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Complexation of peptides with crown ethers. Structure and thermal behaviour of ternary compounds: 18-crown-6/glycylglycine/water and 18-crown-6/L-α-alanyl-L-α-alanine/water

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X-ray structures of ternary complexes composed of small dipeptides, i.e. glycylglycine or L-α-alanyl-L-α-alanine, 18-crown-6 and water molecules are determined based on single-crystal studies. It has been concluded that both dipeptides exist in the complex as zwitterions and are bonded to the 18-crown-6 macrocycle by the -NH_3^+ end group through N-H...O hydrogen bonds. The carboxylic groups at the opposite side of the peptide molecules take part in hydrogen bonding with water molecules. This scheme of water-peptide hydrogen bonding is particularly interesting in the glycylglycine compound where the water content is rather high (approximately 16 moles per mole of crown/dipeptide, 6 of which are found in the X-ray study) and may have interesting relevance with respect to the structure of gel solutions which easily form in these systems. The DSC and TGA thermograms of different hydrated forms of the complexes were obtained. Two types of water, i.e. weakly and strongly bonded, were observed upon heating of the hydrated complex. On further heating the anhydrous complexes have at least two transitions in the range 320–470 K: melting of complexes at 373–383 K and decomposition above 410 K.

INTRODUCTION

Study of crystalline structures of peptide-crown complexes is very important for the development of new molecular receptors for a single dipeptide units in the problems of peptide recognition.[1–3]

In the present paper we describe the crystal structures and the thermal behaviour of the title compounds with different maintenance of water molecules investigated by the X-ray diffraction, differential scanning calorimetry (DSC) and thermogravity (TGA) methods. The complexes are 18-crown-6/glycylglycine/H_2O (I), 18-crown-6/glycylglycine/nH_2O (II) and 18-crown-6/L-α-alanyl-L-α-alanine/$2H_2O$ (III).

RESULTS AND DISCUSSION

Structures of complexes

Conformation of the 18-crown-6 molecule. The conformations of the crown molecule in both II and III are very much alike. It may be described by the sequence of torsion angles: (trans, trans, gauche +, trans, trans, gauche −) repeated three times (starting from C(18)-O(1)-C(2)-C(3), then C(1)-C(2)-C(3)-O(4) etc.). Deviations from the ideal trans angle value (±180°) in III lie within ±3°, except for that of C(8)-C(9)-O(10)-C(11), 172.0(2)°. Those for gauche+ are close to 60° (62.6(3), 67.2(3) and 64.5(3)°), and similarly for gauche− (−67.6(3), −60.3(3), −67.4(3)°). The respective data for I are not quoted here because of the relatively low accuracy, but the data are identical to II within the error limits (±5°). As given above, the geometry of the crown molecules is close to the three-fold, axial symmetry.

Conformation of dipeptide molecules. The glycylglycine molecule has the well-known trans conformation of the N(1G)-C(3G) bond; the torsion angle C(2G)-N(1G)-C(3G)-C(4G) being −175(3)°. The C(2G), C(1G), O(1G), O(2G) moiety is twisted with respect to the rest of the molecule around the C(2G)-N(1G) bond by 80(2)° (the angle between the planes defined

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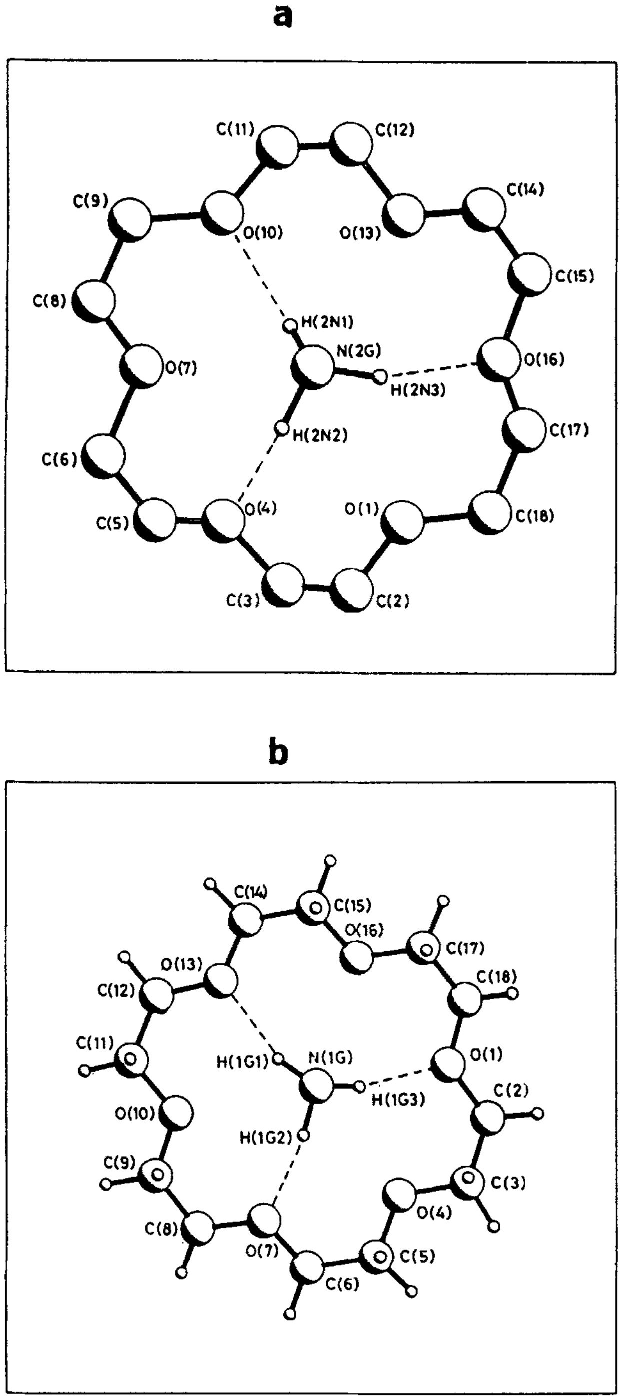

Figure 1 PLUTO projections of 18-crown-6 with the -NH$_3^+$ moiety of glycylglycine (a) and L-α-alanyl-L-α-alanine (b). In (a) hydrogen atoms of the macrocycle are omitted.

by, respectively, N(1G), C(1G), C(2G) and N(2G), C(3G), C(4G)).

The L-α-alanyl-L-α-alanine molecule is in the trans conformation as well, the C(1G)-C(2G)-N(2G)-C(3G) torsion angle being 165.1(1)°. The twist angle between the planes defined by N(1G), C(1G), C(2G) and N(2G), C(3G), C(4G) is 120.6(2)°. From the structure analysis it is assumed that both dipeptides exist in the crystal phases in zwitterionic form. The interatomic C-O bond distances in the carboxylic groups are identical.

Bonding pattern of 18-crown-6 to dipeptide molecules. As illustrated in Figs 1 and 2, both dipeptide molecules are bound to 18-crown-6 through a set of -NH...O

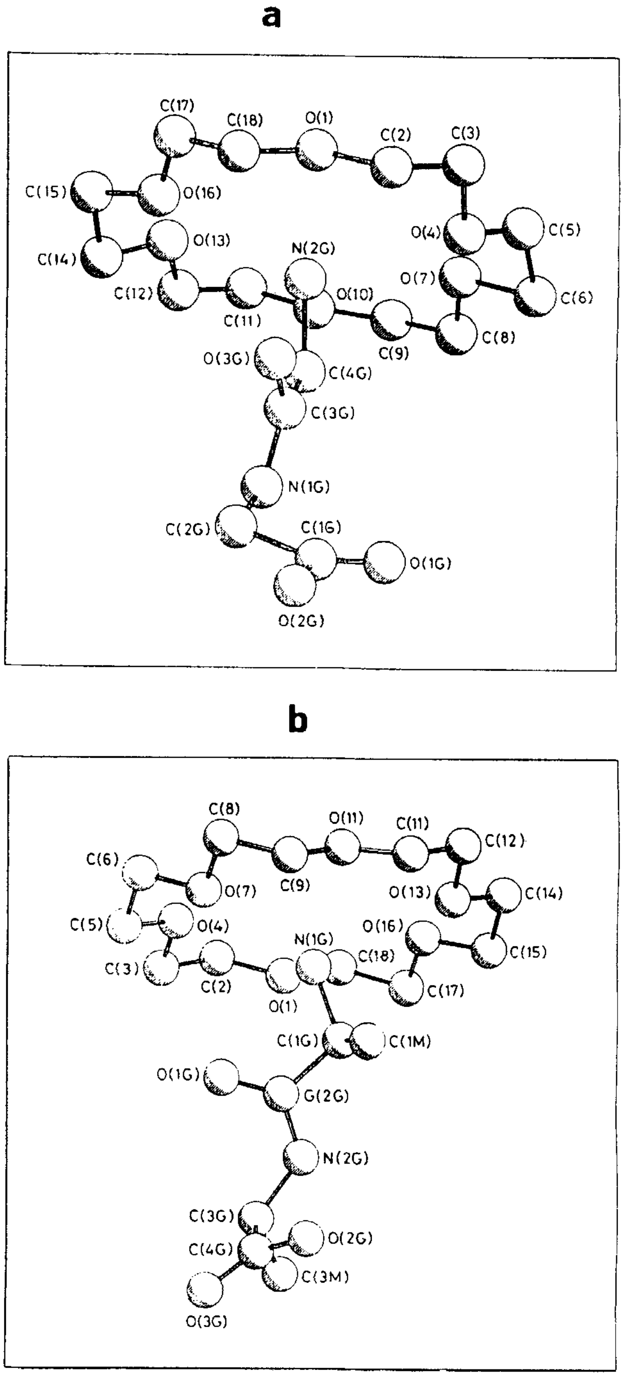

Figure 2 PLUTO projections of the complexes of 18-crown-6 with glycylglycine (a) and L-α-alanyl-L-α-alanine (b) with atom numbering scheme induced.

Table 1 Values of the H(NH_3^+)...O distances and N(1G)-H(NH_3^+)...O angles for III

Atom	*Atom*	*Distance (Å)*	*Angle (°)*
H(1G1)	O(13)	1.96(3)	153(2)
	O(10)	2.41(3)	121(2)
	O(16)	2.71(3)	96(2)
H(1G2)	O(7)	2.01(3)	160(3)
	O(4)	2.63(3)	105(2)
	O(10)	2.86(3)	96(2)
H(1G3)	O(1)	1.95(3)	166(3)
	O(4)	2.50(3)	117(2)
	O(16)	2.76(3)	98(2)

hydrogen bonds. Although bonding to three of the six macrocycle oxygen atoms would be preferred because of the orientation of their lone electron pairs towards the peptide -NH_3^+ group, it has to be noticed that the N-O distances to the remaining three oxygens are within the range of hydrogen bonding. Convenient reference may be made to atomic distances from the mean plane defined by the six macrocycle oxygens. It results that in II atoms denoted as O(1), O(7) and O(13) lie on the side of the plane opposite to the peptide moiety at distances of 0.3, 0.2 and 0.2 Å, respectively, while O(4), O(10), O(16) are at the peptide side at 0.2, 0.1 and 0.2 Å from the plane. The nitrogen atom of the -NH_3^+ group lies 0.8 Å above the plane. The N...O distances are: N(2G) to O(1), 2.94(4); O(4), 2.91(3); O(7), 2.95(3); O(10), 2.88(4); O(13), 2.92(4); O(16), 2.90(4).

In III the pattern is rather similar. The oxygens O(4), O(10) and O(16) lie 0.24, 0.22 and 0.16 Å, respectively, from the plane opposite to the peptide moiety, while O(1), O(7) and O(13) deviate by 0.19, 0.25 and 0.17 Å towards the -NH_3^+ group, the N atom of which lies 1.11 Å out of the plane. The distances N(1G) to macrocycle oxygens are: O(1), 2.892(3); O(4), 3.052(2); O(7), 2.979(2); O(10), 3.123(2); O(13), 2.984(2); O(16), 3.035(3). In Table 1 H(NH_3^+)...O distances and N(1G)-H(NH_3^+)...O angles are listed. It seems rather evident from these data that bonding to O(1), O(7) and O(13) is observed.

The N(1G)-C(1G) bond forms an angle of 70.1(1)° with the mean plane of the macrocycle. An identical value, within experimental error, is observed in II. A significant difference is the "depth of penetration" of the -NH_3^+ groups in the macrocycle cavity. In II the ammonium cation moiety gets closer to the ring by ca. 0.3 Å. This result might, perhaps, be explained in terms of steric hindrances associated with the presence in III of the -CH_3 group in the alpha position to the -NH_3^+ moiety (Fig. 3).

The molecular packing of II and III shows one common feature, i.e. there may be distinguished zones of lower polarity formed by double layers of 18-crown-6 and zones of higher polarity formed by the peptides and water. In III the hydration pattern is relatively simple: one of the two water molecules (O(2W)) forms hydrogen bonds to an oxygen from the carboxylic group of the peptide (O(2G), 2.790(3) Å), to its carbonyl oxygen (O(1G), 2.830(3) Å) and to the other water molecule (O(1W), 2.860(4) Å) which bonds to

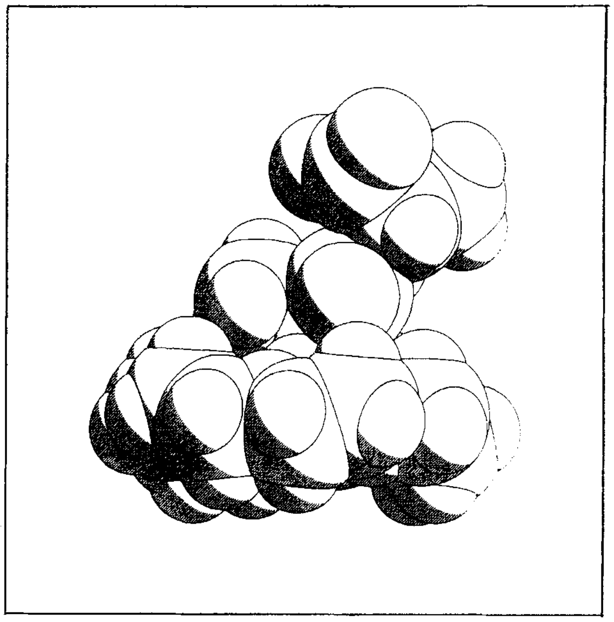

Figure 3 Space-filling model of the complex molecule of III illustrating steric hindrance of alpha-methyl group of L-α-alanyl-L-α-alanine preventing from deeper penetration into the macrocycle cavity.

Table 2 Connectivity in the hydration pattern of II

Starting atom	*Target atom*	*Distance* (Å)*
O(1W)	O(2W)	2.90
	O(3W)	2.72
	O(2W)	2.86
	O(5W)	2.85
O(2W)	O(1W)	
	O(1W)	
	O(4W)	2.78
O(3W)	O(1G)	2.79
	O(1W)	
	O(2G)	2.74
O(4W)	O(5W)	2.75
	O(2W)	
O(5W)	O(1?)	2.91
	O(4W)	
	O(1W)	
O(1?)†	O(5W)	
	O(3G)	2.79
	O(2?)	2.81
O(2?)†	O(3G)	2.72
	O(1?)	

* While each contact is reported twice as A-B and B-A, the distances are given only once.
† O(1?) and O(2?) stand for two positions of one water molecule, each of half occupancy. The distance O(1?)-O(2?) is equal 1.16 Å.

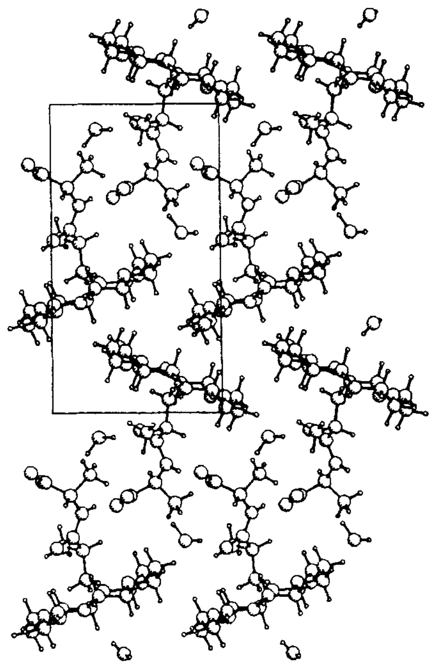

Figure 4 Molecular packing in III as viewed along *b*.

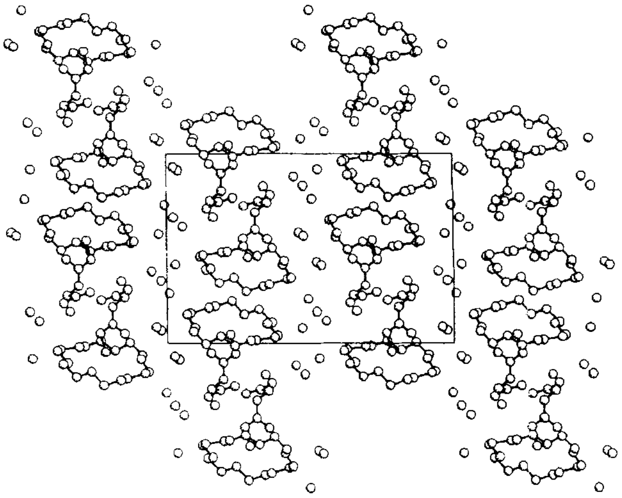

Figure 5 Molecular packing in II viewed along *b*.

the other oxygen from the -COO$^-$ moiety (of a neighbouring peptide molecule).

In II the pattern is more complex. The higher content of water in the crystalline phase of II as compared to III allows formation of a three-dimensional network of hydrogen bonds in which oxygen atoms from the carboxylic group of the peptide are involved in addition to the water molecules. The connectivity in this hydration pattern is presented in Table 2.

An illustration of this packing is given in Figs 4–6, in which 18-crown-6 macromolecules are omitted. The O(1?) and O(2?) water molecules are also missing there but, as seen in these Figs, these waters are important for bonding the layered structures (water + peptide) one to another.

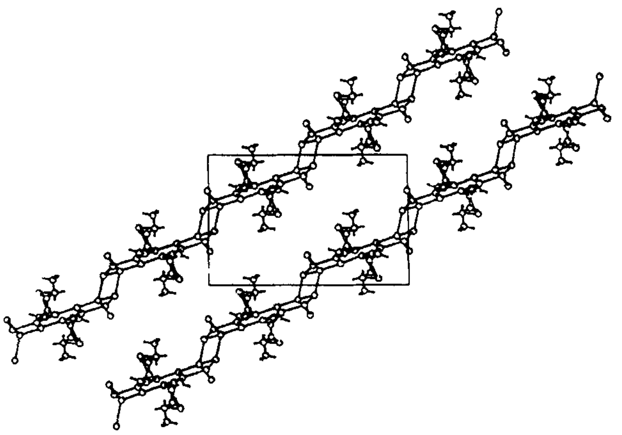

Figure 6 The illustration of the pattern of intermolecular hydrogen bonding in II: in this packing diagram 18-crown-6 molecules are omitted. Thus peptide (glygly) and water are shown.

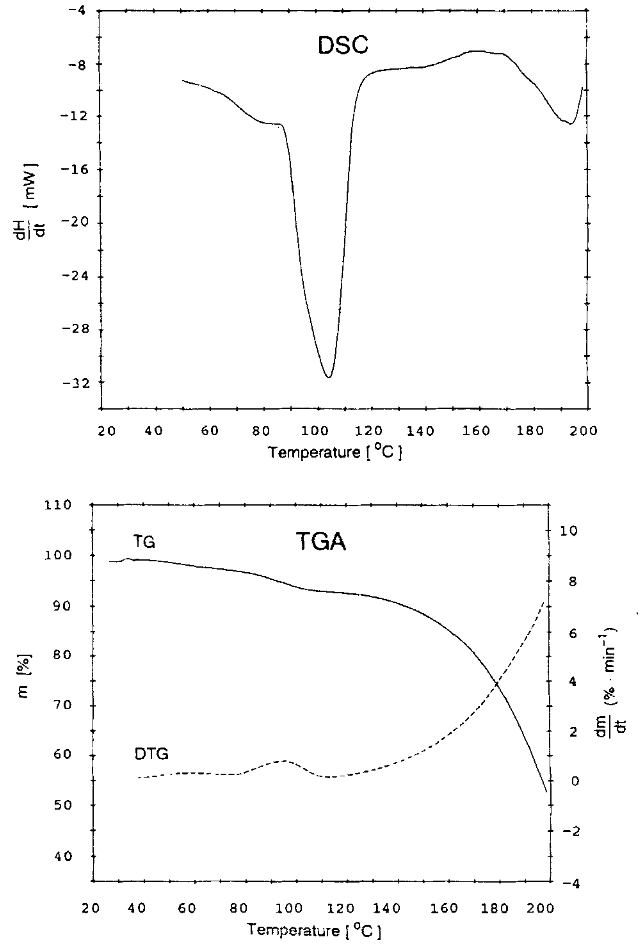

Figure 7 DSC and TGA thermograms of heating of 18-crown-6/glycyl-glycine/H_2O (I).

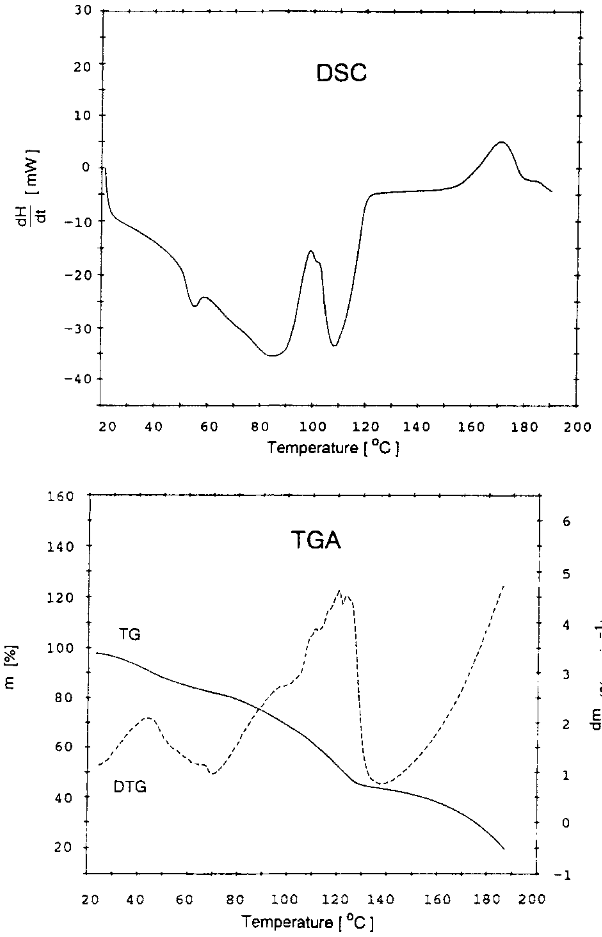

Figure 8 DSC and TGA thermograms of heating of 18-crown-6/glycyl-glycine/nH_2O (II).

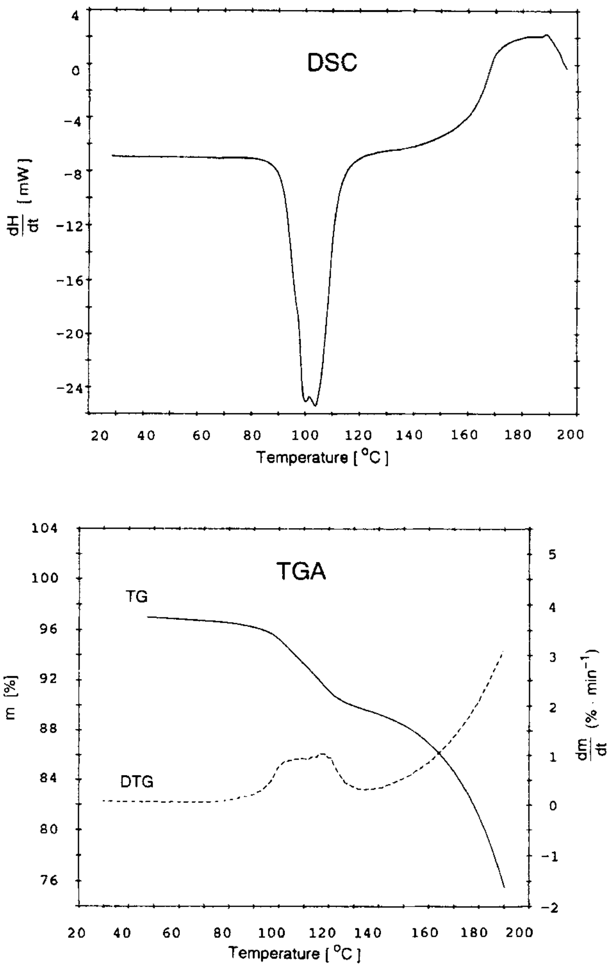

Figure 9 DSC and TGA thermograms of heating of 18-crown-6/L-α-alanyl-L-α-alanine/2H_2O (III).

Thermal behaviour of complexes

For 18-crown-6/glycylglycine/water the I and II forms of complex were investigated by DSC and TGA methods. These data are presented on Figs 7–9 and in Table 3. The previously reported[4] thermogravimetric curves of crystalline peptides did not show a decrease of the weight of the samples up to 470 K. Therefore all the changes in sample mass observed in the complexes must be caused by the evaporation of water or/and crown ethers. The calculation of the decrease in sample mass for I gives the approximate composition 1:1 of the peptide and crown in the complex. The loss of mass at 383 K (evaporation of water) was 5 per cent, corresponding to water molecule in complex I. This compound has two stages of decomposition: (1) melting of the complex at 377.7 K and, probably, (2) chemical decomposition above 450 K (Fig. 7). Thermograms of the hydrated complex 18-crown-6/glycylglycine/nH_2O (II) are more complicated (Fig. 8). At least four clearly separated thermal processes were observed on these curves. These are assumed to be (*1*) evaporation of the weakly bonded water at

Table 3 DSC data collection and thermodynamic characteristics of physico-chemical transformation of complexes

Compounds	T^a *(K)*	ΔH^b *(kJ·mol⁻¹)*
18-Crown-6/glycyclglycine/H_2O (I)		
(1) melting	377.7	127
18-Crown-6/glycyclglycine/nH_2O (II)		
(1) melting of complex	381.9	163
(2) decomposition of complex	443.7	−50.5
(3) dehydration of weakly bonded water	328.7	15.1^c
(4) dehydration of strongly bonded water	358.0	62.8^c
18-Crown-6/L-α-alanyl-L-α-alanine/water (III)		
(1) melting of dihydrate	373.7	117
(2) melting of monohydrate	377.2	
18-Crown-6		
(1) melting	312.5	42.2^c

[a] Temperatures of peaks are presented.
[b] The all values were calculated for 1:1 composition of complexes without water molecules.
[c] These values were calculated taking into account the TGA data on the loss of mass and molar weight of water.

Table 4 Data collection and structure analysis parameters

	II	*III*
Molecular formula	$C_{16}H_{43}N_2O_{21}$*	$C_{18}H_{40}N_3O_{11}$
Crystal size (mm)	0.2·0.5·0.7	0.15·0.4·0.4
Space group	$P2_1/n$	$P2_12_12_1$
Unit cell a (Å)	14.228(7)	8.832(2)
b	8.739(3)	15.781(4)
c	21.867(6)	17.331(7)
β (°)	90.37(3)	—
Z	4	4
Density calc. (g·cm^{-3})	1.21*	1.305
Absorption coeff. (cm^{-1})	8.9*	8.715
Radiation	graphite monochromatized Cu K_α	
Number of reflections		
measured	5801	2910
unique	5454	2883
used in structure analysis	841	2529
Final R values		
unweighted	0.143	0.039
$w = 1/\sigma^2(F \cdot F^*)$	0.136	0.035
Residual extrema in final difference map (e/Å^3)	0.44 −0.38	0.13 −0.17
Maximum shift/error ratio	0.78	0.078

* In II chemical composition and thus density and absorption coefficient calculated on this basis are uncertain within the 5 to 12 water molecules per molecule of the crown-peptide complex. The minimum vs. maximum values are as follows: density: 1.189/1.465, $\mu = 8.55/11.57$.
II at −100 °C.
a(Å) = 14,03(1).
b = 8.685(7).
c = 21.63(2).
β = 90.04(7)°.

Table 5 Fractional atomic coordinates (× 10^4) and mean temperature factors for non-hydrogen atoms of 18-crown-6/L/α-alanyl-L-α-alanine/$2H_2O$ (III)

Atom	*x/a*	*y/b*	*z/c*	*B(eq)*
O(1)	700(2)	5544(1)	983(1)	3.96(5)
C(2)	824(4)	5971(2)	1705(2)	4.8(1)
C(3)	2443(5)	5976(2)	1956(2)	5.03(9)
O(4)	3307(2)	6445(1)	1397(1)	3.83(5)
C(5)	4871(4)	6492(2)	1603(2)	4.8(1)
C(6)	5667(4)	7028(2)	1023(2)	4.8(1)
O(7)	5691(2)	6617(1)	299(1)	3.77(5)
C(8)	6395(4)	7134(2)	−274(2)	4.47(9)
C(9)	6299(3)	6710(2)	−1030(2)	4.25(7)
O(10)	4745(2)	6682(1)	−1262(1)	3.63(5)
C(11)	4596(4)	6387(2)	−2029(2)	4.05(7)
C(12)	2933(4)	6366(2)	−2228(2)	4.12(7)
O(13)	2161(2)	5809(1)	−1715(1)	3.67(5)
C(14)	593(4)	5751(2)	−1909(2)	4.00(7)
C(15)	−170(3)	5184(2)	−1351(2)	4.24(7)
O(16)	−118(2)	5548(1)	−601(1)	3.94(5)
C(17)	−882(4)	5055(2)	−37(2)	4.86(9)
C(18)	−829(4)	5511(2)	705(2)	5.02(9)
C(1G)	3334(3)	4507(1)	−252(1)	2.37(5)
N(1G)	3172(2)	5443(1)	−107(1)	2.53(3)
C(1M)	4465(3)	4365(2)	−901(2)	3.40(7)
C(2G)	3901(2)	4074(1)	472(1)	2.52(5)
O(3G)	4869(2)	4426(1)	877(1)	3.93(5)
N(2G)	3355(2)	3298(1)	584(1)	2.26(3)
C(3G)	4013(2)	2707(1)	1133(1)	2.17(5)
C(3M)	2854(3)	2029(2)	1333(2)	3.05(7)
C(4G)	5469(3)	2274(1)	830(1)	2.65(5)
O(1G)	5670(2)	2242(1)	118(1)	4.22(5)
O(2G)	6306(2)	1957(1)	1323(1)	4.05(5)
O(1W)	2303(2)	795(2)	8039(1)	5.29(7)
O(2W)	980(3)	7861(2)	3722(1)	5.33(7)

328.7 K (loss of mass, 15 per cent), (2) melting and evaporation of the strongly (specifically) bonded water at 358 K (loss of mass, 13.3 per cent), (3) melting of the complex at 381.9 K (endo-effect), and (4) decomposition of the complex at 443.7 K (exo-effect). Therefore, this compound contains approximately 1 mole of 18-crown-6 + 1 mole of glycylclycine + 16 mole of water, 6 mole of which are strongly bonded with the complex. Evidently these molecules are the same which were found in the X-ray study, because of hydrogen bonding with peptide molecules.

Thermograms of the 18-crown-6/L-α-alanyl-L-α-alanine/$2H_2O$ (III) are presented in Fig. 9. Composition of the complex calculated from TGA data approximately equals 1:1 for the peptide-crown relation. Complex III contains also 2 mole of water (loss of mass, 8 per cent at 303 K). Two types of physico-chemical processes take place on heating of this compound: (1) melting at 373.7 and 377.2 K and (2) decomposition of the complex above 430 K. The two peaks of melting are explained by the separate melting of mono- and di-hydrates. Comparison of the two monohydrated title crown/peptide complexes allows the conclusion that their thermal behaviour is similar. However, the enthalpy of melting of II compares to that of III in exactly the same manner as the "depth of penetration" for II compared to that for III.

A complete discussion of the DSC and TGA investigations of some peptide/crown complexes will be published.[5]

EXPERIMENTAL

Preparation of complexes

Single crystals of complexes I and III were prepared by slow evaporation of solvent from equimolar water-ethanol solutions at room temperature. In the case of 18-crown-6/glycylglycine the hydrated form of complex

Table 6 Bond distances for 18-crown-6/L-α-alanyl-L-α-alanine/$2H_2O$ (III)

Atom 1-Atom 2	*Distance (Å)*	*Atom 1-Atom 2*	*Distance (Å)*
O(1)-C(2)	1.427(3)	O(1)-C(18)	1.436(4)
C(2)-C(3)	1.495(5)	C(3)-O(4)	1.436(4)
O(4)-C(5)	1.428(4)	C(5)-C(6)	1.490(4)
C(6)-O(7)	1.413(3)	O(7)-C(8)	1.429(3)
C(8)-C(9)	1.474(4)	C(9)-O(10)	1.432(3)
O(10)-C(11)	1.415(3)	C(11)-C(12)	1.508(5)
C(12)-O(13)	1.423(3)	O(13)-C(14)	1.429(4)
C(14)-C(15)	1.480(4)	C(15)-O(16)	1.423(3)
O(16)-C(17)	1.422(3)	C(17)-C(18)	1.475(4)
C(1G)-N(1G)	1.507(2)	C(1G)-C(1M)	1.521(3)
C(1G)-C(2G)	1.514(2)	C(2G)-O(3G)	1.238(2)
C(2G)-N(2G)	1.330(2)	N(2G)-C(3G)	1.456(2)
C(3G)-C(3M)	1.519(3)	C(3G)-C(4G)	1.549(3)
C(4G)-O(1G)	1.249(2)	C(4G)-O(2G)	1.234(2)

Table 7 Bond angles for 18-crown-6/L-α-alanyl-L-α-alanine/$2H_2O$ (III)

Atom 1-Atom 2-Atom 3	*Angle (°)*
C(2)-O(1)-C(18)	112.6(2)
O(1)-C(2)-C(3)	109.3(2)
C(2)-C(3)-C(4)	108.4(3)
C(3)-O(4)-C(5)	111.9(2)
O(4)-C(5)-C(6)	108.6(2)
C(2)-C(6)-O(7)	110.1(2)
C(6)-O(7)-C(8)	111.2(2)
O(7)-C(8)-C(9)	109.6(2)
C(8)-C(9)-O(10)	108.6(2)
C(9)-O(10)-C(11)	111.3(2)
O(10)-C(11)-C(12)	108.2(2)
C(11)-C(12)-O(13)	109.7(2)
C(12)-O(13)-C(14)	110.9(2)
O(13)-C(14)-C(15)	109.1(2)
C(14)-C(15)-O(16)	109.7(2)
C(15)-O(16)-C(17)	113.1(2)
O(16)-C(17)-C(18)	108.5(2)
O(1)-C(18)-C(17)	109.9(2)
C(1M)-C(1G)-C(2G)	109.3(1)
N(1G)-C(1G)-C(2G)	109.5(1)
N(1G)-C(1G)-C(1M)	109.3(1)
C(1G)-C(2G)-N(2G)	114.6(1)
C(1G)-C(2G)-O(3G)	119.8(1)
O(3G)-C(2G)-N(2G)	125.5(1)
C(2G)-N(2G)-C(3G8)	122.8(1)
N(2G)-C(3G)-C(4G)	113.1(1)
N(2G)-C(3G)-C(3M)	109.4(1)
C(3M)-C(3G)-C(4G)	109.1(1)
C(3G)-C(4G)-O(2G)	116.2(1)
C(3G)-C(4G)-O(1G)	118.1(1)
O(1G)-C(4G)-O(2G)	125.6(2)

II, crystallized in aqueous solution [m(peptide) = 0.6 $\mathrm{mol \cdot kg^{-1}}$, m(crown) = 0.6 $\mathrm{mol \cdot kg^{-1}}$] at room temperature, was also obtained.

Chromatographically homogeneous glycylglycine and L-α-alanyl-L-α-alanine produced by Reanal (Hungary) was used for preparation of the complexes. The purity of the commercially obtained peptides was above 98 molar per cent. Each peptide was purified by recrystallization from water-ethanol and dried under vacuum for 48 h at 330 K. The purity of the commercially obtained 18-crown-6 was above 99 molar per cent and it was used without further purification.

X-ray data

X-ray single crystal intensity data were measured by using an Enraf-Nonius CAD-4 diffractometer. The structures were solved by using SHELXS[6] and refined with SHELX76[7] computer programs. The details of data collection and structure analysis are summarized in Tables 4–7.

Single crystals of the 18-crown-6/glycylglycine/nH_2O (II) complex crystallized in the aqueous solution and 18-crown-6/L-α-alanyl-L-α-alanine/water (III) prepared by slow evaporation from water-ethanol solution were selected for X-ray analysis. The crystals of II and III were placed in thin-wall glass capillaries without any preliminary drying. While with III there were no particular difficulties in the X-ray experimental procedure, with II no good data set could be obtained, neither by using crystals in capillaries with some excess of mother solution nor by going down with the temperature of the experiment. In particular, low temperature experiments showed large variations of both intensity of diffraction and even lattice parameters. These could not be avoided by using different programs of cooling. The structure reported here is based on the best of five data sets.

DSC and TGA analysis

The thermal properties of crystalline complexes in the range 310–470 K were investigated on a Du Pont 1090 installation equipped by DSC and TGA cells. The runs were performed at a scan rate of 5 $\mathrm{K \cdot min^{-1}}$ in an atmosphere of dry argon. The sample mass was 10–30 mg.

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REFERENCES

1. Lehn, J.M. (1988). *J. Inclus. Phenom.* **6,** 351.
2. Hamilton, A.D., Pant, N. and Muehldorf, A. (1988). *Pure & Appl. Chem.* **60,** 533.
3. Sutherland, I.O. (1989). *Pure & Appl. Chem.* **61,** 1547.
4. Badelin, V.G., Kulikov, O.V., Vatagin, V.S., Utzig, E., Zielenkiewicz, A., Zielenkiewicz, W. and Krestov, G.A. (1990). *Thermochim. Acta* **169,** 81.
5. Kulikov, O.V., Zielenkiewicz, W., Utzig, E. and Krestov, G.A. (1992). *Thermochim. Acta* in press.
6. Sheldrick, G.M. (1985). SHELXS-86, In Crystallographic Computing 3, Sheldrick, G.M., Krueger, C. and Goddard R. (Eds.), Oxford University Press, pp. 175–189.
7. Sheldrick, G.M. SHELX-76, Program for Crystal Structure Determination, University of Cambridge, England.