Apart from the hydrogen bonds, there are no intermolecular distances shorter than van der Waals contacts.

I wish to thank Professor K. Wiesner for suggesting this problem and for sending me the crystals. I am also indebted to Dr Maria Przybylska for her constant encouragement and interest in this work. The use of the computer programs of Ahmed, Hall, Pippy & Huber (1966), of *ORTEP* (Johnson, 1965) and of *MGTLS* (Schomaker & Trueblood, 1968) is gratefully acknowledged.

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The Crystal Structure of Tris-Sarcosine Calcium Chloride

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The structure of the room-temperature phase of tris-sarcosine calcium chloride, $CaCl_2.3(CH_3NH_2^+CH_2COO^-)$, has been studied. The crystal is ferroelectric below the Curie point, 127°K [Makita, Y. *J. Phys. Soc. Japan* (1965), **20**, 2073].It is orthorhombic with $a=9{\cdot}156$, $b=17{\cdot}460$, $c=10{\cdot}265$ Å, space group *Pnma* and $Z=4$. The structure was determined by use of the data obtained on a four-circle diffractometer, and the final *R* was 0·059. Out of two kinds of sarcosine, both having a zwitterion form, one is in the mirror plane perpendicular to the *b* axis; the other in the general position is also not far from being planar, and is roughly perpendicular to the *bc* plane. There are only three hydrogen bonds in the crystal, of the kind N-H···Cl. The Ca ion is located in a mirror plane, and is coordinated by 6 oxygen atoms arranged in an octahedron. The crystal has a pseudo-hexagonal symmetry if viewed down the *b* axis, and the complex around the Ca ion and the hydrogen bonds play an important role together in making up the crystal.

Introduction

Tris-sarcosine calcium chloride, $CaCl_2.3(CH_3NH_2^+CH_2COO^-)$, was found to exhibit ferroelectric behaviuor below the Curie point, 127°K (Pepinsky & Makita, 1962). Since then a detailed study of the physical properties of the crystal has been made by Makita (1965), who deduced an order–disorder type ferroelectric phase transition. In view of this physical significance, the structure of the room-temperature phase of the crystal was worked out when one of the authors was at Pennsylvania State University (Ashida & Pepinsky, unpublished). On the other hand, from a chemical viewpoint the structure of this crystal is of significance in the study of interactions between amino acids and some non-transition metal ions commonly found in biological systems. The structure analysis of biologically important substances is the main project which has, for these past ten years, been carried on in this laboratory.

The present paper deals with the complete reanalysis which has been carried out by use of the new diffractometer data.

Experimental

Crystals of tris-sarcosine calcium chloride which were rods elongated along the *a* axis were easily obtained from an aqueous solution containing sarcosine and $CaCl_2$ in stoichiometric ratio. The crystals thus obtained were almost invariably twinned. By adding a large excess of sarcosine to the solution, it was possible to decrease the amount of the twinned crystals. This is very similar to the case of $CaCl_2$.glycylglycylglycine.$3H_2O$ (Van der Helm & Willoughby, 1969).

The crystal is orthorhombic with cell dimensions $a=9{\cdot}156\pm0{\cdot}01, b=17{\cdot}460\pm0{\cdot}005, c=10{\cdot}265\pm0{\cdot}005$ Å. The systematic extinction of reflexions of $(k+l)$ odd for $0kl$ and h odd for $hk0$ suggested the space group to be $Pn2_1a$ or *Pnma*. The centric space group *Pnma* is adopted because of the physical experiment (Pepinsky & Makita, 1962; Makita, 1965) and the $N(z)$ test of the intensity data. The observed density of the crystal, 1·533 g.cm^{-3} (Makita, 1965), suggested the number of the chemical units in a cell to be 4, the calculated density being 1·530 g.cm^{-3}.

The intensity measurements were made on an AFC-II (Rigaku Denki automatic four-circle diffractometer), equipped with a pulse-height analyser. The ω–2θ scan method and Ni-filtered Cu $K\alpha$ radiation were used. The background intensities were measured at the starting and end points of the scan. The size of the crystal used in the experiment is 0·26 × 0·08 × 0·08 mm. 1116 reflexions within a limit of $2\theta=113°$ were collected. The Lp corrections were made as usual, while no absorption correction was made.

Structure determination

The coordinates of the non-hydrogen atoms obtained in the previous unpublished work were used as the initial parameters for the refinement of the structure. The difference electron density map, which was made after several cycles of least-squares refinement, showed up all the hydrogen atoms. The hydrogen atoms were also included in the subsequent refinement. The final electron density distribution is shown in Fig. 1. All the computations were done on a NEAC 2200-500 of the Computation Center of this University. The block-diagonal least-squares refinement program, *HBLS* IV (Ashida, 1967), was used. The weighting scheme was: $w=1$ for $F_o\neq0$ and $w=0$ for $F_o=0$. The scattering factors for Ca^{2+}, Cl^-, O, N, C and H were taken from *International Tables for X-ray Crystallography* (1962).

The final atomic parameters are listed in Tables 1 and 2, and the observed and calculated structure factors are in Table 3. The final R value is 0·059 for non-zero reflexions, and 0·064 if all the reflexions are included. The mean e.s.d.'s of the positional parameters are 0·0015 Å for Ca and Cl, 0·0076 Å for C, N and O in the mirror plane, and 0·0054 Å for C, N and O in the general position.

Discussion

The crystal structure is shown in Figs. 2 and 3. Fig. 2 and the Patterson projection on (100) shown in Fig. 4 show clearly a pseudo-hexagonal symmetry of the

Table 1. *The final atomic coordinates (fractional,* × 10^4*) and thermal parameters* (× 10^4)

Standard deviations are shown in parentheses.
Anisotropic thermal parameters are in the form; $\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)\}$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ca	386 (2)	2500 (0)	2249 (1)	42 (2)	6 (1)	16 (2)	0 (0)	2 (3)	0 (0)
Cl	4912 (2)	833 (1)	7148 (1)	96 (2)	15 (1)	47 (2)	10 (2)	0 (3)	−2 (1)
Molecule 1									
O(11)	1720 (8)	2500 (0)	4142 (6)	120 (10)	38 (3)	40 (6)	0 (0)	−84 (14)	0 (0)
O(12)	4070 (7)	2500 (0)	4718 (5)	76 (8)	27 (2)	34 (6)	0 (0)	44 (11)	0 (0)
N(11)	3511 (8)	2500 (0)	7265 (6)	84 (10)	15 (2)	5 (6)	0 (0)	7 (13)	0 (0)
C(11)	2747 (10)	2500 (0)	4942 (8)	120 (14)	8 (3)	24 (8)	0 (0)	−11 (18)	0 (0)
C(12)	2228 (9)	2500 (0)	6378 (8)	67 (11)	20 (3)	29 (8)	0 (0)	−18 (16)	0 (0)
C(13)	3003 (12)	2500 (0)	8659 (9)	141 (16)	31 (4)	30 (9)	0 (0)	11 (20)	0 (0)
Molecule 2									
O(21)	6588 (5)	1447 (2)	3713 (4)	103 (6)	18 (2)	74 (5)	36 (5)	0 (10)	25 (5)
O(22)	8936 (6)	1601 (3)	3240 (5)	145 (8)	23 (2)	77 (5)	−55 (6)	54 (11)	21 (5)
N(21)	7000 (6)	114 (3)	4937 (5)	91 (7)	10 (2)	42 (5)	−1 (6)	15 (10)	13 (5)
C(21)	7899 (7)	1263 (3)	3732 (5)	91 (8)	10 (2)	25 (5)	−12 (7)	8 (11)	−4 (5)
C(22)	8309 (7)	532 (3)	4464 (6)	55 (7)	13 (2)	42 (6)	9 (6)	16 (11)	10 (6)
C(23)	7380 (9)	−576 (4)	5733 (7)	166 (12)	14 (2)	100 (9)	−12 (9)	−17 (18)	48 (8)

Table 2. *The final parameters of the hydrogen atoms*

	x	y	z	Bonded to
H(11)	0·165	0·193	0·653	C(12)
H(13)	0·410	0·202	0·712	N(11)
H(15)	0·373	0·250	0·910	C(13)
H(17)	0·248	0·193	0·858	C(13)
H(21)	0·878	0·014	0·384	C(22)
H(22)	0·894	0·069	0·530	C(22)
H(23)	0·648	−0·011	0·420	N(21)
H(24)	0·655	0·037	0·546	N(22)
H(25)	0·634	−0·082	0·595	C(23)
H(26)	0·805	−0·025	0·660	C(23)
H(27)	0·808	−0·093	0·521	C(23)

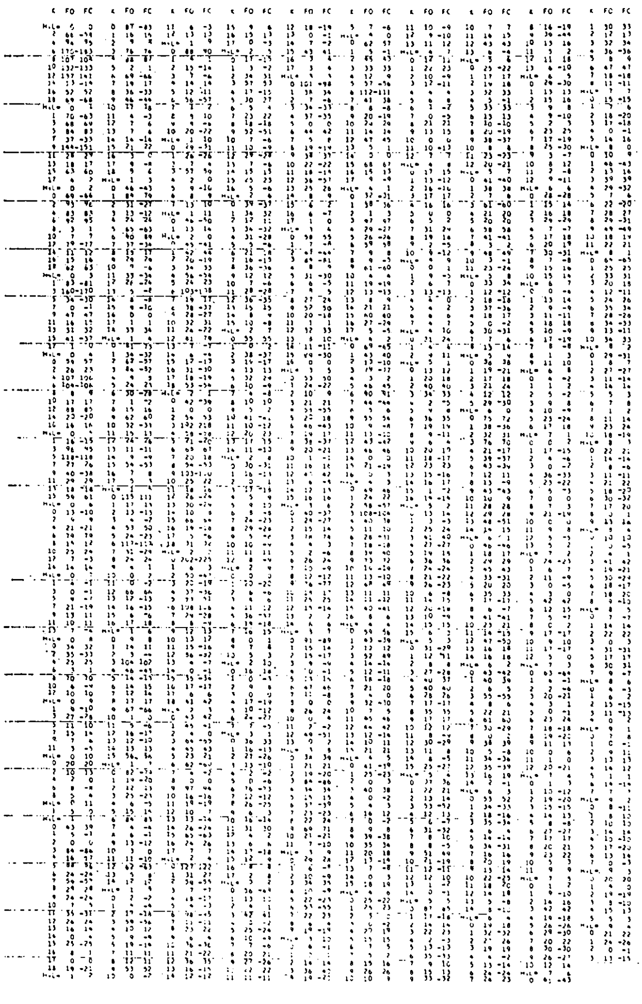
crystal. The twinning, which occurs across the plane (011) in almost every specimen, may be due to the presence of the pseudo-hexagonal symmetry. The detail of the twinning may be similar to that which is outlined elaborately by Bragg (1962) for aragonite with a pseudo-hexagonal symmetry.

There are two kinds of sarcosine molecules in the crystal, each having a zwitterion form. One group, consisting of 4 molecules, lies on the mirror plane perpendicular to the b axis, and hence the skeleton of the molecule is planar. The other kind of molecule (a group of 8 molecules in the general position), is also not far from being planar. The equation of the plane of the carboxyl group with the C_α atom of the molecule (2)* is:

$$0{\cdot}1238X+0{\cdot}5278Y+0{\cdot}8403Z=5{\cdot}2814$$

where X, Y and Z are in Å. The carboxyl group is planar within a maximum atomic displacement of

Table 3. *The observed and calculated structure factors*



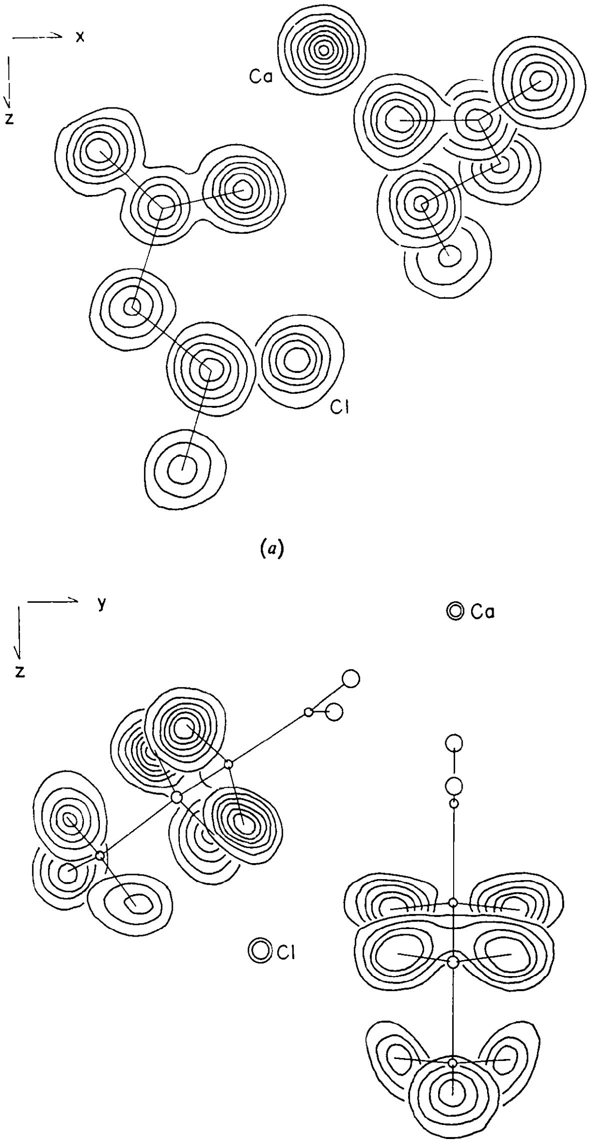


Fig. 1. (a) A composite of sections of the electron density viewed down the b axis. The contours are 2, 4, 6, ... for C, N and O, and 5, 10, 15, ... (e.Å^{-3}) for Ca and Cl. (b) The hydrogen atom electron density in the difference Fourier map viewed down the a axis. The contours are from 0·2 with an interval of 0·1 e.Å^{-3}.

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* The notation of the molecules is shown in Fig. 2.

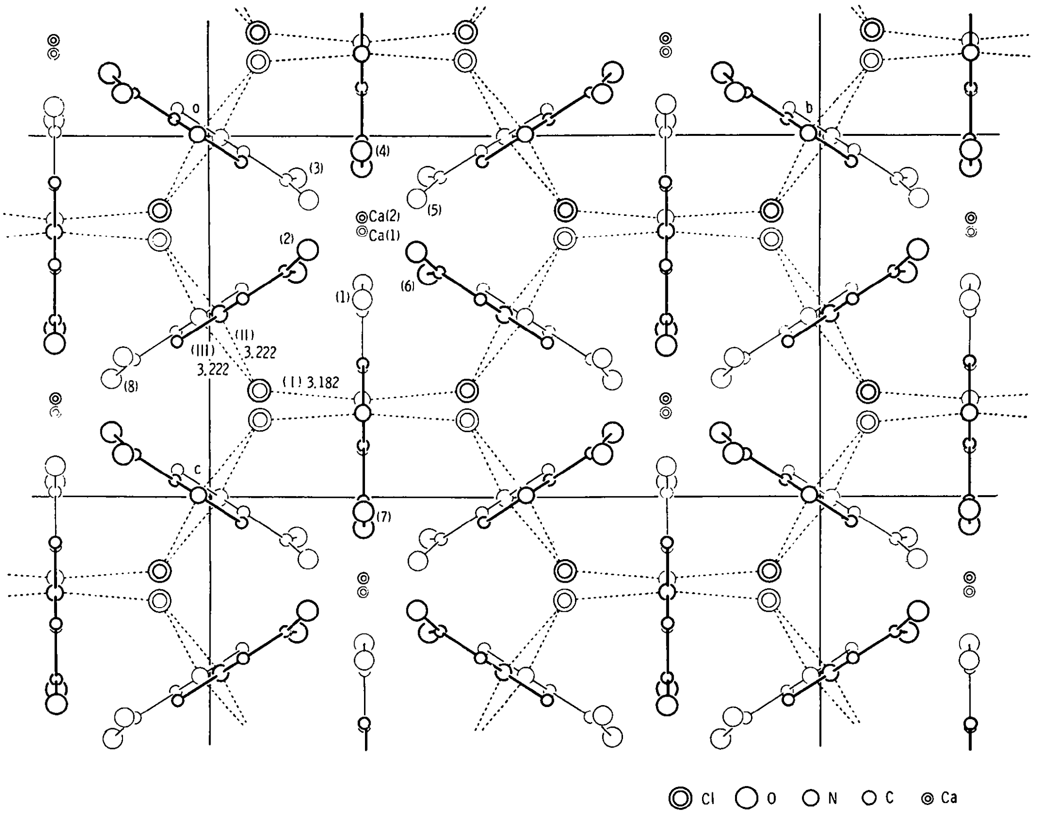

Fig. 2. The structure viewed down the *a* axis. The sarcosine molecules are designated by Arabic numerals, while the hydrogen bonds have Roman numerals.

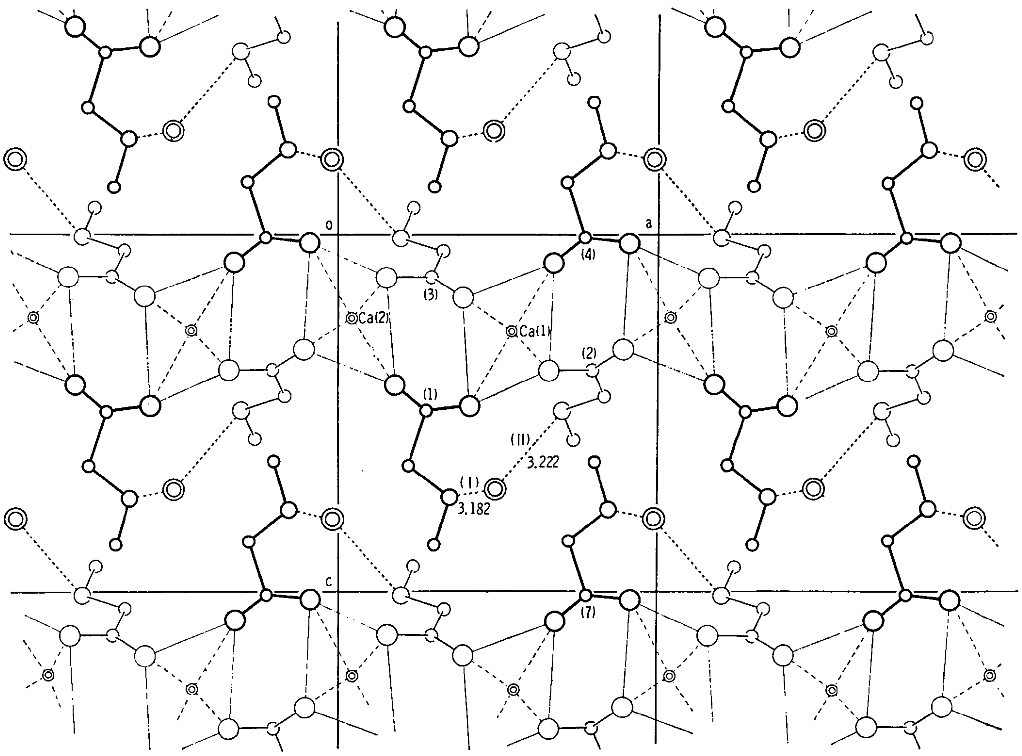

Fig. 3. Projection of half a unit cell along the *b* axis. The other half, left out for the sake of clarity, relates to this part by a centre of symmetry.

0·003 Å. The N(21) atom deviates by −0·124 Å from the plane, while the terminal C(23) deviates by 0·031 Å in the opposite direction. Thus, this molecule lies in the plane (011) and stands on the plane (100); the normal to the molecular plane makes an angle of 82·9° with the *a* axis. The dihedral angle which is made by molecules (1) and (2) is 58·2°. The bond distances and angles in the molecules are shown in Fig. 5. The mean e.s.d.'s are 0·011 Å and 0·6° for the molecule on the mirror plane, and 0·008 Å and 0·4° for the molecule in the general position.

The Ca ion locates on the mirror plane, close to the twofold screw axis at $y=\frac{1}{4}$ and $z=\frac{1}{4}$. The ion is surrounded by 6 oxygen atoms arranged in a slightly distorted octahedron, of which the geometry is shown in Fig. 6. The Ca–O distances are from 2·294 to 2·359 Å with the mean distance of 2·325 Å. This distance is significantly shorter than the distance of 2·40 Å given as the average for the Ca–O distances in the cases of 6-coordination (*International Tables for X-ray Crystallography*, 1962). There is neither direct contact between the Ca ion and the Cl ion, nor contact between the Ca ion and the amino nitrogen atom of the sarcosine molecule. This is just the same as found in $CaCl_2$.glycylglycylglycine.$3H_2O$ (Van der Helm & Willoughby, 1969). The arrangement of the neighbouring molecules around the Ca ion is shown in Figs. 3 and 7. Each sarcosine molecule is shared by two Ca ions which are related to each other by the twofold screw axis at $y=\frac{1}{4}$ and $z=\frac{1}{4}$. Thus the endless chain of the octahedrons is formed around the twofold screw axis.

The sarcosine molecules combine to make a trigonal infinite column along the *a* axis, and the Cl ion is located close to the central axis of the column. The Cl ion accepts three N–H···Cl hydrogen bonds, and these three are the only hydrogen bonds present in this crystal, their dimensions being listed in Table 4. No oxygen atom is involved in the hydrogen bonds. Each N atom is a donor of two hydrogen bonds which protrude laterally to both sides of the molecular plane. Thus, both of the hydrogen bonds and the complex formation of the Ca ion play a key role in making up the crystal structure.

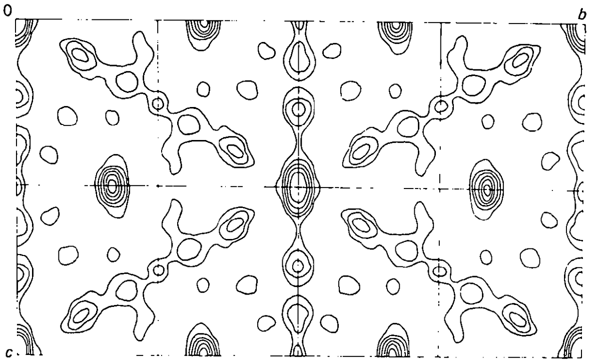

Fig. 4. The Patterson projection on the *bc* plane. The pseudo-hexagonal symmetry is clearly shown.

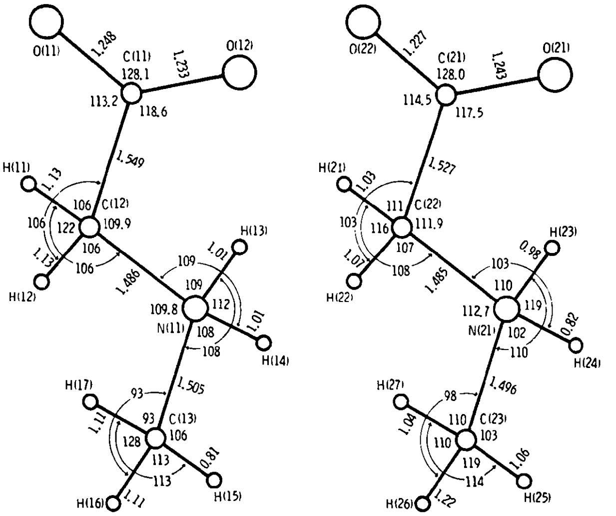

Fig. 5. Bond distances and angles. The left hand molecule is in the mirror plane, and the other is in the general position.

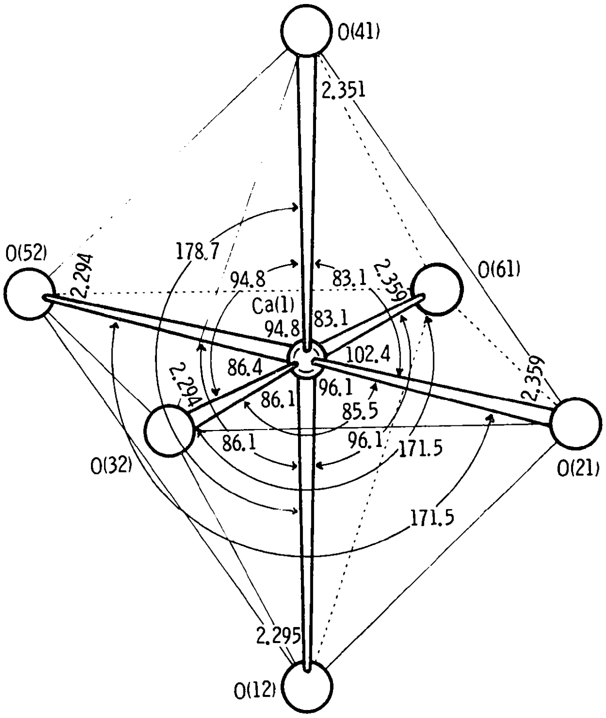

Fig. 6. Geometry of the octahedron around the Ca ion.

Table 4. *Hydrogen bonds*

H-bond*	N···Cl	H···Cl	∠NHCl	$\angle C_\alpha NCl$	$\angle C^M NCl$†
I	3·182 Å	2·20 Å	164°	107·2°	99·2°
II	3·222	2·43	165	121·2	93·9
III	3·222	2·27	166	118·3	94·3

N–Cl–N angle between I and II 128·5°
I and III 106·0
II and III 69·8

* Notation as in Fig. 3.

† C^M: the carbon atom of the methyl group.

The r.m.s. amplitudes of vibrations of atoms in directions parallel and perpendicular to the molecular planes have been deduced from the thermal parameters, and are listed in Table 5; no abnormality is found. All the peaks of atoms in the electron density map, including those of hydrogen atoms in the difference Fourier synthesis, are well defined, as shown in Fig. 1. In order to make clear the detail of the ferroelectric phase transition of the crystal, a further study such as a neutron diffraction experiment seems necessary.

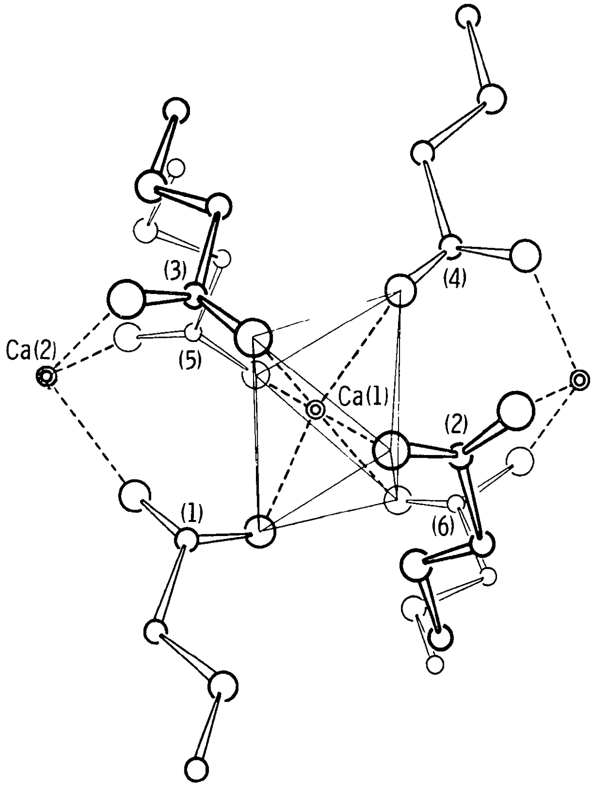

Fig. 7. A sketch of the neighbours of the Ca ion. The molecules (1) and (4) and the Ca ion are in the mirror plane, while the others are in general positions; (2) is the mirror image of (6), and (3) is the mirror image of (5).

Table 5. *R.m.s. displacements of atoms*

u_a: Along the *a* axis.

$u_\perp$: Direction perpendicular to the molecular plane;

For molecule 1 (and Ca, Cl)	Perpendicular to (001)
For molecule 2	Perpendicular to (011)

$u_\parallel$: Direction perpendicular to the *a* axis and parallel to the molecular plane;

For molecule 1 (and Ca, Cl)	Perpendicular to (010)
For molecule 2	Perpendicular to (01$\bar{3}$)

	u_a	$u_\perp$	$u_\parallel$
Ca	0·13 Å	0·10 Å	0·09 Å
Cl	0·20	0·15	0·16
Molecule 1			
O(11)	0·23	0·24	0·14
O(12)	0·18	0·20	0·14
N(11)	0·19	0·15	0·05
C(11)	0·23	0·11	0·11
C(12)	0·17	0·17	0·12
C(13)	0·24	0·22	0·13
mean	0·21	0·18	0·12
Molecule 2			
O(21)	0·21	0·21	0·15
O(22)	0·25	0·22	0·17
N(21)	0·20	0·16	0·11
C(21)	0·20	0·11	0·13
C(22)	0·15	0·16	0·13
C(23)	0·27	0·25	0·11
mean	0·21	0·19	0·13

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