below the phase-transition temperature sterically disfavour the low-spin geometry of the complex.

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Packing Characteristics of the Aliphatic Chains in Bis(n-alkylammonium) Tetrachlorozincate(II) with Even and Odd Numbers of Carbon Atoms

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Abstract

The series of compounds $[(n\text{-}C_mH_{2m+1})NH_3]_2MCl_4$ crystallize in layers alternately formed by the metal complexes and the alkylammonium chains. They exhibit various phase transitions depending on the parity of the number of C atoms included in the chains. To compare the packing characteristics of even and odd members of the Zn series, the structure of $[(C_{13}H_{27})NH_3]_2ZnCl_4$ was solved. The structure is monoclinic, space group $P2_1$, $M_r = 607.48$, $a = 10.644$ (2), $b = 7.3074$ (9), $c = 44.043$ (7) Å, $\beta =$

$94 \cdot 24$ (2)°, $V = 3416 \cdot 3$ Å^3, $Z = 4$, $D_x = 1 \cdot 18$ g cm^{-3}, $\mu = 39 \cdot 5$ cm^{-1}, λ(Cu $K\alpha$) $= 1 \cdot 5418$ Å, $F(000) = 1312$, $T = 293$ K. Final $R = 0 \cdot 06$ for 5081 unique reflections. In the three Zn derivatives with $m = 12$, 13 and 14, the packing of the aliphatic part of the structure differs according to the parity of m. For $m =$ even, the 'cell' defined by the periodic structure of the hydrocarbon part alone is of a new type.

Introduction

Compounds of the type $[(n\text{-}C_mH_{2m+1})NH_3]_2ZnCl_4$ with $m = 1 \ldots 18$ exhibit numerous phase transitions at temperatures varying between 299 and 365 K. Calorimetric studies have shown that the number of transitions depends on the number m of C atoms included in the alkylammonium ion (Socias, Arriandiaga, Tello, Fernandez & Gili, 1980). In all these compounds, the melting of the chains, i.e. the aliphatic part of the molecule, is preceded by one or two transition steps corresponding to order–disorder of rigid chains and conformational changes. For similar compounds with Cd, Cu, Mn or Fe as divalent cation, it has been shown that the transitions are of the same type (Fernandez, Socias, Arriandiaga, Tello & Lopez Echarri, 1982; Blinc et al., 1980; Kind et al., 1979).

This work is part of a study on the structural characteristics of the transitions and their dependence on the parity of m in the Zn family. The room-temperature structures of the compounds with $m = 12$ and 14 have been reported (Ciajolo, Corradini & Pavone, 1977; Zuñiga & Chapuis, 1981). They consist of alternating layers of alkylammonium ions and isolated ZnCl$_4$ tetrahedra. The layers are linked by hydrogen bonds between the N and Cl atoms. Each alkylammonium layer is of the intercalated type, i.e. it consists of interpenetrating chains attached alternately to adjacent ZnCl$_4$ layers.

Owing to the differences in the thermal behaviour between even and odd members of the series, structural differences are also expected. The structure reported in this work contains an odd number of C atoms in the alkylammonium ion ($m = 13$). It is also of the intercalated type but the packing characteristics of the alkyl part differ from those of the other members of the series with even numbers of C atoms.

This compound also exhibits numerous phase transitions in the solid state which have been analysed by X-ray diffraction and calorimetry. The results will be reported elsewhere.

Experimental

The compound was obtained by reaction of equimolar solutions of the starting materials ZnCl$_2$ and $[(C_{13}H_{27})NH_3]Cl$ (Merck). Single crystals were grown by slow evaporation of an ethanolic solution of the compound. Further details on the synthesis and chemistry are to be found in Socias (1980). Single-crystal diffractograms indicated monoclinic symmetry and the systematic absences $0k0$: $k = 2n + 1$. Space group $P2_1$ was chosen on the basis of a statistical test of Bragg intensities and was later confirmed by the successful refinement of the structure. The lattice parameters at 293 K as determined from single-crystal diffractometry are given in the Abstract. Intensities were collected on a Syntex $P2_1$ diffractometer using the θ–2θ scan technique up to (sin θ)/$\lambda = 0 \cdot 5461$ Å^{-1} with Ni-filtered Cu $K\alpha$ radiation. An absorption correction by Gaussian integration was applied to the intensities. The transmission coefficients varied between 0·46 and 0·62 for a specimen with a volume of $7 \cdot 85 \times 10^{-3}$ mm^3. A single asymmetric set of data was collected $(h, k, \pm l)$; 560 intensities were less than $3\sigma(I)$ as derived from counting statistics.

For the reduction of the data and refinement of the structure, the XRAY system of programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) was used. Atomic scattering factors of Zn^{2+}, Cl$^-$, N, C (Cromer & Mann, 1968), and H (Stewart, Davidson & Simpson, 1965) and anomalous-dispersion terms for Zn and Cl (Cromer & Liberman, 1970) were used for the structure factor calculations.

The structure was solved by the Patterson method and refined by least squares with a block-diagonal matrix. The function minimized was $\sum (w\Delta F)^2$ with $w = 1/\sigma(F)$. All the non-hydrogen atoms were refined with anisotropic thermal parameters with the exception of the disordered ones. In the last step of the refinement, H atoms with calculated positions were included in the structure factor calculation but not refined. At the end of the refinement, the maximum shift-to-error ratio was 1·5; the residual values $R_w = 0 \cdot 072$ and $S = 5 \cdot 5$ were obtained. The highest peak on the final difference Fourier synthesis was $0 \cdot 32$ e Å^{-3}.*

Discussion

Atomic parameters, bond distances, bond angles and torsion angles are reported in Tables 1, 2 and 3. The structure is parent to the structures of the compounds with $m = 12$ and 14. It consists of two types of alternating layers stacked along c. One layer is formed by isolated ZnCl$_4$ tetrahedra and the other by interpenetrated alkylammonium chains. Both macro-ions

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and a full list of interatomic distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38487 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates

	x	y	z	U_{eq}* (Å²)
Zn(1)	0·2593 (1)	0·2491	−0·01521 (4)	0·0642
Zn(2)	0·2712 (1)	0·2543 (3)	0·51468 (4)	0·0621
Cl(11)	0·2669 (3)	0·3065 (6)	0·03557 (8)	0·0659
Cl(12)	0·4569 (3)	0·2697 (8)	−0·03050 (8)	0·0732
Cl(13)	0·1707 (3)	−0·0221 (6)	−0·02735 (9)	0·0616
Cl(14)	0·1362 (3)	0·4731 (6)	−0·03791 (9)	0·0623
Cl(21)	0·2532 (3)	0·2065 (6)	0·46377 (8)	0·0624
Cl(22)	0·4763 (3)	0·2442 (8)	0·53164 (8)	0·0713
Cl(23)	0·1624 (3)	0·0357 (6)	0·53655 (8)	0·0596
Cl(24)	0·1838 (3)	0·5318 (6)	0·52513 (8)	0·0574
N(1)	0·1153 (7)	0·707 (1)	0·0296 (2)	0·0593
C(11)	0·2023 (9)	0·799 (2)	0·0514 (2)	0·0645
C(12)	0·1910 (9)	0·728 (2)	0·0841 (2)	0·0617
C(13)	0·295 (1)	0·812 (2)	0·1072 (3)	0·0751
C(14)	0·2860 (9)	0·747 (2)	0·1391 (2)	0·0633
C(15)	0·3857 (9)	0·822 (2)	0·1619 (2)	0·0653
C(16)	0·3769 (8)	0·743 (2)	0·1935 (2)	0·0604
C(17)	0·4795 (9)	0·819 (2)	0·2172 (2)	0·0706
C(18)	0·4680 (8)	0·745 (2)	0·2484 (2)	0·0629
C(19)	0·5692 (9)	0·814 (2)	0·2722 (3)	0·0715
C(110)	0·5568 (8)	0·734 (2)	0·3040 (2)	0·0595
C(111)	0·6546 (9)	0·807 (2)	0·3276 (3)	0·0697
C(112)	0·6450 (9)	0·730 (2)	0·3590 (3)	0·0760
C(113)	0·743 (1)	0·798 (2)	0·3833 (3)	0·1036
N(2)	0·0897 (6)	0·809 (1)	0·4707 (2)	0·0549
C(21)	0·1683 (9)	0·719 (2)	0·4472 (2)	0·0691
C(22)	0·1449 (9)	0·794 (1)	0·4162 (2)	0·0645
C(23)	0·2425 (9)	0·720 (2)	0·3964 (2)	0·0679
C(24)	0·2337 (9)	0·802 (2)	0·3646 (3)	0·0801
C(25)	0·129 (1)	0·739 (2)	0·3422 (3)	0·0771
C(26)	0·132 (1)	0·816 (2)	0·3099 (3)	0·0786
C(27)	0·0315 (8)	0·740 (2)	0·2865 (2)	0·0679
C(28)	0·0413 (9)	0·816 (2)	0·2546 (2)	0·0689
C(29)	−0·0530 (9)	0·742 (2)	0·2311 (2)	0·0697
C(210)	−0·044 (1)	0·823 (2)	0·2002 (3)	0·0770
C(211)	−0·1400 (9)	0·752 (2)	0·1750 (3)	0·0748
C(212)	−0·125 (1)	0·836 (2)	0·1437 (3)	0·0828
C(213)	−0·224 (1)	0·751 (2)	0·1204 (3)	0·0993
N(3)	0·5605 (6)	0·282 (1)	0·4586 (2)	0·0565
C(31)	0·5735 (9)	0·216 (2)	0·4275 (2)	0·0674
C(32)	0·483 (1)	0·303 (2)	0·4058 (2)	0·0661
C(33)	0·4887 (9)	0·234 (2)	0·3740 (2)	0·0659
C(34)	0·3900 (9)	0·315 (2)	0·3499 (3)	0·0682
C(35)	0·3956 (9)	0·234 (2)	0·3187 (2)	0·0610
C(36)	0·2979 (9)	0·317 (2)	0·2961 (2)	0·0667
C(37)	0·3016 (9)	0·243 (2)	0·2638 (2)	0·0670
C(38)	0·206 (1)	0·321 (2)	0·2404 (2)	0·0621
C(39)	0·2150 (8)	0·244 (2)	0·2093 (2)	0·0591
C(310)	0·1183 (9)	0·326 (2)	0·1855 (2)	0·0653
C(311)	0·1215 (9)	0·248 (2)	0·1532 (2)	0·0638
C(312)	0·027 (1)	0·327 (2)	0·1312 (3)	0·0684
C(313)	0·029 (1)	0·241 (2)	0·1001 (3)	0·0986
N(4)†	0·5835 (7)	0·223 (2)	0·0417 (2)	0·0762
C(41)†	0·576 (2)	0·179 (5)	0·0720 (6)	0·0548
C(41)P†	0·609 (3)	0·283 (7)	0·0740 (7)	0·0952
C(42)†	0·562 (2)	0·371 (4)	0·0872 (5)	0·0619
C(42)P†	0·523 (3)	0·196 (5)	0·0912 (8)	0·1140
C(43)	0·522 (1)	0·339 (3)	0·1221 (4)	0·1484
C(44)	0·620 (1)	0·271 (3)	0·1432 (4)	0·1149
C(45)	0·607 (1)	0·316 (2)	0·1771 (4)	0·1059
C(46)	0·703 (1)	0·250 (2)	0·2008 (4)	0·1035
C(47)	0·693 (1)	0·306 (2)	0·2329 (3)	0·0919
C(48)	0·790 (1)	0·244 (3)	0·2549 (4)	0·1196
C(49)	0·786 (1)	0·304 (2)	0·2887 (4)	0·1046
C(410)	0·890 (1)	0·236 (2)	0·3108 (3)	0·0942
C(411)	0·883 (1)	0·295 (2)	0·3431 (3)	0·0909
C(412)	0·979 (1)	0·235 (2)	0·3658 (4)	0·1164
C(413)	0·975 (1)	0·282 (2)	0·3985 (3)	0·1131

* $U_{eq} = \frac{1}{3}(U_1 + U_2 + U_3)$.

† Population parameters: C(41) 0·45 (7), C(41)P 0·55 (7), C(42) 0·49 (4), C(42)P 0·51 (4).

Table 2. Selected distances (Å) and interatomic angles (°)

Standard deviations are given in parentheses. The bonds and angles of the four independent alkylammonium chains do not deviate significantly from the expected values. A full list of distances and angles has been deposited (see deposition footnote).

Zn(1)−Cl(11)	2·271 (4)		N(2)−C(24)	3·241 (9)
Zn(1)−Cl(2)	2·260 (4)		N(2)−Cl(21ᶦ)	3·401 (9)
Zn(1)−Cl(13)	2·243 (4)		N(2)−Cl(23ᶦ)	3·378 (9)
Zn(1)−Cl(14)	2·281 (4)		N(2)−Cl(23ᵛⁱ)	3·343 (8)
Zn(2)−Cl(21)	2·263 (4)		N(2)−Cl(24ᵛⁱ)	3·352 (8)
Zn(2)−Cl(22)	2·256 (3)		N(3)−Cl(21)	3·342 (8)
Zn(2)−Cl(23)	2·233 (4)		N(3)−Cl(22)	3·413 (8)
Zn(2)−Cl(24)	2·292 (5)		N(3)−Cl(22ᶦᶦ)	3·43 (1)
N(1)−Cl(11)	3·341 (9)		N(3)−Cl(23ᶦᶦ)	3·477 (8)
N(1)−Cl(14)	3·451 (9)		N(3)−Cl(24ᶦᶦᶦ)	3·313 (8)
N(1)−Cl(13ᶦ)	3·285 (9)		N(4)−Cl(11)	3·416 (8)
N(1)−Cl(13ᵛᶦᶦ)	3·468 (9)		N(4)−Cl(12)	3·377 (8)
N(1)−Cl(14ᵛᶦᶦ)	3·352 (9)		N(4)−Cl(13ᶦᶦᶦ)	3·31 (1)
			N(4)−Cl(12ᵛ)	3·37 (1)

Cl(11)−Zn(1)−Cl(12)	108·4 (1)		Cl(21)−Zn(2)−Cl(22)	109·4 (1)
Cl(11)−Zn(1)−Cl(13)	112·4 (2)		Cl(21)−Zn(2)−Cl(23)	108·0 (2)
Cl(11)−Zn(1)−Cl(14)	106·1 (2)		Cl(21)−Zn(2)−Cl(24)	109·3 (2)
Cl(12)−Zn(1)−Cl(13)	111·8 (2)		Cl(22)−Zn(2)−Cl(23)	110·7 (2)
Cl(12)−Zn(1)−Cl(14)	109·8 (2)		Cl(22)−Zn(2)−Cl(24)	111·1 (2)
Cl(13)−Zn(1)−Cl(14)	108·2 (2)		Cl(23)−Zn(2)−Cl(24)	108·4 (2)

Symmetry code
(i)	$x, y + 1, z$	(v)	$1 - x, y - \frac{1}{2}, -z$
(ii)	$1 - x, \frac{1}{2} + y, 1 - z$	(vi)	$-x, \frac{1}{2} + y, 1 - z$
(iii)	$1 - x, \frac{1}{2} + y, -z$	(vii)	$-x, \frac{1}{2} + y, -z$
(iv)	$1 - x, y - \frac{1}{2}, 1 - z$		

stereochemical considerations. In these models, atoms N(1) and N(2) are bonded to Cl(11), Cl(13ᶦ), Cl(14ᵛᶦᶦ) and Cl(24), Cl(21ᶦ), Cl(23ᵛⁱ) respectively. In both cases, the strongest H bonds [N(1)···Cl(13ᶦ) and N(2)···Cl(24)] are directed towards Cl atoms located deeper in the cavity. Atoms N(1) and N(2) seem thus to be more strongly bonded than N(3) and N(4). The second type of cavity is characterized by N(3) bonded to Cl(21), Cl(22ᶦᶦ), Cl(24ᶦᶦᶦ) and N(4) bonded to Cl(11), Cl(13ᶦᶦᶦ) and Cl(12ᵛ).

It is important to note the systematically larger thermal ellipsoids of one chain (chain 4) as compared to the other three. The first three C atoms of chain 4 [N(4)...C(413)] are disordered between two positions but only C(41) and C(42) have been split in the refinement of the structure. Owing to the proximity of the two disordered positions, an average position has been refined for atom C(43) explaining thus its large thermal parameters ($U_{eq} = 0.1484$ Å²). The refined population parameters of atoms C(41) and C(42) are reported in Table 1. The two reported population parameters can be considered as identical within the calculated errors. Thus, the two disordered parts of the chains are statistically distributed on two equally probable positions. The other C atoms of the chain are also affected by the disorder as revealed by the temperature factors and the short values of some C—C distances.

are linked by hydrogen bonds between N and Cl atoms. A projection of the structure is given in Fig. 1.

The four independent N atoms are located in two different types of Cl cavities. As a consequence, two different schemes of H bonds linking the N and Cl atoms can be observed. Figs. 2(a), 2(b), 2(c) and 2(d) show the most probable H bonds as derived by

Table 3. *Torsion angles* (°)

|					
N(1)–C(11)–C(12)–C(13)	174 (1)	N(2)–C(21)–C(22)–C(23)	170 (1)	N(3)–C(31)–C(32)–C(33)	−178 (1)
C(11)–C(12)–C(13)–C(14)	180 (1)	C(21)–C(22)–C(23)–C(24)	−175 (1)	C(31)–C(32)–C(33)–C(34)	178 (1)
C(12)–C(13)–C(14)–C(15)	179 (1)	C(22)–C(23)–C(24)–C(25)	−75 (1)	C(32)–C(33)–C(34)–C(35)	−177 (1)
C(13)–C(14)–C(15)–C(16)	−177 (1)	C(23)–C(24)–C(25)–C(26)	−175 (1)	C(33)–C(34)–C(35)–C(36)	180 (1)
C(14)–C(15)–C(16)–C(17)	−180 (1)	C(24)–C(25)–C(26)–C(27)	175 (1)	C(34)–C(35)–C(36)–C(37)	179 (1)
C(15)–C(16)–C(17)–C(18)	178 (1)	C(25)–C(26)–C(27)–C(28)	−178 (1)	C(35)–C(36)–C(37)–C(38)	180 (1)
C(16)–C(17)–C(18)–C(19)	179 (1)	C(26)–C(27)–C(28)–C(29)	179 (1)	C(36)–C(37)–C(38)–C(39)	180 (1)
C(17)–C(18)–C(19)–C(110)	−179 (1)	C(27)–C(28)–C(29)–C(210)	179 (1)	C(37)–C(38)–C(39)–C(310)	−179 (1)
C(18)–C(19)–C(110)–C(111)	−178 (1)	C(28)–C(29)–C(210)–C(211)	−180 (1)	C(38)–C(39)–C(310)–C(311)	−179 (1)
C(19)–C(110)–C(111)–C(112)	−180 (1)	C(29)–C(210)–C(211)–C(212)	−179 (1)	C(39)–C(310)–C(311)–C(312)	179 (1)
C(110)–C(111)–C(112)–C(113)	179 (1)	C(210)–C(211)–C(212)–C(213)	179 (1)	C(310)–C(311)–C(312)–C(313)	−178 (1)
N(4)–C(41)–C(42)–C(43)	168 (2)	C(42)P–C(43)–C(44)–C(45)	−155 (2)	C(47)–C(48)–C(49)–C(410)	180 (2)
N(4)–C(41)P–C(42)P–C(43)	−157 (3)	C(43)–C(44)–C(45)–C(46)	180 (2)	C(48)–C(49)–C(410)–C(411)	180 (2)
C(41)–C(42)–C(43)–C(44)	73 (2)	C(44)–C(45)–C(46)–C(47)	176 (2)	C(49)–C(410)–C(411)–C(412)	180 (2)
C(41)P–C(42)P–C(43)–C(44)	−89 (2)	C(45)–C(46)–C(47)–C(48)	−178 (2)	C(410)–C(411)–C(412)–C(413)	−177 (2)
C(42)–C(43)–C(44)–C(45)	155 (2)	C(46)–C(47)–C(48)–C(49)	178 (2)		
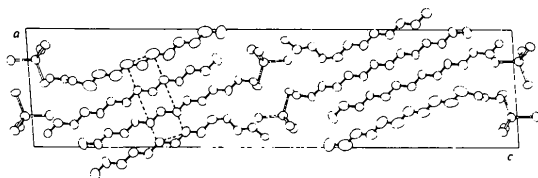
Fig. 1. Projection of the structure along the *b* axis. For the disordered atoms only a single position is represented. The dashed lines shows the *p* cell considered for the packing chains.
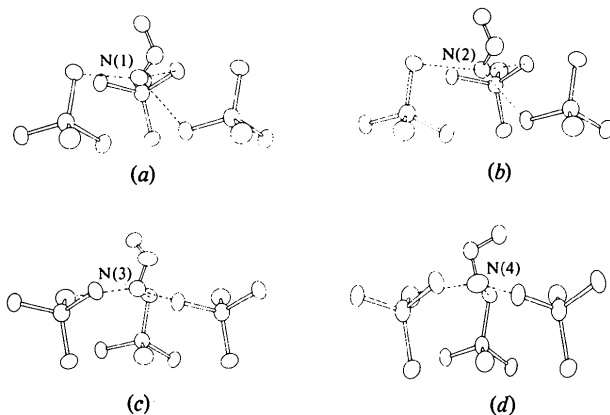

Fig. 2. *ORTEP* (Johnson, 1965) drawing of Cl cavities showing the proposed H-bonding schemes. The first two C atoms of the alkylammonium chains are also represented.

The disorder of chain 4 corresponds to the two symmetric values $\pm\sigma$ of the torsion angle about the second and third C atoms. As mentioned earlier, the organic layers are formed by interpenetrating chains attached to consecutive inorganic layers so as to achieve an optimal packing over the largest part of the organic chains. For atoms near the tetrahedral layer the packing density is reduced by a factor of two and, consequently, the available free space allows the disorder found near the inorganic layer. From the

existence of a phase transition near room temperature (Socias *et al.*, 1980) one can suppose that one of the disordered positions will be favoured by decreasing the temperature. Structural studies of the next high-temperature phase (Zuñiga & Chapuis, 1983) show, however, that all the chains choose the all-*trans* configuration. In that phase, chain 4 is ordered with atom C(41′) nearly in the position of C(41)P and C(42′) in an average position between C(42) and C(42)P.

The main structural differences as compared to compounds with $m = 12, 14$ are found in the packing of the chains. This seems to be associated with the even–odd effect of m as mentioned above. For $m = 13$, the organic chains are bent towards the tetrahedral layers in the *ac* plane. Torsion angles of −75 and 73° respectively are introduced in chains 2 [N(2)...C(213)] and 4 [N(4)...C(413)], whereas for $m = 12, 14$ they are bent in the *bc* plane with a nearly all-*trans* configuration. Slight differences from 180° in the torsion angles are present in both parity groups and are probably the result of an optimal packing of C atoms far from the inorganic layer. In that region, the density of chain packing is 20 Å² per chain (the cross-sectional area perpendicular to the chains). This value is slightly greater than the 18 Å² value found for closely packed aliphatic chains (Kitaigorodskii, 1961). To compare the chain packing of the different Zn derivatives, we have considered the cell formed by the aliphatic C atoms (*p* cell) in the middle area between two adjacent layers of tetrahedra where the influence of the inorganic part is negligible. In Fig. 1, the dashed line shows for $m = 13$ the cell chosen for chain-packing considerations. It is characterized by a close-packing translation of the t_R type as described by Kitaigorodskii (1961) with cell parameters $a' = 5.24$, $b' = 7.31$, $c' = 2.5$ Å and $\beta' = 99°$. According to the classification of Segerman (1965), the chain packing of the *p* cell is O_b. For $m = 12$ or 14, a different packing is observed. It is formed by chain translation of t_R and t_M types with the cell parameters $a' = 10.3$, $b' = 7.9$, $c' = 2.5$ Å and $\beta' = 99°$ (Zuñiga & Chapuis, 1981).

It is evident that the above description with the given p cell does not correspond to the symmetry operations of the whole structure as the alkylammonium chains are only part of it; it is though convenient to compare the various packings of aliphatic chains. The idealized p cell found in $m = 13$ is well known and corresponds to a packing of layers with symmetry $2_1 t$ [2_1 and t are the two orthogonal basic operations used to construct the layer (Kitaigorodskii, 1961)]. For $m = 14$, the packing type is new. To obtain the atomic parameters of the idealized structure of this type of packing, the atomic positions have been refined along with the cell parameters by fitting the observed distances C—C, C—H and H···H to the ideal values given for the t_R and t_M packing translation (see Fig. 3). The DLS-76 (Baerlocher, Hepp & Meier, 1977) program was used for the calculations. The function minimized was $\sum (w \Delta d)^2$ with $w = 1$ for interchain distances and $w = 2$ for intrachain distances. Nearest C—C and C—H distances were initially set to 1·52 and 1·02 Å respectively; distances between C atoms related by translation were set to 4·2 Å and H—H contacts between t_R chains to 2·8 and 2·6 Å. Symmetry $P2_1$ was assumed as it seemed to be the best approximation for the idealized structure. The refined cell parameters are $a = 10·33$, $b = 6·88$, $c = 2·53$ Å and $\beta = 84·8°$. Atomic parameters are given in Table 4 and a comparison between the calculated and the initial distances is given in Table 5.

Table 4. *Atomic coordinates of the idealized chain packing in* $(C_{14}H_{29}NH_3)_2ZnCl_4$ *as obtained by the program DLS-76*

	x	y	z
C(1)	0·0000	0·0624	−0·1500
C(2)	−0·0590	−0·0126	0·3500
C(3)	0·1814	0·5580	−0·0741
C(4)	0·2397	0·4819	0·4259
H(11)	−0·0162	0·2051	−0·1500
H(21)	0·0974	0·0424	−0·1500
H(12)	−0·0439	−0·1546	0·3500
H(22)	−0·1581	0·0094	0·3500
H(13)	0·0837	0·5459	−0·0741
H(23)	0·2042	0·6881	−0·0741
H(14)	0·3383	0·4952	0·4259
H(24)	0·2195	0·3341	0·4259

Table 5. *Comparison between preset and calculated distances* (Å) *after refinement with DLS-76*

	d_{calc}	d_{pre}		d_{calc}	d_{pre}
C(1)—H(11)	1·541	1·520	C(3)—H(32)	0·989	1·020
C(3^{iv})—C(4^{iv})	1·541	1·520	C(4)—H(41)	0·992	1·020
C(3^{iv})—C(2^i)	4·256	4·200	C(4)—H(42)	1·112	1·020
C(4^{iv})—C(1^i)	4·266	4·200			
			H(11)—H(42^{ii})	2·792	2·800
C(1)—H(11)	1·068	1·020	H(12)—H(42^{ii})	2·767	2·800
C(1)—H(12)	0·986	1·020	H(32)—H(21^{iii})	2·916	2·800
C(2)—H(21)	1·061	1·020	H(11)—H(31)	2·706	2·600
C(2)—H(22)	1·006	1·020	H(31)—H(21^{iii})	2·711	2·800
C(3)—H(31)	0·982	1·020			

$R = [\sum w(d_{calc} - d_{pre})]/\sum (w d_{calc}) = 0·029$.

Symmetry code: (i) x, $1 + y$, z; (ii) x, y, $z - 1$; (iii) $1 + x$, y, z; (iv) $1 - x$, $y + \frac{1}{2}$, $\frac{1}{2} - z$.

On the basis of the structural results, one may ask what is the origin of the differences in chain packing between groups of different parity. The analysis of these systems shows that the chains always tend to acquire the all-*trans* configuration. For even values of m, this has been achieved by doubling the cell volume of the p cell as represented in Fig. 3(a). For odd values of m, the chains introduce torsion angles different from 180° near the contact zone of the layers. This energetically unfavourable configuration generates the additional phase transition found in odd members of the series.
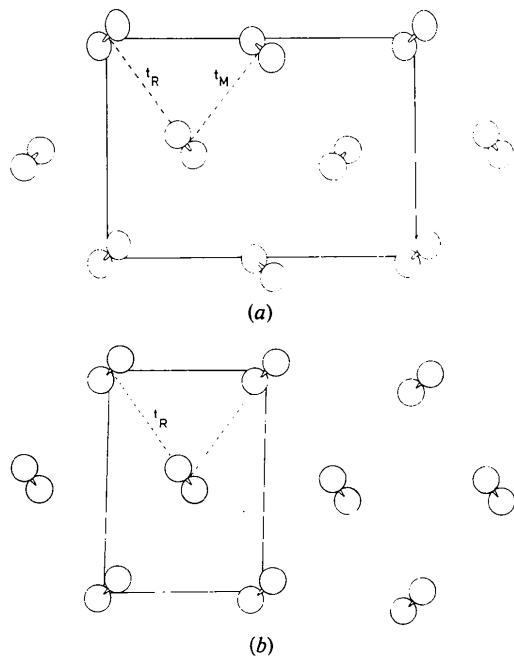

(a)

(b)

Fig. 3. Projection along the chain axis of the alkylammonium packing chains in (a) $m = 14$ and (b) $m = 13$. The t_R and t_M packing translations are indicated.

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[Leu⁵]enkephalin: Four Cocrystallizing Conformers with Extended Backbones that Form an Antiparallel β-Sheet

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Abstract

[Leu⁵]enkephalin (Tyr-Gly-Gly-Phe-Leu) grown from N,N-dimethylformamide(DMFA)/water crystallizes with four quite different conformers side-by-side in the asymmetric unit. The four conformers with extended backbones form an infinite antiparallel β-sheet. β-sheets related by the twofold screw axis are separated by a 12 Å spacing. Side groups protrude above and below the β-sheets and are entirely immersed in a thick layer of solvent occupying the volume between β-sheets. The crystal, stable only in contact with its mother liquor, appears to be a hybrid consisting of rather rigid sheets of peptide molecules separated by spaces filled with mobile solvent, thus having some resemblance to molecules in solution. Many solvent molecules are completely disordered and may be fluid. The space group is $P2_1$ with $a = 18 \cdot 720$ (4), $b = 24 \cdot 732$ (6), $c = 20 \cdot 311$ (5) Å, $\beta = 115 \cdot 86$ (1)°, $V = 8462$ Å³. Composition of the asymmetric unit includes four enkephalin molecules, eight water molecules, eight DMFA molecules, plus an unknown number of disordered solvent molecules: $4C_{28}H_{37}N_5O_7 \cdot 8H_2O \cdot 8C_3H_7NO \cdot X$. The R factor from a restrained least-squares re-

finement (with six-parameter thermal factors) is $11 \cdot 9\%$ for 8155 data with $|F_o| > 0$. The procedure used for phase determination and structure analysis is described. Parameters for an extensive antiparallel β-sheet are presented.

Introduction

Endogenous enkephalin, a linear pentapeptide functioning as a natural analgesic with opiate-like activity, occurs in the brain as [Leu⁵]enkephalin and [Met⁵]-enkephalin in varying proportions, depending upon the species (Hughes, Smith, Kosterlitz, Fothergill, Morgan & Morris, 1975). The extreme flexibility of peptides, as compared to the more rigid molecules of morphine and other opiates, necessitates the delineation of probable conformations for the peptide to facilitate structure–activity studies. In the present study of the crystal structure of [Leu⁵]enkephalin, the serendipitous occurrence of four molecules of the peptide, each having a different conformation, and a large amount of solvent surrounding the peptide may give good indications for the preferred conformations in solution.