is a close chemical analogue of norleucine (Nle). A substitution of the S atom in methionine with an ethylene group, $-CH_2-$, transforms methionine into norleucine. Similarities in crystal packing habits for the two amino acids are thus expected. This is clearly demonstrated in the polymorphism of DL-Met (Taniguchi *et al.*, 1980) and DL-Nle (Dalhus & Görbitz, 1996*b*; Harding *et al.*, 1995). Somewhat unexpectedly, methionine and norleucine form complexes with L-Ile, L-Leu and L-Val with different structural features. The L-Ile complexes of D-Met and D-Nle, in space groups $C2$ and $P2_1$, respectively, have a different number of independent molecules in the asymmetric unit (Dalhus & Görbitz, 1999*a*). Furthermore, in L-Leu:D-Nle (Dalhus & Görbitz, 1999*b*) the D-Nle side chain is disordered over two nearly equally occupied conformations. In the present L-Leu:D-Met complex, **3**, on the other hand, no such disorder exists (Fig. 3). The side chain conformation of D-Met (χ^1 *trans*, χ^3 *trans*, χ^3 *gauche*$^+$; Table 3) does not match either of the conformations of D-Nle in L-Leu:D-Nle. The two complexes L-Val:D-Nle (Dalhus & Görbitz, 1999*b*) and L-Val:D-Met, **7**, crystallize in different crystal systems: L-Val:D-Nle is monoclinic, while L-Val:D-Met is the first known orthorhombic amino acid complex.

An investigation of all known crystal structures of hydrophobic amino acids reveals three major classes of molecular aggregation patterns, I, II and III, each with a unique hydrogen-bond network (Dalhus & Görbitz, 1999*c*). Complexes of category (*b*) and (*c*) belong to either class I or II. In class I, the D- and L-amino acids are related by crystallographic or pseudo-glide planes. In class II, the molecules are related by crystallographic or pseudo-inversion. Thus, the molecular packing arrangements in the L-Val series fall within class I, while the L-Leu complexes belong to class II. In a series of papers (Dalhus & Görbitz, 1999*a*, and references therein), we have focused on the acquisition of geometric information on the hydrogen-bonding network in this class of compounds. The aim of this project is to construct a database for multivariate analysis of correlations between hydrogen-bond parameters in identical hydrogen-bonded frameworks. Experimental and normalized (Taylor & Kennard, 1983) hydrogen-bond geometries for the seven complexes discussed here are listed in Table 8.

Experimental

Aqueous solutions of the seven complexes were prepared by dissolving equimolar amounts (typically 5–10 mg, depending on the solubility properties) of the two selected amino acids in 1 ml deionized water. In order to reduce the rate of crystallization, gelling of the growth medium was performed. The various amino-acid solutions were thoroughly mixed with 0.1 ml tetramethoxysilane, and each resulting mixture was distributed in 10–12 30 × 5 mm test-tubes, sealed with Parafilm, and then left for a couple of minutes to polymerize. Crystals were formed as methanol, ethanol or 2-propanol was diffused into the gels at room temperature. Crystallization experiments with L-Leu/L-Val and D-alanine (D-Ala) have also

been carried out. In L-Leu:D-Ala the two amino acids are separated upon crystallization, giving only L-Leu and D-Ala crystals. For L-Val:D-Ala only extremely thin needles have been obtained.

Compound 1

Crystal data

$C_6H_{13}NO_2{\cdot}C_4H_9NO_2$
M_r = 234.30
Monoclinic
$P2_1$
a = 5.1673 (1) Å
b = 23.9998 (4) Å
c = 5.4029 (1) Å
β = 112.026 (1)°
V = 621.13 (2) Å^3
Z = 2
D_x = 1.253 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 5937 reflections
θ = 3.40–49.72°
μ = 0.096 mm^{-1}
T = 150 (2) K
Plate
0.70 × 0.65 × 0.20 mm
Colourless

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.935, T_{max} = 0.981
16 059 measured reflections
9155 independent reflections

7846 reflections with $I > 2\sigma(I)$
R_{int} = 0.025
θ_{max} = 49.72°
h = −10 → 9
k = −44 → 49
l = −10 → 10
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.136
S = 1.099
9155 reflections
175 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0666P)^2 + 0.1082P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.495 e Å^{-3}
$\Delta\rho_{min}$ = −0.410 e Å^{-3}
Extinction correction: *SHELXTL* (Sheldrick, 1995)
Extinction coefficient: 0.39 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for* **1**

O1*A*—C1*A*	1.2605 (10)	C4*A*—C6*A*	1.531 (2)
O2*A*—C1*A*	1.2596 (9)	O1*B*—C1*B*	1.2582 (10)
N1*A*—C2*A*	1.4929 (10)	O2*B*—C1*B*	1.2625 (9)
C1*A*—C2*A*	1.5389 (10)	N1*B*—C2*B*	1.4897 (10)
C2*A*—C3*A*	1.5360 (12)	C1*B*—C2*B*	1.5371 (10)
C3*A*—C4*A*	1.5357 (14)	C2*B*—C3*B*	1.5304 (13)
C4*A*—C5*A*	1.530 (2)	C3*B*—C4*B*	1.527 (2)
N1*A*—C2*A*—C3*A*—C4*A*	−169.23 (7)		
C2*A*—C3*A*—C4*A*—C5*A*	74.14 (11)		
C2*A*—C3*A*—C4*A*—C6*A*	−163.87 (10)		
N1*B*—C2*B*—C3*B*—C4*B*	165.91 (9)		

Compound 2

Crystal data

$C_6H_{13}NO_2{\cdot}C_5H_{11}NO_2$
M_r = 248.32
Triclinic
$P\overline{1}$
a = 5.1639 (1) Å
b = 5.4076 (1) Å
c = 13.1241 (2) Å
α = 91.779 (1)°
β = 98.138 (1)°
γ = 111.823 (1)°
V = 335.39 (1) Å^3
Z = 1
D_x = 1.229 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 4034 reflections
θ = 1.57–40.26°
μ = 0.093 mm^{-1}
T = 150 (2) K
Plate
0.60 × 0.55 × 0.05 mm
Colourless

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.946, T_{max} = 0.995
5991 measured reflections
4828 independent reflections

4227 reflections with $I > 2\sigma(I)$
R_{int} = 0.012
θ_{max} = 40.26°
h = −9 → 8
k = −9 → 9
l = −23 → 23
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.114
S = 1.083
4827 reflections
190 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0723P)^2 + 0.0294P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.824 e Å^{-3}
$\Delta\rho_{min}$ = −0.229 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 2. *Selected geometric parameters (Å, °) for* **2**

O1*A*—C1*A*	1.258 (2)	O1*B*—C1*B*	1.257 (2)
O2*A*—C1*A*	1.255 (2)	O2*B*—C1*B*	1.265 (2)
N1*A*—C2*A*	1.493 (2)	N1*B*—C2*B*	1.492 (2)
C1*A*—C2*A*	1.546 (2)	C1*B*—C2*B*	1.534 (2)
C2*A*—C3*A*	1.532 (2)	C2*B*—C3*B*	1.548 (2)
C3*A*—C4*A*	1.533 (2)	C3*B*—C4*B*	1.528 (3)
C4*A*—C5*A*	1.522 (3)	C4*B*—C5*B*	1.529 (3)
C4*A*—C6*A*	1.539 (2)		
N1*A*—C2*A*—C3*A*—C4*A*	−169.86 (13)		
C2*A*—C3*A*—C4*A*—C5*A*	75.9 (2)		
C2*A*—C3*A*—C4*A*—C6*A*	−161.68 (13)		
N1*B*—C2*B*—C3*B*—C4*B*	169.96 (15)		
C2*B*—C3*B*—C4*B*—C5*B*	−78.3 (2)		

Compound 3

Crystal data

$C_6H_{13}NO_2{\cdot}C_5H_{11}NO_2S$
M_r = 280.38
Monoclinic
$P2_1$
a = 5.1451 (1) Å
b = 28.0517 (5) Å
c = 5.4068 (1) Å
β = 111.423 (1)°
V = 726.44 (2) Å^3
Z = 2
D_x = 1.282 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 3681 reflections
θ = 2.90–36.20°
μ = 0.232 mm^{-1}
T = 150 (2) K
Plate
0.30 × 0.25 × 0.013 mm
Colourless

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.942, T_{max} = 0.997
8344 measured reflections
3540 independent reflections (plus 1317 Friedel-related reflections)
3354 reflections with $I > 2\sigma(I)$
R_{int} = 0.069
θ_{max} = 36.20°
$h = -8 \rightarrow 8$
$k = -45 \rightarrow 35$
$l = -8 \rightarrow 8$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.081
$wR(F^2)$ = 0.173
S = 1.095
4857 reflections
193 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0670P)^2 + 0.3454P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.637 e Å^{-3}
$\Delta\rho_{min}$ = −0.380 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.1 (1)

Table 3. *Selected geometric parameters (Å, °) for* **3**

O1*A*—C1*A*	1.253 (4)	S1*B*—C5*B*	1.794 (4)
O2*A*—C1*A*	1.257 (3)	S1*B*—C4*B*	1.811 (4)
N1*A*—C2*A*	1.490 (4)	O1*B*—C1*B*	1.258 (4)
C1*A*—C2*A*	1.547 (4)	O2*B*—C1*B*	1.259 (3)
C2*A*—C3*A*	1.529 (4)	N1*B*—C2*B*	1.486 (4)
C3*A*—C4*A*	1.535 (5)	C1*B*—C2*B*	1.537 (4)
C4*A*—C5*A*	1.521 (5)	C2*B*—C3*B*	1.530 (4)
C4*A*—C6*A*	1.526 (6)	C3*B*—C4*B*	1.525 (5)
N1*A*—C2*A*—C3*A*—C4*A*	−169.3 (3)		
C2*A*—C3*A*—C4*A*—C5*A*	76.1 (3)		
C2*A*—C3*A*—C4*A*—C6*A*	−160.8 (3)		
N1*B*—C2*B*—C3*B*—C4*B*	155.4 (3)		
C2*B*—C3*B*—C4*B*—S1*B*	176.1 (2)		
C3*B*—C4*B*—S1*B*—C5*B*	63.7 (3)		

Compound 4

Crystal data

$C_6H_{13}NO_2 \cdot C_5H_{11}NO_2$
M_r = 248.32
Monoclinic
$P2_1$
a = 5.2002 (1) Å
b = 25.1334 (4) Å
c = 5.4157 (1) Å
β = 110.796 (1)°
V = 661.71 (2) Å^3
Z = 2
D_x = 1.246 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 6288 reflections
θ = 1.62–38.52°
μ = 0.094 mm^{-1}
T = 150 (2) K
Block
0.45 × 0.30 × 0.20 mm
Colourless

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.959, T_{max} = 0.981
9106 measured reflections
4831 independent reflections
4717 reflections with $I > 2\sigma(I)$
R_{int} = 0.021
θ_{max} = 38.52°
$h = -8 \rightarrow 9$
$k = -40 \rightarrow 32$
$l = -6 \rightarrow 9$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.095
S = 1.108
4830 reflections
186 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0453P)^2 + 0.1252P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.411 e Å^{-3}
$\Delta\rho_{min}$ = −0.217 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 4. *Selected geometric parameters (Å, °) for* **4**

O1*A*—C1*A*	1.2618 (11)	O1*B*—C1*B*	1.2604 (11)
O2*A*—C1*A*	1.2589 (11)	O2*B*—C1*B*	1.2623 (11)
N1*A*—C2*A*	1.4953 (12)	N1*B*—C2*B*	1.4919 (12)
C1*A*—C2*A*	1.5389 (13)	C1*B*—C2*B*	1.5370 (13)
C2*A*—C3*A*	1.5361 (14)	C2*B*—C3*B*	1.5440 (14)
C3*A*—C4*A*	1.535 (2)	C3*B*—C5*B*	1.526 (2)
C4*A*—C5*A*	1.524 (2)	C3*B*—C4*B*	1.529 (2)
C4*A*—C6*A*	1.529 (2)		
N1*A*—C2*A*—C3*A*—C4*A*	−169.69 (8)		
C2*A*—C3*A*—C4*A*—C5*A*	77.32 (12)		
C2*A*—C3*A*—C4*A*—C6*A*	−160.65 (10)		
N1*B*—C2*B*—C3*B*—C4*B*	153.88 (9)		
N1*B*—C2*B*—C3*B*—C5*B*	−81.67 (10)		

Compound 5

Crystal data

$C_5H_{11}NO_2 \cdot C_4H_9NO_2$
M_r = 220.27
Monoclinic
$P2_1$
a = 9.9562 (1) Å
b = 4.7417 (1) Å
c = 12.7833 (1) Å
β = 106.843 (1)°
V = 577.60 (1) Å^3
Z = 2
D_x = 1.267 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 6288 reflections
θ = 3.07–49.71°
μ = 0.099 mm^{-1}
T = 150 (2) K
Needle
2.00 × 0.25 × 0.20 mm
Colourless

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.820, T_{max} = 0.976
18 959 measured reflections
8952 independent reflections
7932 reflections with $I > 2\sigma(I)$
R_{int} = 0.035
θ_{max} = 49.71°
$h = -21 \rightarrow 21$
$k = -8 \rightarrow 9$
$l = -25 \rightarrow 26$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.104
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.537 e Å^{-3}
$\Delta\rho_{min}$ = −0.434 e Å^{-3}

$S = 1.046$
8952 reflections
178 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0681P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
Extinction correction: *SHELXTL* (Sheldrick, 1995)
Extinction coefficient: 0.15 (1)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 5. *Selected geometric parameters (Å, °) for* **5**

O1*A*—C1*A*	1.2574 (7)	O1*B*—C1*B*	1.2542 (6)
O2*A*—C1*A*	1.2625 (6)	O2*B*—C1*B*	1.2635 (6)
N1*A*—C2*A*	1.4955 (6)	N1*B*—C2*B*	1.4941 (6)
C1*A*—C2*A*	1.5401 (6)	C1*B*—C2*B*	1.5330 (6)
C2*A*—C3*A*	1.5455 (6)	C2*B*—C3*B*	1.5331 (7)
C3*A*—C4*A*	1.5280 (8)	C3*B*—C4*B*	1.5243 (9)
C3*A*—C5*A*	1.5341 (8)		
N1*A*—C2*A*—C3*A*—C4*A*	−176.16 (6)		
N1*A*—C2*A*—C3*A*—C5*A*	−52.63 (6)		
N1*B*—C2*B*—C3*B*—C4*B*	63.23 (7)		

Compound 6

Crystal data

$C_5H_{11}NO_2{\cdot}C_5H_{11}NO_2$
$M_r = 234.30$
Monoclinic
$C2$
$a = 27.2288\ (2)$ Å
$b = 4.7397\ (1)$ Å
$c = 9.9535\ (1)$ Å
$\beta = 96.091\ (1)°$
$V = 1277.31\ (3)$ Å^3
$Z = 4$
$D_x = 1.218$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 6914 reflections
$\theta = 1.50–49.75°$
$\mu = 0.093$ mm^{-1}
$T = 150\ (2)$ K
Block
1.00 × 0.50 × 0.45 mm
Colourless

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.911$, $T_{max} = 0.959$
16 408 measured reflections
9399 independent reflections
8643 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 49.75°$
$h = -58 \rightarrow 56$
$k = -9 \rightarrow 9$
$l = -18 \rightarrow 20$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.097$
$S = 1.110$
9398 reflections
180 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0601P)^2 + 0.0277P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.410$ e Å^{-3}
$\Delta\rho_{min} = -0.258$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 6. *Selected geometric parameters (Å, °) for* **6**

O1*A*—C1*A*	1.2578 (6)	O1*B*—C1*B*	1.2543 (6)
O2*A*—C1*A*	1.2643 (5)	O2*B*—C1*B*	1.2637 (5)
N1*A*—C2*A*	1.4947 (5)	N1*B*—C2*B*	1.4938 (5)
C1*A*—C2*A*	1.5391 (6)	C1*B*—C2*B*	1.5344 (6)
C2*A*—C3*A*	1.5440 (6)	C2*B*—C3*B*	1.5324 (6)
C3*A*—C4*A*	1.5300 (8)	C3*B*—C4*B*	1.5251 (8)
C3*A*—C5*A*	1.5343 (7)	C4*B*—C5*B*	1.5273 (10)
N1*A*—C2*A*—C3*A*—C4*A*	−174.02 (6)		
N1*A*—C2*A*—C3*A*—C5*A*	−50.62 (6)		
N1*B*—C2*B*—C3*B*—C4*B*	58.57 (6)		
C2*B*—C3*B*—C4*B*—C5*B*	177.76 (6)		

Compound 7

Crystal data

$C_5H_{11}NO_2{\cdot}C_5H_{11}NO_2S$
$M_r = 266.36$
Orthorhombic
$P2_12_12_1$
$a = 28.9379\ (2)$ Å
$b = 4.7032\ (1)$ Å
$c = 10.0011\ (1)$ Å
$V = 1361.16\ (3)$ Å^3
$Z = 4$
$D_x = 1.300$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 8192 reflections
$\theta = 2.15–49.99°$
$\mu = 0.244$ mm^{-1}
$T = 150\ (2)$ K
Needle
1.2 × 0.3 × 0.1 mm
Colourless

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.746$, $T_{max} = 0.976$
34 193 measured reflections
7975 independent reflections (plus 4489 Friedel-related reflections)
10 210 reflections with $I > 2\sigma(I)$
$R_{int} = 0.044$
$\theta_{max} = 49.99°$
$h = -62 \rightarrow 62$
$k = -9 \rightarrow 8$
$l = -20 \rightarrow 17$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.109$
$S = 1.168$
12464 reflections
185 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0318P)^2 + 0.2437P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.410$ e Å^{-3}
$\Delta\rho_{min} = -0.370$ e Å^{-3}
Extinction correction: *SHELXTL* (Sheldrick, 1995)
Extinction coefficient: 0.014 (1)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.00 (5)

Table 7. *Selected geometric parameters (Å, °) for* **7**

O1*A*—C1*A*	1.2528 (10)	O2*B*—C1*B*	1.2640 (9)
O2*A*—C1*A*	1.2643 (10)	N1*B*—C2*B*	1.4937 (10)
N1*A*—C2*A*	1.4956 (10)	C1*B*—C2*B*	1.5367 (10)
C1*A*—C2*A*	1.5386 (10)	C2*B*—C3*B*	1.5386 (10)
C2*A*—C3*A*	1.5411 (10)	C3*B*—C4*B*	1.5243 (12)
C3*A*—C5*A*	1.5247 (12)	C4*B*—S1*B*	1.8132 (10)
C3*A*—C4*A*	1.5253 (15)	S1*B*—C5*B*	1.8038 (14)
O1*B*—C1*B*	1.2535 (9)		
N1*A*—C2*A*—C3*A*—C4*A*	−174.80 (10)		
N1*A*—C2*A*—C3*A*—C5*A*	−51.82 (9)		
N1*B*—C2*B*—C3*B*—C4*B*	169.58 (7)		
C2*B*—C3*B*—C4*B*—S1*B*	172.63 (6)		
C3*B*—C4*B*—S1*B*—C5*B*	63.86 (9)		

Table 8. *Hydrogen bond geometry (Å, °) in complexes* **1–7**

N—H···O	N—H	H···O[a]	H···O[b]	N···O	N—H···O[a]
L-Leu:D-Abu, **1**					
N1*A*—H1*A*···O2*A*^{i}	0.88 (2)	1.97 (2)	1.82	2.845 (1)	178 (2)
N1*A*—H2*A*···O1*A*^{ii}	0.92 (2)	1.82 (2)	1.71	2.730 (1)	173 (2)
N1*A*—H3*A*···O2*B*	0.91 (2)	2.01 (2)	1.90	2.899 (1)	165 (2)
N1*B*—H1*B*···O2*B*^{iii}	0.93 (2)	1.93 (2)	1.83	2.846 (1)	169 (2)
N1*B*—H2*B*···O1*B*^{iv}	0.88 (2)	1.87 (2)	1.72	2.747 (2)	177 (2)
N1*B*—H3*B*···O2*A*	0.94 (2)	2.05 (2)	1.97	2.947 (1)	159 (2)
L-Leu:D-Nva, **2**					
N1*A*—H1*A*···O2*A*^{iii}	0.85 (3)	2.01 (3)	1.83	2.855 (2)	176 (3)
N1*A*—H2*A*···O1*A*^{v}	0.90 (3)	1.84 (3)	1.71	2.728 (2)	171 (2)
N1*A*—H3*A*···O2*B*	0.88 (2)	2.05 (2)	1.90	2.909 (2)	166 (2)
N1*B*—H1*B*···O2*B*^{i}	0.94 (2)	1.91 (2)	1.82	2.847 (2)	175 (2)
N1*B*—H2*B*···O1*B*^{vi}	0.87 (3)	1.88 (3)	1.72	2.736 (2)	168 (3)
N1*B*—H3*B*···O2*A*	0.92 (2)	2.07 (2)	1.97	2.922 (2)	154 (2)
L-Leu:D-Met, **3**					
N1*A*—H1*A*···O2*A*^{iii}	0.90 (4)	1.95 (4)	1.82	2.839 (4)	173 (4)
N1*A*—H2*A*···O1*A*^{iv}	0.95 (4)	1.79 (4)	1.72	2.729 (3)	167 (4)
N1*A*—H3*A*···O2*B*	0.86 (4)	2.13 (4)	1.97	2.960 (4)	163 (3)
N1*B*—H1*B*···O2*B*^{i}	0.89 (4)	1.96 (4)	1.82	2.848 (4)	176 (4)
N1*B*—H2*B*···O1*B*^{ii}	0.98 (4)	1.78 (4)	1.73	2.755 (3)	174 (3)
N1*B*—H3*B*···O2*A*	0.89 (4)	2.11 (4)	1.99	2.912 (4)	149 (3)
L-Leu:D-Val, **4**					
N1*A*—H1*A*···O2*A*^{i}	0.91 (2)	1.97 (2)	1.85	2.881 (1)	176 (2)
N1*A*—H2*A*···O1*A*^{ii}	0.89 (2)	1.84 (2)	1.70	2.732 (1)	178 (2)
N1*A*—H3*A*···O2*B*	0.85 (2)	2.09 (2)	1.91	2.919 (1)	166 (2)
N1*B*—H1*B*···O2*B*^{iii}	0.90 (2)	1.97 (2)	1.84	2.858 (1)	170 (2)
N1*B*—H2*B*···O1*B*^{iv}	0.94 (2)	1.81 (2)	1.72	2.753 (2)	177 (2)
N1*B*—H3*B*···O2*A*	0.92 (2)	2.06 (2)	1.95	2.935 (1)	159 (2)
L-Val:D-Abu, **5**					
N1*A*—H1*A*···O2*B*^{vii}	0.94 (2)	1.90 (2)	1.82	2.832 (1)	168 (1)
N1*A*—H2*A*···O2*B*^{iii}	0.93 (1)	1.90 (2)	1.80	2.803 (1)	163 (1)
N1*A*—H3*A*···O1*A*^{viii}	0.95 (1)	1.85 (1)	1.77	2.788 (1)	170 (1)
N1*B*—H1*B*···O2*A*^{vi}	0.91 (1)	1.96 (1)	1.84	2.859 (1)	169 (1)
N1*B*—H2*B*···O2*A*	0.93 (2)	1.95 (2)	1.85	2.845 (1)	162 (1)
N1*B*—H3*B*···O1*B*^{ix}	0.95 (1)	1.82 (1)	1.74	2.757 (1)	171 (1)
L-Val:D-Nva, **6**					
N1*A*—H1*A*···O2*B*^{x}	0.87 (2)	1.97 (2)	1.81	2.827 (1)	170 (1)
N1*A*—H2*A*···O2*B*^{ix}	0.99 (1)	1.85 (2)	1.82	2.791 (1)	157 (1)
N1*A*—H3*A*···O1*A*^{xi}	0.95 (1)	1.84 (1)	1.76	2.785 (1)	173 (1)
N1*B*—H1*B*···O2*A*^{vi}	0.94 (1)	1.92 (1)	1.83	2.853 (1)	172 (1)
N1*B*—H2*B*···O2*A*	0.96 (2)	1.91 (2)	1.84	2.847 (1)	166 (1)
N1*B*—H3*B*···O1*B*^{xii}	0.93 (1)	1.86 (1)	1.76	2.761 (1)	164 (1)
L-Val:D-Met, **7**					
N1*A*—H1*A*···O2*B*^{ii}	0.88 (2)	2.01 (2)	1.86	2.876 (1)	171 (2)
N1*A*—H2*A*···O2*B*^{xiii}	0.87 (2)	2.00 (2)	1.84	2.851 (1)	167 (1)
N1*A*—H3*A*···O1*A*^{xiv}	0.89 (2)	1.90 (2)	1.76	2.782 (1)	172 (1)
N1*B*—H1*B*···O2*A*	0.91 (2)	1.92 (2)	1.80	2.825 (1)	174 (1)
N1*B*—H2*B*···O2*A*^{vi}	0.93 (2)	1.89 (2)	1.80	2.783 (1)	159 (2)
N1*B*—H3*B*···O1*B*^{xv}	0.88 (2)	1.89 (2)	1.74	2.761 (1)	171 (2)

Notes: (*a*) calculated from experimental N—H distance; (*b*) calculated from N—H distance normalized to 1.03 Å (Taylor & Kennard, 1983).

Symmetry codes: (i) $x-1, y, z$; (ii) $x, y, z+1$; (iii) $x+1, y, z$; (iv) $x, y, z-1$; (v) $x, y-1, z$; (vi) $x, y+1, z$; (vii) $x+1, y-1, z$; (viii) $1-x, y+\frac{1}{2}, 1-z$; (ix) $-x, y-\frac{1}{2}, 1-z$; (x) $x, y-1, z-1$; (xi) $-x+\frac{1}{2}, y+\frac{1}{2}, 1-z$; (xii) $\frac{1}{2}-x, y-\frac{1}{2}, 2-z$; (xiii) $x, y-1, z+1$; (xiv) $1-x, y-\frac{1}{2}, \frac{3}{2}-z$; (xv) $1-x, y+\frac{1}{2}, \frac{1}{2}-z$.

Amino-H atoms were refined isotropically, while all the remaining H atoms were kept in idealized positions, refining a single C—H distance for all H atoms connected to the same C atom. A rotating group refinement was utilized for all methyl-H atoms, using the *AFIX*138 card in *SHELXTL* (Sheldrick, 1995). Isotropic displacement parameters for the H atoms were fixed at $1.5U_{eq}$ (for $-CH_3$ and $-NH_3^+$ in L-Leu:D-Met) and $1.2U_{eq}$ (for $-CH_2-$ and $-CH-$) of the bonded C atom. Experimental determination of the absolute structures (Flack, 1983) was only possible for complexes **3** and **7**. For the remaining five complexes, the absolute structures have been assigned according to the chirality of the various amino acids used in the crystallization experiments. Some of the crystals are relatively large, as they were too soft for cutting. The crystals were mounted with the long edge parallel with the ϕ axis.

For all compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structures: *SHELXTL* (Sheldrick, 1995); program(s) used to refine structures: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1063). Services for accessing these data are described at the back of the journal.

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